1-Bridgehead Substituted Norbornenes in Late Transition Metal Polymerisation Catalyst Studies

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By

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Abstract

1-or 4-Substituted norbornene monomers are very attractive because it is a single isomer unlike endo and exo isomers in 5/6 substituted and, syn/anti isomers in 7-substituted norbornene. In this project, the 1-substituted norbornene monomer, norbornene-1-methyl carboxylate monomer, was synthesised from norbornane-2-carboxylic acid in a high yield and in four steps. In each step the product was fully characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. The monomer was subjected to ROMP reactions using 1^{st} , 2^{nd} and modified 2^{nd} generation ruthenium initiators. The polymerisation reaction was monitored by ^{1}H NMR spectroscopy. 1^{st} generation ruthenium initiator showed no evidence for polymerisation, but it indicated the possibility of the formation of a chelating complex as well as an oligomer. When the monomer is inserted at the ruthenium center two different complexes may be formed; a complex via insertion of monomer to the ruthenium center and a complex via chelation of oxygen to the ruthenium center. To isolate the chelated complex, the ROMP reaction of norbornene-1-methyl carboxylate monomer was carried out at the ratio of monomer: 1^{st} generation ruthenium initiator of 1:1. The complex structure could only be identified by ^{1}H NMR spectroscopy and it was not possible to obtain good quality crystals for X-ray crystallography. ROMP reactions using 2^{nd} and modified 2^{nd} generation ruthenium initiators showed that these initiators are efficient for the polymerisation of the norbornene-1-methyl carboxylate monomer. The narrow PDIs indicate reasonably well controlled polymerisation reactions.

Addition polymerisation of norbornene-1-methyl carboxylate monomer was carried out using the palladium initiator $[Pd(H)(MeCN)(PCy_{3)2}][B(C_6F_5)_4]$, (Pd 1388). The result of the GPC analysis showed the existence of two peaks with DP of 2 and 16 which suggest the formation of a dimer and an oligomer. Addition polymerisation of norbornene-1-methyl carboxylate monomer using nickel initiator (η^6-toluene)$Ni(C_6F_5)_2$ was carried out. However, based on the result it has been difficult to determine the outcome of the polymerization reaction. The presence of ester group in 1 position most likely leads to coordination or chelation of the norbornene-1-methyl carboxylate monomer to the nickel or palladium metal center.

ACKNOWLEDGEMENTS

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MEMORANDUM

The work of this thesis was carried out in the Polymer IRC laboratories at Chemistry Department, Durham University between March 2007 and April 2008. This work has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

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Table of Content

Abbreviations

Ac	acetyl
Bu	butyl
$CDCl_3$	deuterated chloroform
Cp	cyclopentyl
CN	cyanide
COD	cyclooctadiene
Cy	cyclohexyl
DMS	dimethyl sulphate
ether	diethyl ether
Et	ethyl group
hr	hours
GPC	gel permeation chromatography
MAO	methyl aluminium oxide
Me	methyl
Mes	mesitylene group
mL	millilitre
NHC	N-heterocyclic carbine
NMR	nuclear magnetic resonance
p	para
PDI	polydispersity Index
Ph	phenyl group
ppm	parts per million
ROMP	ring opening metathesis polymerisation
RT	room temperature

*t*Bu	tertiary butyl group
TCE	tetrachloroethane
TMS	trimethylsilyl
THF	tetrahydrofuran

Chapter 1 Introduction

1.1 Importance of norbornene monomers

Bicyclo[2.2.1]hept-2-ene, better known by its trivial name norbornene,[1] is an example of a strained bicyclic olefin monomer, Figure1.1. Norbornene has a bridged six-membered ring with a double bond. The bridged ring puts extra strain on the double bond, making it highly reactive. The basic structure of norbornene molecule can be modified by incorporating functional groups at various positions.

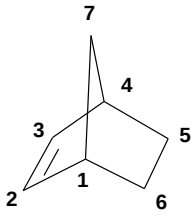
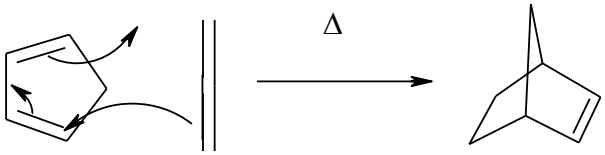


Figure 1.1. Norbornene

1.2 Synthesis of substituted norbornene monomers

Substituted norbornenes are generally synthesised *via* Diels-Alder reactions. Diels-Alder reactions are concerted cycloadditions between a conjugated diene and a dieneophile, and were developed in the 1920s by Otta Diels and Kurt Alder, Scheme 1.1.[2]



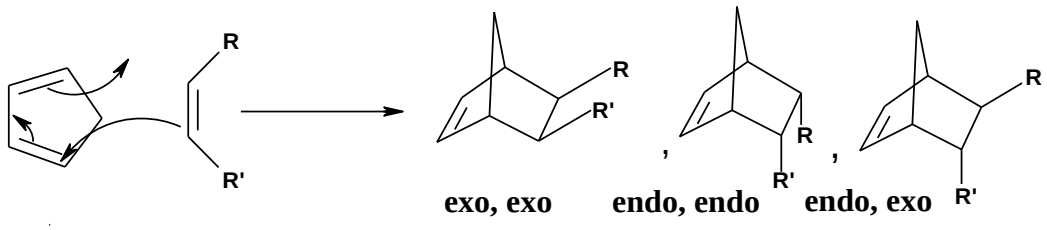
Scheme 1.1. Diels-Alder reaction to form norbornene

The reaction is a concerted [4+2] cycloaddition reaction, and involves the 4π-electrons of the diene and the 2π-electrons of the dieneophile. The driving force for the reaction is the formation of energetically favourable σ-bonds, as they are energetically more stable than π-bonds.

1.2.1 5,6-Substitued norbornenes

5,6-Substitued norbornene monomers are prepared *via* Diels-Alder reaction between a conjugated diene and a difunctional dieneophile, Scheme 1.2. Problem associated with 5,6-substituted norbornenes synthesis is, the reaction gives three different isomers

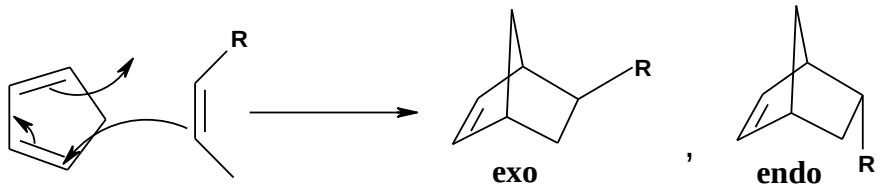
(*endo*, *endo*; *endo*, *exo*; and *exo*, *exo*) and isolation of these isomers is a time-consuming procedure.



Scheme 1.2. Diels-Alder reaction to form 5,6-subsituted norbornenes

1.2.2 5-Substitued of norbornenes

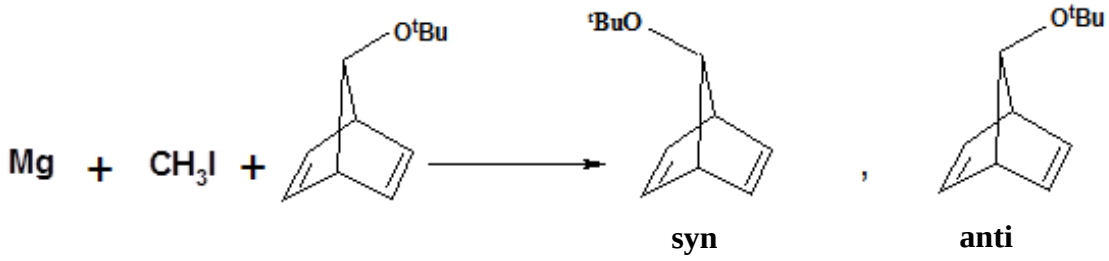
5-Substituted of norbornenes are also produced *via* Diels-Alder reaction between a conjugated diene and a monofunctional dieneophile, Scheme 1.3. The product is also a mixture of *endo* and *exo* isomers and the isolation of the isomers is really problematic.



Scheme 1.3. Diels-Alder reaction to form 5-subsituted norbornenes

1.2.3 7-Subsituted norbornene

7-Substitued norbornenes, Scheme 1.4, are prepared *via* Grignard reaction between magnesium turnings, methyl iodide and 7-tert-butoxynorbornadiene. In the course of reaction of 7-substituted norbornene monomers two (syn and anti) isomers is observed.[3]



Scheme 1.4. Grignard reaction to form 7-subsituted norbornenes

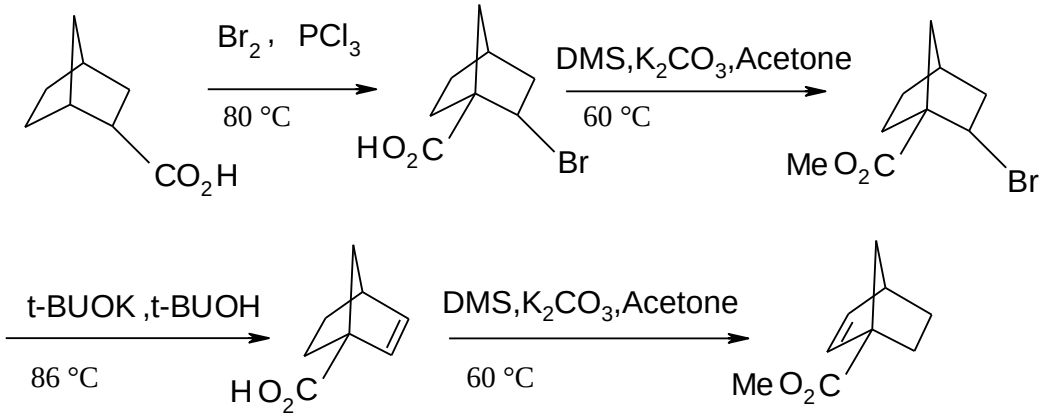
Syn-and anti-7-carbomethoxynorbornene **1(a-b)**, Figure 1.2, were prepared by addition of a syn-7-bromonorbornene to a solution of magnesium in dry ether, under an inert atmosphere.[3]

1.a R=CH_3 **1.b R= CH_3**

Figure 1.2. Syn- and anti-7-carbomethoxynorbornene **1(a-b)**

1.2.4 1-Subsituted norbornene

The incorporation of a substituent in the 1- or 4-positions of the norbornene ring is very attractive as it eliminates the possibility of *endo* and *exo* isomers. The methodology used for the synthesis of norbornene monomers containing substituents in 1 or 4 positions is different to that recognised for other substituted norbornenes. Norbornene-1-methyl carboxylate was synthesised through several steps, Scheme 1.5. The first step is the bromination[4,5] of norbornane-2-carboxylic acid monomer involving Wagner-Meerwein rearrangement.[4,5,6,7] The second step is methylation of 2-bromonorbornane-1-carboxylic acid monomer using K_2CO_3 and DMS (dimethyl sulphate) to 2-bromonorbornane-1-carboxylic acid.[5,8] The next step is de-hydrobromination and hydrolysis of 2-bromonorbornane-1-methyl carboxylate compound using t-BUOH (t-butyl alcohol) and t-BUOK (potassium t-butoxide).[5] The last step is methylation of norbornene-1-carboxylic acid monomer using DMS to obtain norbornene-1-methyl carboxylate.[5,8]



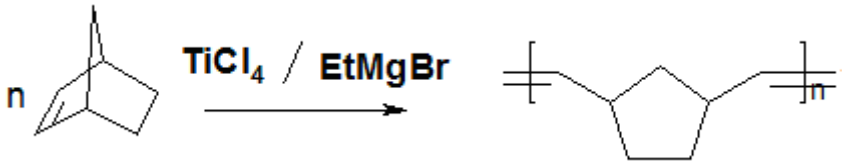
Scheme 1.5. Synthesis steps of norbornene-1-methyl carboxylate monomer

1.3 Polymerisation of norbornene monomers

1.3.1 Ring-opening metathesis polymerisation (ROMP)

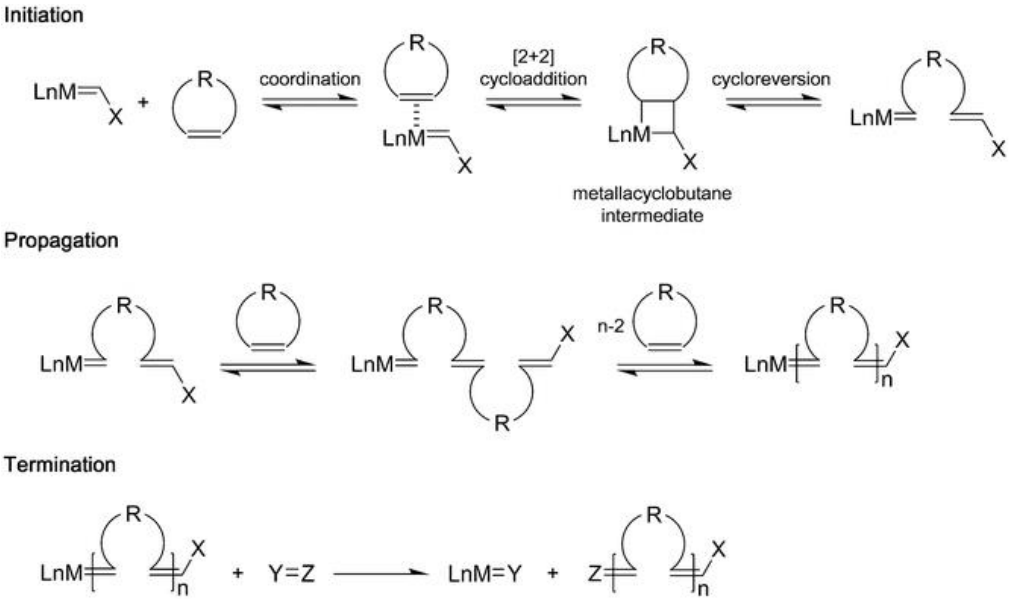
1.3.1.1 Background

Nowadays ring opening metathesis polymerisation (ROMP) is a powerful and applicable way for synthesising macromolecular materials.[9] The first example of ROMP was reported by Anderson and Merckling in 1955,[10] Scheme 1.6, which showed that norbornene polymerised using a mixture of $TiCl_4$ (titanium tetrachloride) and EtMgBr (ethyl magnesium bromide) and resulted in the formation of unsaturated polymers.



Scheme 1.6. Polymerisation of norbornene proposed by Anderson and Merckling in 1955

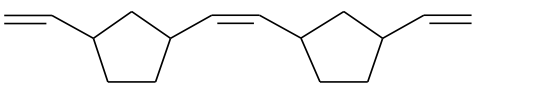
ROMP is a chain-growth polymerisation process in which a cyclic olefins is converted to a polymeric material.[11] The mechanism of this polymerisation is based on olefin metathesis and a metal-mediated carbon–carbon double bond undergoes an exchange process[12] and eventual conversion of unsaturated cyclic monomer into polymer. A general mechanism for the ROMP reaction, based on Chauvin's proposal[13] is shown in Scheme 1.7. According to the mechanism, the initiation step begins with coordination of a transition metal alkylidene complex to a cyclic olefin in a [2+2]-cycloaddition forming a four-membered metallacyclobutane intermediate. The metallacyclobutane is then broken to form a propagating alkylidene allowing the polymer chain to grow. Living ROMP reactions are terminated or quenched by addition of specialised reagent.[14]



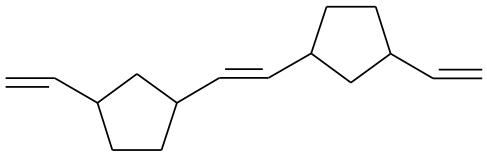
Scheme 1.7. General mechanism for the ROMP reaction, proposed by Chauvin[14]

The way in which a monomer unit incorporates into a polymer chain determines the polymeric microstructure[15-18]. There are four main factors that define the microstructure of polymers formed during the ROMP of norbornene or norbornadiene derivatives.[19]

The backbones of polymers prepared by ROMP contain unsaturated bonds that can be either *cis* or *trans* configuration, Figure 1.3. The ratio and distribution of *cis* or *trans* isomers depends on the monomer, the initiator and, in some cases, other conditions like concentration, temperature, and the solvent.[20] It is possible, with different types of initiator systems and conditions, to prepare unsaturated polymers having either all *cis* or all *trans* configuration.[21-23]



Cis



Trans

Figure 1.3. *Cis* and *trans* configuration of polymer backbone

Not all norbornene and norbornadiene-type monomers are necessarily chiral. Polymers which have chiral carbon atoms exhibit tacticity effects along their backbone.[20,24] Upon polymerisation, there is a possibility that the two tertiary carbon atoms either side of a double bond have the same or different chirality, and form a racemic or meso dyad. The racemic dyads produce syndiotactic polymers, and meso dyads result in isotactic polymers. Polymers with random distribution of meso and racemic dyads are atactic. The combination of meso and racemic dyads with *cis* and *trans* isomerism leads to four possible regular microstructure arrangements, Figure1.4.[25]

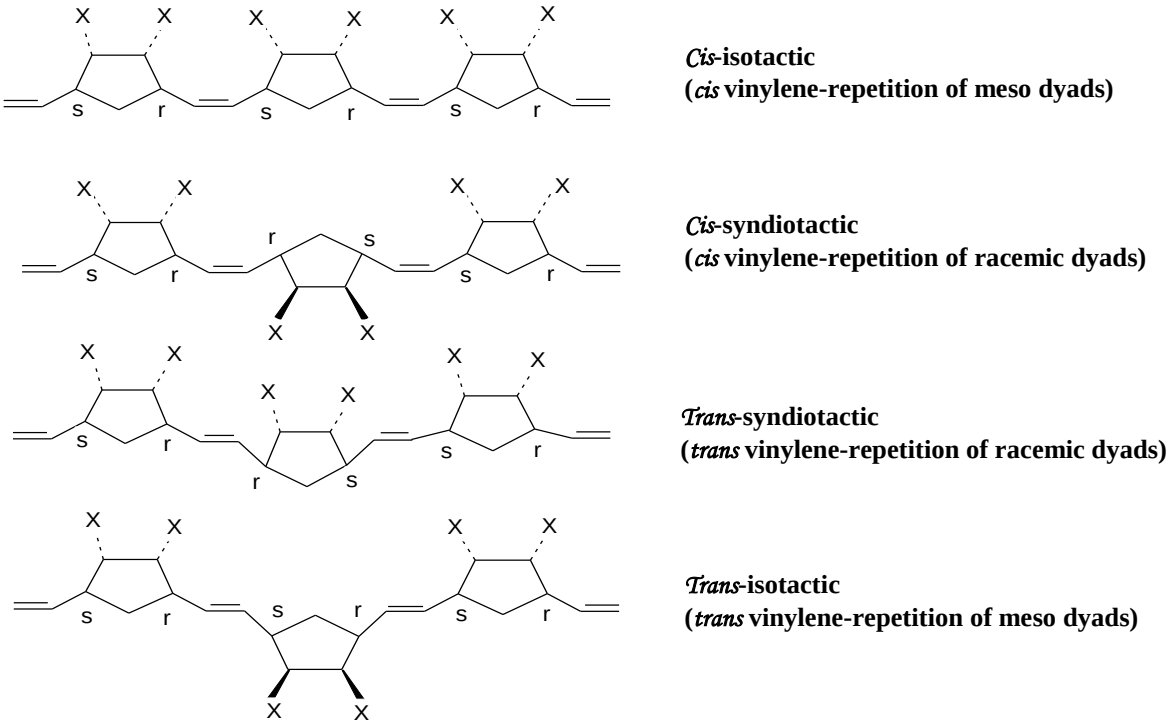


Figure 1.4. The four possible microstructural arrangements of poly(5,6-norbornenes)

The insertion of 1-substituted norbornenes into propagating polymer chains shows that the double bonds are all trans, and there is a strong bias towards an HT structure head/head(HH), head/tail(HT), tail/tail(TT), (1:10:1), Figure 1.5.[26]

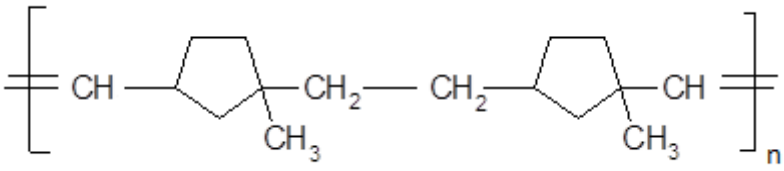


Figure1.5. Head/Tail placement of 1-substituted norbornene monomer

1.3.1.2 Initiator systems for living ROMP reaction

For ROMP, metal-alkylidene complex is required as initiators. These initiator systems are mainly based on groups 4 to 9 of the transition metals and, in particular, Mo, W, Re and Ru complexes. There are two categories for metathesis initiators; ill-defined, and well-defined initiators. Table1.1 shows the toleration of functional groups in the presence of early and late transition metals in olefin metathesis reactions.

Table1.1. Reactivity of functional groups in the presence of early and late transitional metal catalysts.[27]

Ti / Ta	W	Mo	Ru
acids	acids	acids	olefins
alcohols	alcohols	alcohols	acids
aldehydes	aldehydes	aldehydes	alcohols
ketones	ketones	olefins	aldehydes
esters/amides	olefins	ketones	ketones
olefins	esters/amides	esters/amides	esters/amides

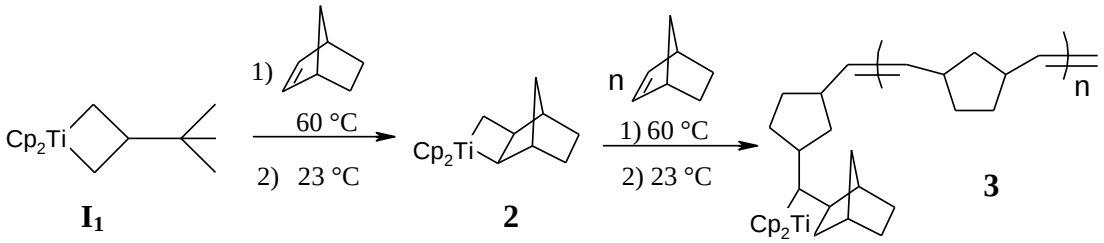
increasing reactivity

The history of ill-defined initiators began when Ziegler oligomerised ethylene in the presence of alkyl aluminium catalysts.[28] interestingly, later on, Ziegler and Natta introduced two different metals and a series of titanium salts that could polymerise ethylene and propylene.[29-34]

Dupont and Natta explored independently the polymerisation of norbornene monomer using different mixtures of Ti, W, or Mo halides with Al compound as a co-initiator.[35-37] Calderon and co-workers also reported a homogeneous system which was a mixture of WCl_6 and $AlEt_2Cl$.[38-40] Although, ROMP reactions with these initiators (homogeneous or heterogeneous) were not living and they required dry, and air-free conditions these systems provided insight into the mechanism of olefin metathesis and they proved the necessity for well-defined initiator systems. More details on the performance of many initiators in the ROMP reaction can be found in the literature.[41-50]

A deep insight into the mechanism of olefin metathesis encouraged scientists to work on developing well-defined initiator. The first well-defined Ti-based initiator (**I_1**) able

to mediate ROMP of norbornene at 60 °C was complex **(I_1)**, Scheme 1.8. (I_1) reacts with norbornene and undergoes [2+2] cycloaddition reaction to produce complex **2**. Complex **2** initiates polymerisation of norbornene when it heated to 60 °C in the presence of norbornene. The resulting polymer showed a narrow Polydispersity Index (PDI<1.2)



Scheme 1.8. ROMP reaction in the presence of titanium-based initiator (I_1)

Schrock[51-52] and co-workers reported molybdenum and tungsten initiators (I_2) and showed that they can polymerise norbornene and norbornadiene derivatives bearing different functional groups such as ethers, esters, acetates, nitriles, halides, and acetate, Figure 1.6. Molybdenum initiators found a wider utility due to their tolerance of a wide range of functional groups, such as preparation of metal clusters and semiconductor materials within a polymeric matrix. These initiators are widely used for the preparation of polymers with different characteristics.[53]

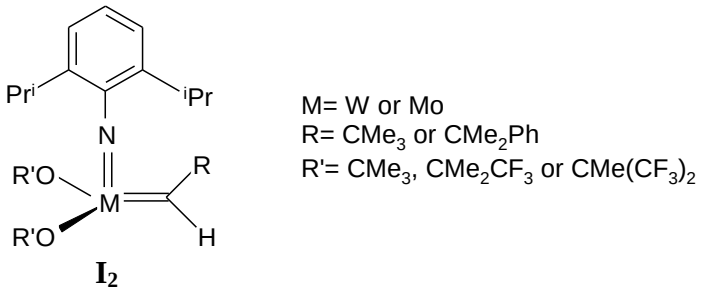


Figure 1.6. Schrock initiator (I_2)

In 1992, the most interesting initiator system, ruthenium initiator (I_3), Figure 1.7, was introduced by Grubbs.[54] These initiator showed a very good stability towards air, water and acids and is a highly active initiator in ROMP. Later on, by exchanging the aryl phosphine with cyclohexyl phosphine ligand in initiator (I_3) ruthenium initiator

(**I$_4$**) was produced. The initiator (**I$_4$**) showed more reactivity for the ROMP reaction and it polymerised relatively unstrained cyclic olefins in protic media.[55]

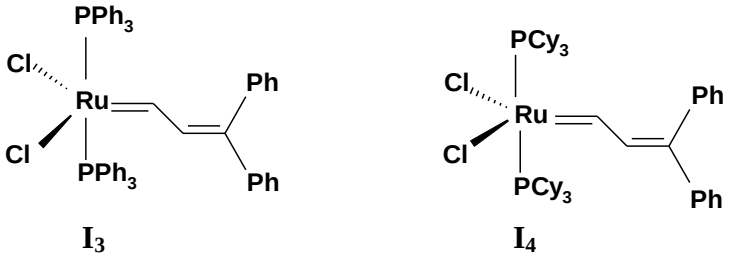
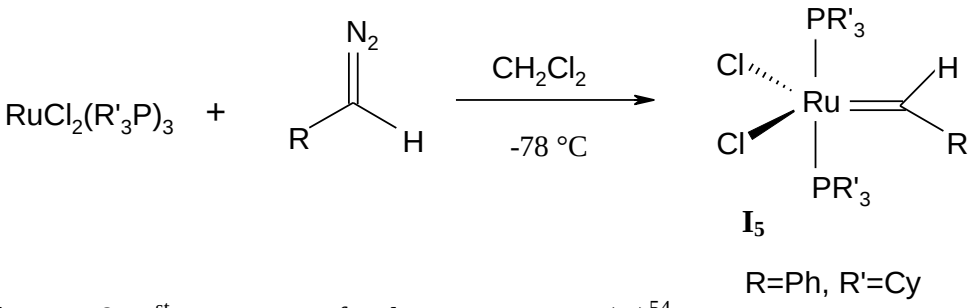


Figure 1.7. Ruthenium Initiators (**I$_3$,I$_4$**)

The main problems with initiator systems (**I$_3$**) and (**I$_4$**) was their low initiation rate and multistep synthesis. Therefore further developments were required, which led to the synthesis of the 1st generation ruthenium initiator (**I$_5$**), Scheme 1.9.

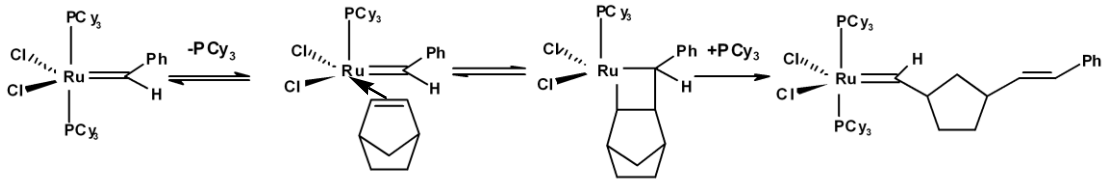


Scheme 1.9. 1st generation of ruthenium initiator (**I$_5$**)[54]

The 1st generation ruthenium initiator (**I$_5$**) has a high activity for the ROMP reaction and it is stable towards functional groups and the mechanism by which each step occurs is established.[56,57] Additionally, each step can be followed by ^{1}H NMR spectroscopy.

Initiation

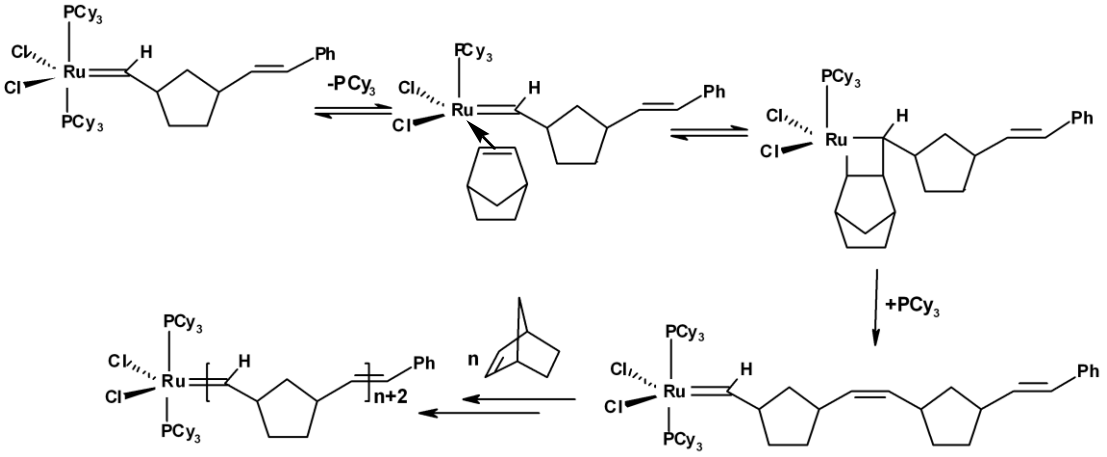
It is well-established that PCy_3 dissociates from $RuCl_2(PCy_3)_2(=C(H)Ph)$ initiator to enable the double bond of the monomer unit to react with the ruthenium-carbon double bond via a [2+2] cyclo-addition reaction to form a metallacyclobutane species. Degenerative cleavage of this four-membered ring results in the formation of the original reactants, whereas productive cleavage (initiation) results in the formation of a new alkylidene species, called the propagating alkylidene, Scheme 1.10.



Scheme 1.10. The initiation step using $RuCl_2(PCy_3)_2(=C(H)Ph)$ for ROMP

Propagation

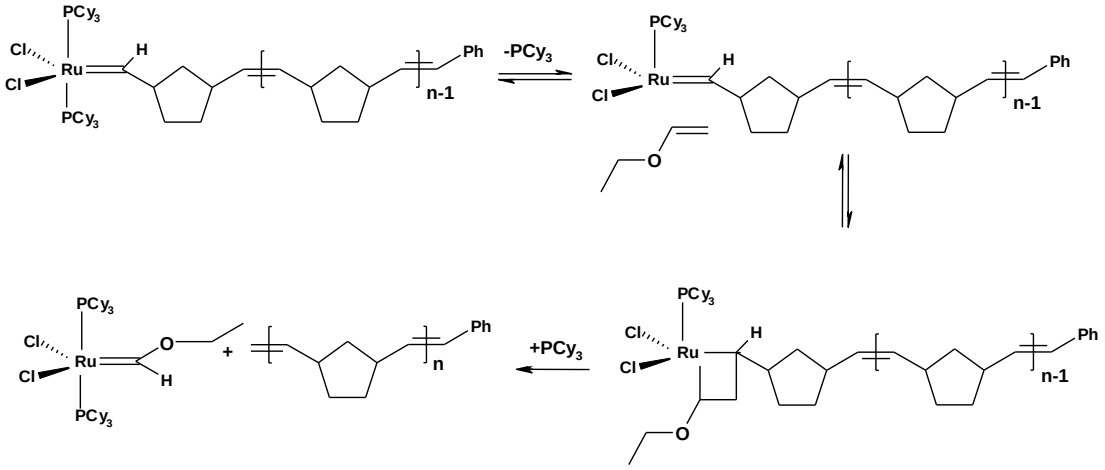
The insertion of subsequent monomer units into the active polymer chain-end is known as the propagation step. The monomer units insert via a [2+2] cyclo-addition reaction, which results in extending the length of the propagating polymer chain and consumption of the monomer, Scheme 1.11.



Scheme 1.11. The propagation steps using $RuCl_2(PCy_3)_2(=C(H)Ph)$ for ROMP

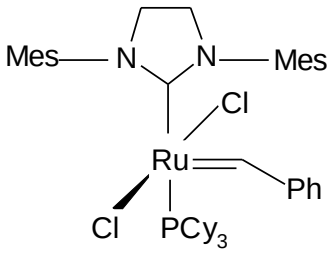
Termination

Once the monomer has been completely consumed, the propagating alkylidene species remain active in solution. If desired, a subsequent batch of a second monomer can be added to form a block copolymer, or the reaction can be terminated by the addition of an acyclic terminating agent. For ROMP reactions mediated by $RuCl_2(PCy_3)_2(=C(H)Ph)$, the most commonly used terminating agent is ethyl vinyl ether. Reaction of propagating ruthenium alkylidene species with ethyl vinyl ether results in almost exclusive formation (98%) of $RuCl_2(PCy_3)_2(=C(H)OEt)$ and CH_2 end-capped polymer, Scheme 1.12.[25]



Scheme 1.12. The termination step using $RuCl_2(PCy_3)_2(=C(H)Ph)$ for ROMP

It can be seen from the mechanism that the olefin metathesis reaction is dissociative in nature. Thus, a phosphine ligand must dissociate from the metal before olefin coordination. So, the 2nd generation of ruthenium initiator (**I_6**) was introduced containing N-heterocyclic carbene (NHC) based ligand, which is a strong σ-donor by comparison to phosphine ligand. Figure 1.8. The imidazole ligand is believed to play two important roles; firstly it is a better electron donor than PCy_3**,** therefore enhancing the initiators' activity towards olefins, and secondly, it is more sterically demanding than PCy_3 which helps to prevent (or to slow down) bimolecular decomposition reactions.[58]

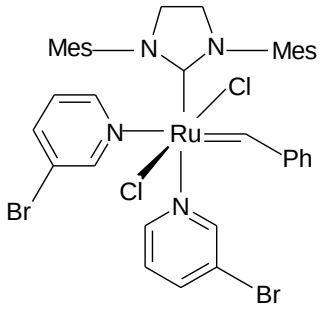


I_6

Figure 1.8. 2nd Generation ruthenium initiator (**I_6**)

The 2nd generation ruthenium initiator (**I_6**) showed good activity in a large number of ROMP reactions.[59] However, this initiator generally provides polymer with uncontrolled molecular weights and broad polydispersities, because the rate of propagation is bigger than the rate of initiation. This lack of control led to the formation of a new generation of ruthenium NHC-bearing complex (**I_7**), Figure 1.9.

This initiator not only displayed extremely high activities towards ROMP reaction but also showed a very fast rate of initiation in comparison to that of propagation. It made it possible to carry out living ROMP reactions of norbornene monomers and produced polymer with a very low PDI, (1.06).



I_7

Figure 1.9. Modified 2nd generation ruthenium initiator (**I_7**)

1.3.1.3 ROMP reaction of 5,6-substituted norbornene monomers

ROMP of monomer 2 (Figure 1.10) using initiators (**I_5**) and (**I_7**) was carried out in CH_2Cl_2.[60] Studies showed, the nature of monomer functional group has effect on polydispersities, molecular weights and properties of the resulting polymer.[61]

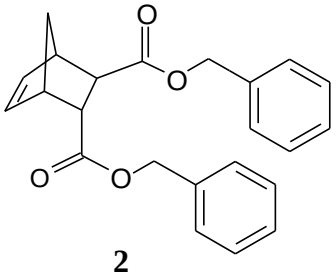


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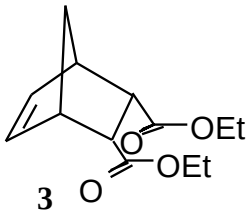
Figure 1.10. *exo, endo*-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dibenzyl ester[62](2)

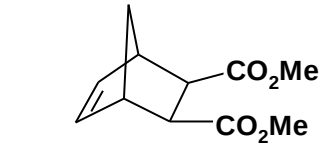
Endo norbornene monomer **3**, Figure 1.11, underwent ROMP reaction in the presence of initiators (**I_3**), and (**I_4**) in either dichloromethane (CH_2Cl_2) or 1,2-dichloroethane ($ClCH_2CH_2Cl$) at room temperature.[63]



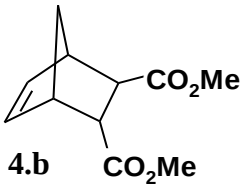
3

Figure 1.11. *Endo, endo*-5,6 diethoxynorbornene (**3**)

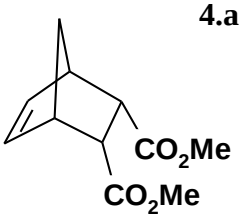
Norbornene derivatives containing oxygen **4(a,b)**, Figure 1.12 can be polymerised via ROMP utilising Grubbs' 1st generation ruthenium initiator (**I_5**) in $CDCl_3$.[64] In order to probe the stereoselectivity of the ruthenium catalytic system $[RuCl_2(p\text{-cymene})]_2$ (**I_8**), it was applied for the ROMP reaction of norbornene 2,3-dimethyl esters monomers **4(a-c)**, Polymerisation reactions were carried out in THF solvent and at 60°C and the resulting polymer showed only 1% yield for *endo, endo,* and *endo, exo* monomers **4(b-c)** whereas the *exo, exo* norbornene monomer 5a afforded a 33% isolated yield.[65]



4.a



4.b



4.c

Figure 1.12. *exo, exo*-5,6-dicarboxylic acid dimethyl ester (**4.a**), *endo, exo*-5,6-dicarboxylic acid dimethyl ester (**4.b**), *endo, endo*-5,6-dicarboxylic acid dimethyl ester (**4.c**)

The kinetic study of ROMP reactions of *exo, endo*-dicarboethoxy norbornene monomer **5** with ruthenium complexes (**I_5**) and (**I_6**), Figure 1.13, was studied and values for the rate of initiation as well as the rate of propagation of the initiators were determined. It revealed that N-heterocyclic carbene-based initiators polymerised with a higher rate of propagation than the rate of initiation, yielding polymers with a broader molecular weight distribution.[66]

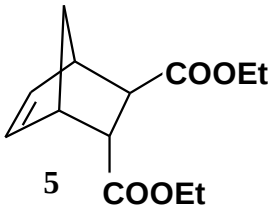


Figure 1.13. *Exo, endo*-dicarboethoxy norbornene monomer (**5**)

1.3.1.4 ROMP reaction of 5-substituted norbornene monomers

Ring-opening metathesis polymerisation of 5-carbomethoxy norbornene monomer **6**, Figure 1.14, was carried out in the presence of (**I_5**) initiator. ^{1}H NMR spectrum of the resulting polymer only showed the effect of head/tail placement of the monomer in the polymer backbone and showed no effects due to chelation.[67]

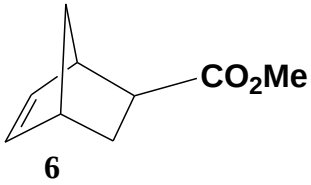


Figure 1.14. 5-Carbomethoxy norbornene monomer (**6**)

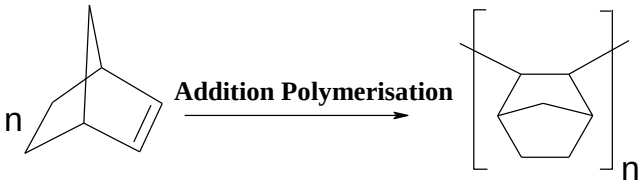
1.3.1.5 ROMP reaction of 1-substituted norbornene monomers

Although norbornene-1-methyl carboxylate compound has previously been synthesised, there are no reports of its polymerisation by ROMP reaction.

1.3.2 Addition polymerisation

Another method for polymerisation of norbornene monomers is addition polymerisation. In addition polymerisation only the double bond of the π-component opens and the product polymer contains saturated bonds, Scheme 1.13. The initiator systems that are used in addition polymerisation are divided into three categories: (a) early transition metals such as Ti-based, Zr-based (b) late transition-metal Pd(II)- and Ni(II)-based initiator ; and (c) less used initiator systems involving Cr and Co complexes.[68]

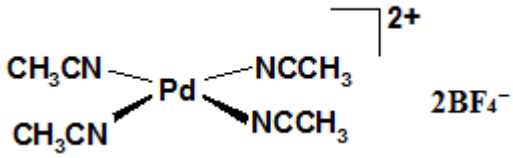
1.3.2.1 Background



Scheme 1.13. Addition polymerisation of norbornene

1.3.2.2 Addition polymerisation using palladium initiators

The first addition polymerisation of norbornene derivatives in the presence of palladium initiator $PdCl_2$ (**I_8**), was observed in 1966.[69,70] Later on, in 1970s, a $Pd(C_6H_5CN)_2Cl_2$ (**I_9**) initiator[71,72,73]and also $Pd(Ph_3P)_2Cl_2$ (**I_{10}**) initiator was used for the polymerisation of norbornene.[73] The most utilised initiator for norbornene polymerisation is the cationic palladium initiator system $[Pd(CH_3CN)_4](BF_4)_2$ (**I_{11}**) which was first introduced by Sen et al. in 1981,[74,75] Figure 1.15.



I_{11}

Figure 1.15. Palladium initiator described by Sen's team (**I_{11}**)

The (**I_{11}**) initiator system has a weakly bound acetonitrile ligand. Addition polymerisation of norbornene in the presence of Sen's initiator with the ratio of monomer to initiator (100:1) in nitromethane (CH_3NO_2) took place and polymer with more than 90% yield was obtained after 5 minutes. The polymer was not soluble in THF, $CHCl_3$, CH_2Cl_2, or C_6H_6 and full characterisation was not possible.[74-76] Later on the addition polymerisation of *exo*-and *endo*-substituted norbornene derivatives including ester groups[77-79] was investigated, but the rate of polymerisation was lower than that for unsubsituted norbornene.[78]

Addition polymerisation in the presence of Pd(II)-based initiator was investigated by Risse et al. in 1991 and the resulting polymer was characterised by GPC.[80,81] The most significant discovery in the research carried out by Risse was the ability of palladium initiator such as (η-allyl)Pd(II)(SbF_6) (**I_{12}**) which tolerated substituted

norbornene monomers, including oxygen-functionalised norbornene monomers such as esters.

Substituted palladium(II) initiator (**I_{13}**), Figure 1.16, were studied by Heitz and Wendorff and based on their observations the yield of the resulting polymers were very similar. The only thing had effect on the polymerisation was the nature of the nitrile residue.[82] Whether it was aromatic or aliphatic ligand. The polydispersity index of these polymers were between 1.3 and 1.5 which was taken as a sign for living polymerisations.

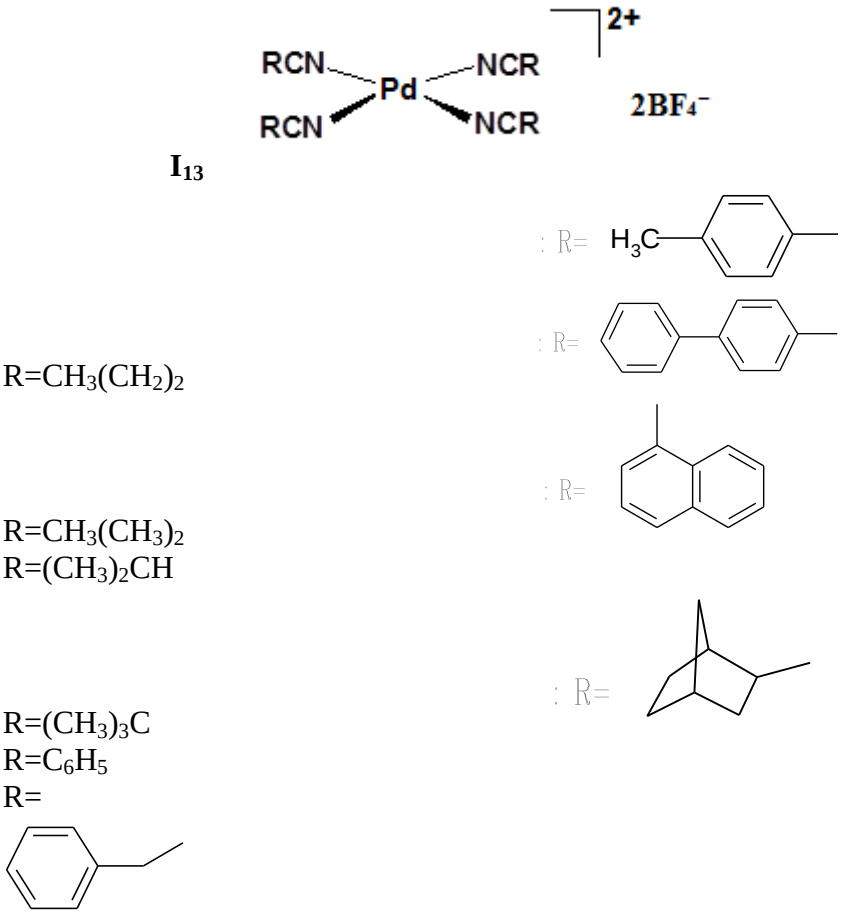
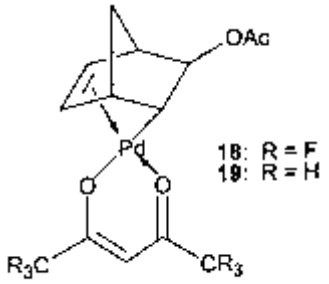


Figure 1.16. Palladium(II) initiator with different substituents were reported by Heitz and Wendorff (**I_{13}**)

A report by Safir and Novak in 1995 introduced a new series of palladium(II)-initiator (**I_{14}**), Figure1.17, for the polymerisation of bicyclic olefins. Their discovery showed a quantitative polymerisation of norbornene monomer in less than 15 minutes even if in wet THF.[83-85]

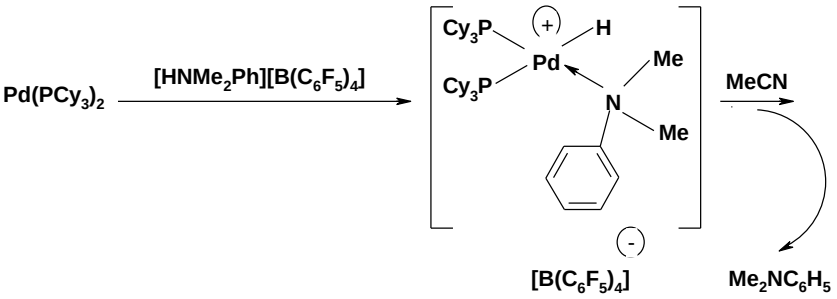


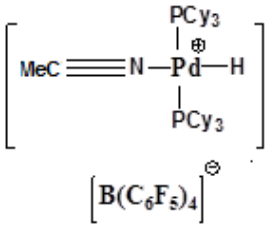
I_{14}

Figure 1.17. Safir and Novak's initiator system (**I_{14}**)

Relevant systems with coordinated cyclooctadiene (COD) ligands were developed and described in a patent by Goodball.[86] Recent research in this area has been extended to palladium phosphine systems. Sen showed that cationic palladium methyl species were effective in the polymerisation of oxygen-functionalised norbornene derivatives.[87] Brookhart reported the synthesis of $[H(OEt)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$, which suggested an alternative route to cationic palladium complexes with weakly coordinating counter ions.[88] Researchers at Promerus LLC developed palladium allyl system $[(\eta\text{-allyl})Pd(PCy_3)_2(ether)][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (**I_{15}**) containing a labile ether ligand and a weakly coordinating anion.[89]

Cationic palladium hydride complex $[Pd(H)(R_3P)_2MeCN)][B(C_6F_5)_4]$ (**I_{16}**) was also introduced as an active species for norbornene polymerisation.[90] One of the palladium initiator developed by Promerus is trans-$[(Pd(H)(Cy_3P)CH_3CN)]$ $[BF_4]$ which is prepared via oxidation of palladium by addition of acids. Another alternative route for producing this initiator is treating $Pd(PCy_3)_2$ with $[HNMe_2Ph][B(C_6F_5)_4]$ in acetonitrile to obtain the $[Pd(H)(Me_2NPh)(PCy_3)_2][B(C_6F_5)_4]$. Dimethylaniline can be easily eliminated by sonication and to produce_$[Pd(H)(MeCN)(PCy_{3)2}][B(C_6F_5)_4]$ (**I_{17}**), Scheme 1.14.[91]



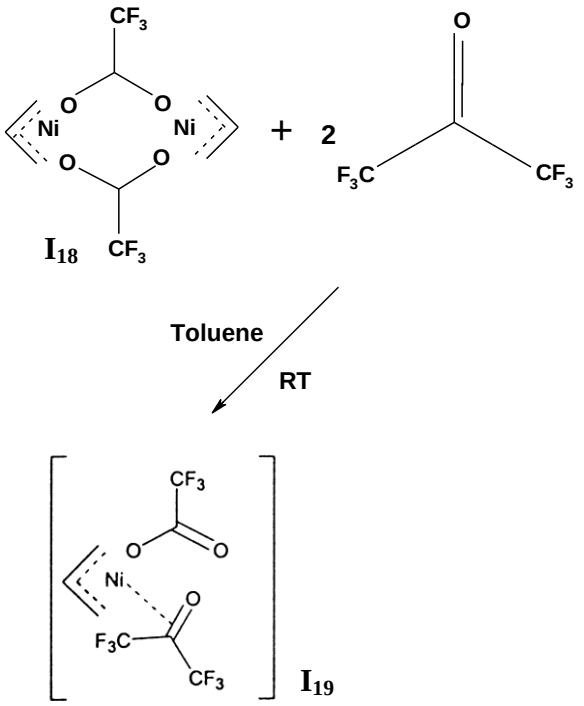


I$_{17}$

Scheme 1.14. Palladium hydride initiator developed by Promerus LLC[91]

1.3.2.3 Addition polymerisation using nickel initiators

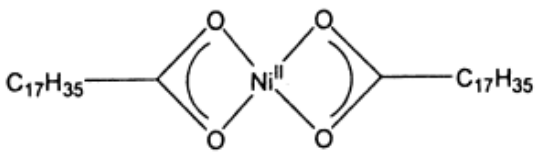
Addition polymerisation using nickel initiators was introduced for the first time in 1993 when Novak and Deming presented the nickel initiator systems (**I$_{18}$**,**I$_{19}$**), Scheme 1.15.[92]



Scheme 1.15. Nickel initiator systems were presented by Novak and Deming (**I_{18},I_{19}**)

Although norbornene monomer was inactive in the presence of **I_{18}** complex, it polymerised in the presence of **I_{19}** initiator.[93] The Addition polymerisation of norbornene monomer with nickel initiator is carried out in the presence of co-initiator MAO.[94,95]

Nickel-stearate initiator **I_{20}**, Figure 1.18, is another nickel complex for polymerisation of norbornene monomers under nitrogen atmosphere in toluene and chlororbenzene at room temperature.

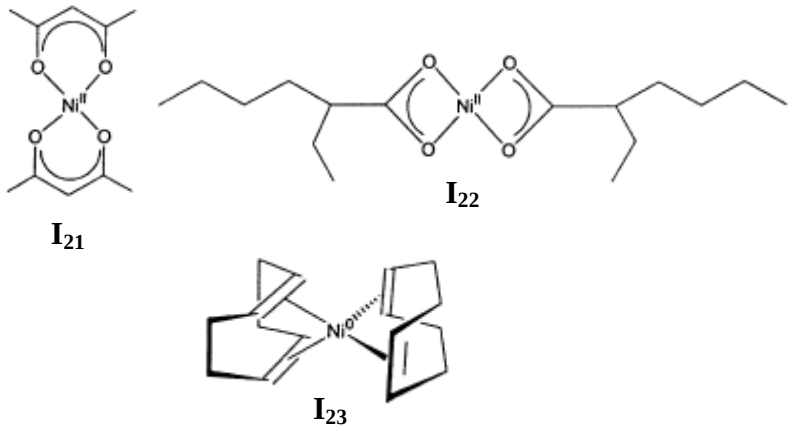


I_{20}

Figure 1.18. Nickel stearate initiator (**I_{20}**)

A report by Arndt and Gosmann showed polymerisation of norbornene using initiator systems: $Ni(acac)_2$ (**I_{21}**), $Ni(2\text{-ethylhexanoate})_2$ (**I_{22}**), and $(COD)_2Ni$

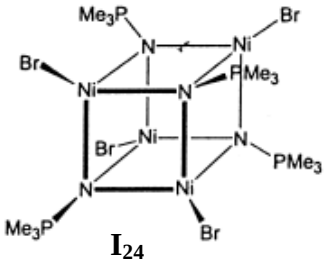
(COD=cyclooctadiene)(**I$_{23}$**), Figure 1.19, each employing MAO as a co-initiator. Polymerisation was carried out under argon atmosphere, in toluene and at room temperature.[95]



I$_{21}$ **I$_{22}$** **I$_{23}$**

Figure 1.19. Arndt and Gosmann initiator systems: Ni(acac)$_2$ (**I$_{21}$**), Ni(2-ethylhexanoate)$_2$ (**I$_{22}$**), (COD)$_2$Ni (COD=cyclooctadiene) (**I$_{23}$**)

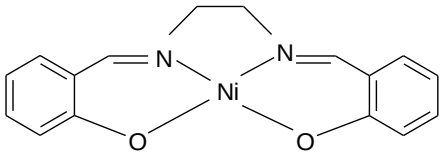
One of the most highly active initiator for the polymerisation of norbornene is the complex [BrNi(NPMe$_3$)]$_4$ (**I$_{24}$**), Figure1.20. In this polymerisation reaction the molar mass of the polynorbornene can be controlled through the variation in the parameters such as temperature, time and the molar ratio of Al:Ni. The molar ratio of Ni and Al has a very important effect on the yield of the reaction.



I$_{24}$

Figure 1.20. [BrNi(NPMe$_3$)]$_4$ nickel initiator (**I$_{24}$**)

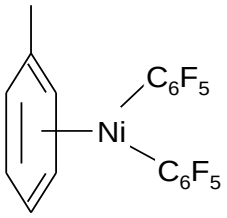
Addition polymerisation of norbornene was investigated by using Nickel (salen) (**I$_{25}$**), Figure1.21, as an initiator in chlorobenzene and the resulting polymer was soluble in 1,2,4-trichlorobenzene.[96]



I25

Figure 1.21. Nickel(Salen) initiator (**I25**)

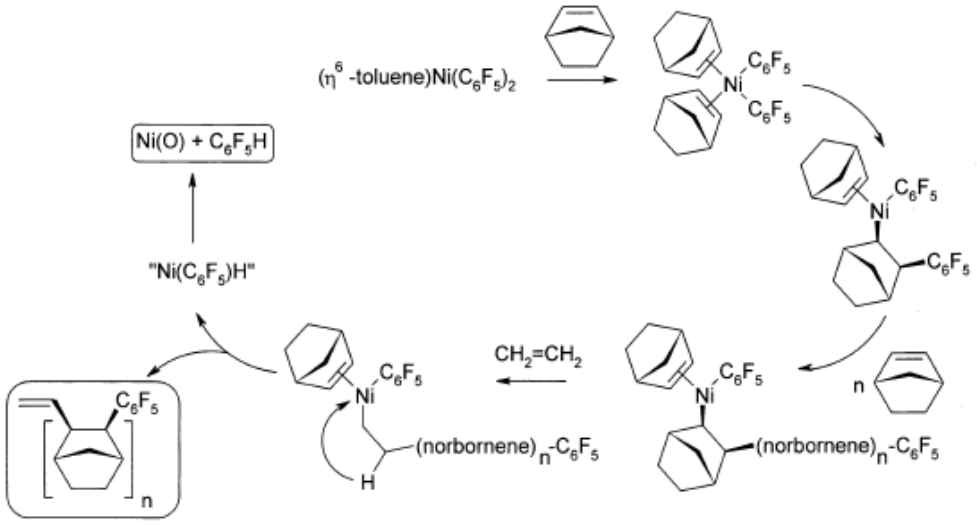
One of the most interesting complexes for norbornene polymerisation, reported by Klabunde, is the complex (η^6-toluene)Ni(C_6F_5)$_2$ (**I26**), Figure 1.22. During the polymerisation reaction, toluene can be easily replaced by a number of neutral, electron donors such as xylene, THF and norbornadiene.[97]



I26

Figure 1.22. (η^6-toluene)Ni(C_6F_5)$_2$ (**I26**)

The polymerisation of norbornene by Ni initiator (**I26**) in the presence of ethylene was reported.[116] Scheme 1.16, below shows the suggested mechanism for this polymerisation.

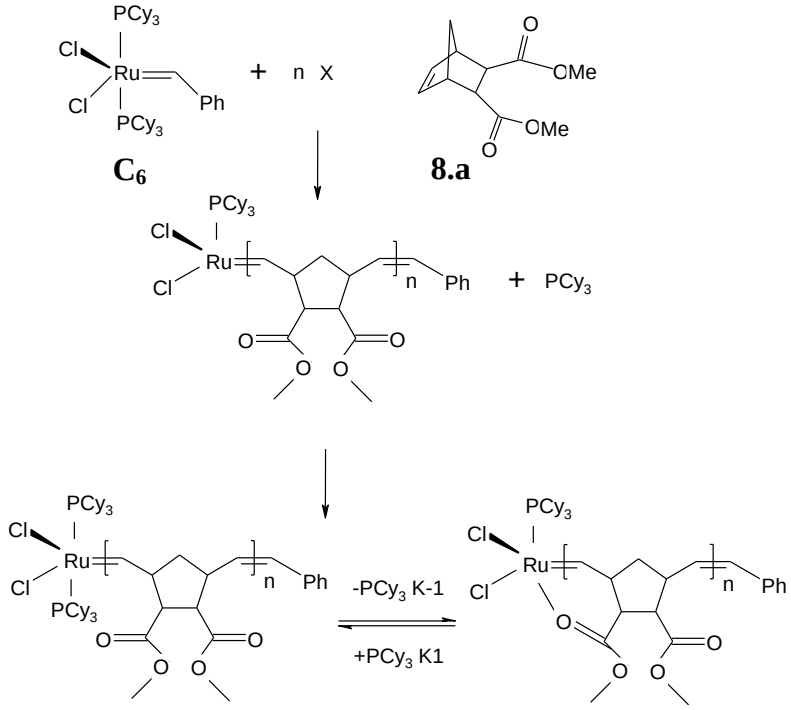


Scheme 1.16. Suggested mechanism for polymerisation of norbornene with (η^6-toluene) Ni(C_6F_5)$_2$ (**I26**) initiator [97]

1.4 Chelation of oxygen-containing functionality to the Ru-based and Pd-based metal centre

1.4.1 Ruthenium initiator

The monomer 8a, shown in Scheme 1.17, is polymerised in the presence of Grubbs 1st generation initiator (**I_5**). The ^{1}H NMR spectrum indicates possible formation of two propagating species (IIa & IIIa) and a residual initiator (I) in the alkylidene region of 17-21ppm see figure 1.24a. The two signals at 19.0-19.5 ppm (IIa) are believed to be the propagating alkylidene species with a pair of PCy_3 ligands bound to the Ru centre whereas, two signals at 18.4-18.8 ppm (IIIa) correspond to the equivalent species with only one PCy_3 ligand, the remaining coordination site being occupied by an oxygen atom emanating from the polymer backbone**,** Scheme 1.17.[98]



Scheme 1.17. ROMP reaction of 5-*exo*, 6-*endo*-dicarbometoxy norbornene monomer with Grubbs 1st generation initiator **(I_5)**

In order to identify species IIa and IIIa, excess of either PCy_3 or CuCl was added to the system. After adding 5 equivalents of PCy_3 only trace signals due to IIIa are observed and the signal due to the IIa increases, Figure1.23b. This is due to the excess phosphine ligand and forcing the equilibrium as it is shown in Scheme 1.17.

towards the two PCy_3 ligand coordinate system (IIa). When CuCl is added to the reaction mixture it acts as a phosphine sponge and PCy_3 ligands are trapped. In this case of the coordination site on the ruthenium centre remains vacant allowing oxygen from the polymer backbone to chelate to the ruthenium centre. Therefore only the signal due to the IIIa species is observed, Figure 1.23c.

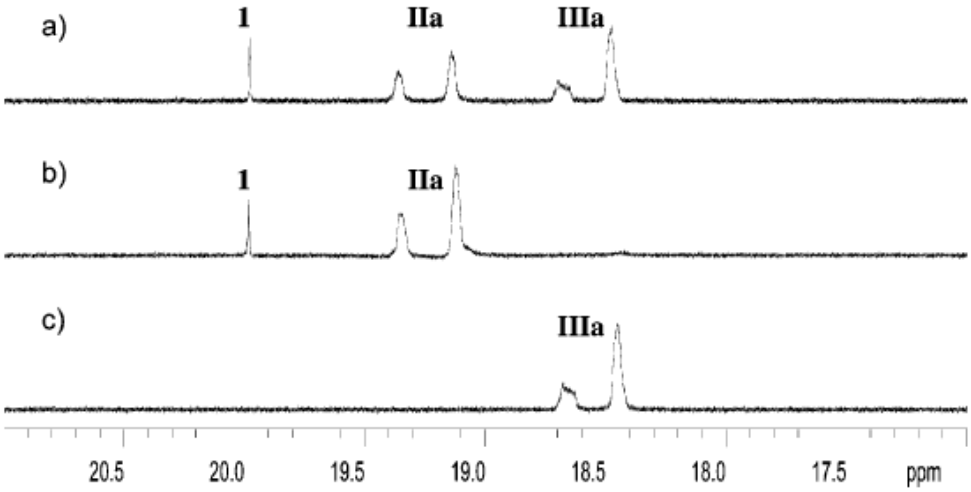


Figure 1.23. Alkylidene region of the ^1H NMR spectrum when (a) is subjected to ROMP reaction with Grubbs 1st generation initiator ($\mathbf{I_5}$), (b) upon the addition of 5 equiv. of Cy_3 and (c) upon the addition of 10 equiv of CuCl. $[M]_0/[I]_0=20$, $[I]_0=15$ mM[98]

1.4.2 Palladium initiator

Polymerisation of *endo*-and *exo*-substituted norbornenes, Figure 1.24, was investigated and found that *endo*-substituted norbornenes are polymerised slower than their corresponding *exo* isomers. The main reason for the slower rate of polymerisation is reported to be the coordinating ability of the *endo*. But the size of the substituent functionality was also found to be important.[99] It was reported that the rate of the polymerisation is decreased by the formation of chelated complex upon the coordination of *endo*-functionalised norbornene to the palladium center.[98]

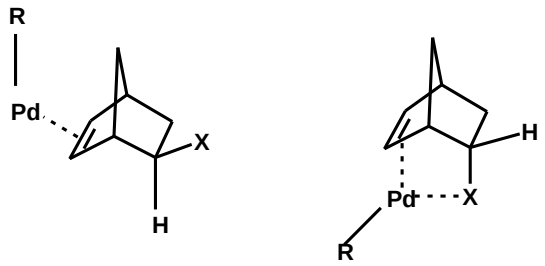


Figure 1.24. Modes of bonding for functionalised norbornene derivatives (X=coordinating functionality)

A report illustrates, formation of a chelated complex had two effects on the rate of polymerisation. Firstly, chelation may strengthen the metal-olefin interaction, thereby raising the barrier for the insertion step. Secondly, it forces insertion through the *endo* face, which is in sharp contrast to the known preference for norbornene to inset into the metal-carbon of metal-hydride bond through the less hindered *exo* face. The *endo* insertion of an *endo*, ester-functionalised norbornene into a metal hydride bond was investigated.[88] Possible *endo* and *exo* binding modes are illustrated in Figure 1.25.

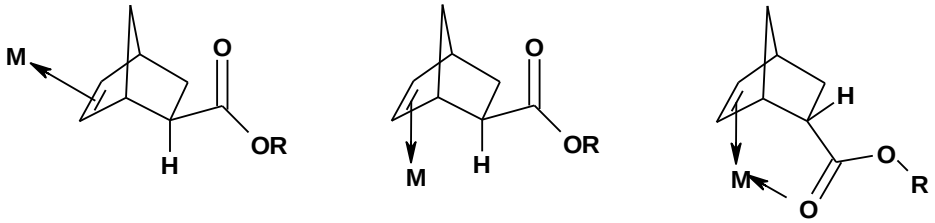


Figure 1.25. Modes of binding for ester-functionalised norbornenes

Sen and coworkers investigated many other cases in which monomer substituents can influence polymerisation activity, using cationic palladium(II)-based initiators.[99] This study showed the preference for *exo* uptake for 5-n-butyl-2-norbornene (Butyl-NB), which does not contain a coordinating functionality. In addition, the rate of polymerisation was shown to decrease in the order butyl-NB> hexyl-NB> decyl-NB. This confirms that coordination of the *endo* functionality is not the sole explanation for this preference. In Figure 1.26, was shown even for coordination and insertion through the *exo* face, for the *endo* isomer there is an unfavourable interaction between the substituent and the vinylic hydrogen that is being rehybridised from sp^2 to sp^3 upon coordination and insertion into the palladium alkyl bond. This raises the energy barrier for the insersion of the *endo* isomer, which results in a decrease in the polymerisation rate.[99]

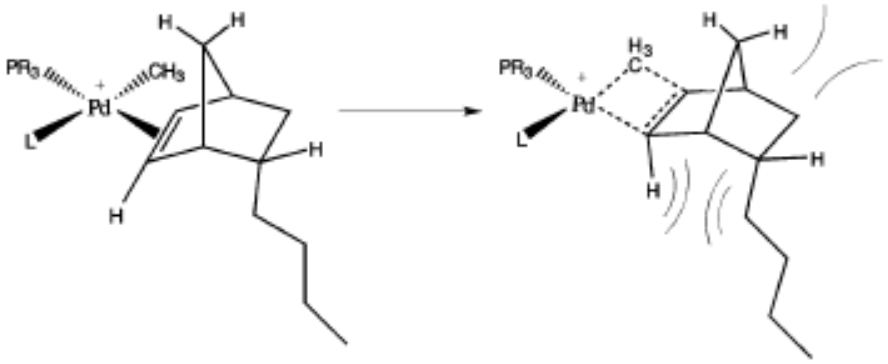


Figure 1.26. Steric compression in the insertion of *endo*-Butyl-NB

In addition to the coordination-chelation and steric effects discussed above, another factor that can diminish the rate of polymerisation of both the *endo* and *exo* isomers is the coordination of the functionality on the monomer to the metal centre, with or without chelation. This was supported by the observation that coordinating solvents such as acetonitrile or ethyl acetate attenuate the polymerisation activity of the initiator. However, when a stable chelate is formed, such as when the ring formed is optimised to 6 members, chelation will also play a major role in slowing down the polymerisation of *endo* isomer.

Chapter 2 Experimental

2.1 Materials

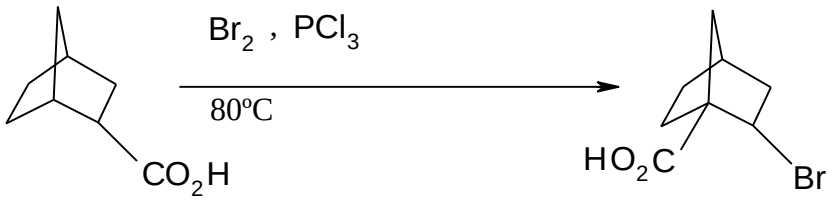
Norbornane-2-carboxylic acid was supplied by Promerus and was used without further purification. PCl_3 (Aldrich), Br_2 (Aldrich), $Na_2S_2O_4$ (Aldrich), $MgSO_4$ (Aldrich), DMS (dimethyl sulphate) (Aldrich), K_2CO_3 (Aldrich), HCl (Aldrich), $NaHCO_3$ (Aldrich), potassium t-butoxide (Aldrich), and NH_4OH (Aldrich), TCE (trichloroethane) (Aldrich), toluene (Aldrich), were used without further purification. Acetone (Fisher Scientific) and t-butyl alcohol (Aldrich) were stored over molecular sieves before use. Ruthenium initiator (Aldrich), palladium initiator $[(PCy_3)_2(CH_3CN)Pd(H)][B(C_6F_5)_4]$(Pd1388) (Promerus), nickel initiator ($\acute{\eta}^6$-toluene)$Ni(C_6F_5)_2$ (Promerus) were used without further purification.

2.2 Analytical measurements

All NMR spectra were recorded using a Bruker-400 or a Varian-VXR 400, both operating at 400 MHz, for ^1H spectra, and 100 MHz for ^{13}C spectra, or Mercury-200 operating at 200 MHz (^1H spectra only), and chemical shifts were recorded in parts per million (δ) referenced to TMS at 0 ppm. Molecular weight analyses were carried out by size exclusion chromatography (SEC) on a Visctek TDA 302 with refractive index, viscosity and light scattering detector (with a 690 nm wavelength laser). Two 300 nm PLgel 5 µm mixed C columns (with a linear range of molecular weight from 200 to 2000 000 $g.mol^{-1}$) were used. THF was used as the eluent with a flow rate of 1.0 $mL.min^{-1}$ at 30 °C.

2.3 Synthesis of norbornene-1-methyl carboxlate monomer

2.3.1 Bromination of norbornane-2-carboxylic acid



2.3.1.1 Small-scale synthesis

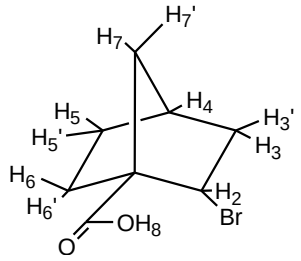
Norbornane-2-carboxylic acid (99.2 g, 0.71 mol) was added into a 3-necked flask equipped with a magnetic stirrer bar and kept under nitrogen. Bromine (40 mL, 0.78 mol) was added in small portions under nitrogen. Phosphorus trichloride (PCl_3) (1.7 mL, 0.02 mol) was then added and the mixture was heated at reflux for 8 hours at 80 °C. Then, more bromine (20 mL, 0.4 mol) was added and the reaction maintained at reflux overnight. A mixture of ether:water (2000 mL, 1:5 v/v) was added to the crude product and the mixture was stirred for 30 minutes. A solution of $Na_2S_2O_4$ (115 g, 0.66 mol) in ether (1500 mL) was added with stirring. The reaction was exothermic and the colour changed from red to pale yellow. The organic layer was separated, dried over $MgSO_4$ and isolated by filtration. Ether was removed on a rotary evaporator resulting in an oily yellowish coloured product. The oily product was then washed with hexane once producing a white powder; 105.12 g, 0.48 mol; yield 68%.

2.3.2.2 Large-scale synthesis

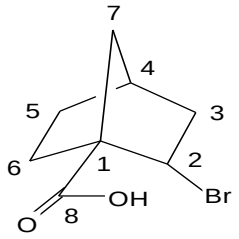
Norbornane-2-carboxylic acid (205.96 g, 1.47 mol) was added into a 3-necked flask equipped with a magnetic stirrer bar and kept under nitrogen. Bromine (82 mL, 1.60 mol) was added in small portions under nitrogen. Phosphorus trichloride (PCl_3) (3.5 mL, 0.04 mol) was added and the mixture was heated at reflux for 8 hours at 80 °C. Then, more bromine (42 mL, 0.82 mol) was added and the reaction maintained at reflux overnight. A mixture of ether:water (5000 mL, 1:5 v/v) was added to the crude product and the mixture was stirred for 30 minutes. A solution of $Na_2S_2O_4$ (181.51 g, 1.04 mol) in ether (2400 mL) was added with stirring. The reaction was exothermic and the colour changed from red to pale yellow. The organic layer was separated,

dried over $MgSO_4$ and isolated by filtration. Ether was removed on a rotary evaporator resulting in an oily yellowish coloured product. The oily product was then washed with hexane once producing a white powder; 149.11 g, 0.68 mol; yield 46.3%.

^{1}H NMR, ($CDCl_3$, 400 MHz) δ (ppm): 11.9 (s, 1H, H^8), 4.17 (s, 1H, H^2), 2.28 (m, 1H, H^4), 2.20 (m, 1H, H^3), 2.06 (m, 1H, $H^{7´}$), 1.97 (m, 1H, $H^{6´}$), 1.63 (m, 1H, $H^{3´}$), 1.59 (m, 1H, $H^{5´}$), 1.57 (m, 1H, H^6), 1.26(m, 1H, H^5), 1.23 (m, 1H, H^7). ^{13}C NMR, ($CDCl_3$, 100 MHz, ^{1}H decoupled 400 MHz) δ (ppm): 179 (s, C^8), 59 (s, C^1), 53 (s, C^2), 44 (s, C^3), 36.59 (s, C^4), 36.57 (s, C^6), 33 (s, C^7), 29 (s, C^5)

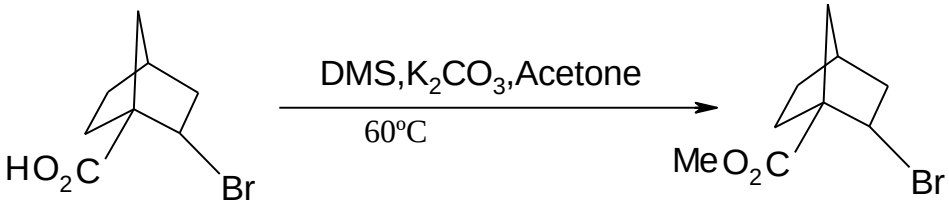


IUPAC assignment of H-atoms within 2-bromonorbornane-1-carboxylic acid



IUPAC assignment of carbon atoms within 2-bromonorbornane-1-carboxylic acid

2.3.2 Methylation of 2-bromonorbornane-1-carboxylic acid



2.3.2.1 Small-scale synthesis

2-Bromonorbornane-1-carboxylic acid (20 g, 0.09 mol) and K_2CO_3 (14.2 g, 0.10 mol) were placed into a 3-necked flask equipped with a magnetic stirrer bar. The flask was kept under reduced pressure for 20 minutes and then kept under nitrogen, acetone (250 mL) was added under N_2 and the mixture was heated to 60 °C to reflux. When the reflux started, DMS (9.7 mL, 0.10 mol) was added in small portions. The mixture was heated at reflux for 6 hours (the colour was yellowish cream). The flask was cooled to room temperature, the mixture was filtered and the filtrate was collected in a one-necked flask. The excess DMS was quenched with NH_4OH (5 mL) and the

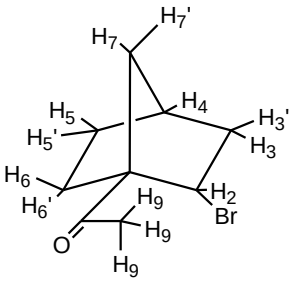
volume was reduced to half and ethyl acetate (50 mL) was added. The mixture was washed with HCl (10%, 40 mL) three times and the organic layer was collected. The organic layer was washed with $NaHCO_3$ (5%) (100 mL) and NaCl (25%) (100 mL). The mixture was then washed three times with water and finally dried over $MgSO_4$. The mixture was filtered and ethyl acetate was removed by a rotary evaporator. A brown oily compound was produced; 15.84 g, 0.07 mol; yield 78%

2.3.2.2 Large-scale synthesis

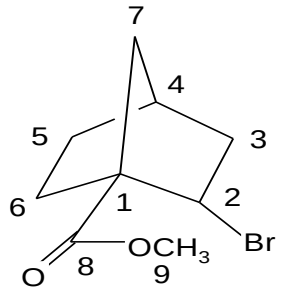
2-Bromonorbornane-1-carboxylic acid (135 g, o.62 mol) and K_2CO_3 (104 g, 0.75 mol) were placed into a 3-necked flask, equipped with a magnetic stirrer bar. The flask was kept under reduced pressure for 20 minutes and then kept under nitrogen, acetone (1500 mL) was added under N_2 and the mixture was heated to 60 °C to reflux. When the reflux started, DMS (100 mL, 1.05 mol) was added in small portions. The mixture was heated at reflux for 6 hours (the colour is yellowish cream). The flask was cooled to room temperature, the mixture was filtered and the filtrate was collected in a one-necked flask. The excess DMS was quenched with NH_4OH (5 mL) and the volume was reduced to half and ethyl acetate (50 mL) was added. The mixture was washed with HCl (10%, 40 mL) three times and the organic layer was collected. The organic layer was washed with $NaHCO_3$ (5%) (600 mL) and NaCl (25%) (600 mL). The mixture was then washed three times with water and dried over $MgSO_4$. The mixture was filtered and ethyl acetate was removed by a rotary evaporator. A brown oily compound was produced; 134 g, 0.58 mol; yield 91.94%.

Note: DMS is very sensitive to moisture, highly toxic and corrosive and therefore careful operation is recommended.

^{1}H NMR, ($CDCl_3$, 400 MHz) δ (ppm): 4.2 (s, 1H, H^2), 3.72 (s, 3H, H^9), 2.34 (m, 1H, H^4), 2.22 (m, 1H, H^3), 2.14 (m, 1H, $H^{7´}$), 1.96 (m, 1H, $H^{6´}$), 1.70 (m, 1H, $H^{3´}$), 1.64 (m, 1H, $H^{5´}$), 1.60 (m, 1H, H^6), 1.28 (m, 1H, H^5), 1.23 (m, 1H, H^7). ^{13}C NMR, ($CDCl_3$, 100 MHz, ^{1}H decoupled 400 MHz) δ (ppm): 173 (s, C^8), 59 (s, C^1), 54 (s, C^2), 52 (s, C^9) 43 (s, C^3), 37.2 (s, C^4), 36.6 (s, C^6), 32 (s, C^7), 29 (s, C^5).

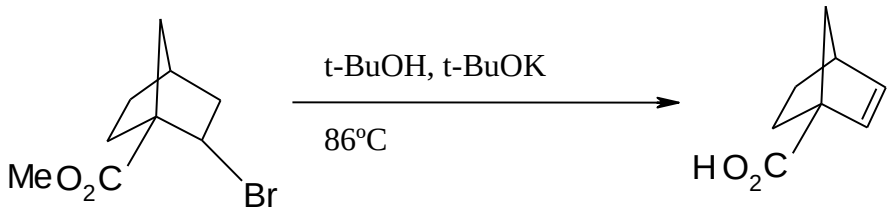


IUPAC assignment of H-atoms within methyl 2-bromonorbornane-1-carboxylate



IUPAC assignment of carbon atoms within methyl 2-bromonorbornane-1-carboxylate

2.3.3 Dehydrobromination of 2-bromonorbornane-1- methyl carboxylate



2.3.3.1 Small-scale synthesis

t-Butyl alcohol (22 g, 0.30 mol) and potassium t-butoxide (11 g, 0.10 mol) were weighed into a 3-necked flask in the glove box. The flask was connected to nitrogen, and 2-bromonorbornane-1- methyl carboxylate (10 g, 0.04 mol) was added drop-wise. The heterogeneous milky cream mixture was heated at reflux at 86 °C for 3 hours after which water (4 mL) was added to the mixture; the colour changed to brown. The reflux was continued for 24 hours. Further water (14 mL) was added and the solvent was distilled off (100 mL total) until the temperature of the material reached to 100 ºC. The caustic residue was chilled, extracted once with ether to remove some oily material, and then strongly acidified with concentrated hydrochloric acid. The precipitated material (norbornene-1-carboxylic acid compound) was collected; 3.5 g, 0.025 mol; yield 58.14%.

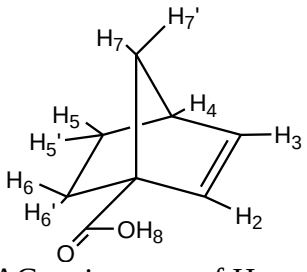
Note: During the distillation MeOH and ^{t}BuOH were collected at 38-80 ºC. More water was added to the mixture and distillation was continued until the distillate temperature reached 100 °C. The distillation was continued until all water was removed.

2.3.3.2 Large-scale synthesis

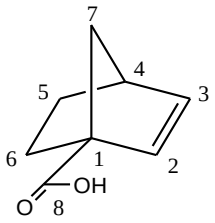
t-Butyl alcohol (242 g, 3.27 mol) and potassium t-butoxide (158 g, 1.41 mol) were weighed into a 3-necked flask in the glove box. The flask was connected to nitrogen, and 2-bromonorbornane-1- methyl carboxylate (130 g, 0.56 mol) was added drop-wise. The heterogeneous milky cream mixture was heated at reflux at 86 °C for 3 hours after which water (57 mL) was added; the colour changed to brown. The reflux was continued for 24 hours. Further water (200 ml) was added and the solvent was distilled off (100 mL total) until the temperature of the material reached to 100 ºC. The caustic residue was chilled, extracted once with ether to remove some oily material, and then strongly acidified with concentrated hydrochloric acid. The precipitated material was collected the impure acid is brown colour; 71.68 g, 0.52 mol; yield 92.86%.

During the distillation MeOH, t-BuOH was collected at 38-80 ºC. More water was added to the mixture and distillation was continued until the distillate temperature reached 100 °C. The distillation was continued until all water was removed. Recrystallisation from water produced fine colourless needles of norbornene-1-carboxylic acid; 38 g, 0.28 mol; yield 50%.

^{1}H NMR, ($CDCl_3$, 400 MHz) δ (ppm): 11.8 (s, 1H, H^8), 6.08 (dm, 2H, H^2, H^3), 2.88 (s,1H, H^4), 1.98 (m, 1H, $H^{6´}$), 1.8 (m, 1H, H^6), 1.58(m, 1H, $H^{7´}$), 1.42 (m, 1H, H^7), 1.28 (m, 1H, $H^{5´}$), 1.04 (m, 1H, H^5). ^{13}C NMR, ($CDCl_3$, 100 MHz, ^{1}H decoupled 400 MHz) δ (ppm): 182(s, C^8), 136 (s, C^3), 134 (s, C^2), 63 (s, C^1), 52 (s, C^7), 43 (s. C^4), 30 (s, C^6), 27 (s, C^5).

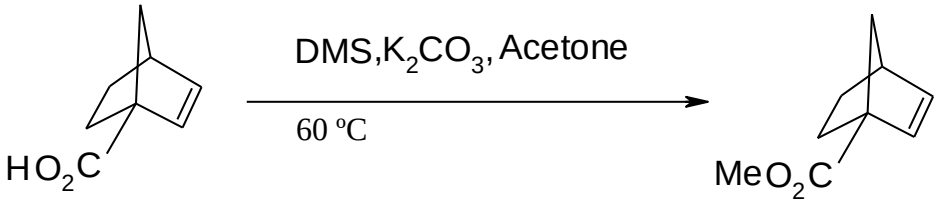


IUPAC assignment of H-atoms within norbornene-1-carboylic acid



IUPAC assignment of carbon atoms within norbornene-1-carboxylic acid

2.3.4 Methylation of norbornene-1-carboxylic acid



2.3.4.1 Small-scale synthesis

Norbornene-1-carboxylic acid (2.32 g, 0.02 mol) and K_2CO_3 (3.32 g, 0.02 mol) were placed into a 3-necked flask equipped with a magnetic stirrer bar. The flask was kept under reduced pressure for 20 minutes and then kept under nitrogen, Acetone (50 mL) was added under N_2 and the mixture was heated at reflux at 60 °C. When the reflux started, DMS (2.3 mL, 0.02 mol) was added in small portions. The mixture was refluxed for 6 hours (the colour was yellowish cream). The flask was cooled at room temperature, and the mixture was filtered. Filtrate was collected into one-necked flask, the excess of DMS was quenched with NH_4OH (l mL) and the volume was reduced to half and ethyl acetate (50 mL) was added. The mixture was washed with HCl (10%, 40 mL) three times and the organic layer was collected. The organic layer was washed with $NaHCO_3$ (5%) (50 mL) and NaCl (25%) (50 mL). The mixture was then washed three times with water and dried over $MgSO_4$. The mixture was filtered and ethyl acetate was removed by a rotary evaporator. The monomer was distilled under reduced pressure (66°C, 6 mbar).

The monomer was dissolved in ether and was washed with a solution of $Na_2S_2O_4$. The organic layer was collected, dried over $MgSO_4$ and was filtered, Ether was removed by a rotary evaporator. A colourless liquid norbornene-1-methyl carboxylate monomer was obtained; 1 g, 0.007 mol; yield 35%. The monomer was stored over molecular sieves.

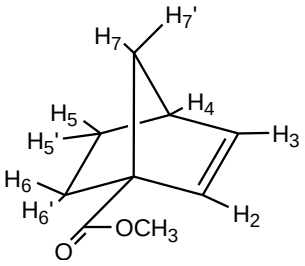
2.3.4.2 Large-scale synthesis

Norbornene-1-methyl carboxylate (37 g, 0.28 mol) and K_2CO_3 (45 g, 0.33 mol) were placed into a 3-necked flask equipped with a magnetic stirrer bar. The flask was kept under reduced pressure for 20 minutes and then kept under nitrogen, Acetone (500 mL) was added under N_2 and the mixture was heated at reflux at 60 °C. When the reflux started, DMS (31 mL, 0.33 mol) was added in small portions. The mixture was

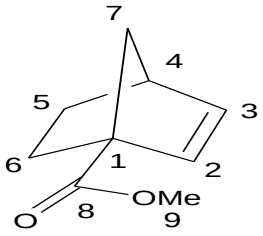
refluxed for 6 hours (the colour is yellowish cream). The flask was cooled at room temperature, the mixture was filtered and the filtrate was collected into a flask. The excess of DMS was quenched with NH_4OH (14 mL) and the volume was reduced to half and ethyl acetate (100 mL) was added. The mixture was washed with HCl (10%, 70 mL) three times and the organic layer was collected. The organic layer was washed with $NaHCO_3$ (5%) (300 mL) and NaCl (25%) (300 mL). The mixture was then washed three times with water and dried over $MgSO_4$. The solution was filtered and ethyl acetate was removed by a rotary evaporator. The monomer was yellow, 20 g, 0.13 mol, yield; 48.15%.

The monomer was dissolved in ether and was washed with a solution of $Na_2S_2O_4$. The organic layer was collected, dried over $MgSO_4$ and was filtered, Ether was removed by a rotary evaporator. A colourless liquid norbornene-1-methyl carboxylate monomer was obtained; 14.84 g, 0.01 mol; yield 37.04%. The monomer was stored over molecular sieves.

^{1}H NMR, ($CDCl_3$, 400 MHz) δ (ppm): 6.17(m, 2H, H^2, H^3), 3.74 (s, 3H, H^9), 2.94 (s, 1H, H^4), 2.0 (m, 1H, $H^{6'}$), 1.82 (m, 1H, H^6), 1.59 (m, 1H, $H^{7'}$), 1.49 (m, 1H, H^7), 1.32 (m, 1H, $H^{5'}$), 1.1 (m, 1H, H^5). ^{13}C NMR, ($CDCl_3$, 100 MHz, ^{1}H decoupled 400 MHz) δ (ppm): 176 (s, C^8), 137 (s, C^3), 134(s, C^2), 52 (s, C^7), 51.86 (s, C^9), 43 (s, C^4), 31 (s, C^6), 27 (s, C^5).



IUPAC assignment of H-atoms within norbornene-1-methyl carboxylate



IUPAC assignment of carbon atoms within norbornene-1-methyl carboxylate

2.4 Polymerisation Reactions

2.4.1 ROMP reaction of norbornene-1-methyl carboxylate monomer

2.4.1.1 ROMP reaction of norbornene-1-methyl carboxylate monomer using ruthenium 1st generation initiator [RuCl2(PCy3)2(=CHPh)]

2.4.1.1.1 Norbornene-1-methyl carboxylate monomer: 1st generation ruthenium initiator (10:1)

The Polymerisation reaction was performed in the glove box at room temperature. Ruthenium initiator, 1st generation, (10 mg, 0.01 mmol) and norbornene-1-methyl carboxylate monomer (10 equivalents, 5.4 mg, 0.036 mmol) were dissolved in $CDCl_3$ (1 mL), in two different vials and were stirred for a few minutes to allow them to dissolve. The monomer solution was transferred into the vial containing initiator and the mixture was stirred for two minutes. The reaction mixture was then transferred to the screw capped NMR tube. The NMR tube was removed from the glove box and the proton NMR spectrum was recorded at different time intervals. The ^1H NMR was taken after 24 hours at room temperature; the ^1H NMR indicated the presence of unreacted monomer therefore the reaction was heated to 40 °C in an oil bath. In order to recover any product the reaction mixture was transferred into the vial, ethyl vinyl ether (0.2 mL) was added to terminate the reaction and stirred for 20 minutes. The volume of the reaction mixture was reduced to one third and then was added dropwise into another vial containing hexane (10-fold excess), resulting in the precipitation of the product. The product was dried under reduced pressure at room temperature overnight.

2.4.1.1.2 Norbornene-1-methyl carboxylate monomer: 1st generation ruthenium initiator (1:1)

The polymerisation reaction was performed in the glove box at room temperature. Ruthenium initiator, 1st generation, (60 mg, 0.073 mmol) and norbornene-1-methyl carboxylate monomer (11.8 mg, 0.078 mmol) were dissolved in $CDCl_3$ (1 mL), in two different vials and were stirred for a few minutes to allow them to dissolve. The monomer solution was transferred into the vial containing (0.073 mmol/mL) initiator and the mixture was stirred for two minutes. The reaction mixture was then

transferred to the screw capped NMR tube. The NMR tube was removed from the glove box and the proton NMR spectrum was recorded at different time intervals.

2.4.1.1.3 Scaling up ROMP reaction using norbornene-1-methyl carboxylate monomer: 1st generation ruthenium initiator (1:1)

The polymerisation reaction was performed in the glove box at room temperature. The initiator (1980 mg, 2.41 mmol) and monomer (365 mg, 2.40 mmol) were dissolved in $CDCl_3$ (6.7 mL), in two different vials and stirred for few minutes to allow its content to dissolve. The monomer solution was transferred into the vial containing initiator and the mixture was stirred for few minutes. The course of the reaction was monitored by NMR at different time intervals.

2.4.1.2 ROMP of exo-N-ethylhexyl norbornene-5,6-dicarboxyimide using the chelated product as an initiator; monomer:chelated product of 10:1

The polymerisation reaction was performed in the glove box at room temperature. The product of the reaction 2.4.1.1.2 (27.5 mg, 0.04 mmol) and monomer (10 equivalents, 109 mg, 0.4 mmol) were dissolved in toluene-d_8 (1 mL), in two different vials and were stirred for few minutes to allow them to dissolve. The monomer solution was transferred into the vial containing the product of reaction 2.4.1.1.2 and the mixture was stirred for few minutes. The reaction mixture was then transferred to the screw capped NMR tube. The NMR tube was removed from the glove box and the spectrum was recorded at different time intervals. The first NMR was taken after 15 minutes at room temperature; the NMR indicated the presence of unreacted monomer therefore the reaction mixture was heated to 100 °C in an oil bath. In order to recover the product the reaction mixture was transferred into the vial, ethyl vinyl ether (0.2 mL) was added to terminate the reaction and stirred for 20 minutes. The volume of the reaction mixture was reduced to one third and then was added dropwise into another vial containing hexane (10-fold excess); resulting in the precipitation of the product. The product was dried under reduced pressure at room temperature overnight.

The experiment 2.4.1.1.2 was repeated. The product of the reaction 2.4.1.1.2 (27.5 mg, 0.04 mmol) and monomer (10 equivalents, 107 mg, 0.39 mmol) were dissolved in toluene-d_8 (1 mL), in two different vials and were stirred for few minutes to allow

them to dissolve. The monomer solution was transferred into the vial containing the product of reaction 2.4.1.1.2 and the mixture was stirred for two minutes. The reaction mixture was then transferred to the screw capped NMR tube. The NMR tube was removed from the glove box and the spectrum was recorded at different time intervals. The NMR was taken after 24 hours at room temperature; the NMR indicated the presence of unreacted monomer therefore the reaction mixture was heated to 100 °C in an oil bath. In order to recover the product the reaction mixture was transferred into the vial, ethyl vinyl ether (0.2 mL) was added to terminate the reaction and stirred for 20 minutes. The volume of the reaction mixture was reduced to one third and was added to hexane (10-fold excess); resulting in the precipitation of the product. The product was dried under reduced pressure at room temperature overnight.

2.4.1.3 ROMP reaction of norbornene-1-methyl carboxylate monomer using 2nd ruthenium initiator [$RuCl_2(PCy_3)(IMes)(=CHPh)$]; monomer:initiator of 10:1

The polymerisation reaction of norbornene-1-methyl carboxylate monomer was performed in the glove box at room temperature. The initiator (10 mg, 0.0118 mmol) and monomer (10 equivalents, 5.5 mg, 0.036 mmol) were dissolved in $CDCl_3$ (1 mL), in two different vials and were stirred for a few minutes to allow them to dissolve. The monomer solution was transferred into the vial containing initiator and the mixture was stirred for a few minutes. The reaction mixture was then transferred to the screw capped NMR tube. The NMR tube was removed from the glove box and the spectrum was recorded at different time intervals. The NMR was taken at room temperature. In order to recover the product the reaction mixture was transferred into the vial, ethyl vinyl ether (0.2 mL) was added to terminate the reaction and stirred for 20 minutes. The volume of the reaction mixture was reduced to one third and then was added dropwise into another vial containing hexane (10-fold excess); resulting in the precipitation of the product. The product was dried under reduced pressure at room temperature overnight.

2.4.1.4 ROMP reaction of norbornene-1-methyl carboxylate monomer using modified 2nd generation ruthenium initiator [$RuCl_2(BrPyr)_2)(IMesH_2)(=CHPh)$]; monomer:initiator of 10:1

The polymerisation reaction was performed in the glove box at room temperature. The initiator (9.97 mg, 0.01125 mmol) and monomer (10 equivalents, 17.1 mg, 0.1125 mmol) were dissolved in $CDCl_3$ (1 mL), in two different vials and were stirred for a few minutes to allow them to dissolve. The monomer solution was transferred into the vial containing initiator and the mixture was stirred for a few minutes. The reaction mixture was then transferred to the screw capped NMR tube. The NMR tube was removed from the glove box and the spectrum was recorded at different time intervals. The NMR was taken after 90 minutes at room temperature; the NMR indicated the presence of unreacted monomer therefore the reaction mixture heated to 40°C in an oil bath**.** In order to recover the product the reaction mixture was transferred into the vial, ethyl vinyl ether (0.2 mL) was added to terminate the reaction and stirred for 20 minutes. The volume of the reaction mixture was reduced to one third and then was added dropwise into another vial containing hexane (10-fold excess); resulting in the precipitation of the product. The product was dried under reduced pressure at room temperature overnight.

2.4.2 Vinylic Polymerisation (Addition polymerisation) of norbornene-1-methyl carboxylate monomer

2.4.2.1 Vinylic polymerisation using palladium initiator $[Pd(H)(MeCN)(PCy_{3)2}][B(C_6F_5)_4]$

2.4.2.1.1 Norbornene-1-methyl carboxylate monomer:Palladium initiator of 1:1

The polymerisation reaction was performed in the glove box at room temperature. The palladium initiator (183 mg, 0.1318 mmol) was dissolved in trichloroethane-d_2 (0.8 mL), and was stirred for few minutes to allow it to dissolve. Monomer (equivalent, 20 mg, 0.1316 mmol) was weighed in the 2nd vial, the initiator solution was then added to the vial containing monomer solution. The reaction mixture was then transferred to the screw capped NMR tube. The NMR tube was removed from the glove box and the spectrum was recorded at different time intervals. The reaction mixture was then heated to 70 °C in an oil bath. In order to recover the product the

volume of the reaction mixture was reduced to one third under reduced pressure and was then added dropwise to methanol (10-fold excess) resulting in the precipitation of the product which was dried under vacuum at 25 °C.

The polymerisation reaction was repeated. The initiator (200 mg, 0.14409 mmol) was dissolved in trichloroethane-d_2 (0.8 mL), and was stirred for few minutes to allow it to dissolve. Monomer (equivalent, 20 mg, 0.1316 mmol) was weighed into the 2nd vial, the initiator solution was then added to the vial containing monomer solution. The reaction mixture was then transferred to the screw capped NMR tube. The NMR tube was removed from the glove box and the spectrum was recorded at different time intervals. The reaction mixture was then heated to 70 °C in an oil bath. In order to recover the product the volume of reaction mixture was reduced to one third under reduced pressure and then was added dropwise into another vial containing methanol (10-fold excess) resulting in the precipitation of the product which was dried under reduced pressure at room temperature.

2.4.2.1.2 Norbornene-1-methyl carboxylate monomer:Palladium initiator of 100:1

The polymerisation reaction was performed in the glove box at room temperature. Palladium initiator (45 mg, 0.0324 mmol) was dissolved in trichloroethane-d_2 (0.6 mL), and was stirred for few minutes to allow it to dissolve. Monomer (100 equivalents, 500 mg, 3.29 mmol) was dissolved in trichloroethane-d_2 (0.6 mL) in another vial. The initiator solution was then added to the vial containing monomer. The reaction mixture was then transferred to the screw capped NMR tube. The NMR tube was removed from the glove box and the spectrum was recorded at different time intervals. The reaction mixture was then heated to 70 °C in an oil bath. In order to recover the product the volume of reaction mixture was reduced to one third under reduced pressure and then was added dropwise into another vial containing methanol (10-fold excess) resulting in the precipitation of the product which was dried under reduced pressure at room temperature.

2.4.2.2 Vinylic polymerisation using nickel in (η^6-toluene) $Ni(C_6F_5)_2$

2.4.2.2.1 Norbornene-1-methyl carboxylate monomer : Nickel initiator (1:1)

The polymerisation reaction was performed in the glove box at room temperature. The initiator (64 mg, 0.1319 mmol) and monomer (equivalent, 20 mg, 0.1316 mmol) were dissolved in cold toluene-d_8 (1 mL), in two different vials and were stirred for few minutes to allow them to dissolve. The initiator solution was transferred into the monomer vial and the mixture was stirred for few minutes. The reaction mixture was then transferred to the screw capped NMR tube. The NMR tube was removed from the glove box and the spectrum was recorded at different time intervals. The NMR spectrum was taken at room temperature. In order to recover the product the volume of reaction mixture was reduced to one third and then was added dropwise into another vial containing methanol (10-fold excess) resulting in the precipitation of the product which was dried under reduced pressure at room temperature. The NMR indicated the presence of unreacted monomer.

2.4.2.2.2 Norbornene-1-methyl carboxylate monomer: Nickel initiator (100:1)

The polymerisation reaction was performed in the glove box at room temperature. The Nickel initiator (31.90 mg, 0.0658 mmol) and monomer (100 equivalents, 1000 mg, 6.58 mmol) were dissolved in cold toluene-d_8 (1 mL), in two different vials and were stirred for few minutes to allow them to dissolve. The initiator solution was transferred into the monomer vial and the mixture was stirred for few minutes. The reaction mixture was then transferred to the screw capped NMR tube. The NMR tube was removed from the glove box and the spectrum was recorded at different time intervals. In order to recover the product the volume of reaction mixture was reduced to one third and then was added dropwise into another vial containing methanol (10-fold excess) resulting in the precipitation of the product which was dried under reduced pressure at room temperature. The NMR indicated the presence of unreacted monomer.

Chapter 3 Results and Discussion

3.1 Synthesis of and characterisation of monomers

3.1.1 Norbornane-2-carboxylic acid

Norbornane-2-carboxylic acid was supplied by Promerus and was fully characterised at Durham. Both ^{1}H NMR and ^{13}C NMR spectra confirm the structure of norbornane-2-carboxylic acid. The ^{1}H NMR spectrum, Figure 3.1, shows a broad signal at 9.28 ppm due to the proton of the carboxylic acid. It also shows a peak at 3.72 ppm corresponding to the proton on (C^{2}), confirming the attachment of the carboxylic acid group. The resonances at 2.58 ppm and 2.82 ppm are due to the protons of (C^{1}) and (C^{4}), respectively. The resonances due to other protons of the monomer can also be observed.

^{13}C NMR spectrum, Figure 3.2, shows a signal at 180.05 ppm due to the carbon of the carboxylic acid (C^{8}). It also shows a signal at 45.60 ppm corresponding to the carbon with the carboxylic acid group (C^{2}). The resonances at 40.05 ppm and 36.50 ppm are due to (C^{1}) and (C^{4}), respectively. The resonances due to other carbons can also be observed.

The DEPT spectrum further confirms the proposed assignments.

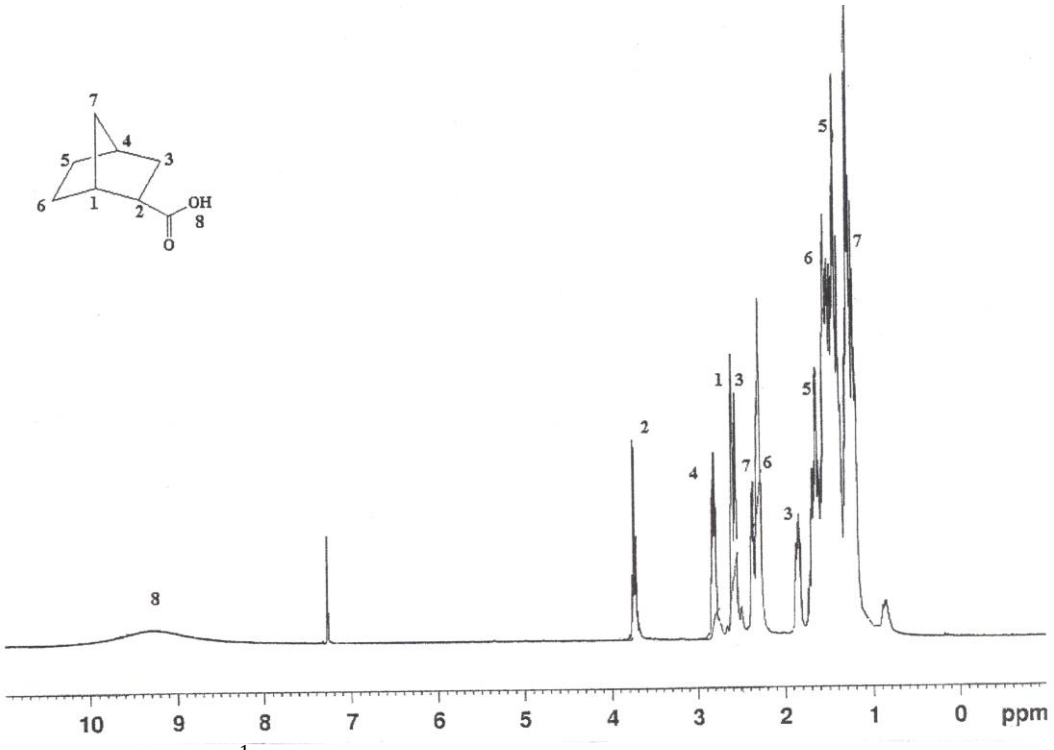


Figure 3.1. 400 MHz ^{1}H NMR spectrum of norbornane-2-carboxylic acid in $CDCl_3$

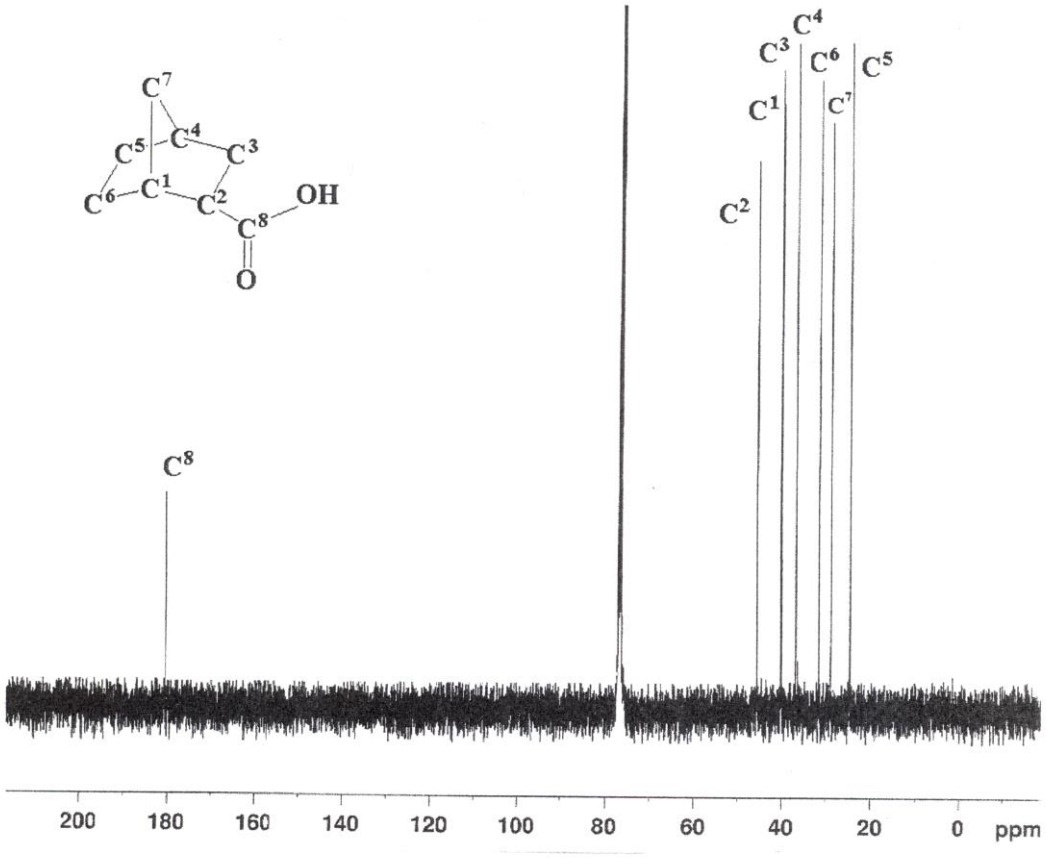


Figure 3.2. 400 MHz ^{13}C NMR spectrum of norbornane-2-carboxylic acid in $CDCl_3$

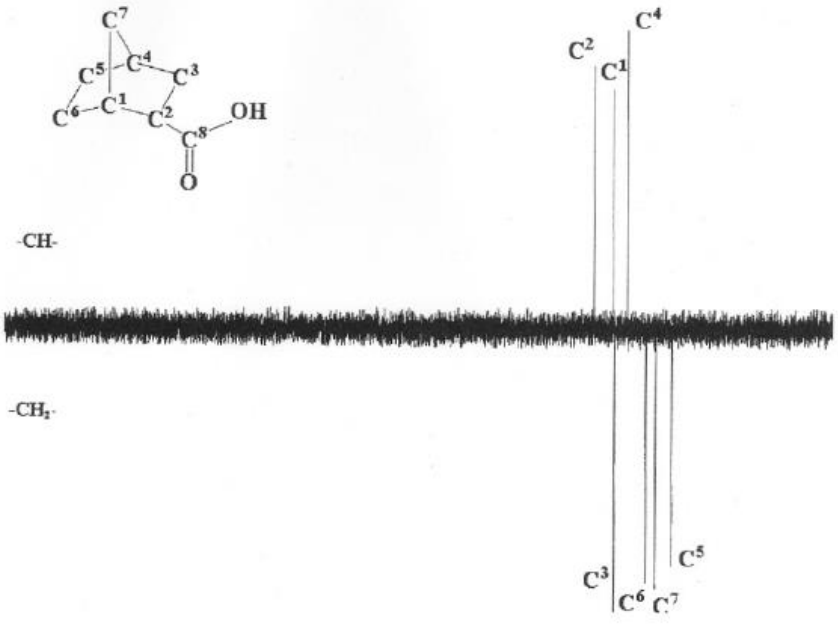
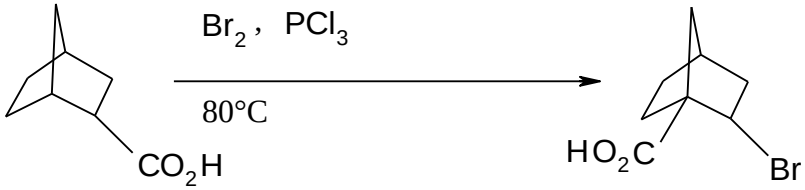


Figure 3.3. 265 MHz DEPT spectrum of norbornane-2-carboxylic in $CDCl_3$

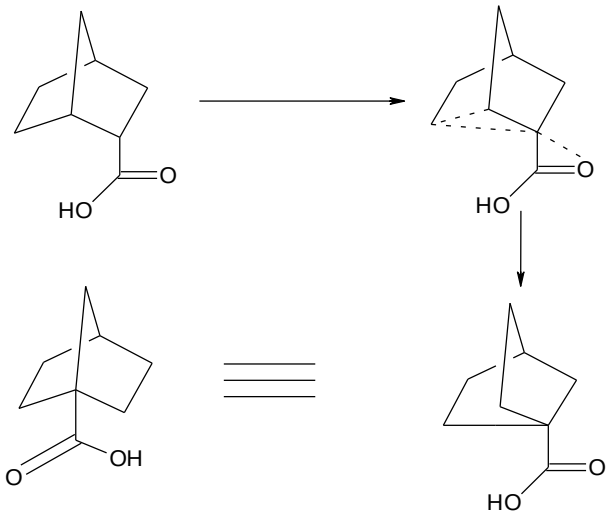
3.1.2 Synthesis of 2-bromonorbornane-1-carboxylic acid

Norbornane-2-carboxylic acid was brominted according to the reaction scheme 3.1 and 2-bromonorbornane-1-carboxylic acid was successfully prepared.



Scheme 3.1. Bromination of norbornane-2-carboxylic acid

Bromination reaction was carried out via heating the norbornane-2-carboxylic acid with bromine (Br_2) and phosphorus trichloride (PCl_3) at reflux for 8 hours at 80 °C under an inert atmosphere (N_2 gas). The bromination reaction was carried out first in a small scale in order to test the efficiency of the reaction and then it was scaled up. The average yield of white powder product was 57%. The mechanism of this bromination reaction is based on Wagner-Meerwein rearrangement, which is a carbocation 1,2 rearrangement reaction in which a hydrogen, alkyl or aryl group migrates from one carbon to an adjacent carbon, Scheme 3.1.[4] This is an intramolecular rearrangement, and the starting material and product are structural isomers, although other substituents can be added during the course of the reaction, as with the bromination in Scheme 3.1. The Wagner-Meerwein rearrangement is quite a common reaction for bicyclic compounds,[5] and it is an extremely useful synthetic tool in the synthesis of bridgehead-substituted polycyclics. The mechanism of the Wagner-Meerwein rearrangement proceeds via a carbocation transition state, is stabilised by the carboxylic acid, Scheme 3.2.[4,5,6,7]



Scheme 3.2. Mechanism of Wagner-Meerwein rearrangement showing carbocation stabilisation by carboxylic acid functionality

The comparison of the ^{1}H NMR spectrum of 2-bromonorbornane-1-carboxylic acid, Figure 3.4, with norbornane-2- carboxylic acid, Figure 3.1, showed that the product was successfully synthesised. The broad signal due to the proton of carboxylic acid is observable, but shifted from 9.28 ppm to 11.94 ppm indicating rearrangement of carboxylic acid group from C^2 to C^1. The resonance due to the proton of the (C^2) is shifted from 3.72 ppm to 4.19 ppm indicating the replacement of the carboxylic group with the bromine group. The signal due to the proton of (C^1) at 2.58 ppm disappeared whereas the signal at 2.35 ppm due to the protons of (C^4) is still present. This confirms the presence of the carboxylic group on the (C^1). Resonances due to other protons of the product can also be observed.

The comparison of the ^{13}C NMR spectrum of 2-bromonorbornane-1-carboxylic acid, Figure 3.5, with norbornane-2-carboxylic acid, Figure 3.2, also showed that the product had been successfully synthesised. The signal at 179.88 ppm due to the carbon of the carboxylic acid (C^8) is observed. The resonances due (C^1) significantly shifted from 40.05 ppm to 59.27 ppm, indicating rearrangement of the carboxylic acid group from (C^2) to (C^1). The resonance due to (C^2) is shifted from 45.60 ppm to 53.19 ppm, indicating the replacement of the carboxylic group with the bromine group. Resonances due to other carbons of the product can also be observed.

The DEPT spectrum, Figure 3.6 further confirms the assignments.

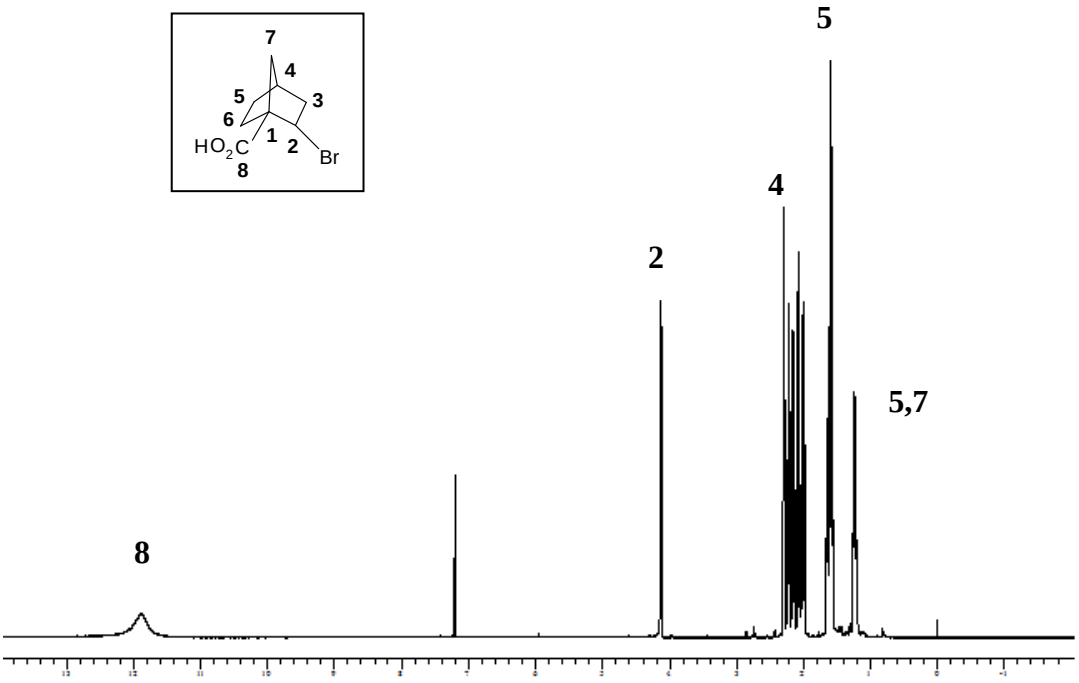


Figure 3.4. 500 MHz ^{1}H NMR spectrum of norbornane-2-carboxylic acid in $CDCl_3$

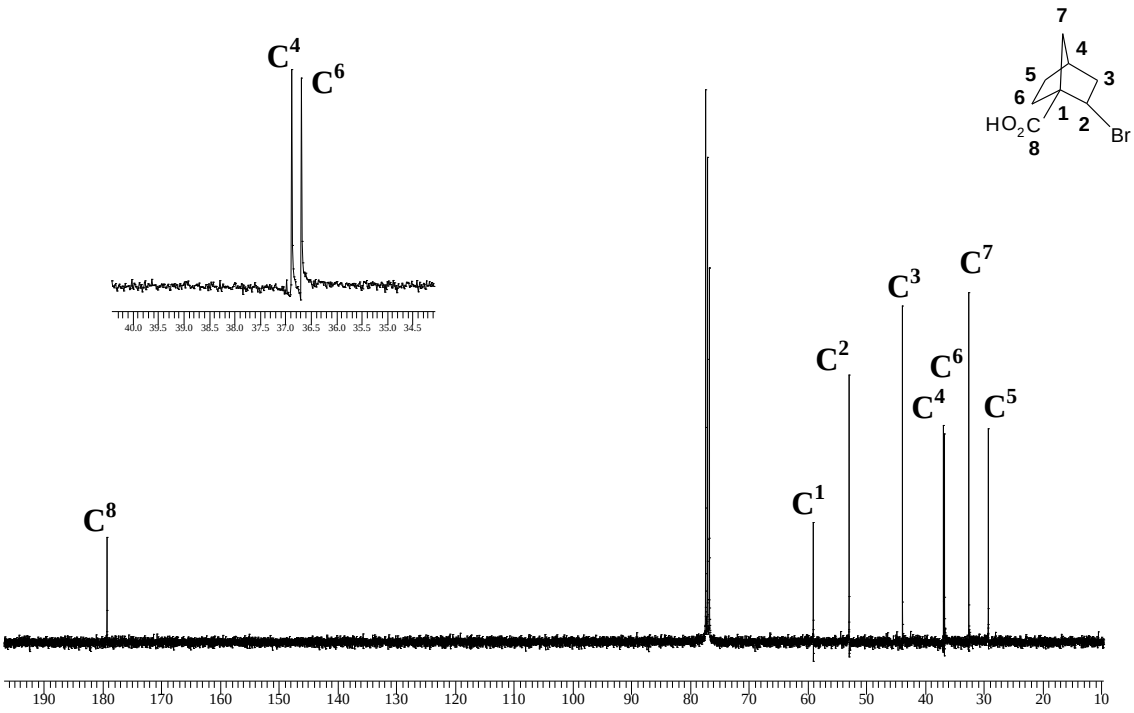


Figure 3.5. 500 MHz ^{13}C NMR spectrum of 2-bromonorbornane-1-carboxylic acid in $CDCl_3$

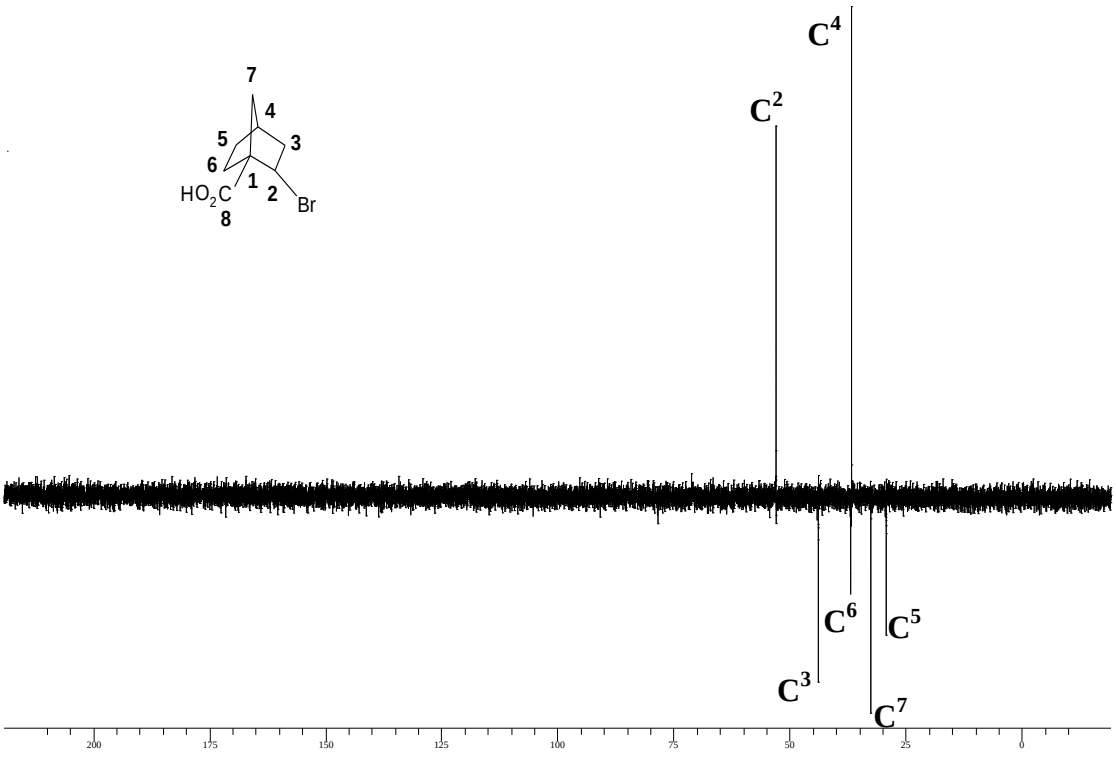
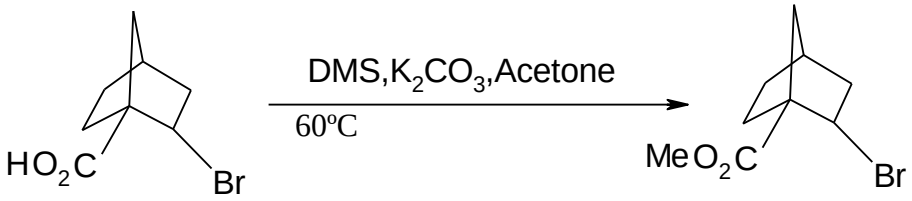


Figure 3.6. 500 MHz DEPT spectrum of 2-bromonorbornane-1-carboxylic acid in $CDCl_3$

3.1.3 Synthesis of 2-bromonorbornane-1-methyl carboxylate

2-Bromonorbornane-1-carboxylic acid was methylated according to the reaction Scheme 3.3 and 2-bromonorbornane-1-methyl carboxylate was successfully prepared.



Scheme 3.3. Methylation of 2-bromonorbornane-1-carboxylic acid

2-Bromonorbornane-1-carboxylic acid was methylated in a small scale first to test the efficiency of the reaction and then it was scaled up. The reaction was carried out by adding K_2CO_3 and DMS (dimethyl sulphate) to 2-bromonorbornane-1-carboxylic acid and refluxing the reaction mixture for 6 hours at 60°C under inert atmosphere (N_2 gas). The average yield of oily brown product was 85%.

There is an alternative route to methylate carboxylic acid and that is via acid chloride (thionyl chloride; $SOCl_2$) /Pyridine followed by adding dry methanol. But this procedure was tedious and involved a very sensitive acid chloride intermediate, so it was not selected for methylation of 2-bromonorborane-1-carboxylic acid. Dimethyl sulphate appeared to be the most efficient reagent for synthesising 2-bromonorbornane-1-methyl carboxylate. However, it is seldom considered for esterification of carboxylic acid, because of the side reactions by the basic medium and hydrolysis of the ester once it is formed. Several base –solvent mixtures have been employed to avoid these side reactions. It was observed that when carboxylic acid is treated by DMS and potassium carbonate anhydrous (K_2CO_3; 10% excess), followed by three hours reflux in dry acetone the reaction is successful and gives a yield of more than 95%.

A comparison of the ^1H NMR spectrum of 2-bromnorbornane-1-methyl carboxylate , Figure 3.7, with 2-bromonorbornane-1-carboxylic acid, Figure 3.4, showed that the product was successfully synthesised. Signal due to the three protons of methyl group (C^9) at 3.74 ppm is appeared whereas the broad signal due to the proton of the carboxylic acid (C^8) at 11.94 ppm disappeared. The proton of (C^2) is still observed at 4.18 ppm which indicates the presence of bromine functionality on (C^2). Also ^1H NMR spectrum shows that none of the other proton resonances have changed which means that the reaction has gone to completion successfully without any side reactions.

A comparison of the ^{13}C NMR spectrum of 2-bromnorbornane-1-methyl carboxylate, Figure 3.8, with 2-bromonorborane-1-carboxylic acid, Figure 3.5, also showed that the product was successfully synthesised. The signal at 51.72 ppm due to the carbon of the methyl group (C^9) is observed. The resonance due to the (C^8) is also shifted from 179.88 ppm to 173.42 ppm indicating the replacement of the carboxylic group with ester group. Signal of the (C^2) is still observed at 53.77 ppm which shows the presence of bromine functionality on (C^2).

The DEPT spectrum, Figure 3.9, further confirms the correct assignments.

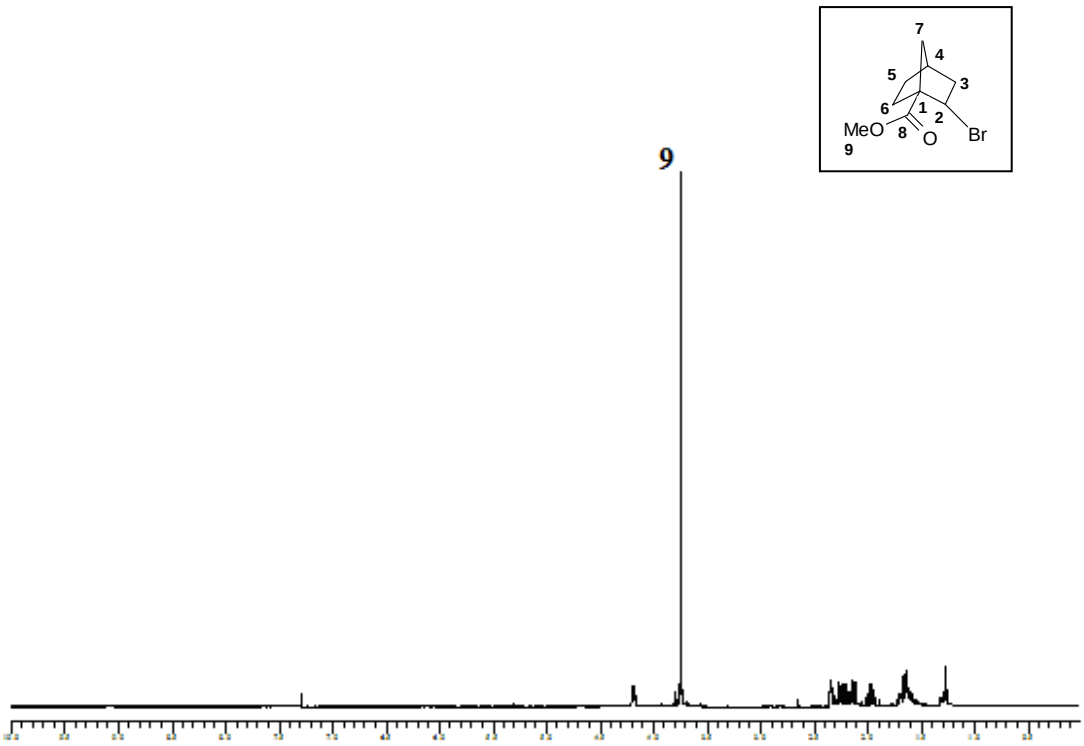


Figure 3.7. 200 MHz ^{1}H NMR spectrum of 2-bromonorbornane-1-methyl carboxylate in $CDCl_3$

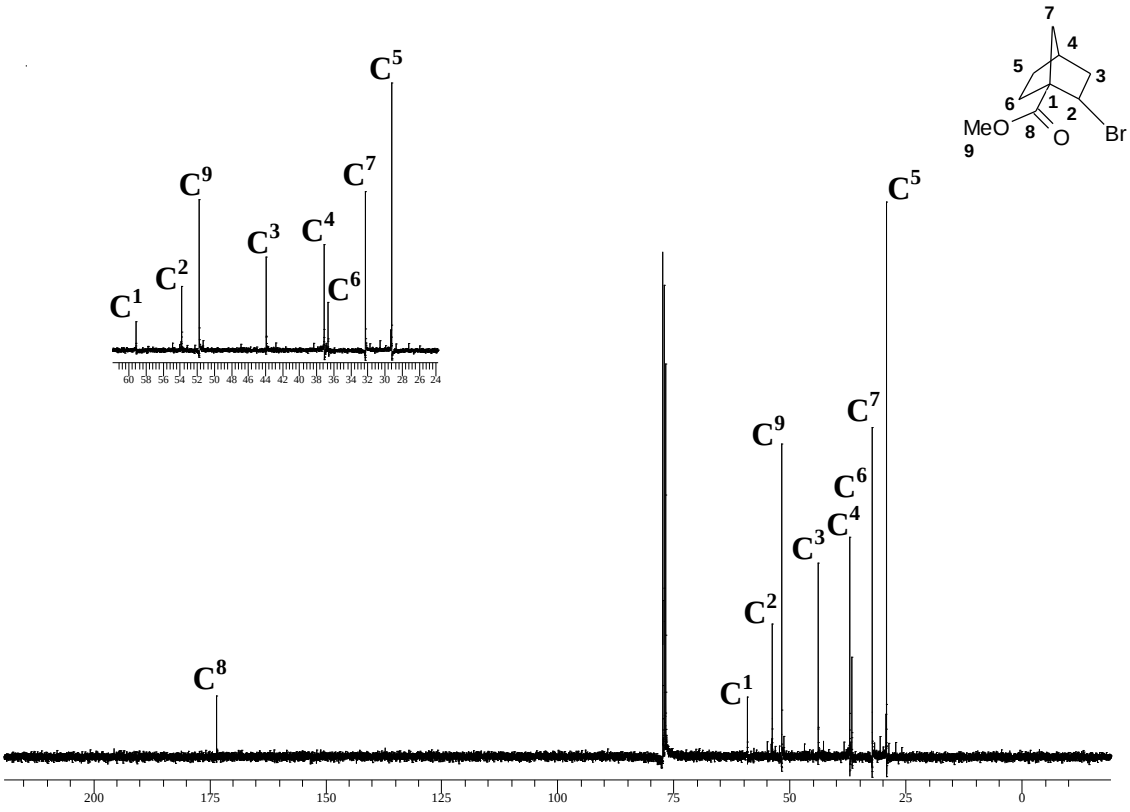


Figure 3.8. 200 MHz ^{13}C NMR spectrum of 2-bromonorbornane-1-methy carboxylate in $CDCl_3$

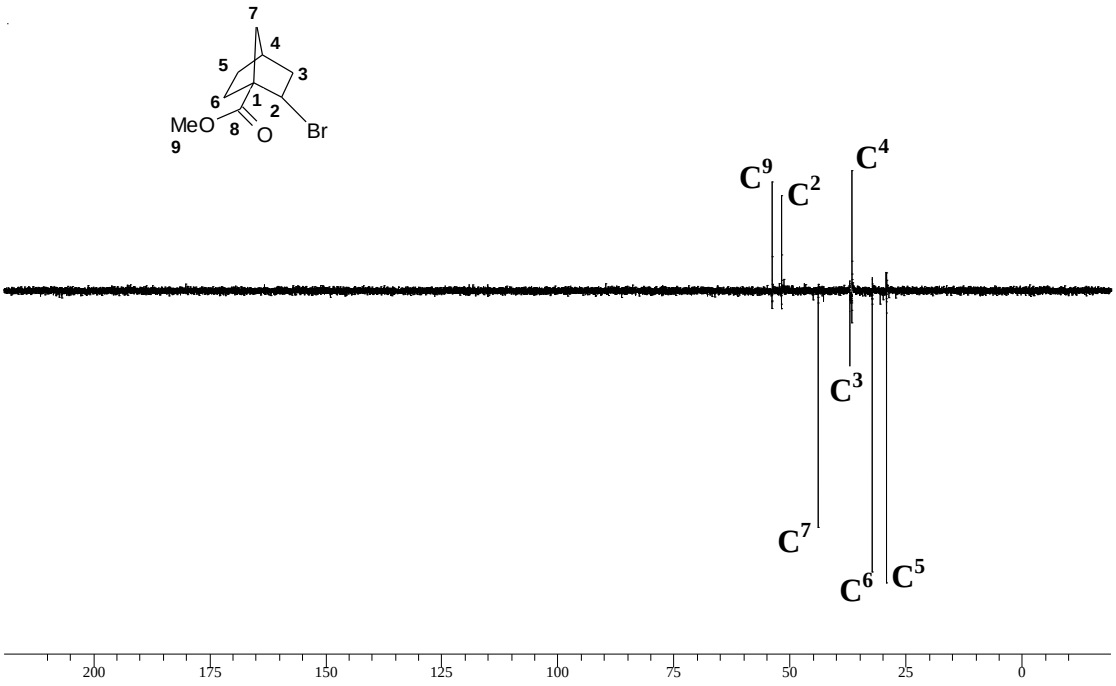
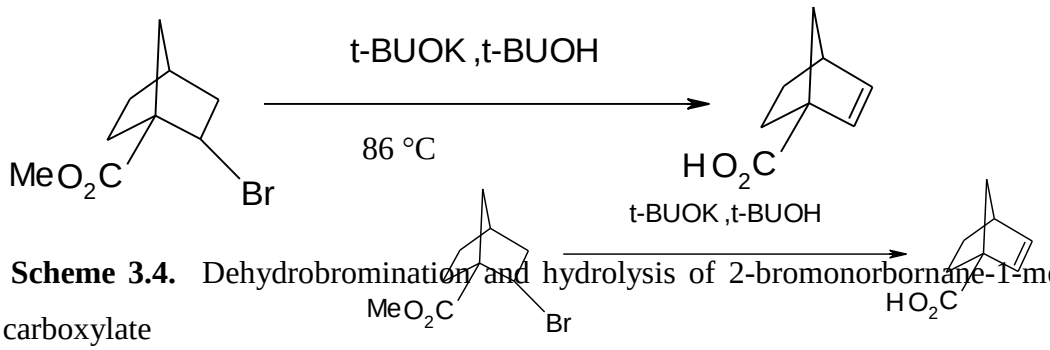


Figure 3.9. 200 MHz DEPT spectrum of 2-bromonorbornane-1-methyl carboxylate in $CDCl_3$.

3.1.4 Synthesis of norbornene-1-carboxylic acid

2-Bromonorbornane-1-methyl carboxylate was dehydrobrominated and hydrolysed according to the reaction scheme 3.4 and norbornene-1-carboxylic acid was successfully prepared.



Scheme 3.4. Dehydrobromination and hydrolysis of 2-bromonorbornane-1-methyl carboxylate

Dehydrobromination of 2-bromonorbornane-1-methyl carboxylate was carried out on a small scale first in order to test the efficiency of the reaction and then it was scaled up. In each reaction 2-bromonorbornane-1-methyl carboxylate was reacted with t-butyl alcohol and potassium t-butoxide and was heated at reflux for 3 hours at 86 °C.

Then water was added to the reaction mixture and the reflux was continued for 24 hours. The average yield of impure brown solid product was 75.5%. In order to purify the product it was recrystallised from water and the average yield of fine white needle product was 50%. Dehydrohalogenation is a reaction in which an alkene is obtained from an alkyl halide, and also known as β-elimination reaction. There are two possible mechanisms for β-elimination, depending on the base used. Applying a strong base such as K^tOBu, makes the reaction proceed via an E_2 elimination (bimolecular elimination) mechanism, Scheme 3.5; in this case the rate is affected by the concentration of base, which means that at high base concentration, the E_2 (bimolecular elimination) mechanism is favoured.

A comparison of the ^1H NMR spectrum of norbornene-1-carboxylic acid, Figure 3.10, to 2-bromonorbornane-1-methyl carboxylate, Figure 3.7, shows that the product was successfully synthesised. The signal due to the three protons of the methyl group at 3.74 ppm disappeared whereas a broad signal due to the proton of carboxylic acid proton (C^8) at 11.59 ppm is observed. Also, a doublet of doublet signals due to the vinylic proton (C^2) at 6.12 ppm and (C^3) 6.19 ppm is observed. The signal due to the proton of (C^2) is shifted from 4.18 ppm to 6.12 ppm which indicating the disappearance of bromine group on (C^2) and the formation of the vinylic group.

The comparison of the ^{13}C NMR spectrum of norbornene-1-carboxylic, Figure 3.11, with 2-bromonorbornane-1-methyl carboxylate, Figure 3.8, also shows that the product was successfully synthesised. Signals due to the (C^2) and (C^3) are changed significantly; signal due to the (C^2) is shifted from 53.77 ppm to 133.87 ppm and signal corresponding to the (C^3) is shifted from 43.87 ppm to 136.57 ppm. This proves that the debromination and hydrolysis have taken place and that a double bond is formed. ^{13}C NMR spectrum also shows the resonance of (C^7) is shifted from 32.25 ppm to 52.06 ppm. Also the signal at 51.72 ppm due to the (C^9) is disappeared which is due to the replacement of the methyl group with the hydrogen group.

DEPT spectrum, Figure 3.12, further confirms the correct assignments.

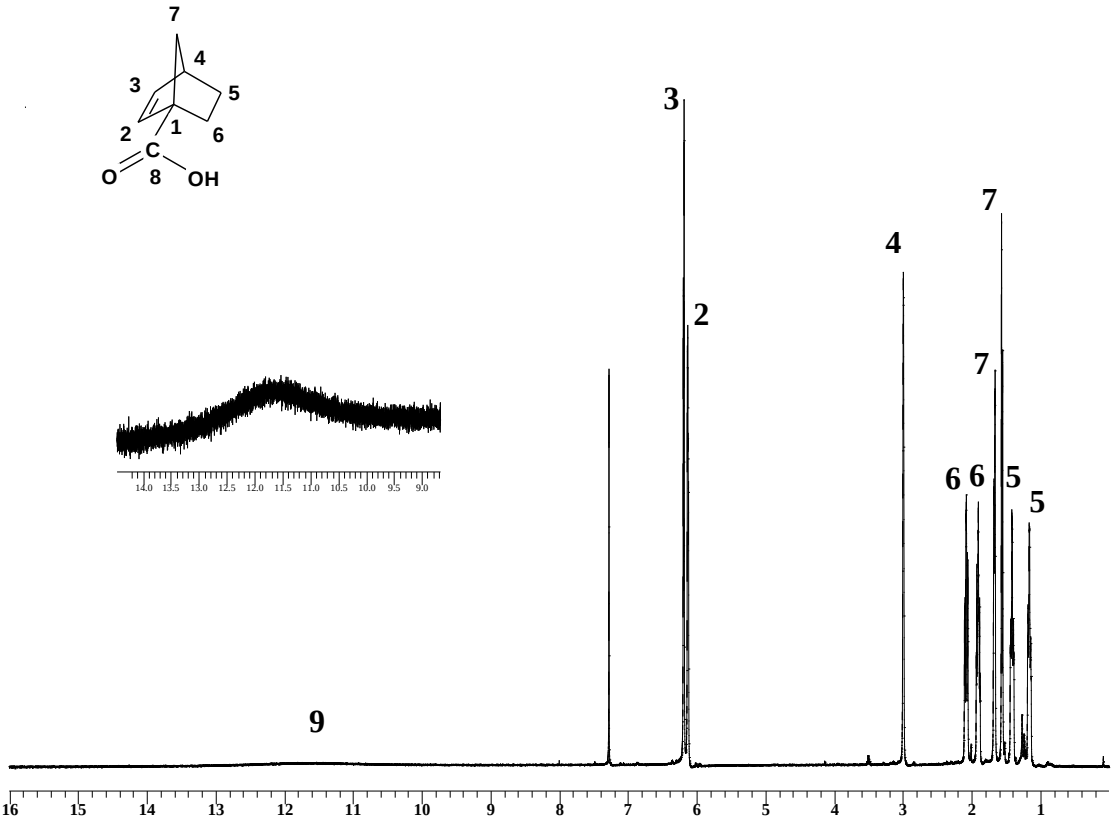


Figure 3.10. 500 MHz ^{1}H NMR spectrum of norbronene-1-carboxylic acid in $CDCl_3$

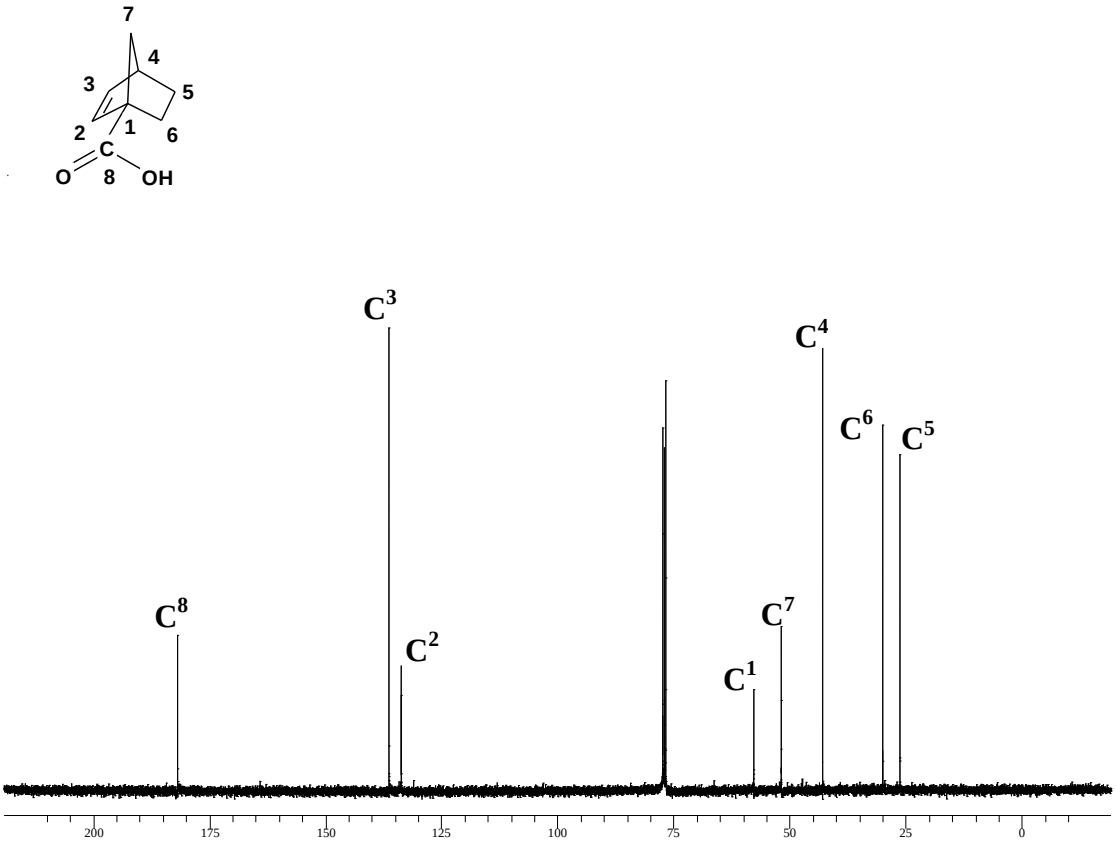


Figure 3.11. 500 MHz ^{13}C NMR spectrum of norbornene-1-carboxylic acid in $CDCl_3$

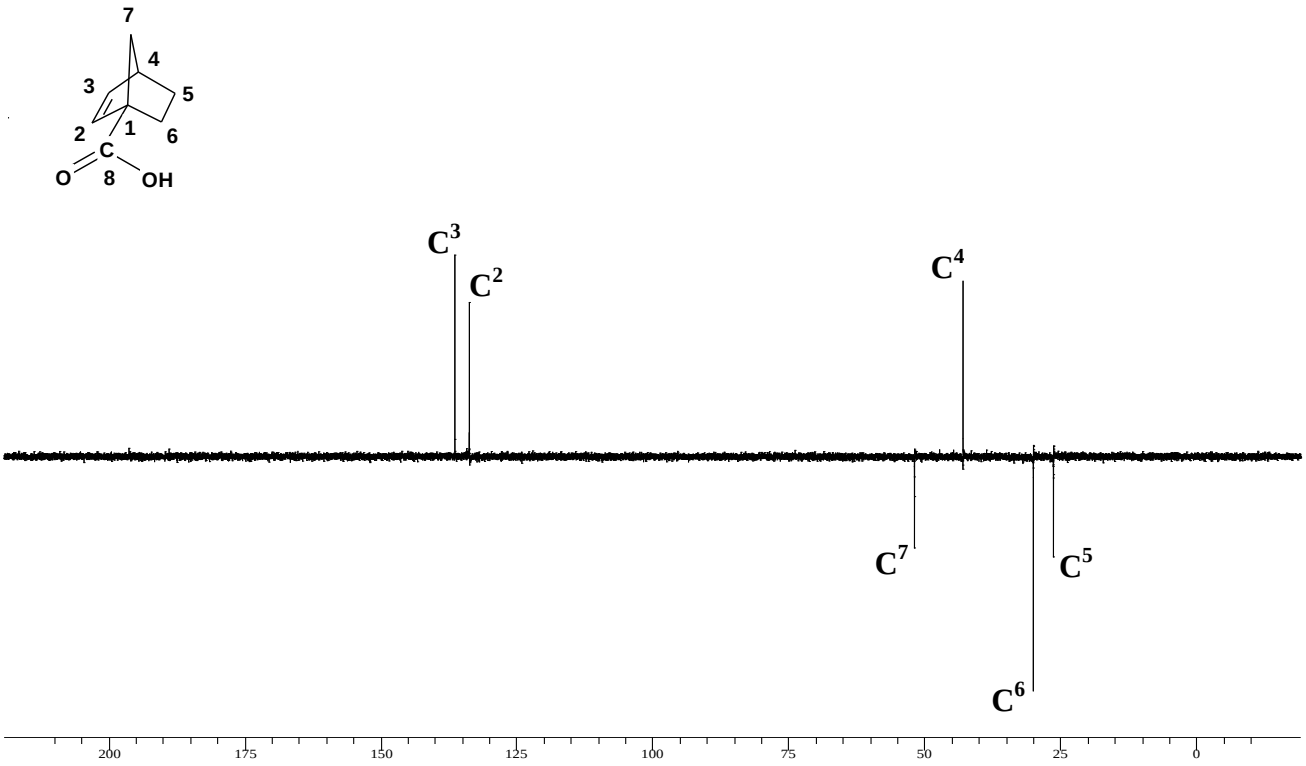
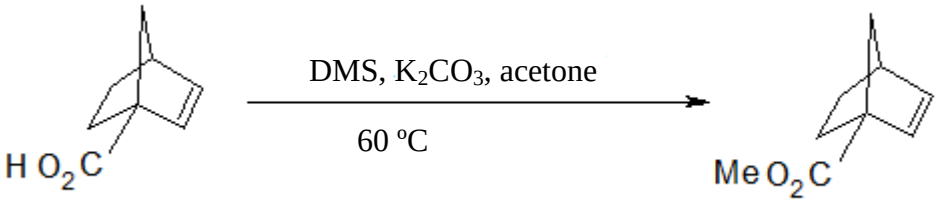


Figure 3.12. 500 MHz DEPT spectrum of norbornene-1-carboxylic acid in $CDCl_3$

3.1.5 Synthesis of norbornene-1-methyl carboxylate

Norbornene-1-carboxylic acid was methylated according to the reaction scheme 3.6 and norbornene-1-methyl carboxylate was successfully prepared.



Scheme 3.6. Reaction of methylation of norbornene-1-carboxylic acid

Methylation of norbornene-1-carboxylic acid was carried out twice, on a small scale to evaluate the feasibility of the reaction and large-scale reaction. Potassium carbonate, DMS (dimethyl sulphate) and acetone were added to norbornene-1-carboxylic acid followed by heating the reaction mixture at reflux under inert

atmosphere (N_2 gas) at 60°C for 6 hours. The average yield was 36% and norbornene-1-methyl carboxylate as a colorless liquid was obtained. The reason for using dimethyl sulphate for esterification of norbornen-1-carboxylic acid was explained in 3.1.3. A comparison of the ^{1}H NMR spectra of norbornene-1- methyl carboxylate, Figure 3.13, with norbornene-1-carboxylic acid, Figure 3.10, showed that the monomer was successfully synthesised. The broad signal due to the proton of carboxylic acid (C^8) at 11.59 ppm is disappeared whereas the signal at 3.73 ppm due to there protons of methyl group is appeared. Also a doublet doublet signal due to the vinylic proton of (C^2) and (C^3) is slightly shifted. Resonance due to the proton of (C^2) is shifted from 6.12 ppm to 6.07 ppm and signal corresponding to the proton of (C^3) is shifted from 6.19 ppm to 6.13 ppm which is believed to be due to the replacement of the carboxylic group with the methyl ester group.

A comparison of ^{13}C NMR spectrum of norbornene-1-methyl carboxylate, Figure 3.14, with norbornene-1-carboxylic acid, Figure 3.11, also shows that the monomer was successfully synthesised. The signal due to the methyl group (C^9) at 51.93 ppm is observed. Also the resonance of (C^8) is slightly shifted from 181.71ppm to 175.63 ppm, indicating to transformation of the acid group into the ester group.

The DEPT spectrum of norbornene-1-methyl carboxlate, Figure 3.12, further confirms the correct assignment.

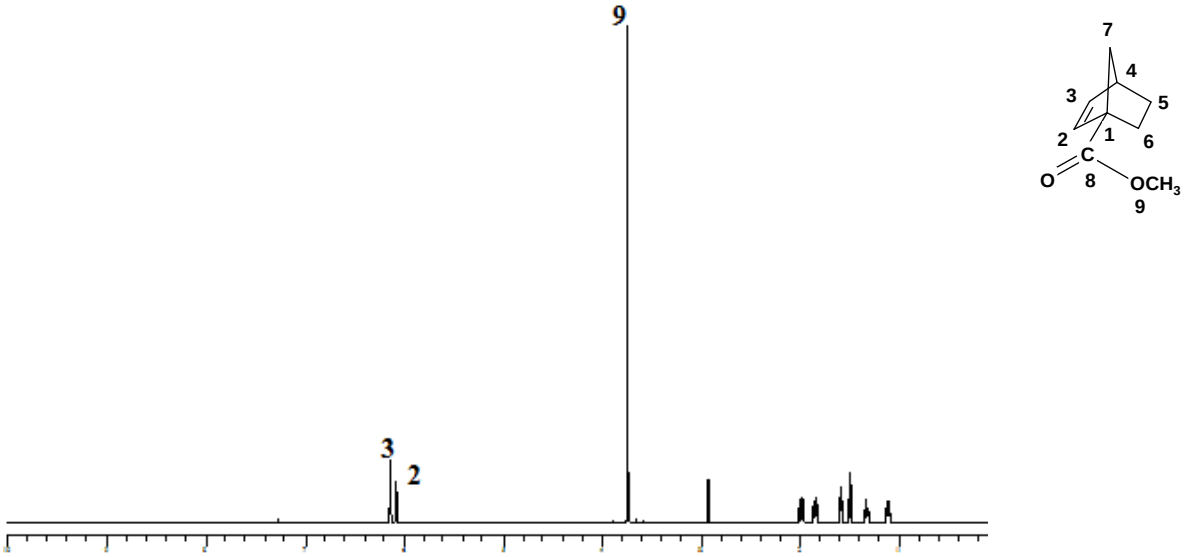


Figure 3.13. 500 MHz ^{1}H NMR spectrum of norbornene-1-methyl carboxylate in $CDCl_3$

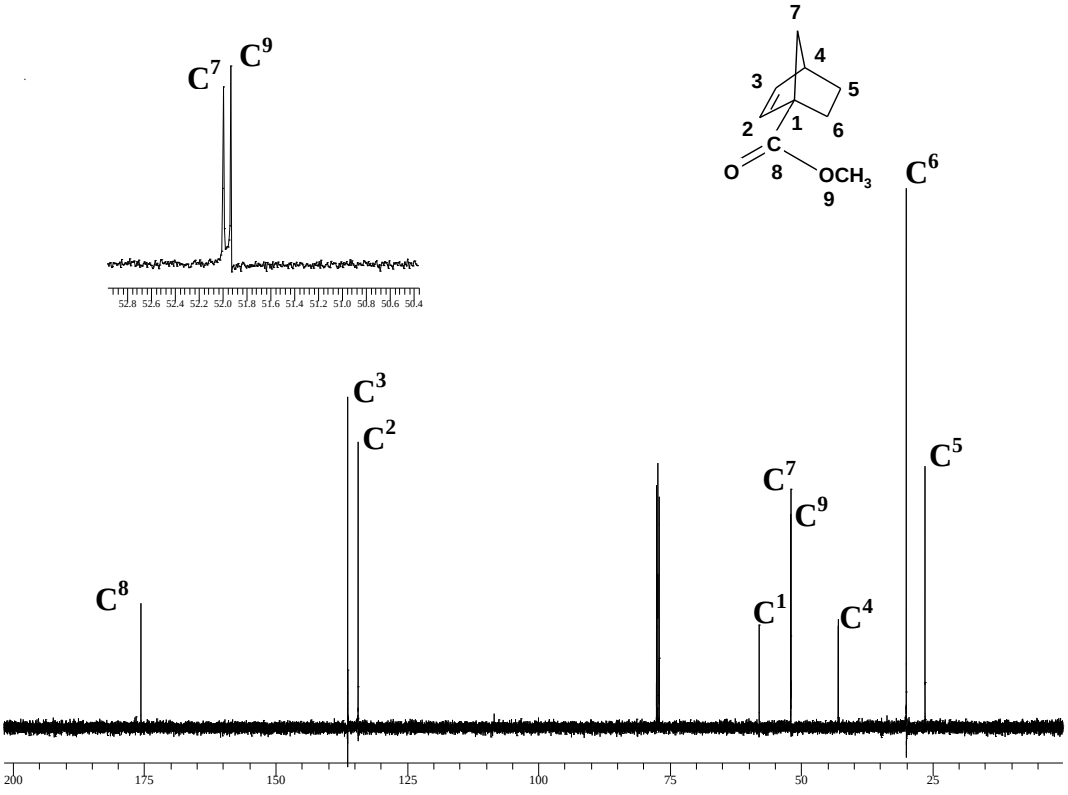


Figure 3.14. 500 MHz ^{13}CNMR spectrum of norbornene-1-methyl carboxylate in $CDCl_3$

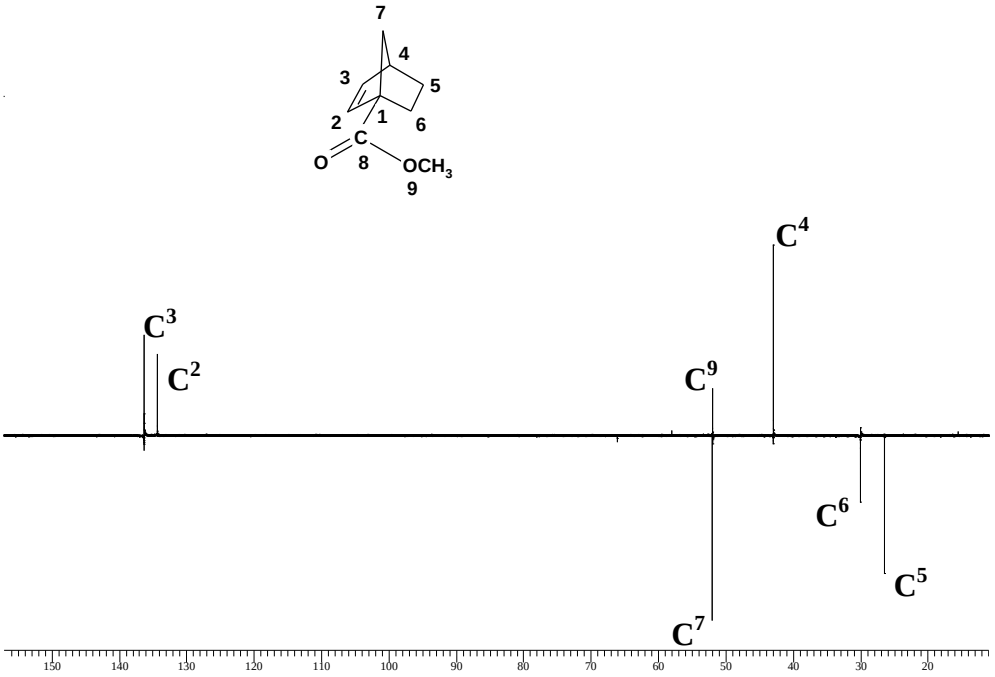
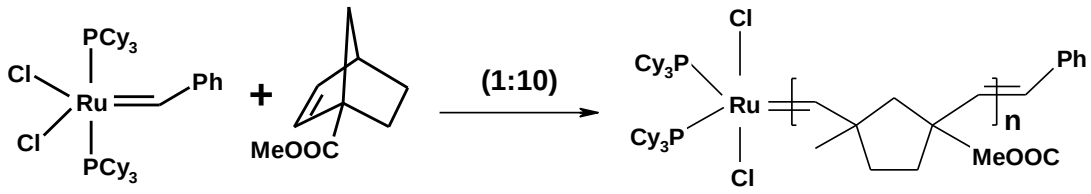


Figure 3.15. 500 MHz DEPT spectrum of norbornene-1-methyl carboxylate in $CDCl_3$

3.2 Ring-opening metathesis polymerisation

3.2.1 ROMP reaction of norbornene-1-methyl carboxylate monomer using 1st generation ruthenium initiator [RuCl2(PCy3)2(=C(H)Ph)].

The ROMP reaction of norbornene-1-methyl carboxylate monomer was carried out using 1st generation ruthenium initiator using the ratio of monomer: initiator of 10:1, in $CDCl_3$, Scheme 3.7.



1: 1st generation ruthenium initiator
10: norbornene-1-methyl carboxylate monomer

Scheme 3.7. ROMP reaction of norbornene-1-methyl carboxylate monomer using 1st generation ruthenium initiator

The ^{1}H NMR spectrum taken after 30 minutes showed that the initiator alkylidene signal at 19.67 ppm is consumed and a new alkylidene signal appeared as a doublet at 17.01 ppm, see Figure 3.17. The signal due to the methyl group of the monomer at 3.73 ppm is observed but a new weak signal due to CH_3 group also appeared at 4.08 ppm, see Figure 3.18. The signals due to the vinylic protons of the monomer are also seen at 6.14 ppm. However, no signal is observed for the vinylic protons of the polymer at 5.20-5.80 ppm.

The reaction was followed for 48 hours and the ^{1}H NMR spectrum were recorded at different reaction time intervals. The ^{1}H NMR spectrum after 16 hours showed the doublet at 17.01 ppm and the appearance of a multiplet at 16.92 ppm in the alkylidene region. The intensity of the doublet at 17.01 ppm is reduced and the intensity of the multiplet at 16.92 ppm is increased as the reaction time was increased to 24 hours and 48 hours. Only a trace of the doublet at 17.01 ppm is left after 48 hours of reaction, Figure 3.17. Although the integration of the vinylic protons of the monomer at 6.05 ppm against the TMS (internal standard) with the time showed that the insentiy of signal slightly reduced. Enough evidence for polymerisation of norbornene-1-methyl carboxylate monomer was not observed.

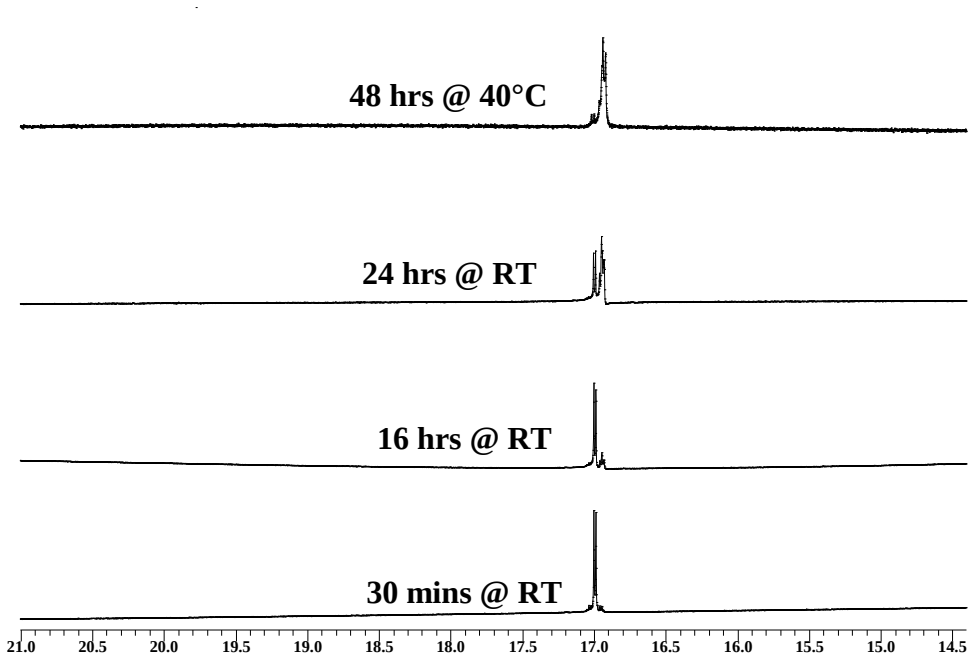


Figure 3.17. 400 MHz ^{1}H NMR spectra showing the alkylidene region for the ROMP reaction of norbornene-1-methyl carboxylate monomer using first generation of ruthenium initiator with the ratio of monomer: initiator of 10:1 in $CDCl_3$

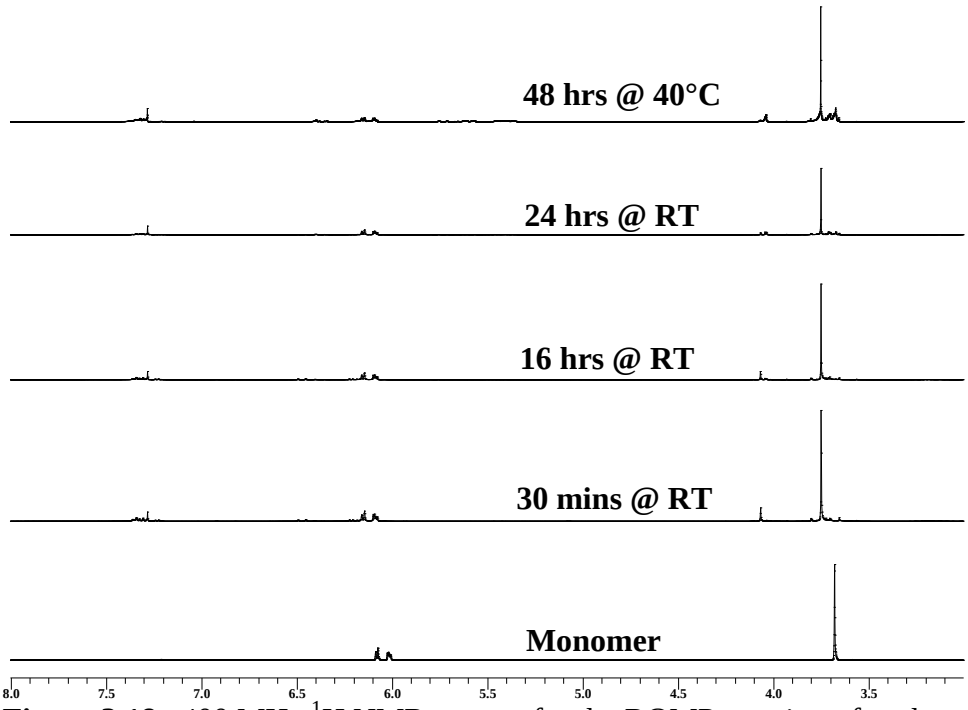


Figure 3.18. 400 MHz ^{1}H NMR spectra for the ROMP reaction of norbornene-1-methyl carboxylate monomer using 1st generation of ruthenium initiator with the ratio of Monomer: Initiator of 10:1 in $CDCl_3$.

It was anticipated that a complex is possibly formed through chelation of, most likely, ether oxygen to the ruthenium centre. This was supported by the appearance of new signals in the alkylidene region.

In order to investigate the possibility of the formation of a complex due to the chelation of the oxygen to the ruthenium centre, the ROMP reaction of norbornene -1-methyl carboxylate monomer with 1st generation ruthenium initiator was carried out at the ratio of monomer: initiator of 1:1, in $CDCl_3$.

The ^{1}H NMR spectrum taken after 15 minutes showed the presence of the alkylidene proton of the initiator at 19.97 ppm and also the appearance of a new doublet at 16.98 ppm, see Figure 3.19. The signal due to the methyl group of the monomer at 3.68 ppm is observed as well as a new weak signal at 3.98 ppm due to a new CH_3 group. The intensity of the signals at 6.03 ppm and 6.07 ppm due to the vinylic hydrogens of the monomer is reduced. However, no signal is observed for the vinylic protons of the polymer at 5.20-5.60 ppm, see Figure 3.20.

The reaction was followed for 150 minutes and the ^{1}H NMR spectrum were recorded at different time intervals. The intensity of the initiator alkylidene at 19.97 ppm is reduced and the intensity of the doublet at 16.96 ppm is increased as the reaction time

was increased from 30 minutes to 150 minutes, see Figure 3.19. The signal due to the vinylic hydrogens of the monomer at 6.03 ppm and 6.07 ppm disappeared and new signals due to the new vinylic hydrogens appeared as the reaction time were increased to 150 minutes. The ^{1}H NMR taken after 150 minutes showed only the presence of the doublet at 16.96 ppm and complete disappearance of the initiator signal at 19.97 ppm.

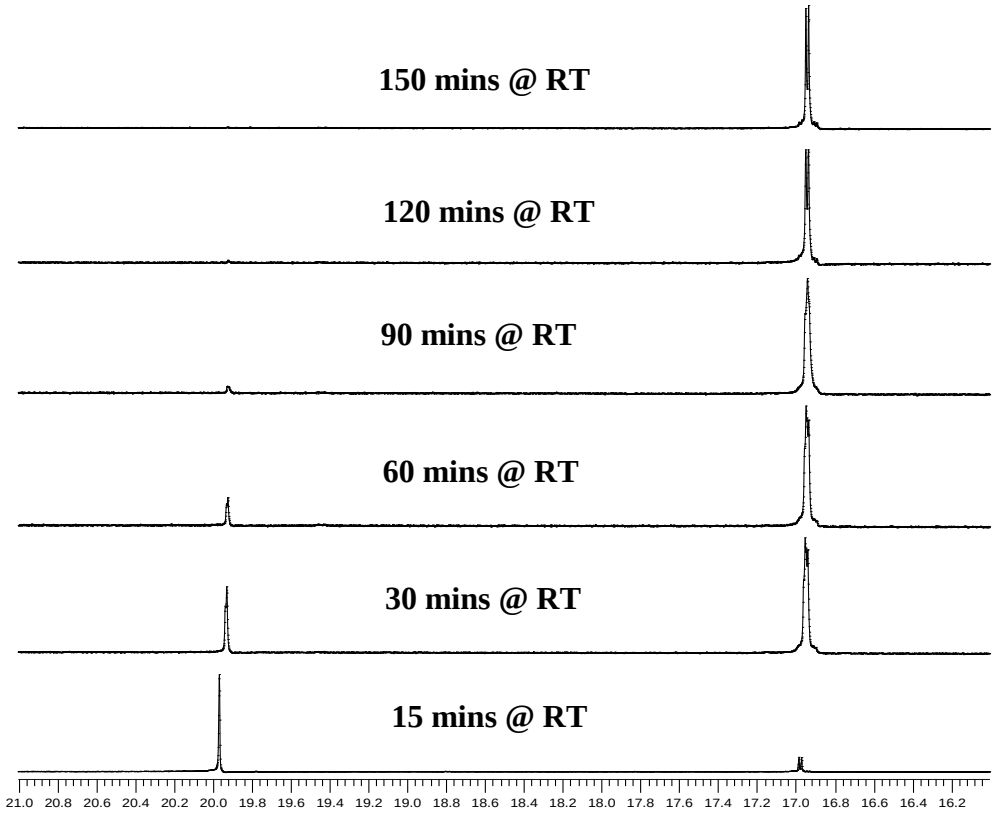


Figure 3.19. 400 MHz ^{1}H NMR spectra showing the alkylidene region for the ROMP reaction of norbornene-1-methyl carboxylate monomer using first generation of ruthenium initiator with the ratio of monomer: initiator of 1:1 in $CDCl_3$

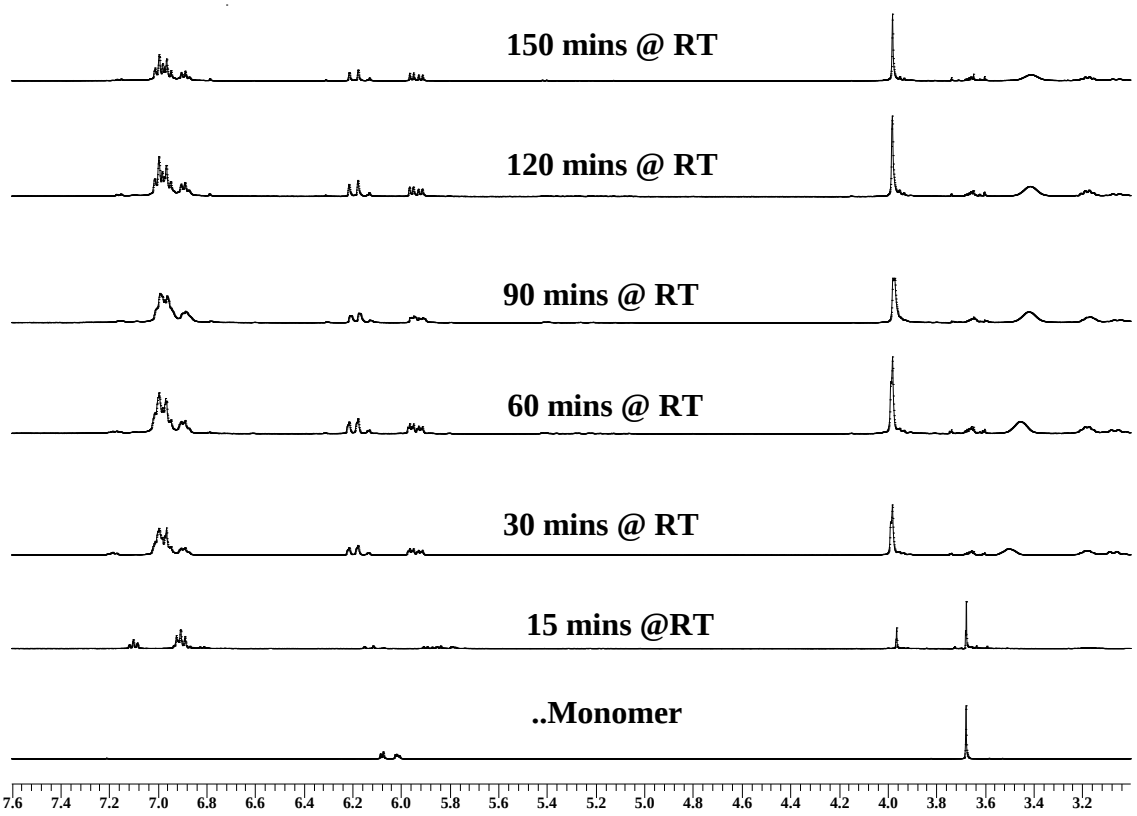


Figure 3.20. 400 MHz ^{1}H NMR spectra for the ROMP reaction of norbornene-1-methyl carboxylate monomer using 1st generation of ruthenium initiator with the ratio of monomer: initiator of 1:1 in $CDCl_3$

The ^{1}H NMR spectrum taken after 30 minutes shows that the signal at 3.68 ppm disappeared and that two signals appeared close to each other at 3.98 ppm. As the reaction time is increased, the intensity of the signal on the left is increased and that of the signal on the right is decreased and eventually disappeared at 120 minutes. So, only one peak at 3.98 ppm is observed after 150 minutes of reaction time.

The signals at 6.88-7.12 ppm and also those at 5.90 ppm and 6.24 ppm are believed to be due the phenyl groups and the vinylic protons respectively of the inserted and chelated compounds.

The integrations of the initiator and new alkylidene signals against TMS as the internal standard are shown in Table 3.1. The result shows the eventual disappearance of the initiator alkylidene signal at 19.97 ppm and eventual appearance of the new alkylidene signal at 16.96 ppm.

Table 3.1. The integration of the signals in the alkylidene reign against TMS (Internal standard)

Entry	Time (minutes)	Initiator alkylidene signal at 19.97 ppm	New alkylidene signal at 16.96 ppm (%)
1	15	4.7(100%)	0.7
2	30	1.0(21.3%)	1.8
3	60	0.4(8.5%)	1.5
4	90	0.14(3.0%)	2.4
5	120	0.0(%)	1.5

The ROMP reaction of the monomer with 1st generation with the ratio of monomer: initiator of 1:1 in $CDCl_3$ was repeated and the same results were obtained.

It is concluded that when the monomer is inserted at the ruthenium centre complex A is formed (Figure 3.21 A) which gives rise to the appearance of a new signal for the methyl group at 3.98 ppm (signal on the right). This is then followed by the formation of complex B through chelation of oxygen to the ruthenium centre which gives rise to another signal for the methyl group at 3.98 ppm (signal on the left) (Figure 3.21 B).

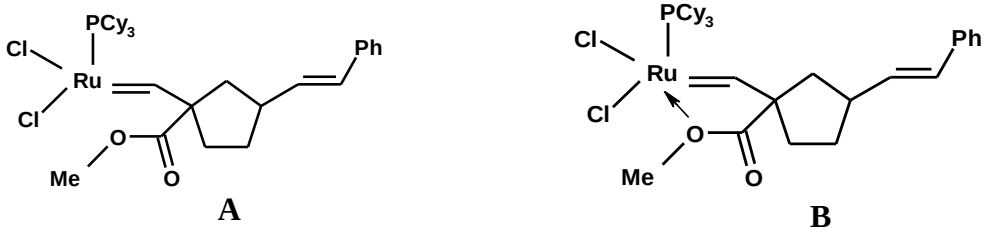
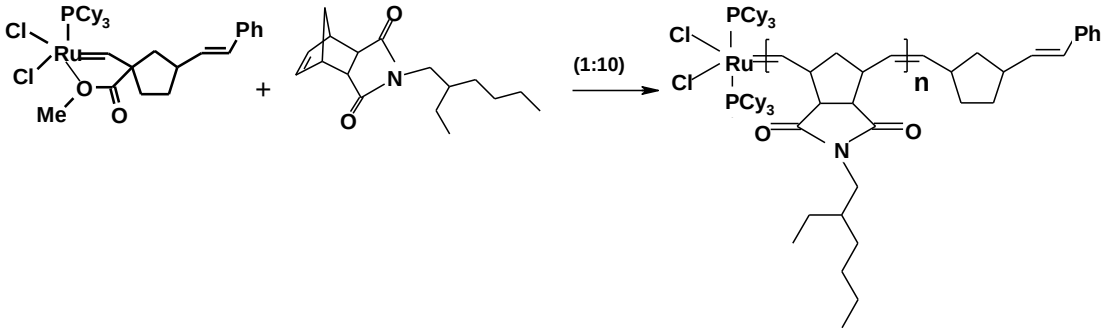


Figure 3.21. (A) insertion of monomer to ruthenium centre, (B) chelation via oxygen to the ruthenium centre

3.2.2 ROMP reaction of exo-N-ethylhexyl norbornene-5,6-dicarboxyimide monomer using chelated product of reaction 3.2.1.

The ROMP reaction of exo-N-ethylhexyl norbornene-5,6-dicarboxyimide monomer was carried out using the product of reaction 3.2.1. using the ratio of monomer: chelated product of 10:1, in Toluene-d_8, Scheme 3.8.



Scheme 3.8. ROMP reaction of exo-N-ethylhexyl norbornene-5,6-dicarboxyimide monomer using the product of reaction 3.2.1.

The ^{1}H NMR spectrum taken after 15 minutes of reaction at room temperature showed the presence of the doublet at 16.92 ppm due to the alkylidene proton of the chelated complex used as an initiator, see Figure 3.22. It also showed the signal due to the olefinic proton of the monomer at 5.77 ppm, Figure 3.23. The multiplet signals for protons in the 1 and 4 positions in the norbornene ring of the monomer and also for protons of the carbon next to nitrogen are observed at 3.32 ppm.

The reaction was heated to 100 °C for 48 hours and the ^{1}H NMR spectrum were recorded at different time intervals. The ^{1}H NMR spectrum after 2 hours reaction showed the disappearance of the alkylidene signals at 16.92 ppm, Figure 3.22. It also showed the disappearance of the vinylic protons of the monomer at 5.80 ppm and appearance of the olefinic protons of the polymer at 5.74 ppm and 5.78 ppm, Figure 3.23. The signal at 3.32 ppm shifted to 3.43 ppm as a broad signal due to the formation of polymer. The resonances due to phenyl end groups are also observed. However, the ^{1}H NMR spectrum taken after 6 hours, 24 hours and 48 hours remained the same.

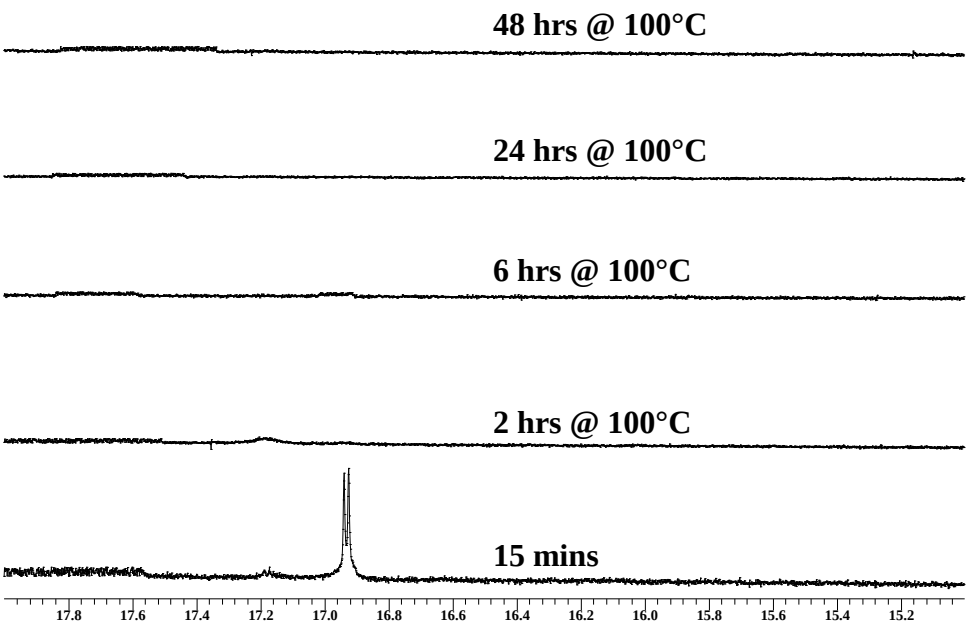


Figure 3.22. 400 MHz ^{1}H NMR spectra showing the alkylidene region for the ROMP reaction of exo-N-ethylhexyl norbornene-5,6-dicarboxyimide monomer using chelated product of (3.2.1) as an initiator with the ratio of monomer: initiator (10:1) in C_7D_8

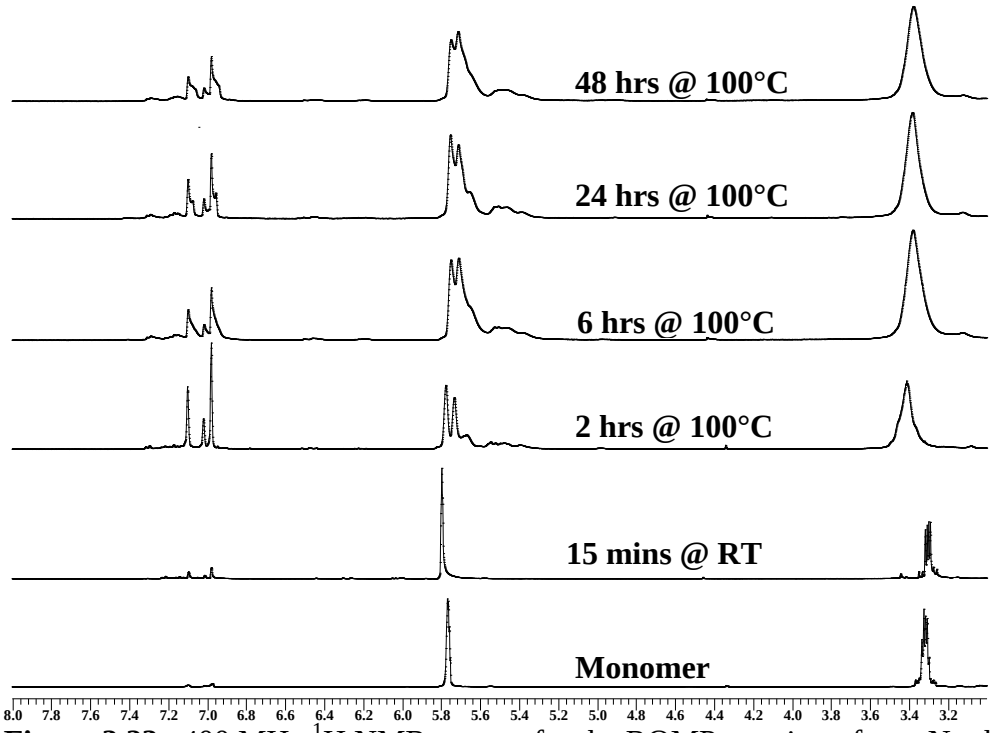


Figure 3.23. 400 MHz ^{1}H NMR spectra for the ROMP reaction of exo-N-ethylhexyl norbornene-5,6-dicarboxyimide monomer using chelated product of (3.2.1) as an initiator with the ratio of monomer: initiator (10:1) in C_7D_8

The integration of the alkylidene signal and also the vinylic protons of the monomer against TMS as an internal standard are shown in Table 3.2. The result confirms the complete consumption/disappearance of the alkylidene signal at 16.92 ppm.

Table 3.2. The integration of the signals in the alkylidene reigon and vinylic proton of the monomer reign against TMS (Internal standard)

Entry	Time	Temp.	Alkylidene signal at 16.92 ppm
1	15mins	RT	1.0(100%)
2	2hrs	100°C	0.25(25%)
3	5hr30mins	100°C	0(%)
4	24 hrs	100°C	0(%)
5	48 hrs	100°C	0(%)

The result of the ^{1}H NMR experiment indicates the complete conversion of monomer to polymer. GPC analysis shows the polymer has Mn=16,990, Mw=47,500 and PDI=2.80. The GPC trace has a low molecular weight shoulder which explains why PDI is broad. The calculated molecular weight is 2,750. The Mn values are relative to polystyrene standard and they are not reliable due to the difference in the hydrodynamic volumes. However, the large difference between the calculated and found Mn indicates that the polymerisation reactionis not well-defined. This is supported by the broad PDI value of 2.80.

The ROMP reaction was repeated in order to leave the reaction for longer time at room temperature to evaluate the efficiency of the chelated product as an initiator.

The ^{1}H NMR spectrum taken after 5 hours of reaction at room temperature showed the presence of the doublet at 16.95 ppm due to the alkylidene proton of the chelated complex (used as an initiator), see Figure 3.24. It also showed the signal due to the olefinic proton of the monomer at 5.78 ppm, Figure 3.25. The signal for protons in the 1 and 4 positions in the norbornene ring of the monomer and also for protons of the carbon next to nitrogen are observed at 3.33 ppm. A broad signal is also observed at 3.45 ppm due the presence of these protons in the polymer.

The ^{1}H NMR spectrum taken after 24 hours of reaction time at room temperature, Figure 3.24, showed the disappearance of the alkylidene signals at 16.95 ppm. It also showed the appearance of the olefinic protons of the polymer at 5.56-5.84 ppm, Figure

3.25, showed the area under the peak of the signal at 3.32 ppm is reduced and the area under the peak of the signal at 3.45 ppm is increased. The reaction was heated to 100°C for 24 hours and the ^{1}H NMR spectra were recorded at different time intervals. The ^{1}H NMR spectrum, Figure 3.25, after 2 hours reaction showed resonances due olefinic protons of the polymer at 5.72 ppm and 5.76 ppm. The signal at 3.33 ppm completely disappeared and only the broad signal at 3.45 ppm was observable. It also showed the resonances due to phenyl end groups. The ^{1}H NMR spectrum taken after 24 hours remained the same.

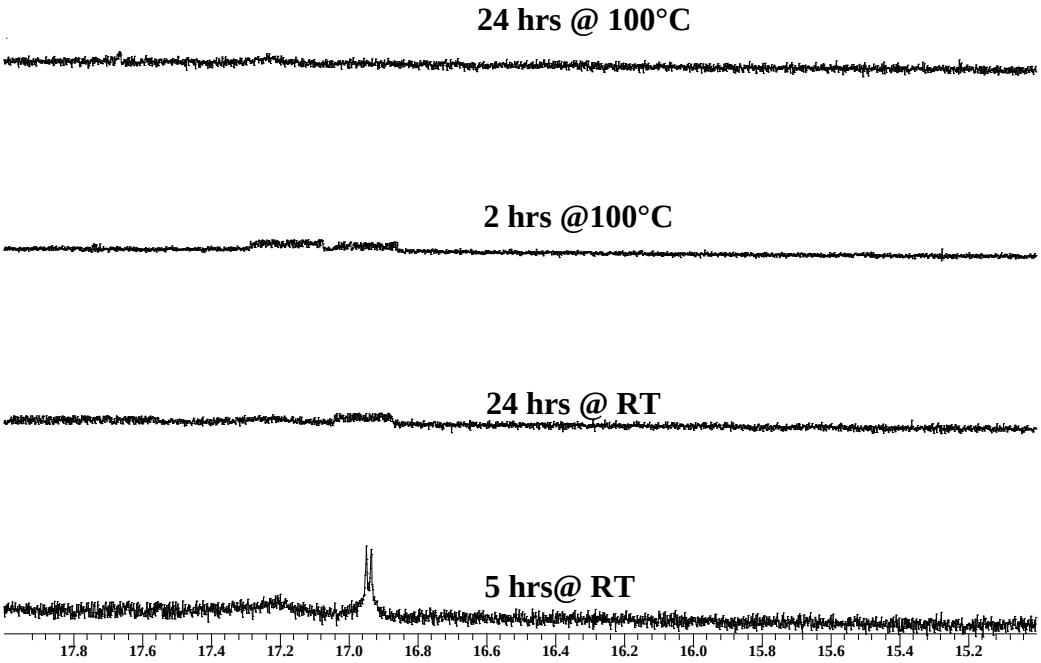


Figure 3.24. 400 MHz ^{1}H NMR spectra showing the alkylidene region for the ROMP reaction of exo-N-ethylhexyl norbornene-5,6-dicarboxyimide monomer using chelated product of (3.2.1) as an initiator with the ratio of monomer: initiator (10:1) in C_7D_8

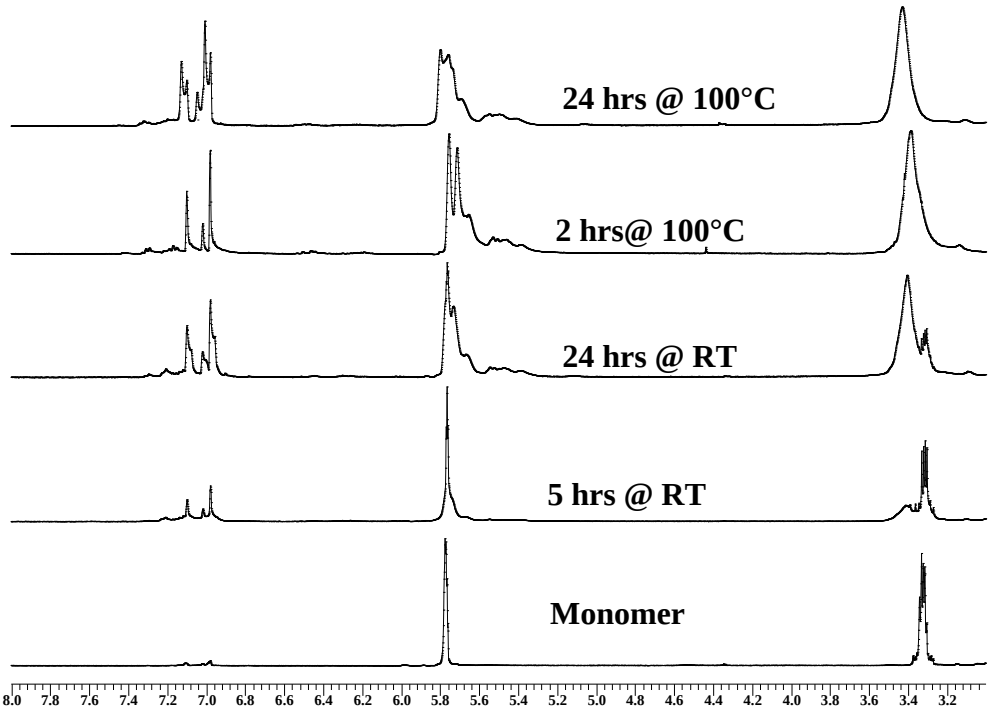
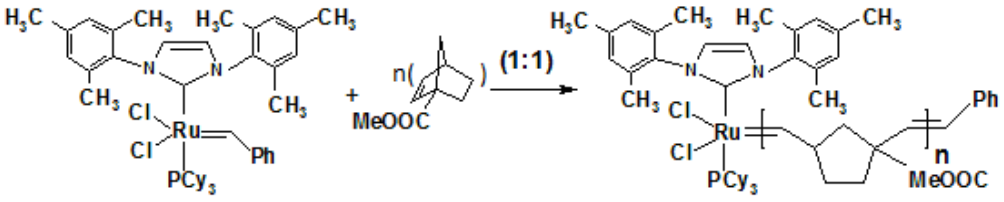


Figure 3.25. 400 MHz ^{1}H NMR spectra for the ROMP reaction of exo-N-ethylhexyl norbornene-5,6-dicarboxyimide monomer using chelated product of (3.2.1) as an initiator with the ratio of monomer: initiator (10:1) in C_7D_8

The results confirms the conclusion made earlier for the first ROMP reaction using the chelated complex as an initiator.

3.2.3 ROMP reaction of norbornene-1-methyl carboxylate monomer using 2nd generation ruthenium initiator [RuCl2(PCy3)(IMes)(=CHPh)].

The ROMP reaction of norbornene-1-methyl carboxylate monomer was carried out using the 2nd generation ruthenium initiator with a ratio of monomer: initiator of 10:1, in $CDCl_3$, Scheme 3.9.



Scheme 3.9. ROMP reaction of norbornene-1-methyl carboxylate monomer using 2nd generation ruthenium

The ^{1}H NMR spectrum taken after 30 minutes showed the presence of the initiator alkylidene at 19.12 ppm and new alkylidene signal at 16.00 ppm, see Figure 3.26. The signal due to the methyl group of the monomer at 3.68 ppm is still observed. It also showed the appearance of new signals due to the methyl group, a broad and a sharp signal at 3.89 ppm and at 3.63 ppm, respectively. The signals due to the vinylic protons of the monomer at 6.02-6.08 ppm are observed but no signal is observed for the vinylic protons of the polymer expected at 5.20-5.80 ppm, see Figure 3.27. The spectrum also showed resonances in the aromatic region at 6.98-7.31 ppm due to the phenyl end groups.

The reaction was followed for 48 hours at room temperature and the ^{1}H NMR spectra were recorded at different time intervals. The ^{1}H NMR spectrum after 1 hour showed the presence of the initiator alkylidene signal at 19.12 ppm and of a multiplet signal at 16.11 ppm. The intensity of the multiplet signal at 16.11 ppm was increased as the reaction time was increased to 48 hours. The ^{1}H NMR spectrum taken after 48 hours showed the presence of the initiator alkylidene signal at 19.12 ppm as well as the multiplet signal at 16.11 ppm, Figure 3.26. The intensity of the methyl signal at 3.68 ppm was reduced as the reaction time was increased and at the same time the intensity of other signals due to methyl group at 3.71-3.99 ppm were increased. The signals at 3.57 ppm and 3.62 ppm disappeared with time and instead other signals due to the methyl groups appeared. Resonances due to the olefinic protons of the polymer at 5.01-5.71 ppm appeared after 24 hours of reaction time, the intensity of these signals increased after 48 hours. The intensity of the resonances in the aromatic region at 6.98-7.31 ppm due to the phenyl end groups also increased as the reaction time increased to 48 hours. The ^{1}H NMR spectrum taken after 48 hours shows multiple resonances due to the methyl groups as well as resonances due to the olefinc protons of both the monomer and the polymer. It also shows the resonances due to phenyl end groups.

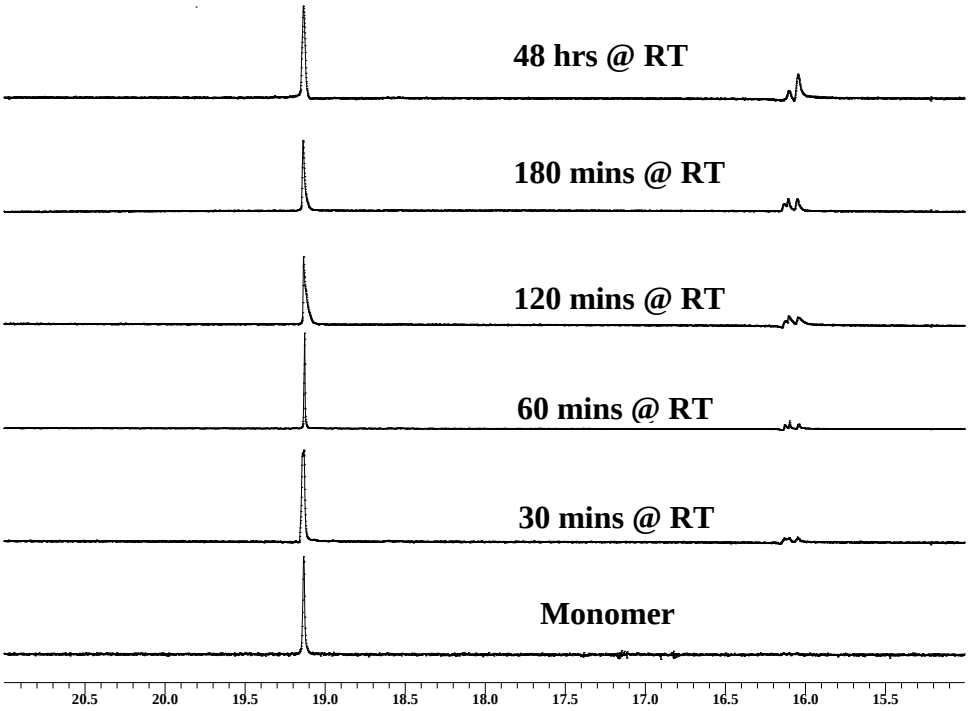


Figure 3.26. 400 MHz ^{1}H NMR spectra showing the alkylidene region for the ROMP reaction of norbornene-1-methyl carboxylate monomer using 2nd generation of ruthenium initiator with the ratio of monomer : initiator of (10:1) in $CDCl_3$

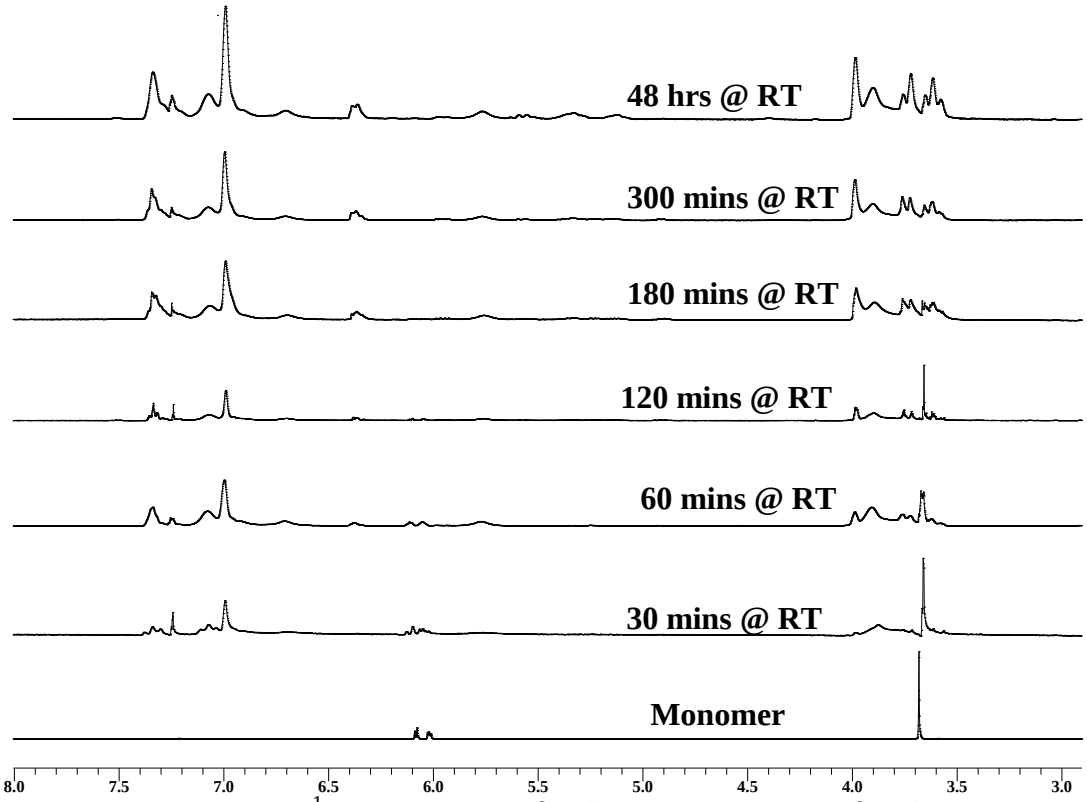
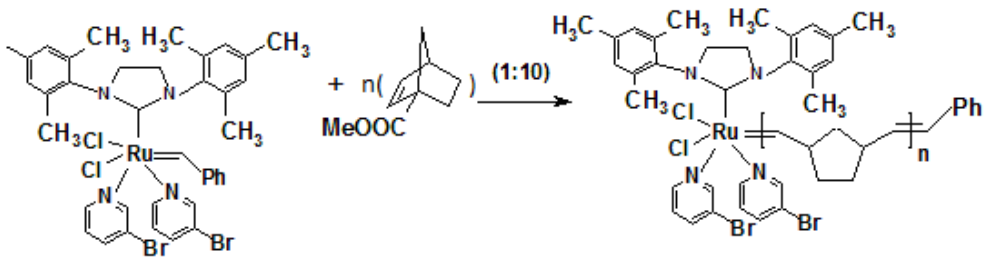


Figure 3.27. 400 MHz ^{1}H NMR spectra for the ROMP reaction of norbornene 1-methyl carboxylate monomer using 2nd generation of ruthenium initiator with the ratio of monomer: initiator of (10:1) in $CDCl_3$

The result shows that norbornene-1-methyl carboxylate monomer polymerised in the presence of the 2nd generation ruthenium initiator. GPC analysis of the product shows that a polymer is obtained, Mn=1,810, Mw=2,420, PDI=1.34. The Calculated Mn for the polymer is found to be 1,520. The experimentally determined Mn value is equivalent to polystyrene and for the reason explained in section 3.2.2. it is not reliable. However, there is a good correlation between the calculated and found Mn values. The fact that PDI is narrow (1.34) indicates a reasonably well controlled polymerisation reaction.

3.2.4 ROMP reaction of norbornene-1-methylester carboxylate monomer using modified 2nd generation ruthenium initiator [$RuCl_2(BrPy)_2(IMesH_2)(=CHPh)$]

The ROMP reaction of norbornene-1-methyl carboxylate monomer was carried out using modified 2nd generation ruthenium initiator using the ratio of monomer: initiator of 10:1, in $CDCl_3$, Scheme 3.10.



Scheme 3.10. ROMP reaction of norbornene-1-methyl carboxylate monomer using modified 2nd generation ruthenium

The ^1H NMR spectrum taken after 30 minutes of the reaction mixture at room temperature showed the disappearance of the initiator alkylidene signal at 19.12 ppm and the presence of a set of alkylidene signals at 16.04 ppm and a major one at 16.14 ppm, see Figure 3.28. The signal due to the methyl group of the monomer at 3.68 ppm is still observed. It also shows the signals due to the methyl group of the monomer at 3.68 ppm, and a new one at 3.69 ppm. A broad signal is also observed in the methyl region at 4.00 ppm, Figure 3.29. The signals due to the vinylic protons of the monomer at 6.04-6.11 ppm are observed but no signal is observed for the vinylic protons of the polymer at 5.20-5.80 ppm, see Figure 3.29. The spectrum also shows resonances in the aromatic region at 6.98-7.33 ppm due to the phenyl end groups.

The ^{1}H NMR spectrum taken after 90 minutes of reaction at room temperature showed the intensity of the alkylidene peak at 16.14 ppm decreased, Figure 3.28. The reaction was heated to 45°C for 48 hours and the ^{1}H NMR spectra were recorded at different time intervals. The ^{1}H NMR spectrum after 40 minutes reaction showed further decrease in the intensity of the alkylidene peak at 16.14 ppm and the disappearance of the singlet peak at 3.69 ppm. The intensity of the alkylidene signals at 16.14 ppm continued decreasing and the alkylidene signal at 16.04 ppm became broader as the reaction time was increased to 48 hours. Moreover, the intensity of the signal due to methyl group at 3.69 ppm was also reduced and the intensity of other signals due to methyl group increased. The ^{1}H NMR spectrum taken after 48 hours showed the presence of a broad alkylidene signal at 16.07 ppm, Figure 3.28. Broad resonances due the methyl group at 3.64 ppm and 4.05 ppm as well as resonances due to the olefinc protons of both the monomer (6.01-6.08 ppm) and the polymer (5.11-5.51 ppm). It also shows the resonances due to phenyl end groups, Figure 3.29.

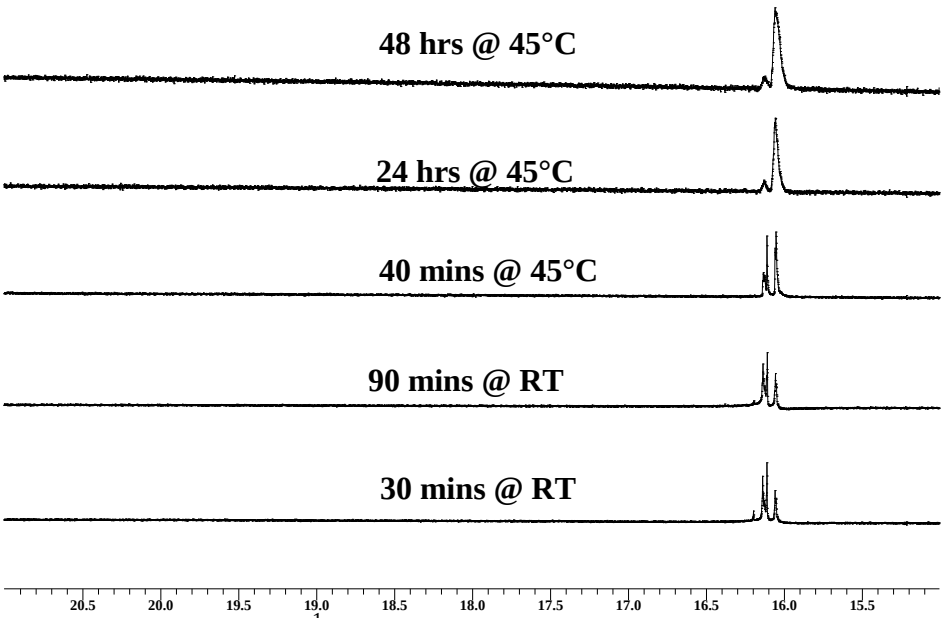


Figure 3.28. 400 MHz ^{1}H NMR spectra showing the alkylidene region for the ROMP reaction of norbornene-1-methyl carboxylate monomer using modified 2nd generation of ruthenium initiator with the ratio of monomer: initiator of (10:1) in $CDCl_3$

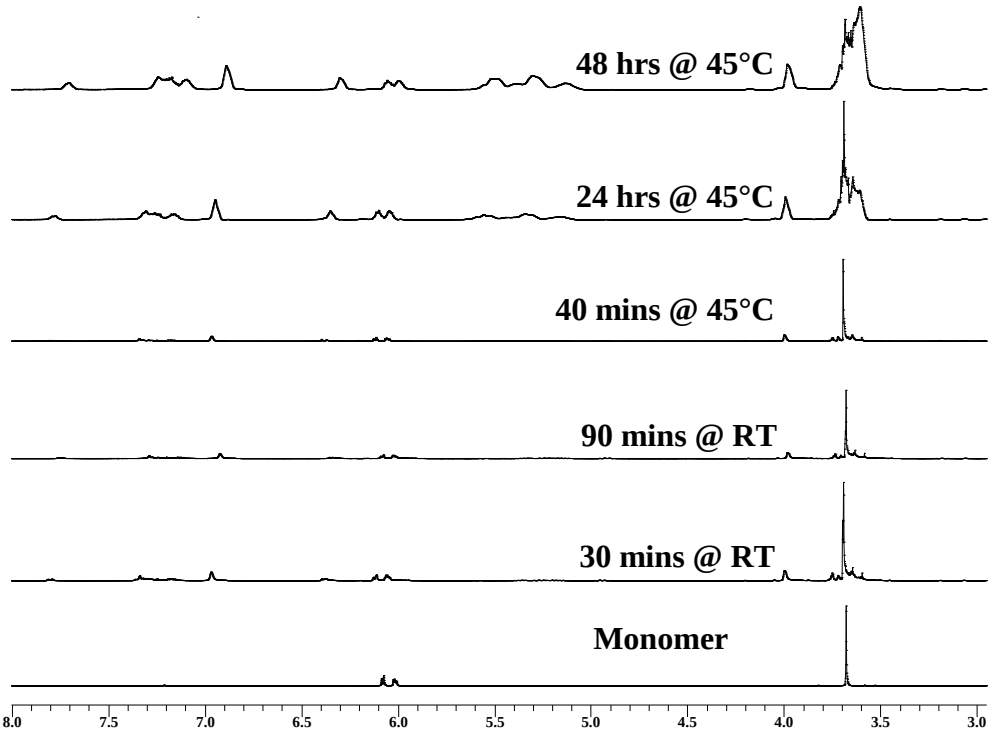


Figure 3.29. 400 MHz ^{1} H NMR spectra for the ROMP reaction of norbornene-1-methyl carboxylate monomer using modified 2nd generation of ruthenium initiator with the ratio of monomer: initiator of (10:1) in $CDCl_3$

The result shows that the modified 2nd generation ruthenium initiator polymerised norbornene-1-methyl carboxylate monomer. GPC analysis of the product shows that the polymer is formed, Mn=2,746, Mw=3,655 and PDI=1.33. The narrow PDI (1.33) indicated a well controlled polymerisation reaction.

3.2 Addition (Vinylic) polymerisation of norbornene-1-methyl carboxylate monomer

3.2.1 Addition Polymerisation of norbornene-1-methyl carboxylate monomer using palladium initiator [Pd(H) $(PCy_3)_2(CH_3CN)][B(C_6F_5)_4]$, (Pd 1388)

Addition polymerisation of norbornene-1-methyl carboxylate monomer was carried out using palladium initiator $(Pd(H)(PCy_3)_2(CH_3CN)$, (Pd 1388) using the ratio of monomer: initiator of 1:1, in TCE-d_2.

The ^{1}H NMR spectrum taken after 30 minutes of reaction at room temperature showed signals due to the vinylic protons of the monomer at 6.08 ppm and 6.13 ppm and also a signal due to the methyl group of the monomer at 3.73 ppm, see Figure 3.30. The spectrum also showed a triplet due to the hydride of the Pd 1388, at -15.47 ppm, Figure 3.31. The reaction was heated to 70°C and ^{1}H NMR spectra were taken

at different time intervals. ^{1}H NMR spectrum taken after 1 hour reaction showed the same signals seen at room temperature. It also showed the appearance of new multiplet signals at 3.92 ppm and a doublet at 3.68 ppm due to possibility new methyl group. The intensity of the signals at 3.92 ppm, 3.68 ppm is increased as the reaction time was increased to 4 hours, Figure 3.30. The intensity of the hydride signal is reduced as the reaction is heated to 70°C and the reaction time is increased to 4 hours, Figure 3.31. The colour of the solution turned into a dark-green colour from light-green colour after 4 hours at 70°C and signals appeared at 7.22 ppm.

The ^{31}P NMR spectrum taken after 30 minutes of the start of the reaction at room temperature showed a signal as a doublet at 44.30 ppm and 44.35 ppm due to the Pd 1388, Figure 3.32. The spectrum taken after 1 hour of the reaction at 70°C showed the appearance of several signals at 41.73, 35.56, 34.55, and 26.41 ppm, the intensity of which increased with the time at the expense of the doublet at 44.30 ppm and 44.35 ppm. The identity of these signals is not known. In the ^{31}P NMR spectrum signal at 11.43 ppm due to free tricyclohexyl phosphine was not observed.

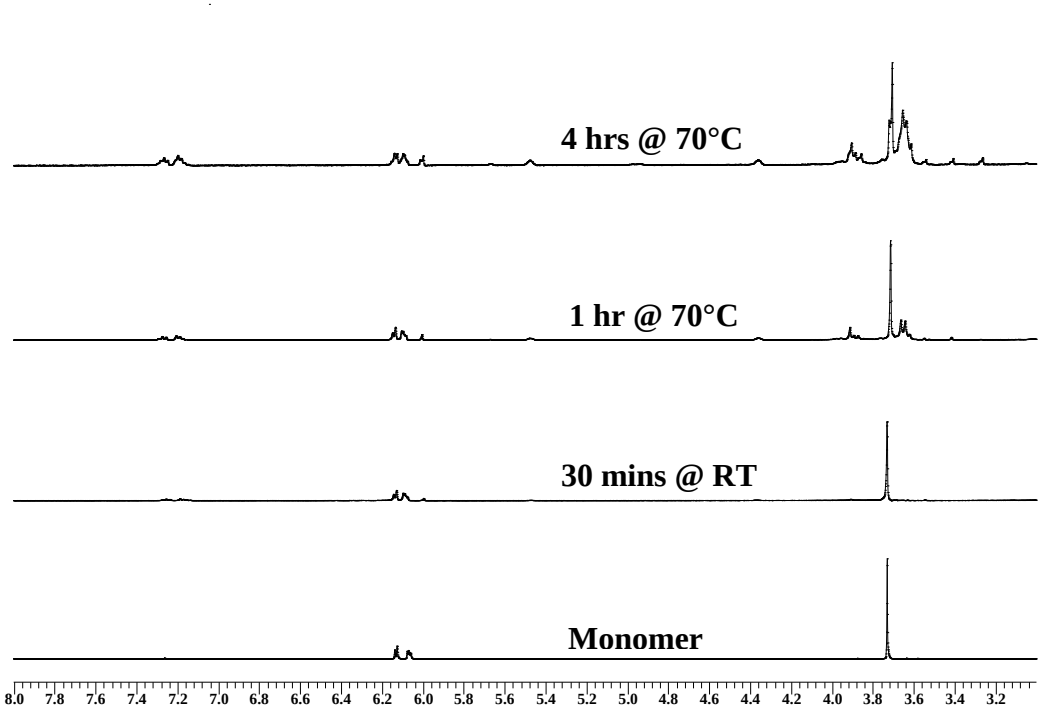


Figure 3.30. 400 MHz ^{1}H NMR spectra for addition polymerisation of norbornene-1-methyl carboxylate monomer using palladium initiator with the ratio of monomer : initiator (1:1) in TCE-d_2

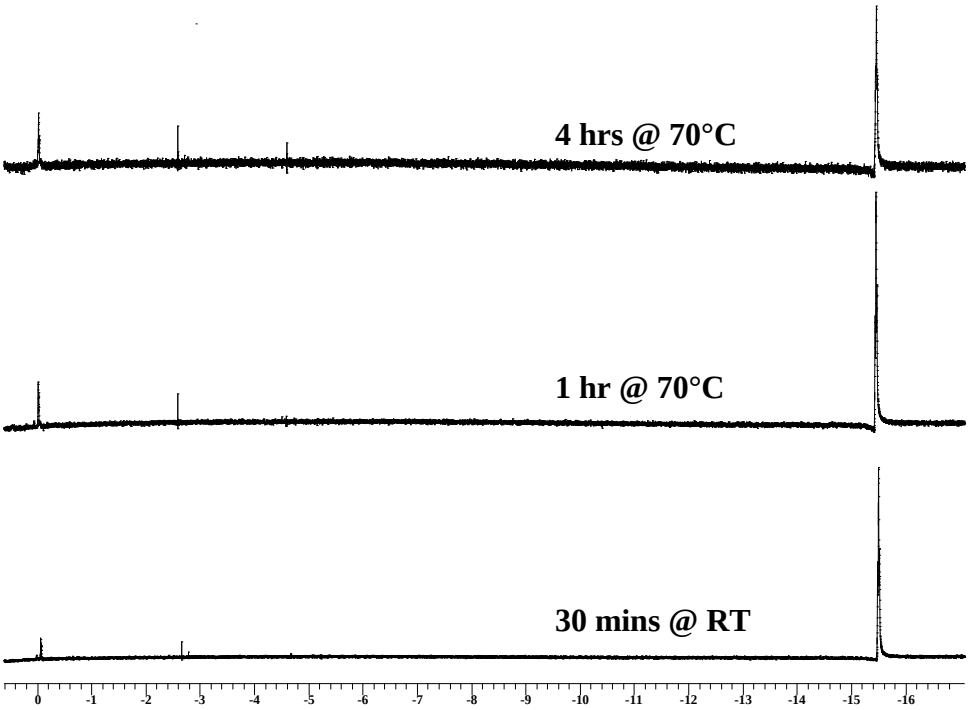


Figure 3.31. 400 MHz ^{1}H NMR spectra showing the hydride region for addition polymerisation of norbornene-1-methyl carboxylate monomer using palladium initiator with the ration of monomer: initiator of 1:1 in TCE-d_2

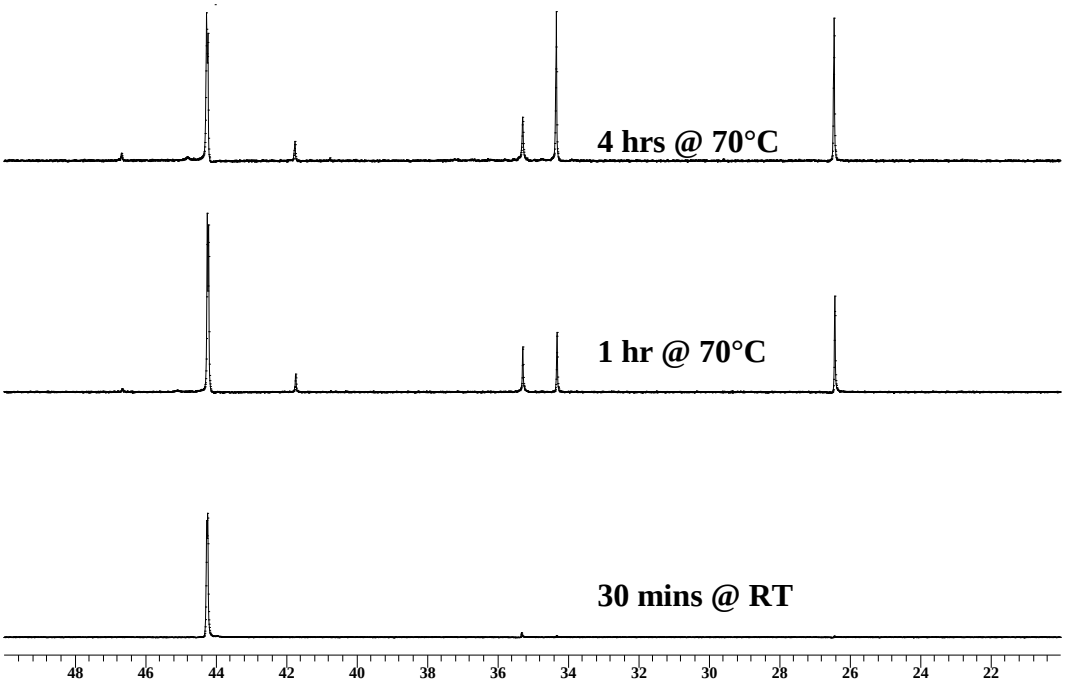


Figure 3.32. 162 MHz ^{31}P NMR spectra for of norbornene-1-methyl carboxylate monomer using palladium initiator with the ratio of monomer : initiator (1:1) in TCE-d_2

The reaction was repeated once more under similar conditions and the same results were observed.

The integration of the hydride signal of the initiator and the vinylic protons of the monomer against TMS are shown in Table 3.3. It shows the reduction of the intensity of the signal as the reaction is heated to 70°C and the reaction time is increased.

Table 3.3. The integration of the signals due to the vinylic protons of the monomer against TMS.

Entry	Time	Temp.	Monomer vinylic hydrogen signal at 6.08 & 6.13 ppm	Initiator hydride signal at -15.47 ppm	Monomer methyl Group at 3.74 ppm
1	30min	RT	11(100%)	7.5(100%)	88(100%)
2	1 hr	70°C	7.5(68.2%)	6.5(86.7%)	57.5(65.34%)
3	4 hr	70°C	2.5(22.7%)	3.5(46.7%)	23.5 (26.70%)

In order to investigate the possibility of addition polymerisation, the addition polymerisation of norbornene-1-methyl carboxylate monomer was carried out using palladium initiator ($Pd(H)(PCy_3)_2(CH_3CN)$), (Pd 1388) using the ratio of monomer: initiator of 100:1, in TCE-d_2.

The ^1H NMR spectrum taken after 30 minutes showed two signals at 3.57 ppm and 3.59 ppm and signals at 5.96 and 6.02 ppm due to the methyl protons and vinylic protons of the monomer respectively, Figure 3.33. The reaction was heated to 70°C and spectra were recorded at different reaction time intervals, Figure 3.33. The signals at 5.95 ppm and 6.02 ppm appeared to remain unchanged, as the reaction time was increased to 4 days. However, as the reaction increased the intensity of the signals at 3.59 ppm increased and that at 3.57 ppm decreased. The signal at 3.59 ppm was the only one observed after 4 days of reaction at 70°C.

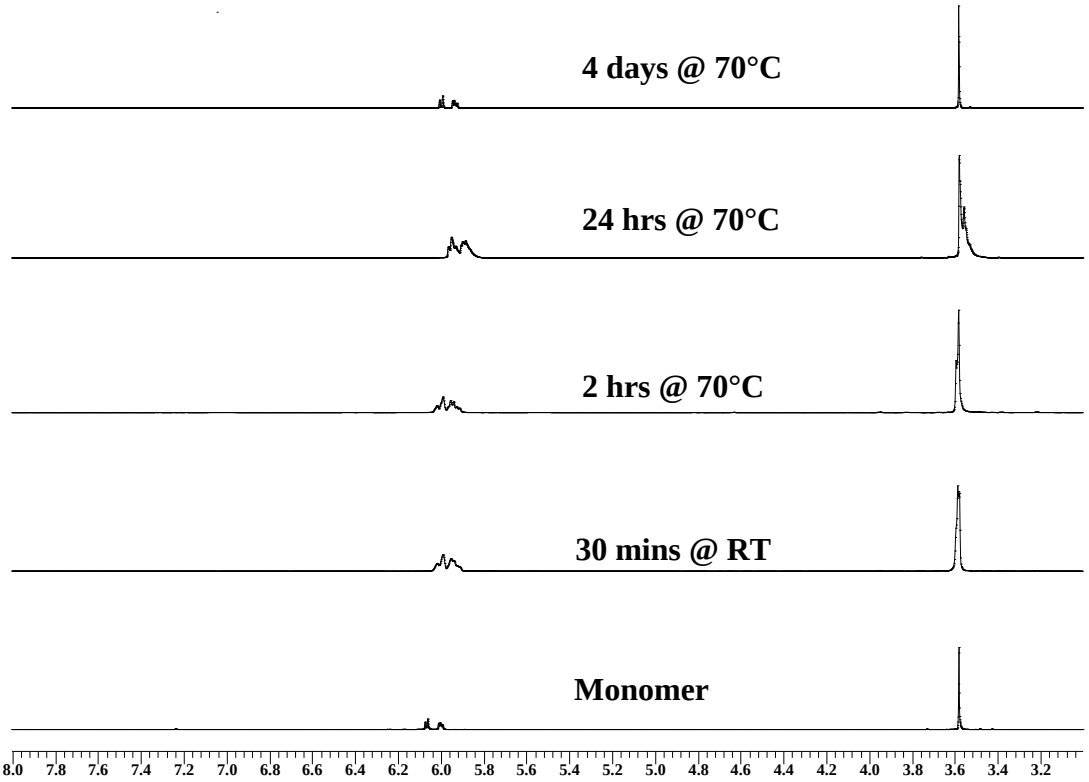


Figure 3.33. 400 MHz ^{1}H NMR spectra for addition polymerisation of norbornene-1-methyl carboxylate monomer using palladium initiator with the ratio of monomer : initiator (100:1) in TCE-d_2

No signal due to hydride of the initiator was observed after 30 minutes of reaction at room temperature. This may be due to low concentration of initiator in comparison with the monomer. The ^{31}P NMR spectrum taken after 30 minutes reaction at room temperature showed a sharp signal at 44.30 ppm due to the Pd1388 initiator and three weak signals at 34.15 ppm, 33.75 ppm, and 26.28 ppm.

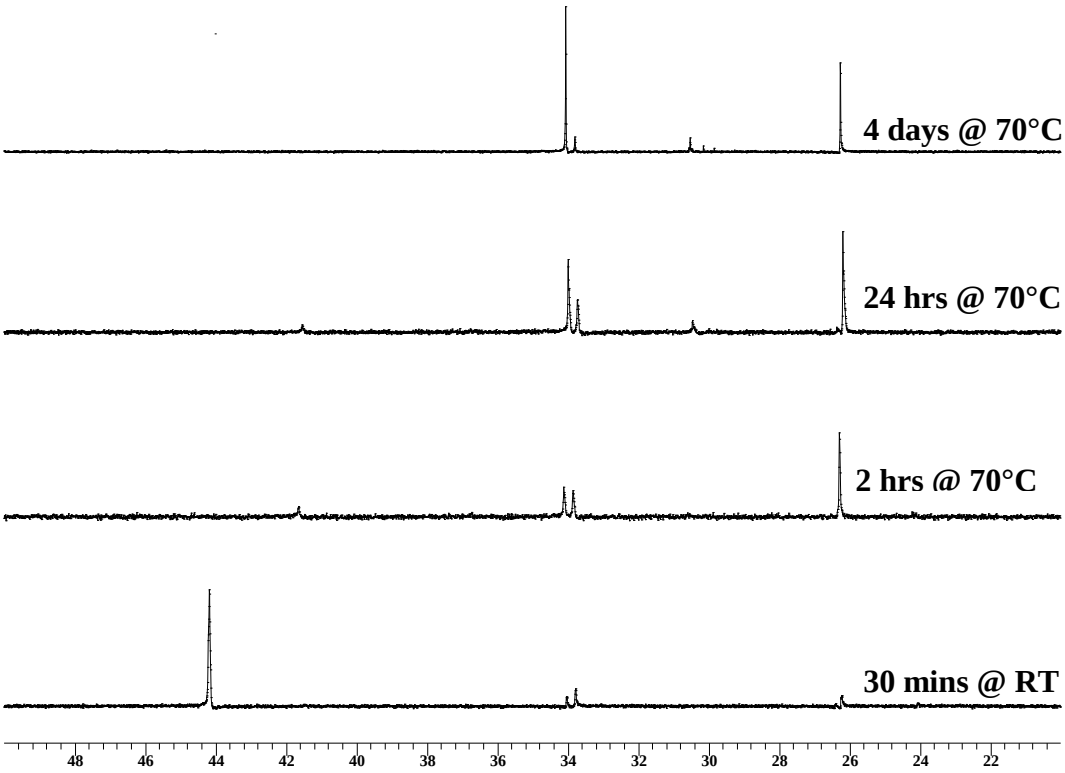
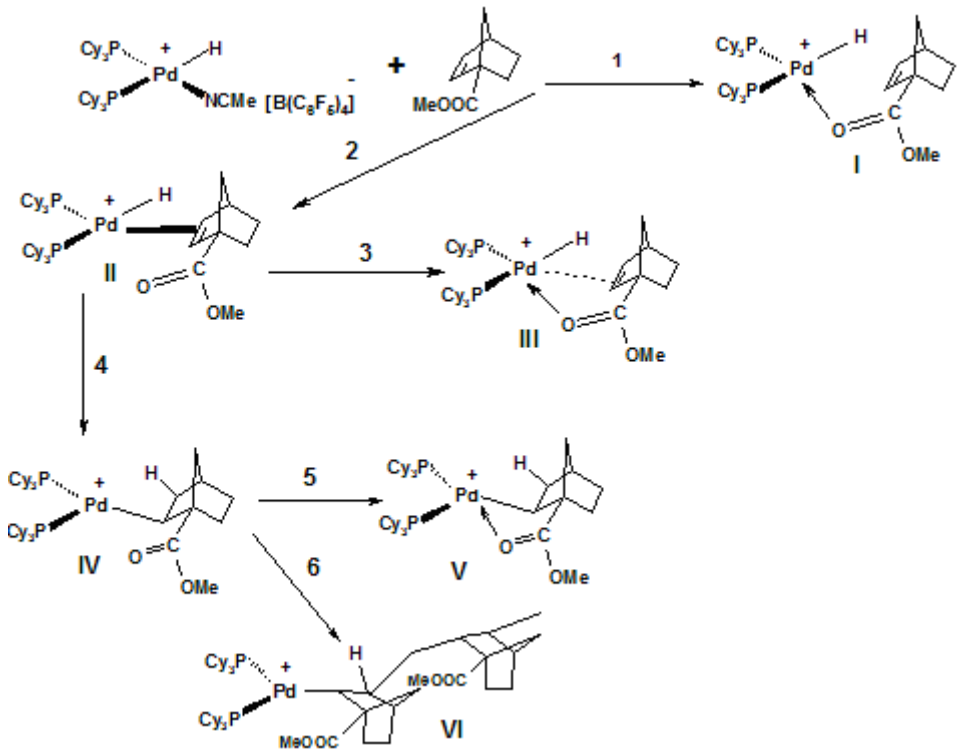


Figure 3.34. 162 MHz ^{31} P NMR spectra for of norbornene-1-methyl carboxylate monomer using palladium initiator with the ratio of monomer : initiator (100:1) in TCE-d_2

The spectra taken after 2 hours reaction at 70°C showed that the intensity of the signals at 34.15, 33.75, and 26.28 ppm was increased and that the signal at 44.30 ppm had disappeared. The intensity of the peak at 34.15 ppm increased and the intensity of the peak at 26.28 ppm decreased as the reaction time was increased to 24 hours. The identity of these signals are not known. They are believed to be due to the decomposition protons of the initiator. The result of the GPC analysis showed the existence of two peaks with DP(degree of polymerisation) of 2 and 16 which suggest the formation of a dimmer and an oilgomer.

The ester functionality in 1 position of the norbornene-1-methyl carboxylate monomer has the ability to chelate to the metal centre. Scheme 3.11, suggested possible monomer-initiator complexes (I-VI) for addition polymerisation using Pd 1388 initiator.



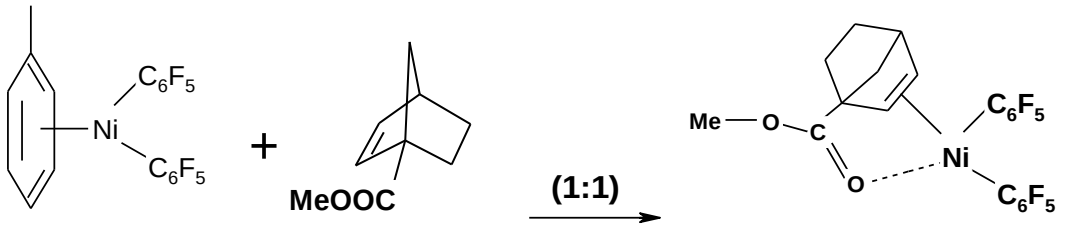
Scheme 3.11. Addition polymerisation of norbornene-1-methyl carboxylate monomer using palladium initiator $[Pd(H)(PCy_3)_2(CH_3CN)][B(C_6F_5)_4]$

The coordination/chelation ability monomer's ester functional group may play an important role in catalytic activity of Pd1388. The monomer can simply chelate to Pd1388 initiator and form I. This mode of action may prevent further insertion of monomer. The monomer can simply coordinate to the Pd centre without chelation forming II, which could either lead to coordination as well as chelation III or insertion forming IV. The inserted monomer can then promote the chelation forming V or further insertion of monomer may take place forming oligomers or polymer VI. The formation of I-III is expected to result in no change in the intensity of the vinylic hydrogens of the monomer or the hydride of the Pd1388. Although, their formation may result in small changes in the chemical shifts. However, the formation of IV-VI is expected to result in disappearance of the vinylic hydrogens of the monomer and hydride of the initiator. The results in Table 3.3 show reduction in the intensities of the signals for both vinylic protons and hydride, but not complete disappearance as both signals are present after 4 hours at 70°C. The signal due to the methyl of the monomer is also reduced but not completely. At the same time some new methyl groups have appeared in the NMR spectra which support the formation compounds

having methyl groups experiencing different environments. Moreover, the GPC analysis indicates the formation dimmers and oligomers, pointing towards repeated insersion of the monomer at the Pd centre. Based on the result discussed here, it has been difficult to determine which route is the dominant one in this reaction.

3.3.2 Addition polymerisation of norbornene-1-methyl carboxylate monomer using nickel initiator (η^6-toluene)Ni(C_6F_5)$_2$

The addition polymerisation of norbornene-1-methyl carboxylate monomer was carried out using the nickel initiator (η^6-toluene)Ni(C_6F_5)$_2$ using the ratio of monomer:initiator of 1:1, in C_7D_8, Scheme 3.13.



Scheme 3.13. Vinylic polymerisation of norbornene-1-methyl carboxylate monomer using Nickel initiator (η^6-toluene) Ni(C_6F_5)$_2$

The ^{1}H NMR spectrum taken after 30 minutes of reaction at room temperature showed resonances due to monomer only; vinylic protons at 5.83 ppm and 6.19ppm and Methyl at 3.40ppm, Figure 3.35. The ^{19}F NMR spectrum taken after 30 minutes of the reaction at room temperature also showed the resonances due to the initiator; -118.63ppm (dd, meta-F), -164.11ppm (t, para-F) and -168.23ppm (t, ortho-F), Figure 3.36. The reaction was therefore heated to 70˚C in C_7D_8. Both ^{1}H NMR and ^{19} F NMR spectra taken after 2 hours at 70˚C showed no change.

The decomposition of the Ni initiator is known to give resonances in ^{19} F NMR spectrum at 139.10, 164.92 & 162.60 ppm for penta fluoro benzene and 138.50, 151.30 & 161.34 ppm for deca fluoro bi-phenyl. None of these resonances are observed in the ^{19} F NMR spectrum take after 30 minutes of the reaction at room temperature and after 2 hours at 70˚C. In order to investigate the possibility of addition polymerisation, the addition polymerisation of norbornene-1-methyl carboxylate monomer was carried out using Ni initiator using the ratio of monomer: initiator of 100:1, in C_7D_8.

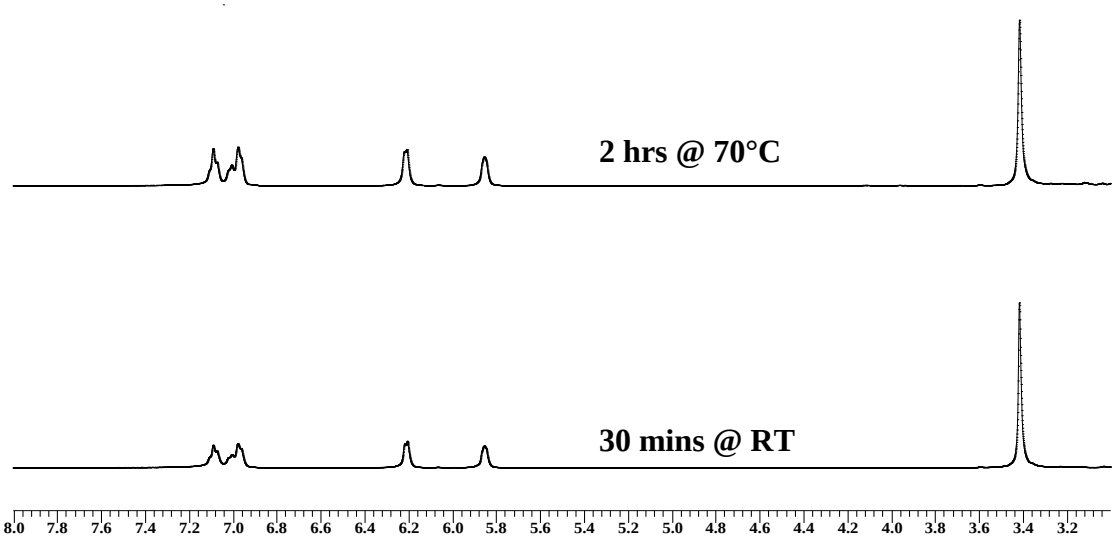


Figure 3.35. 400 MHz ^{1} H NMR spectra for of norbornene-1-methyl carboxylate monomer using nickel initiator with the ratio of monomer: initiator (1:1) in C_7D_8

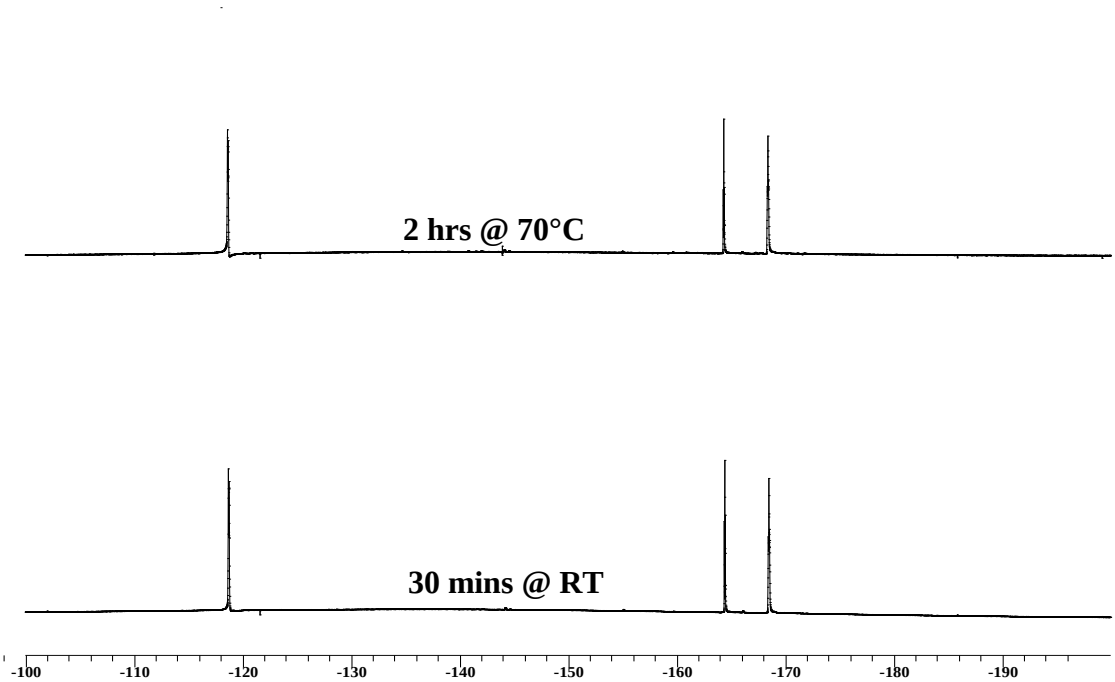


Figure 3.36. 376 MHz ^{19}F NMR spectra for of norbornene-1-methyl carboxylate monomer using nickel initiator with the ratio of monomer: initiator (1:1) in C_7D_8.

The ^{1}H NMR spectrum taken after 30 minutes and 1 hour of the reaction at room temperature showed only resonances due to the vinylic and methyl protons of the monomer, Figure 3.37. The reaction was therefore heated to 50 °C and was

monitored by NMR spectroscopy after 45 minutes, 105 minutes, 24 hours at 50 °C and the ^{1}H NMR spectra showed no changes in the intensity of vinylic protons, Figure 3.37.

Due to low concentration of the catalyst in the reaction mixture it was difficult to observe any signals due to the initiator in the the ^{19}F NMR spectrum.

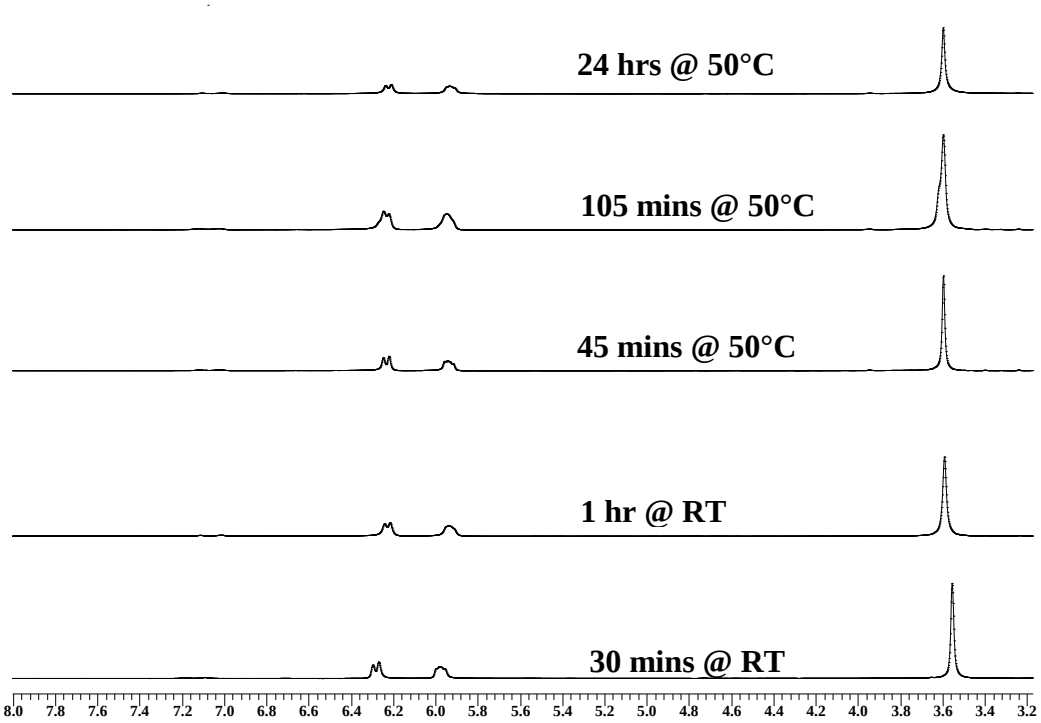
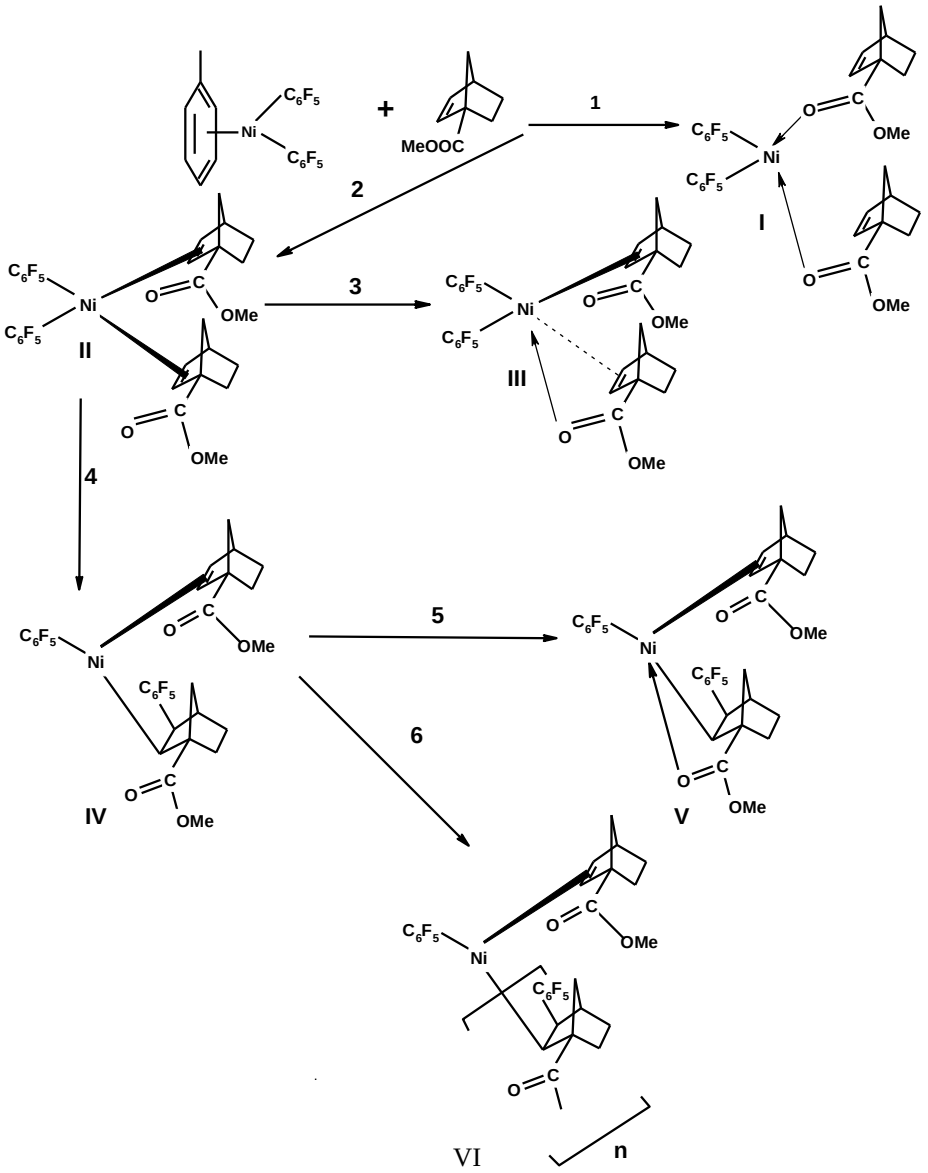


Figure 3.37. 400 MHz ^{1}H NMR spectra for of norbornene-1-methyl carboxylate monomer using nickel initiator with the ratio of monomer: initiator (100:1) in C_7D_8.

The monomer contains an ester group in 1 position, and the ester functional group has the ability to chelate to the metal centre. Therefore, in addition polymerisation using the nickel initiator (η^6-toluene)Ni(C_6F_5)$_2$, the coordination and chelation ability of the monomer is considered and it is expected to give several possible monomer-initiator complexes Scheme 3.12.

The coordination/chelation ability monomer's ester functional group may play an important role in catalytic activity of Ni initiator. The monomer can simply chelate to the initiator and form I. This mode of action may prevent further insertion of monomer. The monomer can simply coordinate to the Ni centre without chelation forming II, which could either lead to coordination as well as chelation III or insertion forming IV. The inserted monomer can then promote the chelation forming V or further insertion of monomer may take place forming oligomers or polymer VI. The formation of I-III is expected to result in no change in the intensity of the vinylic

hydrogens of the monomer. Although, their formation may result in small changes in the chemical shifts particularly for the vinylic hydrogens. However, the formation of IV-VI is expected to result in disappearance of the vinylic hydrogens of the monomer. The ^{1}H NMR spectra of the reaction mixtures taken at several interval at both room temperature and elevated temperature showed no shifts in the resonances of the monomer and no reduction in the intensity of the resonances. Moreover, we have not been able to collect any polymer products from these reactions. Consequently, based on the result discussed here, it has been difficult to determine the outcome of the polymerisation reaction involving the Ni initiator.



Scheme 3.12. Addition polymerisation of norbornene-1-methyl carboxylate monomer using nickel initiator (η^6-toluene)Ni(C_6F_5)$_2$

Chapter 4 Conclusion and Future Work

4.1 Conclusion

Norbornene-1-methyl carboxylate monomer was synthesised in several steps, in each step the final product was characterised by ^{1}H NMR and ^{13}C NMR spectroscopies. In the first step, norbornane-2-carboxylic acid monomer was brominated based on the Wagner-Meerwein rearrangement and 2-bromonorbornane-1-carboxylic acid was successfully prepared. In the second step, 2-bromonorbornane-1-carboxylic acid was methylated in the presence of K_2CO_3 and DMS (dimethyl sulphate) and 2-bromonorbornane-1-methyl carboxylate monomer was prepared. In the next step, 2-bromonorbornane-1-methyl carboxylate was de-hydrobrominated and hydrolysised using t-butyl alcohol and potassium t-butoxide and norbornene-1-carboxylic acid was synthesised. In the last step, norbornene-1-carboxylic acid was methylated and norbornene-1-methyl carboxylate monomer was successfully synthesised.

Norbornene-1-methyl carboxylate monomer was subjected to ring opening metathesis polymerization (ROMP) and additional polymerisation. The ROMP reaction of norbornene-1-methyl carboxylate monomer was carried out using 1st generation ruthenium initiator, the result showed no evidence for polymerisation, but it indicated the possibility of formation of a chelating complex as well as an oligomer. It was anticipated that a complex is possibly formed through chelation of the ether oxygen to the ruthenium center. In order to investigate the possibility of the formation of the complex, the ROMP reaction of norbornene-1-methyl carboxylate monomer with 1st generation ruthenium initiator was carried out at the ratio of monomer: initiator of 1:1. It was concluded that when the monomer is inserted at the ruthenium center two different complexes may form; a complex via insertion of monomer to the ruthenium center and a complex via chelation of oxygen to the ruthenium center.

ROMP reaction of norbornene-1-methyl carboxylate monomer using 2nd generation ruthenium initiator and modified 2nd generation ruthenium initiator was carried out and the GPC analysis confirmed the presence of the polymer. Although, the Mn value is not reliable because is equivalent to polystyrene standard and due to the difference in the hydrodynamic volumes but the narrow PDI (1.34) indicates a reasonably well controlled polymerisation reaction.

Addition polymerisation of norbornene-1-methyl carboxylate monomer was carried out using palladium catalyst $Pd(H)(PCy_3)_2(CH_3CN)$, (Pd 1388). The result of the GPC analysis showed the existence of two peaks with DP of 2 and 16 which suggest

the formation of a dimmer and an oligomer. The ester group in the 1-position has the ability to chelate to the metal centre. In addition polymerisation using Pd 1388 initiator, the coordination and chelation of the monomer to the palladium metal center suggested possible monomer-initiator complexes. However, based on the result discussed here it has been difficult to determine which complex is dominant in this polymerisation reaction.

Addition polymerisation of norbornene-1-methyl carboxylate monomer was carried out using nickel initiator (η^6-toluene)Ni(C_6F_5)$_2$. The presence of an ester group in the 1-position most likely leads to coordination or chelation to the nickel metal center. However, based on the result it has been difficult to determine the outcome of the polymerization reaction involving the nickel initiator.

4.2 Future Work

ROMP reaction using 1st generation ruthenium initiator and additional polymerisation using palladium catalyst (Pd(H)(PCy_3)$_2$(CH_3CN), (Pd 1388) and nickel initiator (η^6-toluene)Ni(C_6F_5)$_2$ did not proceed, due to the possible formation of the chelating complex. In order to investigate the possibility of the formation of the complex via chelation of either ester oxygen or carbonyl oxygen to the metal centre, it is suggested that norbornene-1-dimethyl ether and norbornene-1-methyl monomers should be synthesised. Norbornene-1-methyl carboxylate monomer can be reduced in the presence of $LiALH_4$ to obtain norbornene-1-methyl alcohol, which then can be reacted with methyl iodide or methyl bromide to obtain norbornene-1-dimethyl ether monomer. Polymerisation of norbornene-1-dimethyl ether monomer will provide evidence for the possibility of chelation via ether oxygen. Norbornene-1-methyl alcohol can be reacted with mesyl chloride to obtain norbornene-1-methyl mesylate. Then, norbornene-1-methyl mesylate can be reduced to norbornene-1-methyl monomer in the presence of $LiAlH_4$ to obtain norbornene-1-methyl. In this case, the possibility of the formation of the chelated complex during polymerisation reaction is eliminated. Moreover, it provides evidence for the polymerisability of 1-substituted norbornenes.

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