Ring opening metathesis polymerisation of phenylnorbornene dicarboxyimide derivatives

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A thesis submitted for the degree of Master of Science

at the University of Durham

By

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First degree in Chemistry (Fort Hare, South Africa)

September 2003

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MSc 2003

ABSTRACT

The work described in this thesis illustrates that a series of exo-phenyl norbornene dicarboxyimide derivatives are synthesised and characterised using several spectroscopic methods. It also demonstrates that polymeric material can be prepared from phenylnorbornene dicarboxyimide derivatives using ROMP. Three well-defined initiators, ruthenium $Cl_2[(C_6H_{11})_3P]_2Ru{=}CHC_6H_5$, t-butoxy molybdenum $Mo[CHC(CH_3)_3][C_{10}H_{17}N][OC(CH_3)_3]_2$, Mo (1), and hexafluoro-t-butoxy molybdenum $Mo[CHC(CH3)_2C_6H_5][C_{10}H_{17}N][OC(CF_3)_2CH_3]_2$, Mo (2), were used. The polymers prepared were fully characterised using ^{1}H NMR, ^{13}CNMR, elemental analysis, GPC and DSC.

The cis / trans contents of the polymers are readily determined from the ^{1}H NMR spectrum from the integration of the resonance attributable to cis and trans olefinic hydrogen. Generally the trans vinylene content for polymers prepared by ruthenium initiator is about 83%, for the polymers prepared by t-butoxy molybdenum initiator is about 97% and for the polymers prepared by hexafluoro-t-butoxy molybdenum initiator is about 31%. The t-butoxy molybdenum initiator produced polymers with narrow PDI compared to hexafluoro-t-butoxy molybdenum and ruthenium initiators. This is an indication of a well-controlled living polymerisation reaction. The hexafluoro-t-butoxy molybdenum initiator produced polymers with broader PDI. This can be attributed to the secondary metathesis reactions or to the rate of propagation being faster than the rate of initiation. Polymers obtained by ruthenium initiator also gave polymers with broader PDI due to secondary metathesis reaction.

The Tg for the polymers prepared by t-butoxy molybdenum initiator were about 15°C higher than the polymers produced using hexafluoro-t-butoxy molybdenum and the ruthenium initiators, suggesting that the higher the trans content of the polymer, the higher the Tg. It was also found that the longer the alkyl chain in the polymer, the lower the glass transition temperatures. The Tg for the polymers prepared from of exo-phenyl norbornene dicarboxyimides are generally higher than the polymers obtained from exo-alkyl norbornene dicarboxyimides.

ACKNOWLEDGEMENTS

First, I would like to thank my supervisor, Dr Ezat Khosravi for his support and guidance throughout my work in the department. I would like to thank the NMR staff: Dr Alan Kenwright, Mr Ian McKeag and Mrs Catherine Heffernan, GPC staff, mass spectroscopy staff: Miss Lara Turner and Dr M. Jones, Leeds University for DSC: Peter Hine, and elementary analysis staff: Mrs Joroslava Dostal. I would like also to thank my colleagues in Dr Ezat's group and all the IRC colleagues. I would also like to thank Ruth First scholarship friends, African & Caribbean society friends, Durham Amigos friends, and Dr Luthando Adams for their support throughout my stay in Durham and, finally my family for their prayers.

MEMORANDUM

The work of this thesis was carried out in the IRC Chemistry laboratories of the University of Durham between October 2002 and September 2003. This work has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

FINANCIAL SUPPORT

I gratefully acknowledge the funding provided by Ruth First Scholarship and Durham University.

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Chapter 1

General introduction and background

1.1 Aims and objectives

Dicyclopentadiene (DCPD) has been widely used as a monomer for polymer processing methods like Ring Opening Metathesis Polymerisation (ROMP)-Reaction Injection Moulding (RIM) and ROMP-Resin Transfer Moulding (RTM) for producing material with good mechanical properties, figure 1.1.[1, 2] Although this has resulted in important commercial applications, there are some drawbacks like strong monomer odours, strongly exothermic reaction and problems surrounding the cross-linked material.[3]

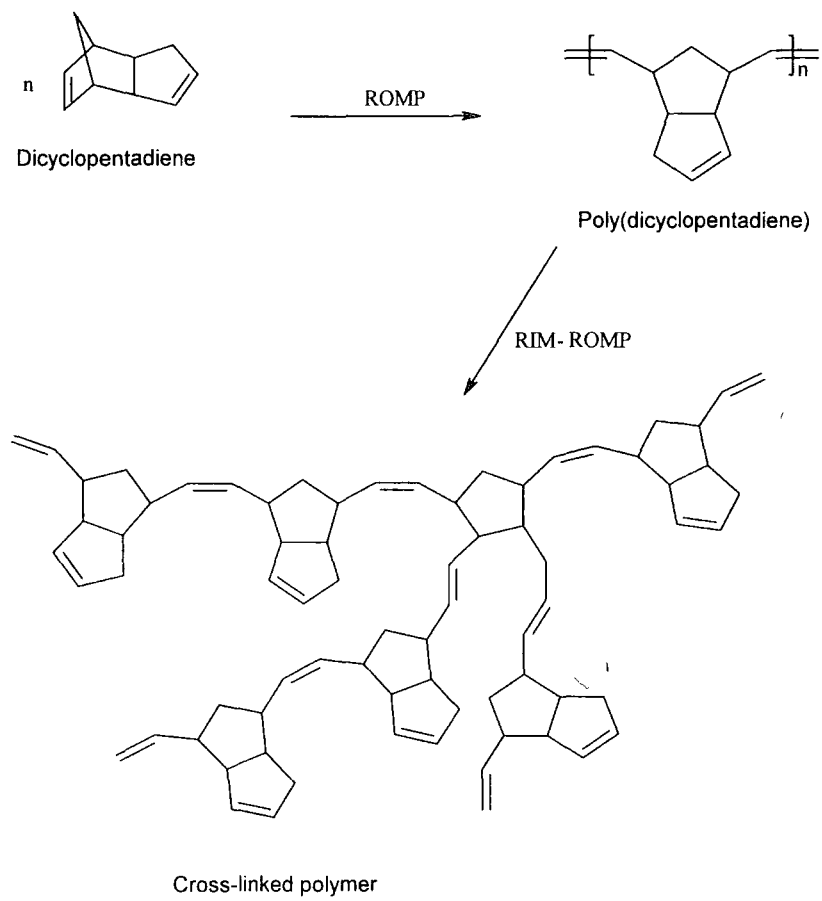


Figure 1.1: Cross linking in dicyclopentadiene

In the earlier work[4], a series of mono functional n-alkyl norbornene dicarboxyimides and difunction n-alkylene dinorbornene dicarboxyimides was successfully synthesised, figure 1.2. The monomers were subjected to ROMP using classical initiators and also well-defined molybdenum initiators; the t-butoxy molybdenum initiator

$Mo[CHC(CH_3)_3][C_{10}H_{17}N][OC(CH_3)_3]_2$, and hexafluoro-t-butoxy molybdenum initiator $Mo[CHC(CH3)_2C_6H_5][C_{10}H_{17}N][OC(CF_3)_2CH_3]_2$. This work served as a benchmark towards the synthesis and characterisation of polymeric material using RIM-ROMP and RTM-ROMP.

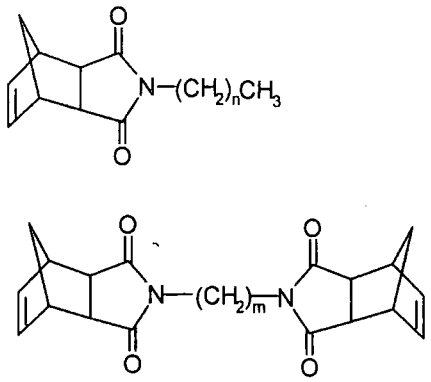


Figure 1.2: Structure of the (a) monofuntional monomer and (b) the difuntional monomer

The work[5] that followed explored further the physical and thermal properties and provided guidelines and basic parameters for ROMP-RTM processing of norbornene dicarboxyimides. The initiator used for ROMP reactions was well defined ruthenium initiator $Cl_2[(C_6H_{11})_3P]_2Ru=CHC_6H_5$. The Copolymerisation of monofunctional and difunctional monomers produced well-defined crosslinked materials, figure 1.3.

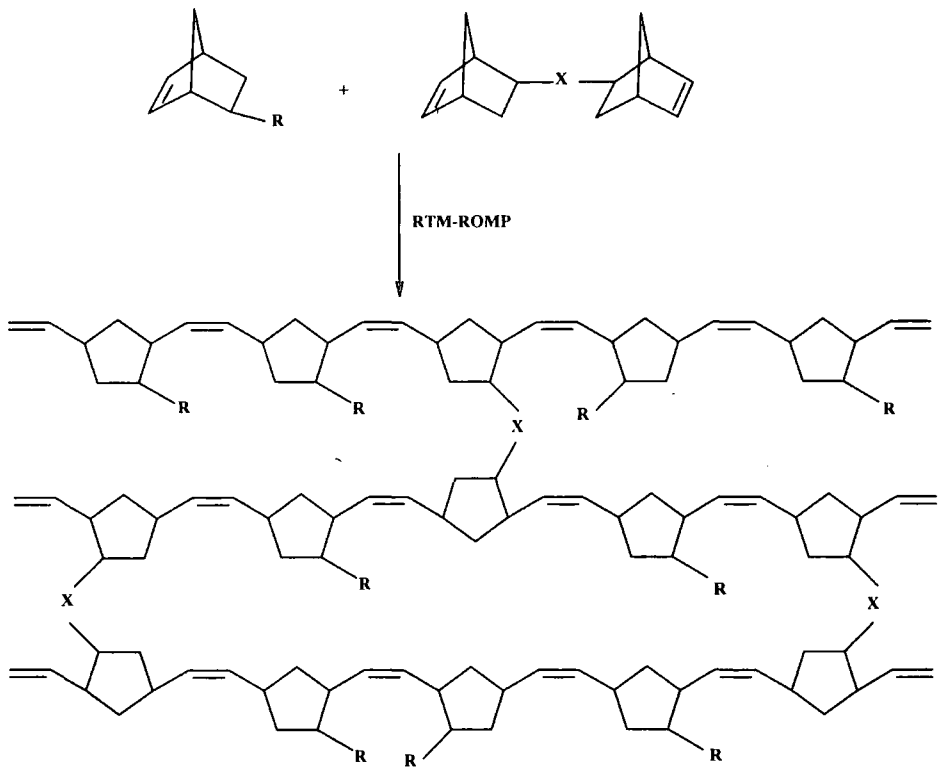


Figure 1.3: Cross linking in substituted norbornene

The physical and mechanical properties of the crosslinked materials were comparable or better than some engineering polymers such as polycarbonates and Telene 1100, table 1.1.

Polymer	**Tg** (°C)	**Density** kg/m^3	**Modulus** GPa	**Yield/Fracture Strength (Mpa)**
C4M/2%C12D	~120	1136	2.7+- 0.2	61+- 15 (F)
C5M/2%C12D	106	1120	2.2+- 0.2	72 +- 2 (Y)
C6M/2%C12D	87	1092	1.9 +- 0.1	59 +- 3 (Y)
Polycarbonate	150	1200	2.3	62 (Y)
Poly(DCPD) Telene1100	145	1030	1.9	45

Table 1.1: Shows the comparison of the new polymeric material with poly(dicyclopentadiene)

However, the Tg of the crosslinked materials were lower than the commercial materials based on Poly(DCPD).

The aim of this work was to improve the glass transition temperature of the material produced by ROMP-RTM. According to the literature the presence of the phenyl ring on the side chain of the polymer would raise the glass transition temperature.[6] Therefore the objective of the work presented in this thesis was to synthesise and fully characterise a series of exo-phenyl norbornene dicarboxyimide derivatives, figure 1.4, subject them to ROMP using well-defined Grubbs ruthenium initiator, and evaluate their Tgs of the resulting polymers.

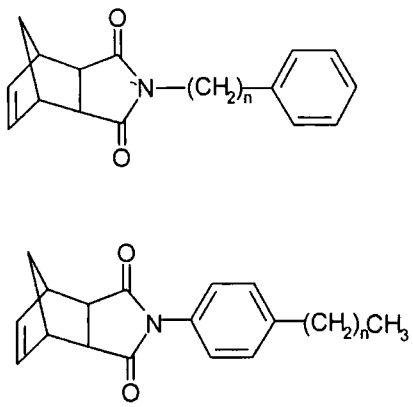


Figure 1.4: Structures of phenyl norbornene dicarboxyimide

This work is divided into 4 chapters. The first chapter deals with the historical background to ROMP and the latest developments on the initiators used in this process. The second chapter deals with the synthesis and characterisation of monomer, the third chapter deals with the polymer synthesis and characterisation and the last chapter deals with conclusion and proposal for future work.

1.2 Ring Opening Metathesis polymerisation (ROMP)

1.2.1 Definition and historical background of olefin metathesis

Olefin metathesis was discovered in 1920s. It was only 50 years later that it found usefulness in polymer chemistry and only recently that a lot of useful materials are produced through this method. Olefin metathesis can be described as the catalytically induced bond reorganisation reaction that lead to the breaking and making of carbon-carbon double bonds without losing the total and type of chemical bond in the process. For acyclic olefins the process lead to the exchange of alkylidene units (a) and, for

cyclic olefins the process lead to ring scission and the formation of linear polymer (b), figure 1.5.

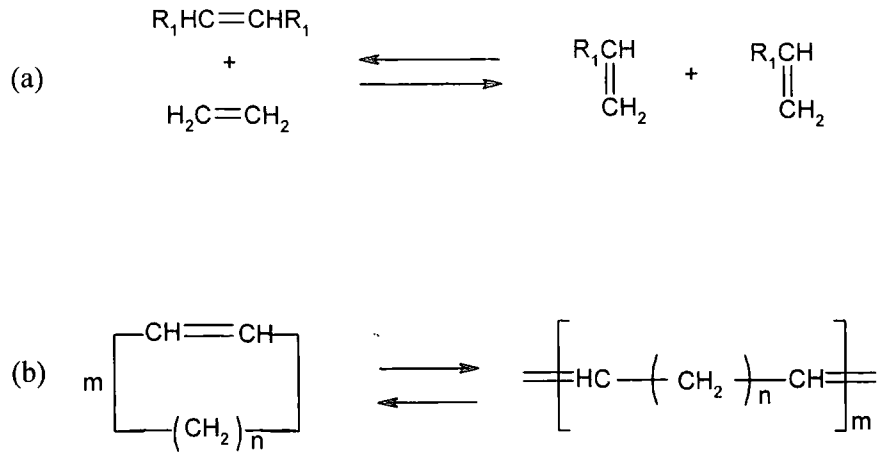


Figure 1.5: Schematic presentation of olefin metathesis

(a) Schematic representation for acyclic olefins

(b) Schematic representation for cyclic olefins

The reaction for acyclic olefins was first reported by Banks and Barley in 1964 and was termed 'olefin disproportionation'.[7] Three years later, in 1967, Calderon *et al* acknowledged that acylic disproportionation of olefins and ring scission of cyclic olefins to form linear polymers were example of the same process and hence they commonly name these reactions 'olefin metathesis'.[8] Anderson and Merkling, in 1955, discovered evidence of olefin metathesis although it was only reported in the 1960s.[9] In the experiment they successfully polymerised bicyclo[2.2.1]hept-2-ene using a mixture of titanium tetrachloride and ethylmagnesium bromide to initiate the polymerisation, figure 1.6.

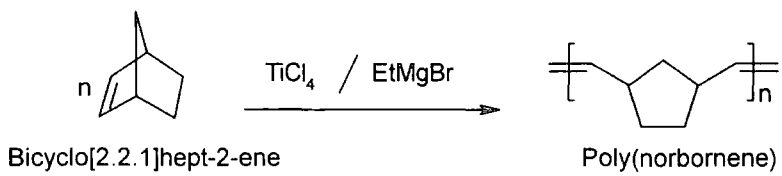


Figure 1.6: Romp of norbornene

Several mechanisms were proposed for the olefin metathesis reaction.[10-12] The widely accepted mechanism was proposed by Chauvin. The mechanism involved cycloaddition reaction between metal alkylidene complex and the olefin. The addition proceeds via an intermediate metallacyclobutane that breaks up to give new alkylidene and a new olefin, figure 1.7. This mechanism was a break through to catalyst development as it provided the basis for the understanding of the way the catalyst system work. This resulted in the development of single component and well-defined homogeneous catalyst in 1970s and 1980s.[14] These new catalysts will be discussed under ROMP initiators

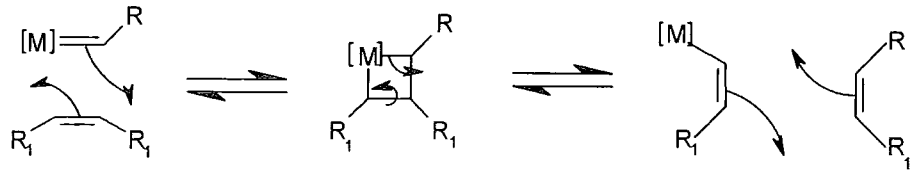


Figure 1.7: Chauvin's mechanism for olefin metathesis

1.2.2 ROMP mechanism

Ring opening metathesis polymerisation (ROMP) is a variant of olefin metathesis in which cyclic olefins are used and new olefin remains attached to the catalyst as part of the growing chain, figure 1.8. Although ROMP has the same mechanism as the one Chauvin proposed, the difference is with the second step of ROMP, which is in most cases is irreversible. With advancement in catalyst development, ROMP system are considered as living system as there is no termination step, which means that the polymer chain ends remain active and on addition of the same monomer, the chain continue to grow until termination is induced. The sequential addition of the monomers results in the synthesis of block polymers.[6]

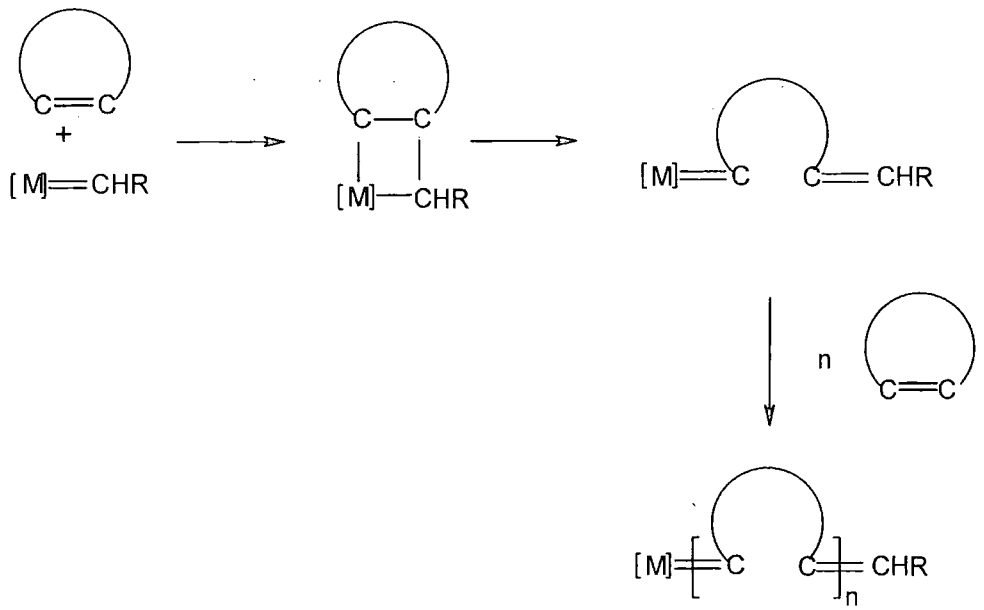


Figure 1.8: Mechanistic pathway for ROMP

1.2.3 ROMP initiators

The initiator systems used for ROMP are based on group IV to group IX transition elements such as Ti, V, Nb, Ta, Mo, W, Re, Ru, Os, and Ir.[4,15] The history of initiators started as early as in 1960's with development of catalyst that were ill-defined but useful at the time to the present catalyst that are well-defined. The initiators are therefore categorised into two systems, namely classical (ill-defined systems) and single component initiators (well-defined systems).

1.2.3.1 Ill-defined initiators

Classical initiators are multiple component systems and are derived from chlorides, oxides, and oxychlorides of Mo, W, and Re. Cocatalyst for these systems are usually $EtAlCl_2$ and R_4Sn were R= Ph, Bu or Me and promoters being O_2, EtOH and PhOH. These systems can be homogeneous, e.g. $WCl_6/EtAlCl_2/EtOH$ and heterogeneous, e.g. MoO_3/AlO_3. These initiators suffer from a lot of drawbacks such as:

- The precise nature of the active site at the metal centre is unknown, thus the system is ill-defined
- The metal carbene must be generated before initiation and subsequent propagation can commence and this process usually proceeds in a very low yield
- The activity of a given initiation system is dependent upon its chemical, thermal and mechanical history, and upon the order and rate of mixing of the catalyst, co-catalyst and monomer
- They have limited tolerance towards functional groups in the monomer or solvent,
- There is a lack of control of molecular weight and molecular weight distribution due to intra and intermolecular reactions with the double bond
- They display an element of irreproducibility

1.2.3.2 Well-defined initiators

Although classical initiators are still having their place in commercial applications, the development of single component initiators has promoted a lot of research in ROMP and resulted in synthesis of polymers with complex architectures that would not have been possible with ill-defined initiators. Most of this success is due to the fact that the development of single component initiators has set a benchmark for more improved initiators with greater functional group tolerance.

The Fischer carbene, which was heteroatom stabilised complex, was the first isolated metal carbene species to be reported in 1964, figure 1.9.[16] The discovery of Casey carbene, a diphenyl complex followed this in 1973, figure 1.9.[17] Although Casey carbene was not heteroatom stabilised complex, it was proved to be more reactive capable of polymerising less strained olefins.

Fischer carbene Casey carbene

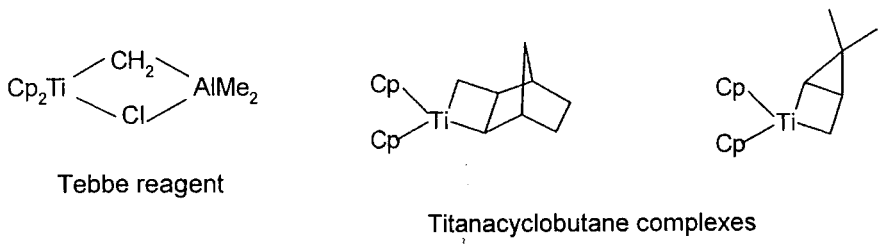
Figure1.9: Structural representation of Fischer and Casey carbene

Table 1.2 show the advancement of functional group tolerance of the initiators from Titanium initiator, which was only reactive to olefins but could not survive other functional groups to ruthenium, which is tolerant to wide range of functional groups. Due to this tolerance, ruthenium has gained a lot of attention in ROMP and this has lead to more research done to improve the initiation capability of this initiator. Researchers have noticed that the development of more reactive initiators has a cost on the stability of the initiator. There is a growing interest to develop initiators that would be more reactive but maintain the stability.

Titanium	**Tungsten**	**Molybdenum**	**Ruthenium**
Alcohol, water	Alcohol, water	Alcohol, water	**OLEFINS**
Acids	Acids	Acids	**ALCOHOL, WATER**
Aldehydes	Aldehydes	Aldehydes	**ACIDS**
Ketones	Ketones	**OLEFINS**	**ALDEHYDES**
Esters, amides	**OLEFINS**	**KETONES**	**KETONES**
OLEFINS	**ESTERS, AMIDES**	**ESTERS, AMIDES**	**ESTERS, AMIDES**

Figure 1.2: Outline of different initiators and their respective tolerance to a range of functional groups. The tolerance is increased from left to right. The reactivity of the functional groups is increased from bottom to top.

Tebbe *et al* prepared a bimetallic methyledene[18,19] (Tebbe reagent), which can be classified as a well defined Ti carbene that is stabilised by coordination of Me_2AlCl and this carbene set as the benchmark for the discovery of living polymerisation. Titanacyclobutane complexes shown in figure 1.10 produced the first living polymerisation of cycloolefin.[20-23] These Ti complexes were prepared from Tebbe reagent. Although these complexes were capable of forming polynorbornene with narrow molecular weight distribution, the disadvantages were that the polymerisation required a temperature of 50°C and the functional group tolerance was limited to olefins.



Tebbe reagent

Titanacyclobutane complexes

Figure 1.10: Structural representation of Tebbe reagent and Titanacyclobutane complexes

Tungsten alkylidene complexes were the next to be isolated. Kress and Osborn prepared the first well-defined tungsten alkylidene complex[24], which required a strong Lewis acid co-catalyst such as $GaBr_3$ for increased activity, figure 1.11. The functional group tolerance was extended esters and amides. Schrock and co-workers reported well-defined tungsten and molybdenum complexes with bulky alkoxide and arylimido ligands, figure 1.12.[25] The bulky alkoxide groups and imido ligand of both complexes served as a shield towards intermolecular reactions. Moreover, molybdenum complexes showed better tolerance, compared to tungsten, which extended functional group tolerance to ketones.

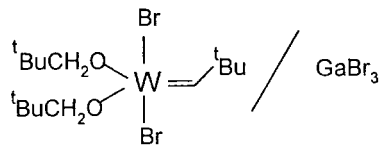


Figure 1.11: Structural representation of Kress and Osborn complex

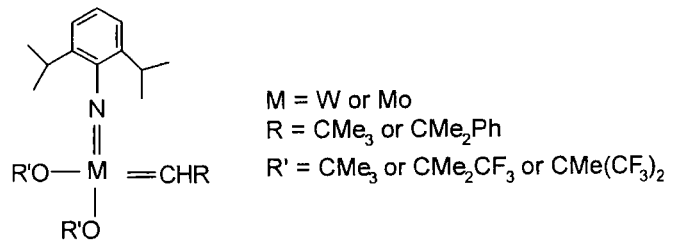
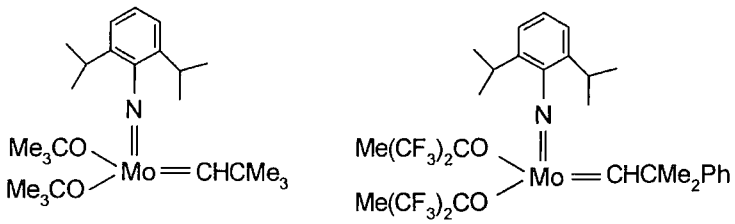


Figure 1.12: Structural representation of Schrock's initiators

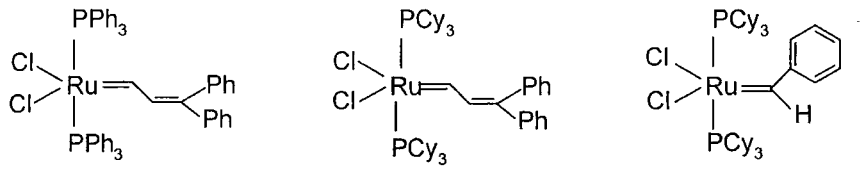
The most widely studied are t-butoxy substituted molybdenum initiator (complex **1**) and hexafluoro-t-butoxy substituted molybdenum initiator (complex **2**), figure 1.13. [4,25-29] Molybdenum complex **2** was found to be the most reactive of all the molybdenum derivatives.



1 **2**

Figure 1.13: Structural representation of two molybdenum complexes and ruthenium complex.

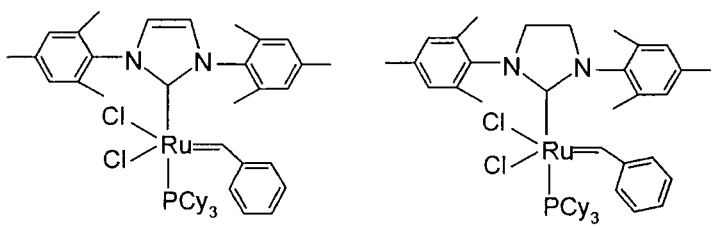
The discovery of ruthenium alkyledene complexes extended the scope to a wide range of functional group tolerance and hence they have been widely studied in recent years. The history of ruthenium based initiators started with the simple salts to well-defined ruthenium alkyledene complexes. Ruthenium salts did not get much exposure in ROMP because of low reactivity and limited functional group tolerance. Other attempts resulted in ROMP but with longer reaction time and the complexes were only limited to highly strained substrates[14]. The isolation of ruthenium alkyledene complex **3** was a breakthrough in ruthenium catalyst development, figure 1.14.[30] Although the discovery of this complex was a step forward, the drawback was that the complex was limited to only highly strained monomers. The research work that followed, led to the discovery of the second series of these ruthenium alkylidene complexes, complex **4**[31] and **5**[32], figure1.14. The work focused on modification of the ligand environment so as to extend the activity to low strained monomers. Complex **4,** was found to have a broader metathesis activity that incorporated metathesis of acyclic olefins and an increased[33] tolerance to most functionalities. However, complex **5** was found to be the most active complex of the series.



3 **4** **5**

Figure 1.14: Series of ruthenium complexes

Further work led to the discovery of a family of mesityl-substituted N-heterocyclic carberne, figure 1.15. It was reported that complexes **6**[34] and **7**[35] were more reactive than complex **5** and complex **7**[35] was the most reactive. These complexes expanded the scope of the monomers to sterically hindered olefins.[34,36]



6 **7**

Figure 1.15: Mesityl-substituted N-heterocyclic carbenes

The drawback to complex **5** or its most active derivative **7** was broad polydispersity indices (between 1.3 and 1.5), which are attributed to unfavourable rate of initiation (k_i) as compared to propagation (k_p) and secondary metathesis. This has resulted in synthesis of a new family of Ru-based initiators by substituting one of PCy_3 ligand with different phosphines. Gibson and co-worker established that the initiation efficiency of **5** can be enhanced by replacing one of the PCy_3 ligand with $Cy_2PCH_2Si(CH)_3$ to form a new initiation complex **8**, figure 1.16.[37] The enhanced initiation was attributed to lower basicity and smaller size of $Cy_2PCH_2Si(CH_3)_3$.

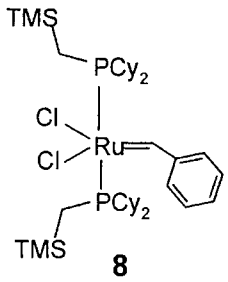


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Figure 1.16: TMS ligand exchange in ruthenium initiator

Work by Grubbs *et al* showed that the olefin metathesis reaction catalysed by ruthenium complexes **5** or **7** proceed via a dissociative mechanism which can either bind to free PCy_3 to form the initial alkyledene complex or bind to the substrate and undergo metathesis, figure 1.17.[38]

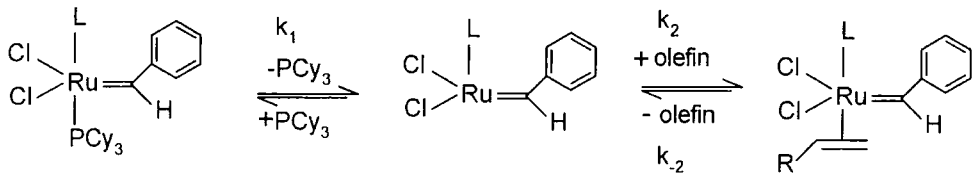


Figure 1.17: Dissociative mechanism of olefin metathesis

Recent research by Bielawski and Grubbs has shown that addition of phosphine in the polymerisation reaction can enhance the initiation efficiency, without having to synthesize a new complex. The PDIs in a particular experiment improved from 1.25 without the added phosphine to 1.04, depending on the type and number of equivalents of phosphine added and also to the number of equivalents of monomer. This was due to the fact that the rate of phosphine exchange is faster, as the result the formation of a new complex with labile phosphine can occur before initiation. They concluded that polymers with narrow polydispersity could be achieved this way, figure 1.18.[39]

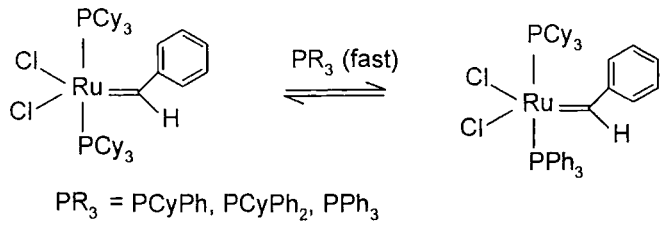


Figure 1.18: Schematic representation of phosphine exchange mechanism

1.2.4 Microstructure of polymer chains and stereoregularity

For ROMP systems there are three main factors that define the microstructure of the polymers:

- Cis/trans vinylene ratios and distribution
- Tacticity effect
- Head to head, head to tail and tail-to-tail arrangements

(i) Cis/trans vinylene ratios and distribution.

The repeating units in the backbone of the polymer chain are distributed in a cis and trans configuration, figure 1.19. The distribution depends on the type of solvent, monomer and catalyst system and concentration. For example for molybdenum catalyst systems, the molybdenum (1) catalyst gives high trans distribution whereas molybdenum (2) gives high cis configuration.[4]

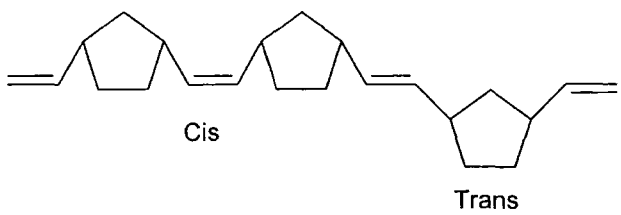


Figure 1.19: Cis / trans double bonds in polynorbornene

(ii) Tacticity effect

The repeating units of polymers like polynorbornene have chiral centres and each configurational unit of a polymer chain is the dyad, figure 1.20. A meso dyad is observed when the chiralities of the two chiral carbons adjacent to the double bond are opposite and a series of meso dyads gives isotactic polymers. A racemic dyad on the other hand is observed when the chiralities of the two chiral carbons adjacent to double bond are the same and a series of racemic dyads gives syndiotatic polymers.

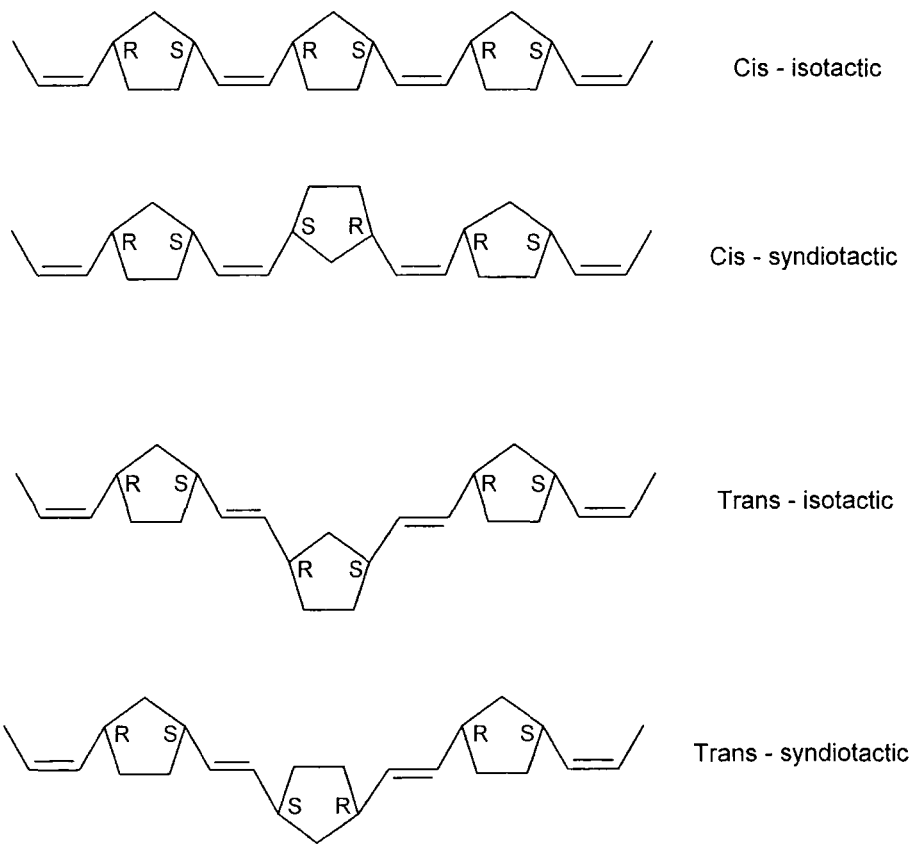


Figure 1.20: Tacticity effect in polynorbornene

(iii) Head to head, head to tail and tail-to-tail arrangements.

Unsymmetrically substituted monomers give rise to head to head, head to tail or tail-to-tail form. Figure 1.21 shows the different forms. The polymers prepared from this thesis are synthesized from symmetrically substituted monomer and therefore, the polymers will not experience the tail / head effects.

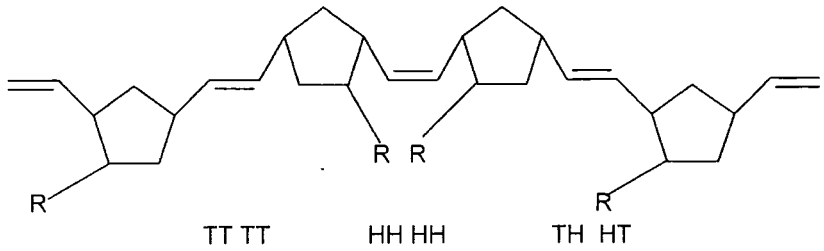


Figure 1.21: Head / Tail effects in the polymer of unsymmetrical substituted monomer

Chapter 2

Synthesis and characterisation of the monomers

2.1 Introduction

The focus of this chapter is on the synthesis of monofunctional phenylnorbornene dicarboxyimide derivatives. These are synthesised in two steps. The first step is the Diels-Alder cycloaddition reaction of maleic anhydride and dicyclopentadiene to give a mixture of exo / endo -norbornene-5,6-dicarboxyanhydride. This is followed by recrystallisation in acetone for several times (at least five times) to give pure exo-norbornene dicarboxyanhydride (exo-AN). The second step is the reaction of the pure exo-AN with phenylamines to produce phenylnorbornene dicarboxyimide derivatives. Only exo-monomers are synthesized in this work, as they have proved in previous work to be very reactive for ROMP reactions.[5,40]

2.2 Diels-Alder reaction

The reaction involves conjugate addition of a conjugated diene to an alkene, dienophile, to produce a cyclohexene. It is one of the few methods available for forming cyclic molecules and hence it is also called cycloaddition as the reaction produce cyclic products.[41] The simplest example is the reaction of 1,3-butadiene with alkene to form cyclohexene. The reaction proceeds through a cyclic transition state in a single step process.[42]

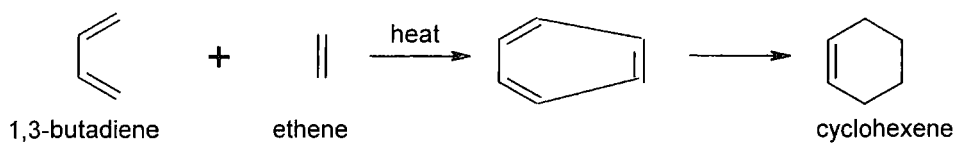


Figure 2.1: The Diels-Alder reaction between a conjugated diene and dienophile.

It is a widely used and studied method in organic synthesis ever since it was first reported in 1928.[43] It has gained synthetic applicability in the synthesis of compounds such as drugs, dyes and polymers chemistry. The experimental procedures for this reaction are usually simple and it produces good yields. For Diels-Alder cycloaddition

to occur under normal conditions the dienophile must contain electron withdrawing group and the diene must contain electron-donating group.

Diels-Alder reaction is stereospecific with respect to both the diene and dienophile as the result the stereochemistry of the dienophile determines the stereochemistry of the resulting product.[41] Most importantly the diene must be in the cis conformation in order to react.[44] This relationship is illustrated in figure 2.2.

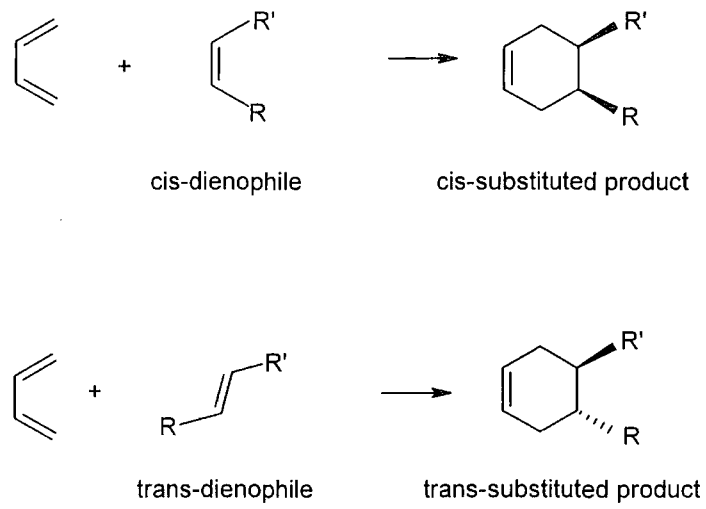


Figure 2.2: A schematic representation showing the dependence of the stereochemistry of the product on the stereochemistry of the dienophile in a Diels-Alder reaction.

The stereoisomeric product of cyclic dienes depends on the orientation of dienophile to the diene in the transition state and that results in two possible additions that is endo and exo.[45] If the dienophile lies under the diene an endo product is formed and if the dienophile lies away form the diene the exo is formed. Endo product is usually the major product due to kinetic control and due to the best overlap when the two reactant lies on top of each other.[46,47]

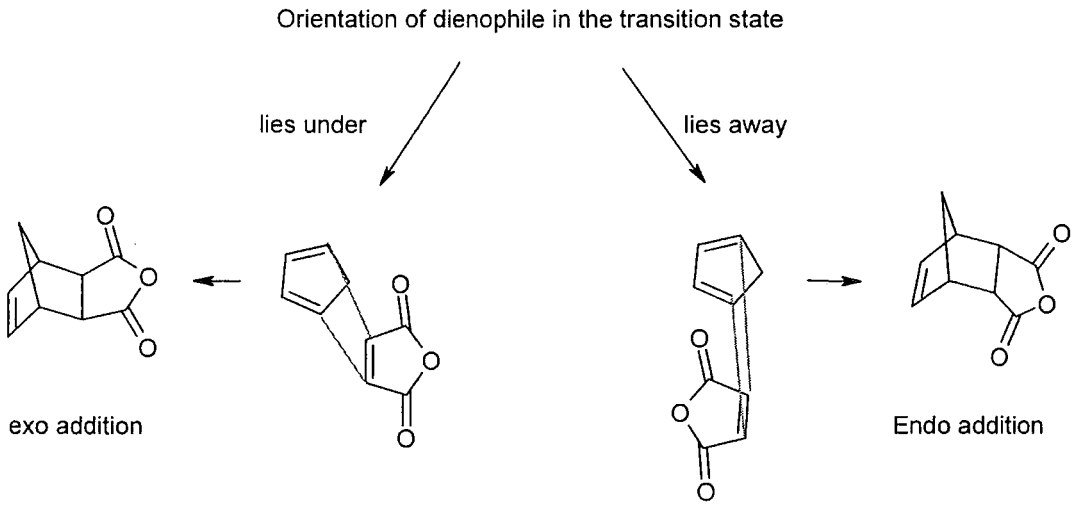


Figure 2.3: The schematic representation showing the dependence of type of addition on the orientation of the dienophile from the diene in the transition state of a Diels-Alder reaction.

2.2.1 Synthesis and characterisation of exo-norbornerne-5,6-dicarboxyanhydride

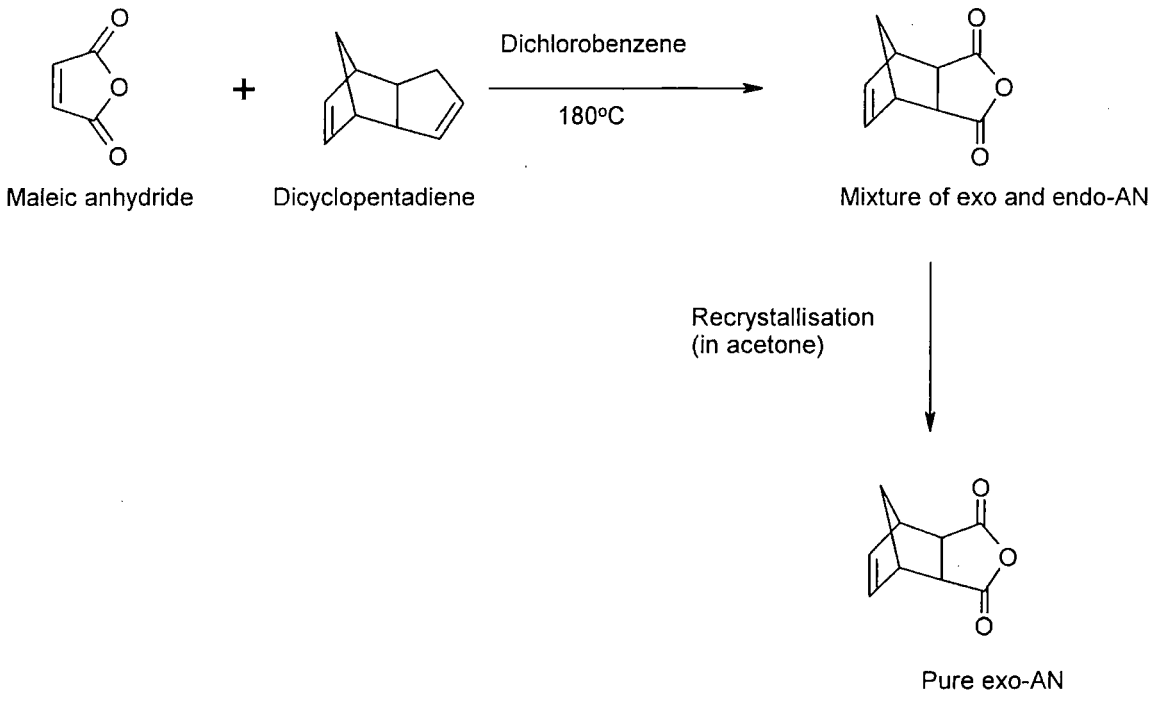


Figure 2.4: Outline of the synthetic route for exo-AN

The synthesis of exo-norbornene-5,6-dicarboxyanhydride (exo-AN) was the result of a Diels-Alder reaction between maleic anhydride and dicyclopentadiene.[4,5,48] The

reaction was carried out at 180°C in dichlorobenzene as the solvent for 16 hours. At this temperature, which is the boiling point of dichlorobenzene, dicyclopentadiene was cracked into two cyclopentadiene, which then react with the maleic anhydride.. The product formed by the reaction was the mixture of exo and endo-norbornene-5,6-dicarboxyanhydride. In order to get a pure exo-adduct, the mixture was recrystallised several times from acetone (at least five times). The product was clear, crystalline solid. Analytical methods like ^{1}H and ^{13}C NMR, elemental analysis, and mass spectroscopy were used to confirm the product. The mass spectrum showed a parent peak (M^{+}) at 164, which corresponded with the molecular weight of exo-AN and the peak at 66 correspond to cyclopentadiene. The mass spectrum is shown in figure 2.5. The peaks in the ^{1}H and ^{13}C NMR are similar to the peaks for exo-AN in the previous work[5] and the spectrum is shown in figure 2.6. The results are found in the experimental section of this chapter.

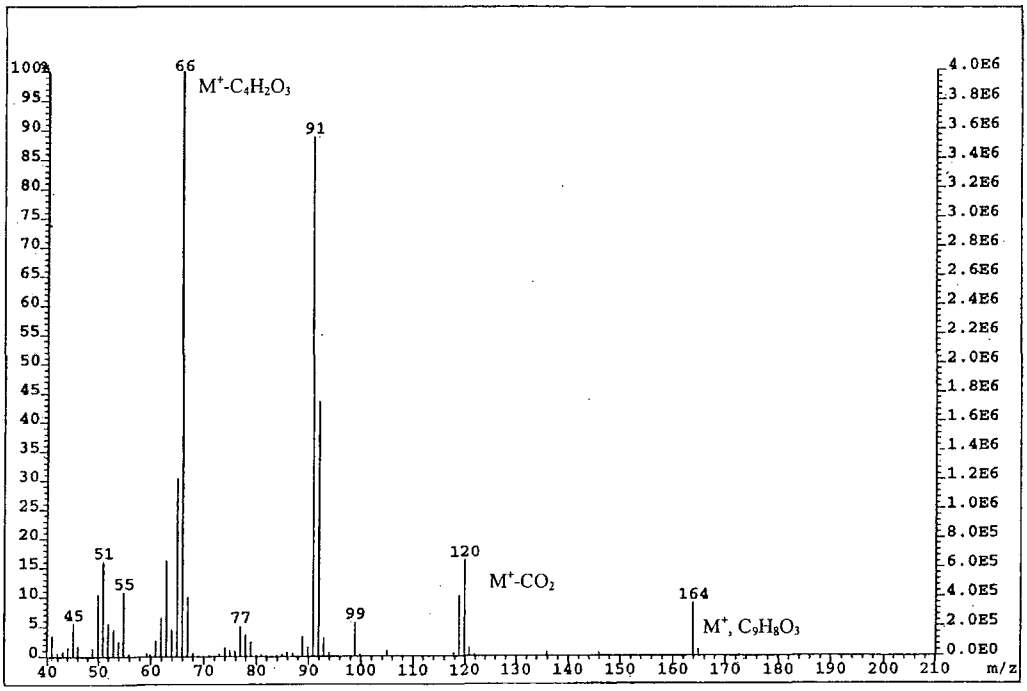


Figure 2.5: Mass spectrum of exo-norbornene-5,6-dicarboxyanhydride

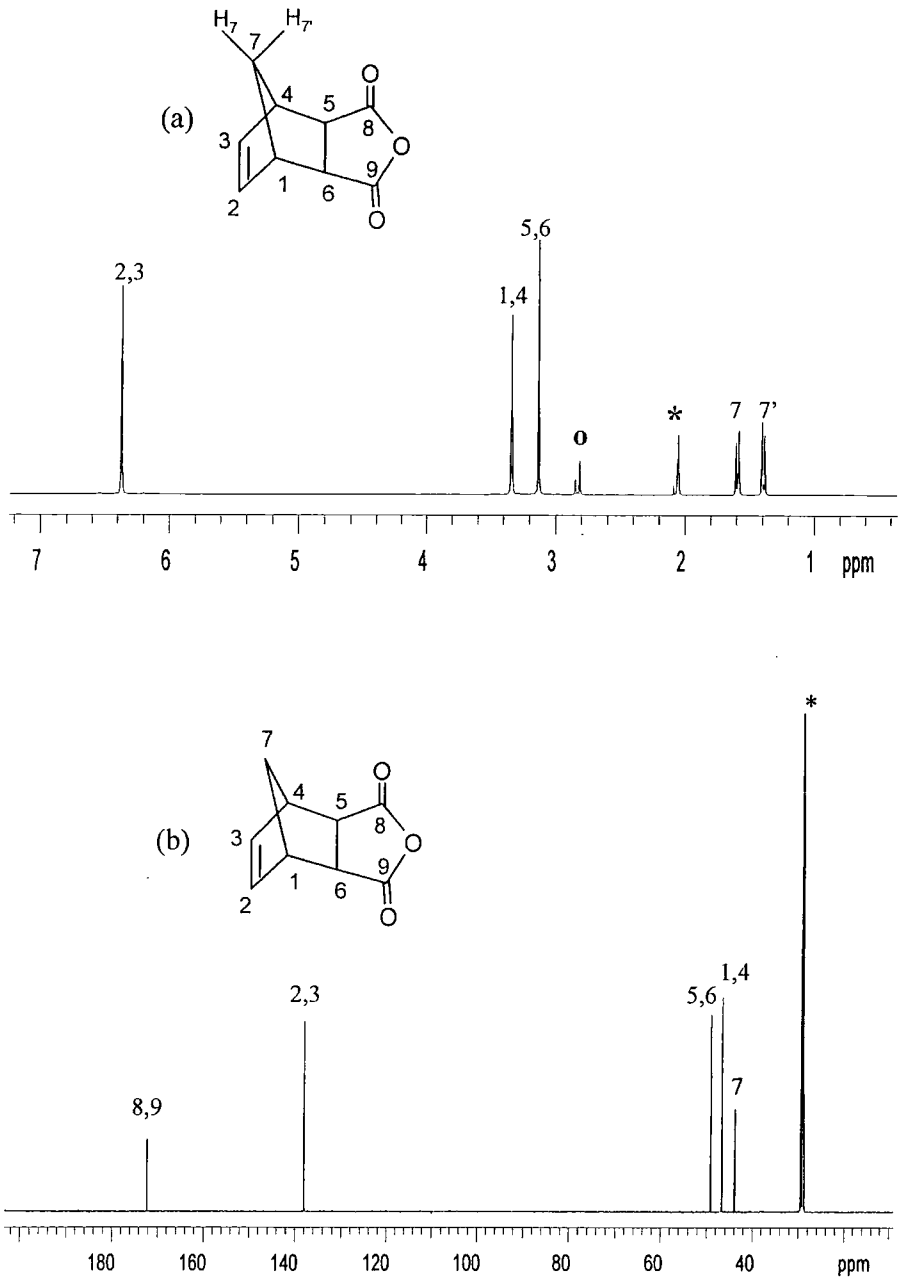


Figure 2.6: (a) ^{1}HNMR spectrum of exo-AN in acetone

(b) ^{13}CNMR spectrum of exo-AN in acetone

* Residual hydrogen in acetone

o Water in acetone

2.3 Synthesis and characterisation of exo-phenylnorbornene dicarboxyimides

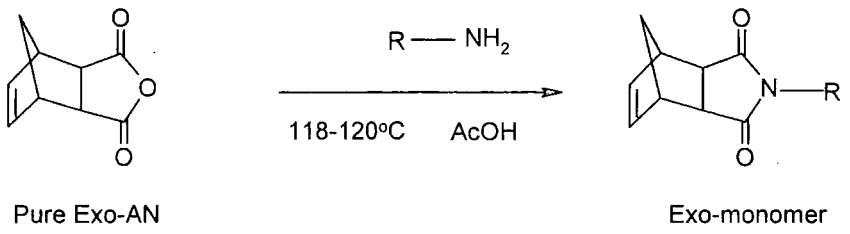


Figure 2.7: Outline of the synthetic route for exo-monomers where R-NH_2 is phenyl amines

Synthesis of exo-monofuntional and exo-difuntional monomers using aliphatic amines has been done successfully in the previous work using Diels-Alder reaction giving product in high yields. In this work the focus was on the use of a series of phenyl amines. The synthesis of the monomers was the result of a reaction between the pure exo-AN and a series of phenyl amines. The reaction was carried out at 120°C using the solvent glacial acetic acid. At this temperature, amines were added drop wise for a certain period of time to react with exo-AN. After the addition was complete, the reaction mixture was left for a further two hours to reflux. All monomers were recovered as solids except exo-C_6M, which was recovered as the clear liquid. A single recrystallisation was necessary to purify the solid monomers, while exo-C6M was purified by distillation. All monomers were soluble in chlorinated solvents. Analytical methods like ^1H and ^{13}C NMR, elemental analysis, and mass spectroscopy were used to confirm the product. Figure 2.8 shows an example of one of the monomers.

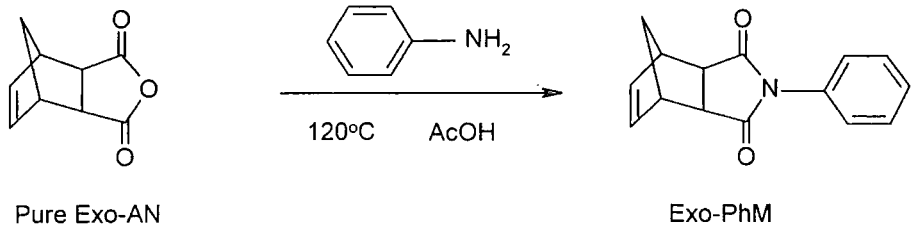


Figure 2.8: Outline of the synthetic route for exo-N-phenylnorbornene-5,6-dicarboxyimide

The NMR analysis of these monomers was similar to that of the previous work, with the phenyl protons found in the region from 7.26 to 7.47ppm and the phenyl carbons in the region from 126.03-151.89ppm. The result for mass spectroscopy showed that the parent peak (M^+) of each spectrum corresponded with the molecular weight of the corresponding monomer and in addition there were two peaks, (66) and (M^+-66), which are characteristic peak of reverse Diels-Alder reaction. The result found for elemental analysis was close and in some cases the same as the calculated values. The results of these monomers are found in the experimental section of this chapter. To illustrate the characterisation of the monomers, figure 2.9 shows the mass spectrum of the exo-PhM monomer and figure 2.10 shows the ^1H NMR and ^{13}C NMR. The expanded part in figure 2.10 (a) and (b) shows the proton and carbon signal in the phenyl ring respectively.

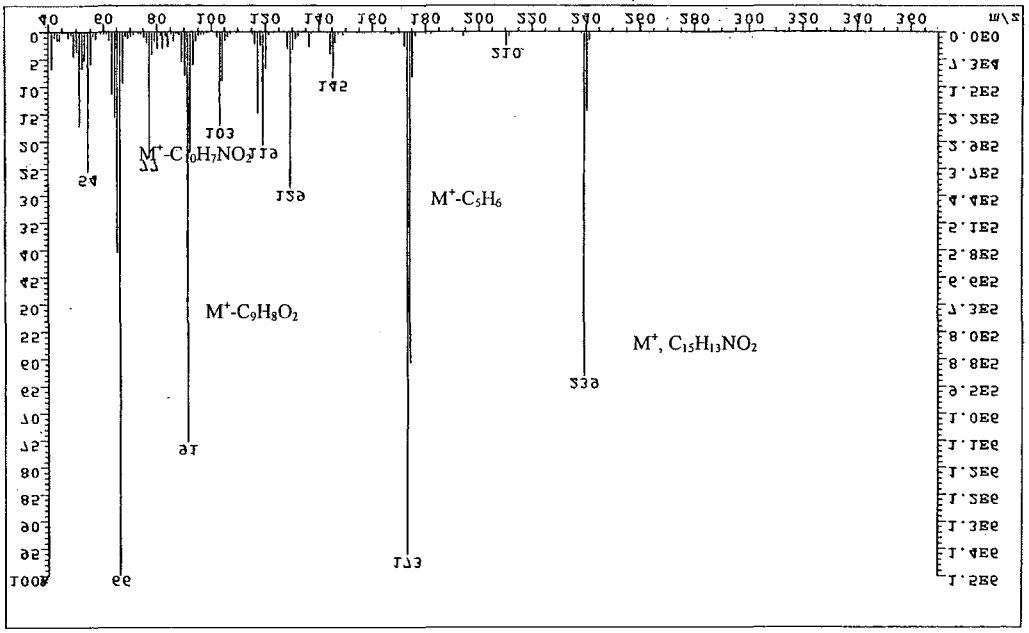


Figure 2.9: Mass spectrum of exo-N-phenlynorbornene-5,6-dicarboxyimide

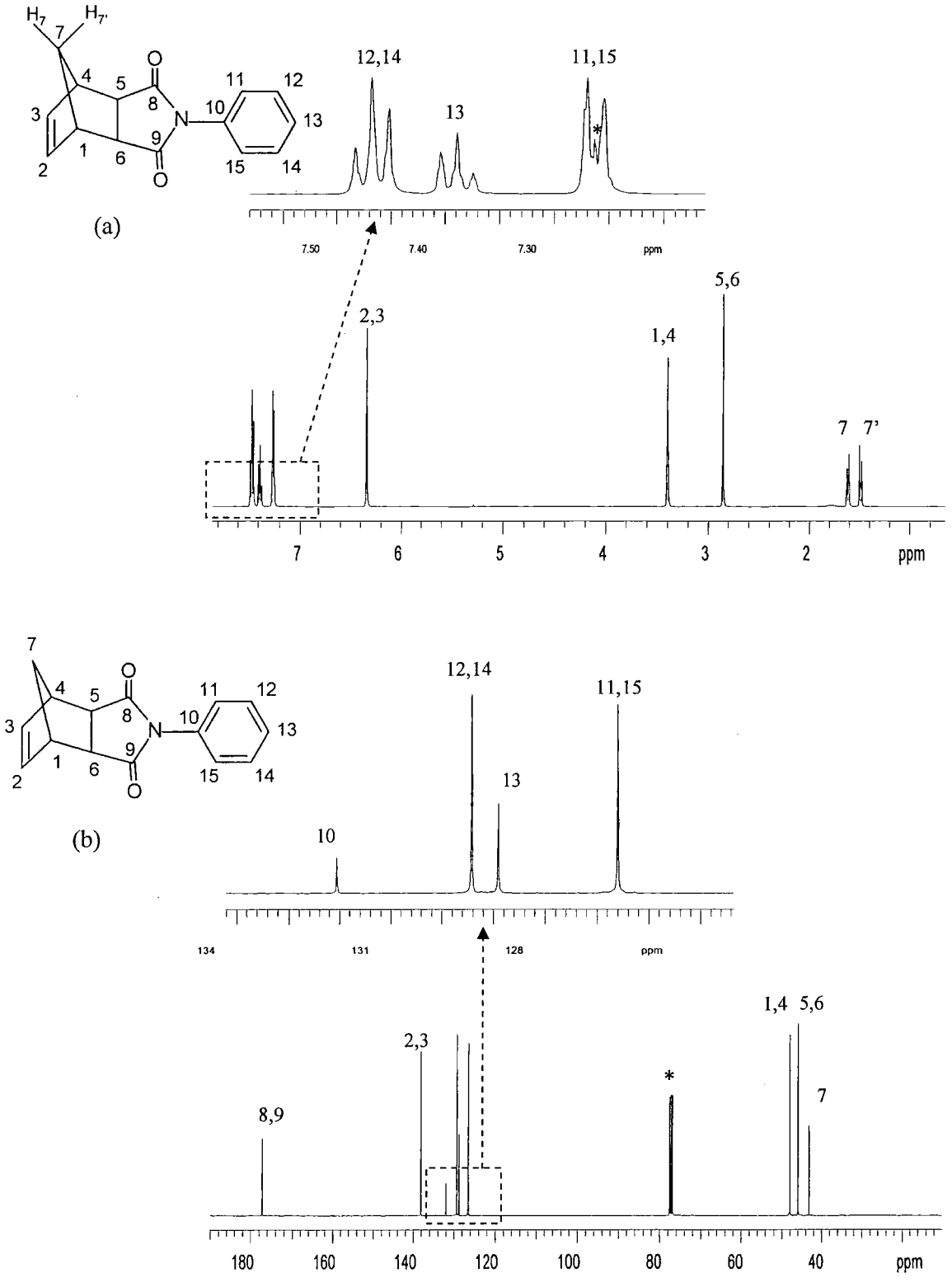


Figure 2.10: (a) ^{1}HNMR spectrum of exo-PhM in $CDCl_3$

(b) ^{13}CNMR spectrum of exo-PhM in $CDCl_3$

* Residual hydrogen in $CDCl_3$

2.4 Experimental

Reagents

Maleic anhydride, dicyclopentadiene, 1.2-diclorobenzene, n-alkylamine and n-phenylamines were purchased from Aldrich Company Ltd, acetic acid, acetone were purchased from BDH Chemical Company Ltd. All reagents and solvents were used without further purification.

2.4.1 Synthesis and characterisation of exo-norbornerne-5,6-dicarboxyanhydride

Maleic anhydride (490.2g, 5.0mol) and 1,2-dichlorobenzene (500ml) were placed in a, 3-necked round bottom flask (1000ml). The flask was fitted with a stopper, a condenser and a dropping funnel. The mixture was heated to 180°C and dicyclopentadiene (335ml, 2.5mol) was added via a dropping funnel. The mixture was left overnight to reflux and brown solution was formed. The product was recovered from the solution by filtration and dried in the vacuum oven. The product was yellow crystals, which was a mixture of exo and endo-norbornene dicarboxyanhydride. The product was recrystallised five times in hot acetone to give 100% pure exo-norbornene-5,6-dicarboxyanhydride.

(a) Elemental analysis of $C_9H_8O_3$: calculated (found)

C = 65.85% (65.75%), H = 4.91% (4.89%), O = 29.24% (29.36%)

(b) ^{1}H NMR (see appendix x), $CDCl_3$, 500 MHz, δ (ppm)

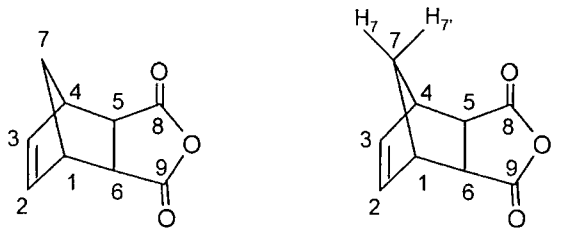
6.37 (s, 2H, $H_{2,3}$), 3.34 (s, 2H, $H_{1,4}$), 3.13 (s, 2H, $H_{5,6}$), 1.59 (d, 1H, H_7), 1.39 (d, 1H, $H_{7'}$)

(c) ^{13}C NMR (see appendix y), $CDCl_3$, 500 MHz, δ (ppm)

177.37 ($C_{8,9}$), 138.05 ($C_{2,3}$), 49.13 ($C_{5,6}$), 46.73 ($C_{1,4}$), 43.95 (C_7).

(d) Mass spectrum (see appendix z), (EI^+):

164 (M^+, $C_9H_8O_3$), 120 (M^+- CO_2), 66 (M^+- $C_4H_2O_3$)



Assignment of C and H atoms of exo-AN

2.4.2 Synthesis and characterisation of exo-N-phenylnorbornene-5,6-dicarboxyimide: (exo-PhM)

Exo-norbornene-5,6-dicarboxyanhydride (5.003g, 0.03mol) and glacial acetic acid (35ml) were placed in a 3-necked round-bottomed flask (100ml). The flask was fitted with a suba-seal, condenser and a thermometer. The top of the condenser was fitted with drying tube. The mixture was heated to 120°C and aniline (2.84g, 0.03mol) was added drop wise for 25min using a disposable syringe via a suba seal. The resulting yellow solution was left to reflux for 2 hours. The solution was then poured into cold distilled water (50ml) and a white precipitate was formed. Dichloromethane (50ml) was added twice to extract the monomer. The monomer was then washed twice with distilled water (50ml). The monomer was then dried over anhydrous magnesium sulphate. Dichloromethane was removed under reduce pressure to give pale yellow crystals. The monomer was recrystallised from toluene and was dried using a vacuum oven (5.6g, 0.023mol, 77%, mpt: 201°C).

(a) Elemental Analysis of $C_{15}H_{13}NO_2$: calculated (found)

C = 75.30% (75.40%), H = 5.48% (5.47%), N = 5.85% (5.89%), O = 13.37% (13.24%)

(b) ^{1}H NMR (see appendix x), $CDCl_3$, 500 MHz, δ (ppm)

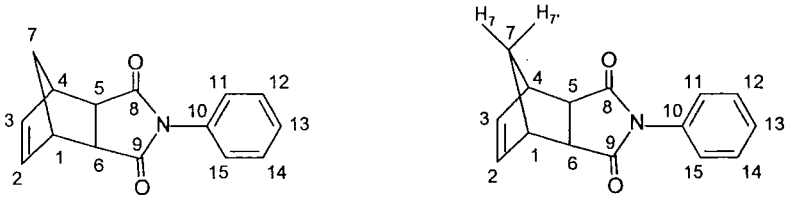
7.47 (t, 2H, $H_{12,14}$), 7.39 (t, 1H, H_{13}), 7.26 (d, 2H, $H_{11,15}$), 6.35 (s, 2H, $H_{2,3}$),
3.41 (s, 2H, $H_{1,4}$), 2.86 (s, 2H, $H_{5,6}$), 1.62 (d, 1H, H_7), 1.49 (d, 1H, $H_{7'}$)

(c) ^{13}C NMR (see appendix y), $CDCl_3$, 500 MHz, δ (ppm)

177.32 ($C_{8,9}$), 138.23 ($C_{2,3}$), 132.05 (C_{10}), 129.42 ($C_{12,14}$), 128.91 (C_{13}), 126.60 ($C_{11,15}$),
48.10 ($C_{5,6}$), 46.06 ($C_{1,4}$), 43.20 (C_7).

(d) Mass spectrum (see appendix z), (EI^+).

239 (M^+, $C_{15}H_{13}NO_2$), 173 (M^+- C_5H_6), 91 (M^+- $C_9H_8O_2$), 66 (M^+- $C_{10}H_7NO_2$)



Assignments for C and H atoms of exo-PhM

2.4.3 Synthesis and characterisation of exo-N-benzylnorbornene-5,6-dicarboxyimide: (exo-PhCM)

The same procedure as in section 2.4.2 was followed using exo-AN (5.004g, 0.03mol) and benzylamine (3.26g, 0.030mol). The monomer was recovered as white crystals, which was recrystallised in hexane to give white solid (4.93g, 0.020mol, 64% yield, mpt: 103°C).

(a) Elemental Analysis of $C_{16}H_{15}NO_2$: calculated (found)

C = 75.87% (75.92%), H =5.97% (5.96%), N = 5.53% (5.53%), O =12.63% (12.59%)

(b) ^1H NMR (see appendix x), $CDCl_3$, 500 MHz, δ (ppm)

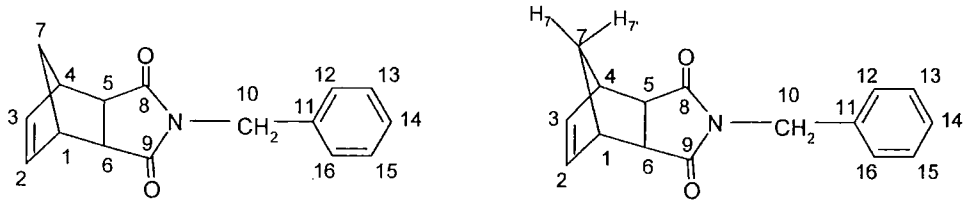
7.38 (d, 2H, $H_{12,16}$), 7.30 (t, 2H, $H_{13,15}$), 7.28 (t, 1H, H_{14}), 6.27 (s, 2H, $H_{2,3}$), 4.61 (s, 2H, H_{10}), 3.24 (s, 2H, $H_{1,4}$), 2.67 (s, 2H, $H_{5,6}$), 1.40 (d, 1H, H_7), 1.06 (d, 1H, $H_{7'}$)

(c) ^{13}C NMR (see appendix y), $CDCl_3$, 500 MHz, δ (ppm)

177.93 ($C_{8,9}$), 138.16 ($C_{2,3}$), 136.13 (C_{11}), 129.11 ($C_{12,16}$), 128.88 ($C_{13,15}$), 128.15 (C_{14}), 48.02 ($C_{5,6}$), 45.52 ($C_{1,4}$), 42.87 (C_7), 42.58 (C_{10})

(d) Mass spectrum (see appendix z), (EI^+).

253 (M^+, $C_{16}H_{15}NO_2$), 187 (M^+- C_5H_6), 91 (M^+- $C_9H_8NO_2$), 66 (M^+- $C_{11}H_9NO_2$)



Assignment of C and H atoms for exo-PhCM

2.4.4 Synthesis and characterisation of exo-N-phenylethylnorbornene-5,6-dicarboxyimide: (exo-PhC$_2$M).

The same procedure as in section 2.4.2 was followed using exo-AN (5.002g, 0.03mol) and phenylethylamine (3.69g, 0.030mol). The monomer was recovered as yellow liquid, which then solidified at room temperature. The monomer was recrystallised in ether to give white solid (5.29g, 0.020mol, 65% yield, mpt: 94°C).

(a) Elementary Analysis of $C_{17}H_{17}NO_2$: calculated (found)

C = 76.38% (76.41%), H = 6.41% (6.41%), N = 5.24% (5.03%), O = 11.97% (12.15%)

(b) ^{1}H NMR (see appendix x), $CDCl_3$, 500 MHz, δ (ppm)

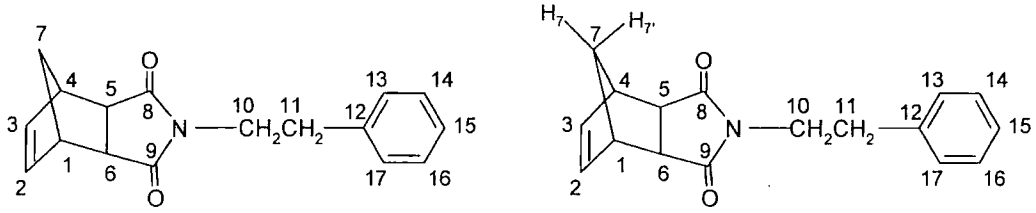
7.28 (t, 2H, $H_{14,16}$), 7.23 (d, 2H, $H_{13,17}$), 7.22 (t, 1H, H_{15}), 6.26 (s, 2H, $H_{2,3}$), 3.72 (t, 2H, H_{10}), 3.22 (s, 2H, $H_{1,4}$), 2.88 (t, 2H, H_{11}), 2.63 (s, 2H, $H_{5,6}$), 1.41 (d, 1H, H_7), 1.02 (d, 1H, $H_{7'}$)

(c) ^{13}C NMR (see appendix y), $CDCl_3$, 500 MHz, δ (ppm)

178.10 ($C_{8,9}$), 138.04 ($C_{2,3}$), 137.93 (C_{12}), 129.06 ($C_{13,17}$), 128.76 ($C_{14,16}$), 126.92 (C_{15}), 48.00 ($C_{5,6}$), 45.33 ($C_{1,4}$), 42.86 (C_7), 39.91 (C_{10}), 33.70 (C_{11}).

(d) Mass spectrum (see appendix z), (EI^+).

267 (M^+, $C_{17}H_{17}NO_2$), 104* (M^+- $C_9H_9NO_2$), 91 (M^+- $C_{10}H_{10}NO_2$), 66 (M^+- $C_{12}H_{11}NO_2$)



Assignment of C and H atoms of exo-PhC$_2$M

2.4.5 Synthesis and characterisation of exo-N-phenylpropylnorbornene-5,6-dicarboxyimide: (exo-PhC$_3$M)

The same procedure as in section 2.4.2 was followed using exo-AN (5.001g, 0.03mol) and phenylpropylamine (4.12g, 0.030mol). The monomer was recovered as white crystals, which was recrystallised in ether to give pale yellow solid (6.49g, 0.023mol, 76% yield, mpt: 64°C)

(a) Elementary Analysis of $C_{18}H_{19}NO_2$: calculated (found)

C = 76.84% (76.86%), H = 6.81% (6.82%), N = 4.98% (4.88%), O = 11.37% (11.44%)

(b) ^{1}H NMR (see appendix x), $CDCl_3$, 500 MHz, δ (ppm)

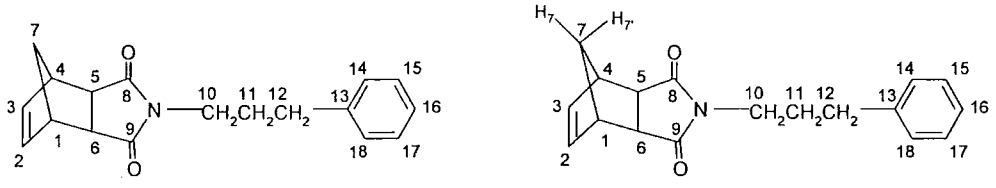
7.26 (t, 2H, $H_{15,17}$), 7.23 (d, 2H, $H_{14,18}$), 7.22 (t, 1H, H_{16}), 6.26 (s, 2H, $H_{2,3}$), 3.52 (t, 2H, H_{10}), 3.25 (s, 2H, $H_{1,4}$), 2.63 (t, 2H, H_{12}), 2.61 (s, 2H, $H_{5,6}$), 1.89 (p, 2H, H_{11}), 1.48 (d, 1H, H_7), 1.20 (d, 1H, $H_{7'}$)

(c) ^{13}C NMR (see appendix y), $CDCl_3$, 500 MHz, δ (ppm)

178.28 ($C_{8,9}$), 141.17 (C_{13}), 138.04 ($C_{2,3}$), 128.66 ($C_{15,17}$), 128.52 ($C_{14,18}$), 126.30 (C_{16}), 48.02 ($C_{5,6}$), 45.37 ($C_{1,4}$), 42.98 (C_7), 38.75 (C_{10}), 33.55 (C_{12}), 29.33 (C_{11}).

(d) Mass spectrum (see appendix z), (EI^+).

281 (M^+, $C_{18}H_{19}NO_2$), 177 (MH^+-C_8H_9), 117* (M^+- $C_9H_{10}NO_2$), 91 (M^+- $C_{11}H_{12}NO_2$), 66 (M^+- $C_{13}H_{13}NO_2$)



Assignment of C and H atoms of exo-PhC$_3$M

2.4.6 Synthesis and characterisation of exo-N-phenylbutylnorbornene-5,6-dicarboxyimide: (exo-PhC$_4$M)

The same procedure as in 2.4.2 was followed using exo-AN (5.002g, 0.03mol) and phenylbutylamine (4.553g, 0.030mol). The monomer was recovered as white crystals, which was recrystallised in toluene to give white solid (4.93g, 0.021mol, 68% yield, mpt: 115°C).

(a) Elementary Analysis of $C_{19}H_{21}NO_2$: calculated (found)

C = 77.26% (77.32%), H = 7.17% (7.19%), N = 4.74% (4.73%), O = 10.83% (10.76%)

(b) ^{1}H NMR (see appendix x), $CDCl_3$, 500 MHz, δ (ppm)

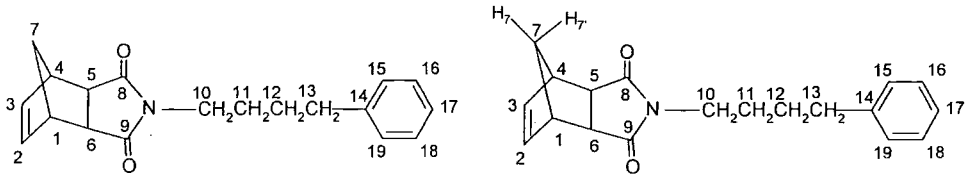
7.26 (t, 2H, $H_{16,18}$), 7.16 (t, 1H, H_{17}), 7.15 (d, 2H, $H_{15,19}$), 6.27 (s, 2H, $H_{2,3}$), 3.48 (t, 2H, H_{10}), 3.25 (s, 2H, $H_{1,4}$), 2.65 (s, 2H, $H_{5,6}$), 2.62 (t, 2H, H_{13}), 1.60 (t, 4H, $H_{11,12}$), 1.49 (d, 1H, H_7), 1.20 (d, 1H, $H_{7'}$)

(c) ^{13}C NMR (see appendix y), $CDCl_3$, 500 MHz, δ (ppm)

178.33 ($C_{8,9}$), 142.17 (C_{14}), 138.06 ($C_{2,3}$), 128.64 ($C_{15,19}$), 128.59 ($C_{16,18}$), 126.08 (C_{17}), 48.04 ($C_{5,6}$), 45.39 ($C_{1,4}$), 42.98 (C_7), 38.67 (C_{10}), 35.58 (C_{11}), 29.05 (C_{12}), 27.64 (C_{13}).

(d) Mass spectrum (see appendix z), (EI^+).

295 (M^+, $C_{19}H_{21}NO_2$), 230 (MH^+-C_5H_6), 91 (M^+- $C_{12}H_{14}NO_2$), 66 (M^+- $C_{14}H_{15}NO_2$)



Assignment of C and H atoms of exo-PhC_4M

2.4.7 Synthesis and characterisation of exo-N-tert-butylphenylnorbornene-5,6-dicarboxyimide: (exo-C_4PhM)

The same procedure as in figure 2.4.2 was followed using exo-AN (5.008g, 0.03mol) and 4-tert-butylaniline (3.26g, 0.030mol). The monomer was recovered as white crystals, which was recrystallised in toluene to give white solid (4.556g, 0.020mol, 68% yield, mpt: 165°C).

(a) Elemental Analysis of $C_{19}H_{21}NO_2$: calculated (found)

C = 77.26% (77.39%), H = 7.17% (7.19%), N = 4.74% (4.73%), O = 10.83% (10.69%)

(b) ^{1}H NMR (see appendix x), $CDCl_3$, 500 MHz, δ (ppm)

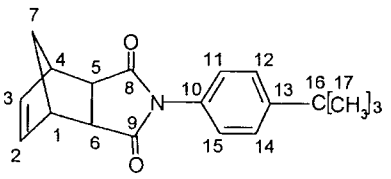
7.47 (d, 2H, $H_{11,15}$), 7.18 (d, 2H, $H_{12,14}$), 6.33 (s, 2H, $H_{2,3}$), 3.39 (s, 2H, $H_{1,4}$), 2.84 (s, 2H, $H_{5,6}$), 1.60 (d, 1H, H_7), 1.48 (d, 1H, $H_{7'}$), 1.32 (s,9H, H_{17}).

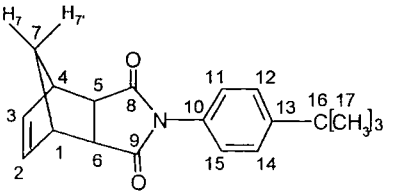
(c) ^{13}C NMR (see appendix y), $CDCl_3$, 500 MHz, δ (ppm)

177.51 ($C_{8,9}$), 151.89 (C_{10}), 138.23 ($C_{2,3}$), 129.33 (C_{13}), 126.46 ($C_{11,15}$), 126.03 ($C_{12,14}$), 48.08 ($C_{5,6}$), 46.05 ($C_{1,4}$), 43.19 (C_7), 34.98 (C_{16}), 31.51 (C_{17}).

(d) Mass spectrum (see appendix z), (EI^+).

295 (M^+, $C_{19}H_{21}NO_2$), 280 (M^+-CH_3), 229 (M^+- $C_{14}H_{15}NO_2$), 214 (M^+-CH_3-C_5H_6), 66 (M^+- $C_{14}H_{15}NO_2$)





Analysis data for exo-C4PhM

2.4.8 Synthesis and characterisation of exo-N-pentylphenylnorbornene-5,6-dicarboxyimide: (exo-C_5PhM).

The same procedure as in figure 2.4.2 was followed using exo-AN (5.006g, 0.03mol) and benzylamine (4.978g, 0.03mol). The monomer was recovered as pink crystals, which was recrystallised in hexane to give pinkish solid (8.1g, 0.026mol, 86% yield, mpt: 108°C)

(a) Elemental Analysis of $C_{20}H_{23}NO_2$: calculated (found)

C = 77.64% (77.90%), H = 7.49% (7.53%), N = 4.53% (4.55%), O = 10.34% (10.02%)

(b) ^{1}H NMR (see appendix x), $CDCl_3$, 500 MHz, δ (ppm)

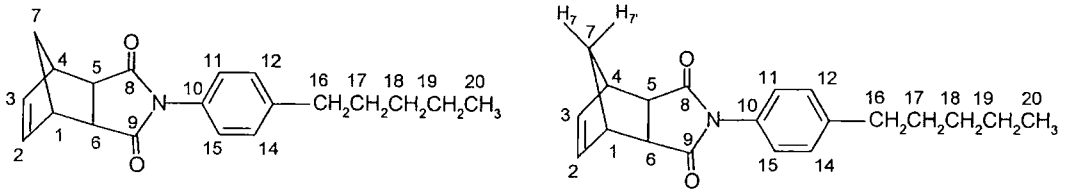
7.27 (d, 2H, $H_{11,15}$), 7.15 (d, 2H, $H_{12,14}$), 6.34 (s, 2H, $H_{2,3}$), 3.39 (s, 2H, $H_{1,4}$), 2.84 (s, 2H, $H_{5,6}$), 2.62 (H_{16}), 1.61 (m, 3H, H_{17} and H_7), 1.48 (d, 1H, $H_{7'}$), 1.32 (m, 4H, $H_{18,19}$), 0.89 (t, 3H, H_{20}).

(c) ^{13}C NMR (see appendix y), $CDCl_3$, 500 MHz, δ (ppm)

177.50 ($C_{8,9}$), 143,91 (C_{10}), 138.22 ($C_{2,3}$), 129.52 (C_{13}), 129.42 ($C_{11,15}$), 126.32 ($C_{12,14}$), 48.07 ($C_{5,6}$), 46.03 ($C_{1,4}$), 43.18 (C_7), 35.86 (C_{16}), 31.67 (C_{17}), 31.21 (C_{18}), 22.75 (C_{19}), 14.26 (C_{20}).

(d) Mass spectrum (see appendix z)

309 (M^+, $C_{20}H_{23}NO_2$), 243 (M^+-C_5H_6), 186 (M^+-C_6H_5-C_4H_9), 66 (M^+- $C_{15}H_{17}NO_2$)



Assignment of C and H atoms for exo-C_5PhM

2.4.9 Synthesis and characterisation of exo-N-hexylphenylnorbornene-5,6-dicarboxyimide: (exo-C_6PhM).

The same procedure as in 2.4.2 was followed using exo-AN (4.631g, 0.028mol) and benzylamine (5.000g, 0.028mol). The monomer was recovered as white crystals, which was recrystallised in hexane to give white solid (7.7g, 0.024mol, 84% yield, mpt: 96°C)

(a) Elemental Analysis of $C_{21}H_{25}NO_2$: calculated (found)

C = 77.99% (77.93%), H = 7.79% (7.73%), N = 4.33% (4.23%), O = 9.89% (10.11%)

(b) ^{1}H NMR (see appendix x), $CDCl_3$, 500 MHz, δ (ppm)

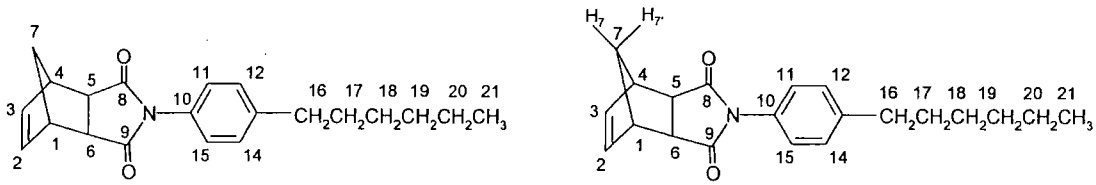
7.26 (d, 2H, $H_{11,15}$), 7.15 (d, 2H, $H_{12,14}$), 6.34 (s, 2H, $H_{2,3}$), 3.39 (s, 2H, $H_{1,4}$), 2.84 (s, 2H, $H_{5,6}$), 2.62 (H_{16}), 1.61 (m, 3H, H_{17} and H_7), 1.48 (d, 1H, $H_{7'}$), 1.30 (m, 6H, $H_{18\text{-}20}$), 0.88 (t, 3H, H_{21}).

(c) ^{13}C NMR (see appendix y), $CDCl_3$, 500 MHz, δ (ppm)

177.49 ($C_{8,9}$), 143.92 (C_{10}), 138.22 ($C_{2,3}$), 129.51 (C_{13}), 129.41 ($C_{11,15}$), 126.31 ($C_{12,14}$), 48.07 ($C_{5,6}$), 46.03 ($C_{1,4}$), 43.18 (C_7), 35.90 (C_{16}), 31.93 (C_{17}), 31.50 (C_{18}), 29.20 (C_{19}), 22.83 (C_{20}), 14.35 (C_{21}).

(d) Mass spectrum (see appendix z)

323 (M^+, $C_{21}H_{25}NO_2$), 257 (M^+-C_5H_6), 186 (M^+- C_6H_5 – C_5H_{11}), 66 (M^+- $C_{16}H_{19}NO_2$)



Assignment of C and H atoms for exo-C_6PhM

2.4.10 Synthesis and characterisation of exo-N-hexylnorbornene-5,6-dicarboxyimide: (exo-C_6M).

The same procedure as in 2.4.2 was followed using exo-AN (10.09g, 0.060mol) and hexylamine (6.16g, 0.060mol). The monomer was recovered as pale yellow liquid, which was distilled to give colourless liquid (87% yield, bpt: 130 @ 4mmbar).

(a) Elemental Analysis of $C_{15}H_{21}NO_2$: calculated (found)

C = 72.84% (72.49%), H = 8.56% (8.52%), N = 5.66% (6.80%), O = 12.94% (12.19%)

(b) ^{1}H NMR (see appendix x), $CDCl_3$, 500 MHz, δ (ppm)

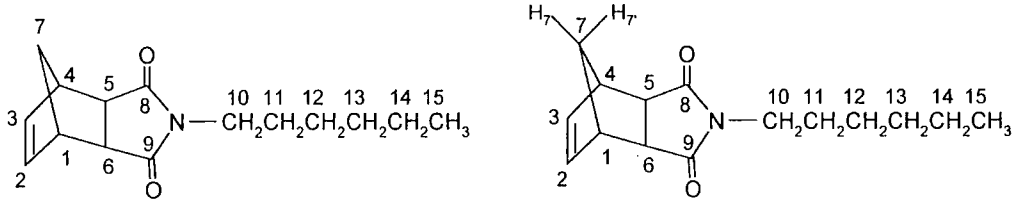
6.28 (s, 2H, $H_{2,3}$), 3.45 (t, 2H, H_{10}), 3.27 (s, 2H, $H_{1,4}$), 2.67 (s, 2H, $H_{5,6}$), 1.52 (m, 3H, H_{11} and H_7), 1.28 (m, 6H, $H_{12\text{-}14}$), 1.23 (d, 1H, $H_{7'}$), 0.87 (t, 3H, H_{15}).

(c) ^{13}C NMR (see appendix y), $CDCl_3$, 500 MHz, δ (ppm)

178.33 ($C_{8,9}$),138.04 ($C_{2,3}$), 48.00 ($C_{5,6}$), 45.36 ($C_{1,4}$), 42.91 (C_7), 38.96 (C_{10}), 31.52 (C_{11}), 27.93 (C_{12}), 26.82 (C_{13}), 22.68 (C_{14}), 14.20 (C_{15}).

(d) Mass spectrum (see appendix z)

247 (M^+, $C_{15}H_{21}NO_2$), 182 (M^+-C_5H_6), 186 (M^+- C_5H_6 – C_5H_{11}), 66 (M^+- $C_{10}H_{15}NO_2$)



Assignment of C and H atoms for exo-C_6M

Chapter 3

Polymer synthesis and characterisation

3.1 Introduction

The focus of this chapter is on the synthesis of linear polymers via ROMP of exo-phenyl norbornene dicarboxyimide monomers using well-defined initiators. The initiators used for polymerisation reaction were well defined ruthenium carbene initiator $\{Cl_2[(C_6H_{11})_3P]_2Ru{=}CHC_6H_5\}$, the t-butoxy substituted molybdenum initiator $\{Mo[CHC(CH_3)_3][C_{10}H_{17}N][OC(CH_3)_3]_2\}$, Mo (1), and hexafluoro-t-butoxy substituted molybdenum initiator $\{Mo[CHC(CH3)_2C_6H_5][C_{10}H_{17}N][OC(CF_3)_2CH_3]_2\}$, Mo (2).
NMR scale ROMP reactions were carried out to provide information on the reactivity of a series of exo- phenyl norbornene dicarboxyimides. The ROMP reactions were scaled up to provide polymer samples for ^{1}H NMR, ^{13}C NMR, and elemental analysis, the molecular weight measurement by GPC and thermal properties evaluation by DSC (differential Scanning Calorimetry) and DMTA (dynamic mechanical thermal analysis). The cis and trans content of the polymers were estimated from ^{1}HNMR and ^{13}CNMR spectra.

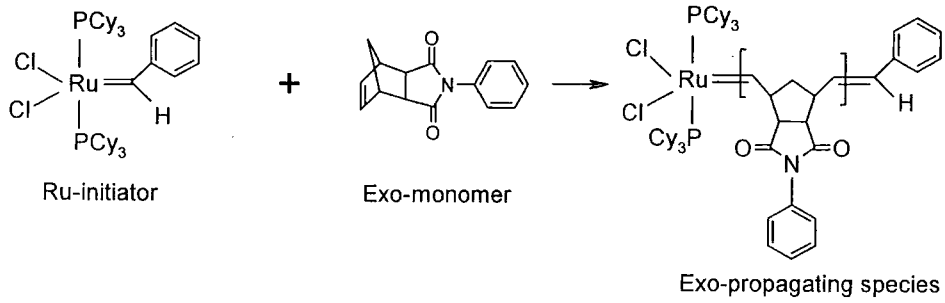
3.2 NMR scale solution polymerisation of exo-phenylnorbornene dicarboxyimide monomers

3.2.1 Polymerisation using ruthenium initiator

Polymerisation reactions were performed in the glove box (Braun) at room temperature. The initiator (10 mg) and monomer (10 equivalents) were dissolved in $CDCl_3$, in two separate 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 NRM tube was removed from the glove box and the spectrum was recorded. The polymerisation reaction is illustrated in figure3.1. In all cases, the monomer was consumed within ten minutes of the reaction. This was shown by the disappearance of the monomer signal at 6.30ppm in the ^{1}H NMR spectra of the reaction mixture.
The alkylidene region in the ^{1}H NMR spectra showed signals due to initiator alkylidene hydrogens at 19.98 ppm and signals due to the propagating alkylidene hydrogens was at 19.52 ppm and 18.67 ppm. A typical example is shown in figure 3.2. On addition of 20 equivalents of the monomer, the polymerisation was continued; the initiator signal was reduced with subsequent growth in the propagation signal. This suggested that the polymerisation was living. The initiator signal was still observable after the addition of

70 equivalents of the monomer. This indicates that the rate of propagation is faster than the rate of initiation i.e. $k_p >> k_i$.

(a) Initiation



(b) Propagation

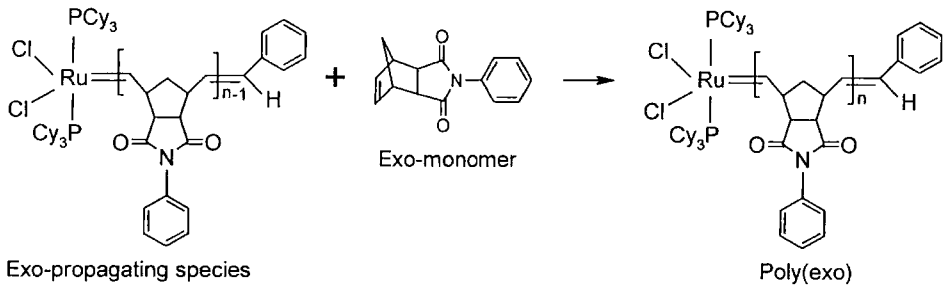


Figure 3.1: (a) Outline of the initiation reaction by well defined Ru-initiator.
(b) Outline of the propagation step.

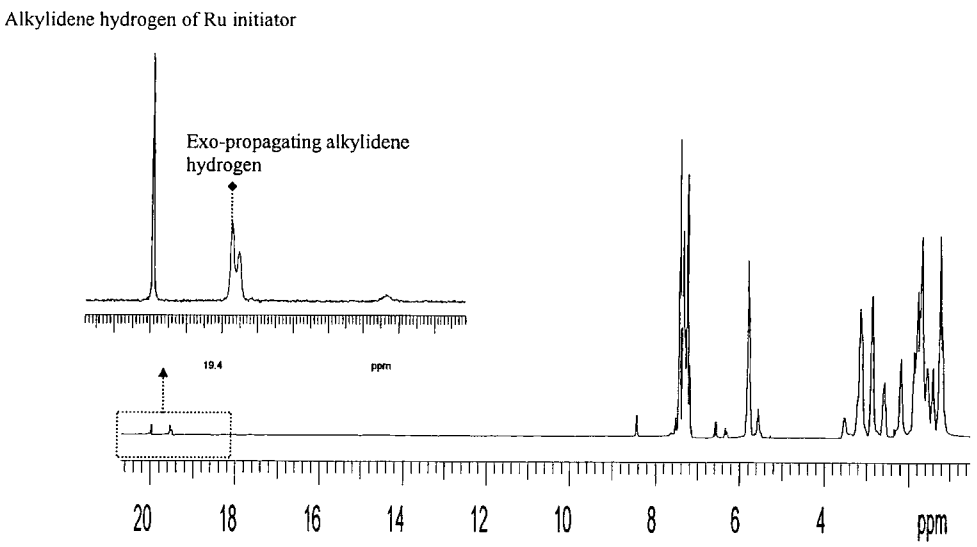
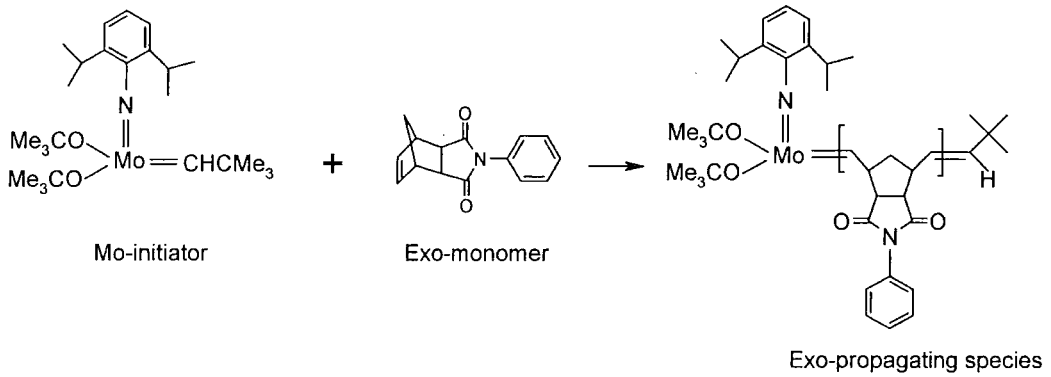


Figure 3.2: ^{1}H NMR spectra from polymerisation of exo-monomer by well-defined ruthenium initiator.

3.2.2 Polymerisation using t-butoxy substituted molybdenum initiator

The same procedure as in section 3.2.1 was followed using t-butoxy substituted molybdenum initiator. The polymerisation reaction is illustrated in figure 3.3. The alkylidene region in the ^1H NMR spectra showed signals due to initiator alkylidene hydrogens at 11.21 ppm and signals due to the propagating alkylidene hydrogens was at 11.59 ppm. A typical example is shown in figure 3.4.

(a) Initiation



(b) Propagation

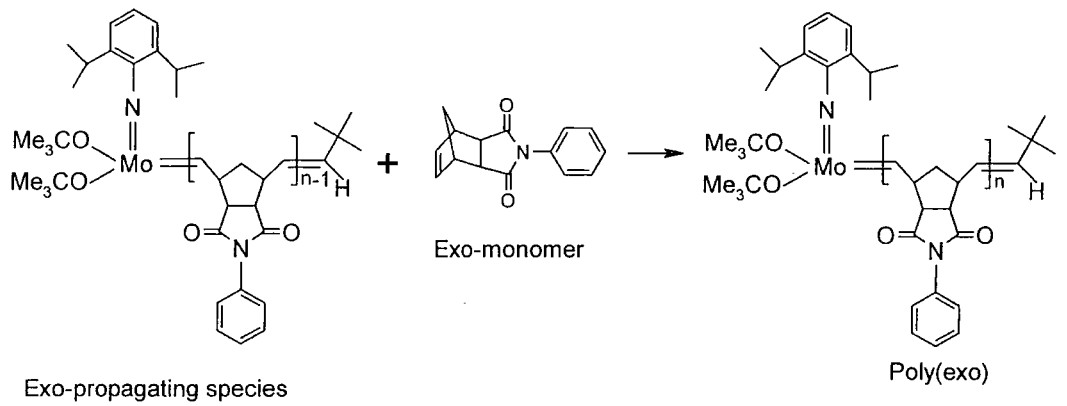


Figure 3.3: (a) Outline of the initiation reaction by well defined Mo (1) initiator.
(b) Outline of the propagation step.

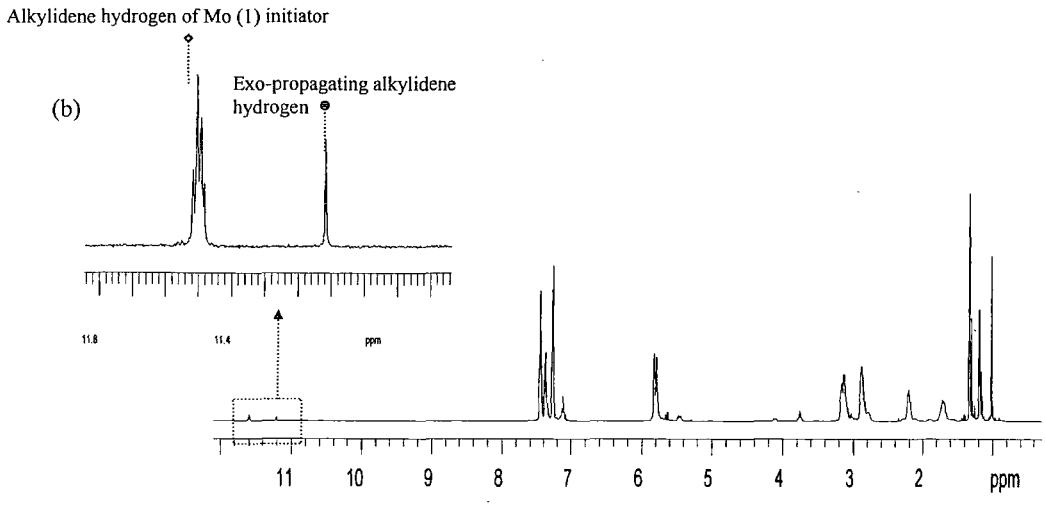
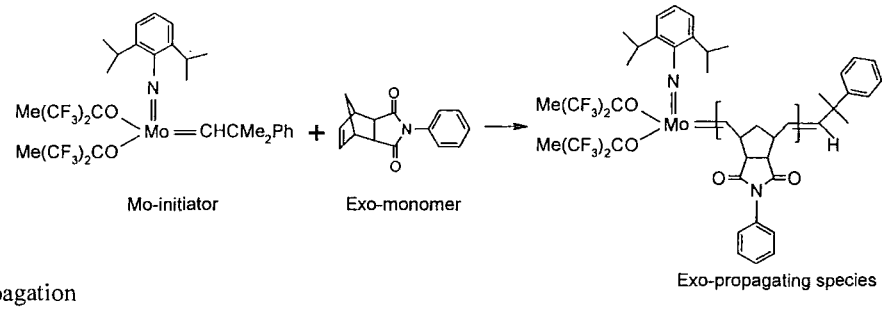


Figure 3.4: ^{1}H NMR spectra from polymerisation of exo-monomer by well-defined Mo (1) initiator.

3.2.3 Polymerisation using hexafluoro-t-butoxy substituted molybdenum initiator

The same procedure as in section 3.2.1 was followed using t-butoxy substituted molybdenum initiator. The polymerisation reaction is illustrated in figure 3.5. The alkylidene region in the ^{1}H NMR spectra showed signals due to initiator alkylidene hydrogens at 12.40 ppm and signals due to the propagating alkylidene hydrogens was at 12.77 ppm. A typical example is shown in figure 3.6.

(a) Initiation



(b) Propagation

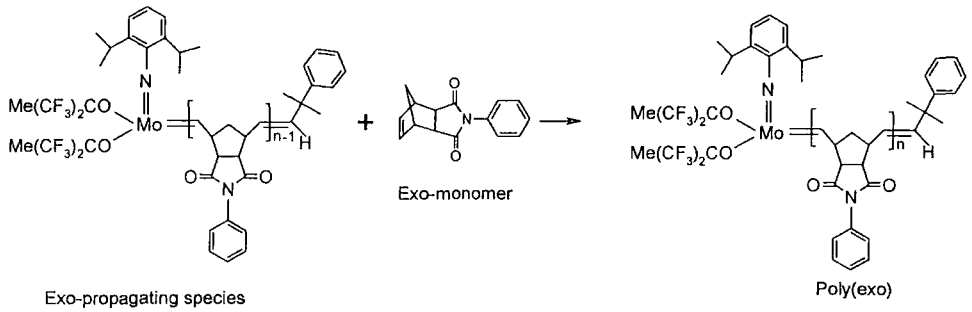


Figure 3.5: (a) Outline of the initiation reaction by well defined Mo (2)-initiator.
(b) Outline of the propagation step.

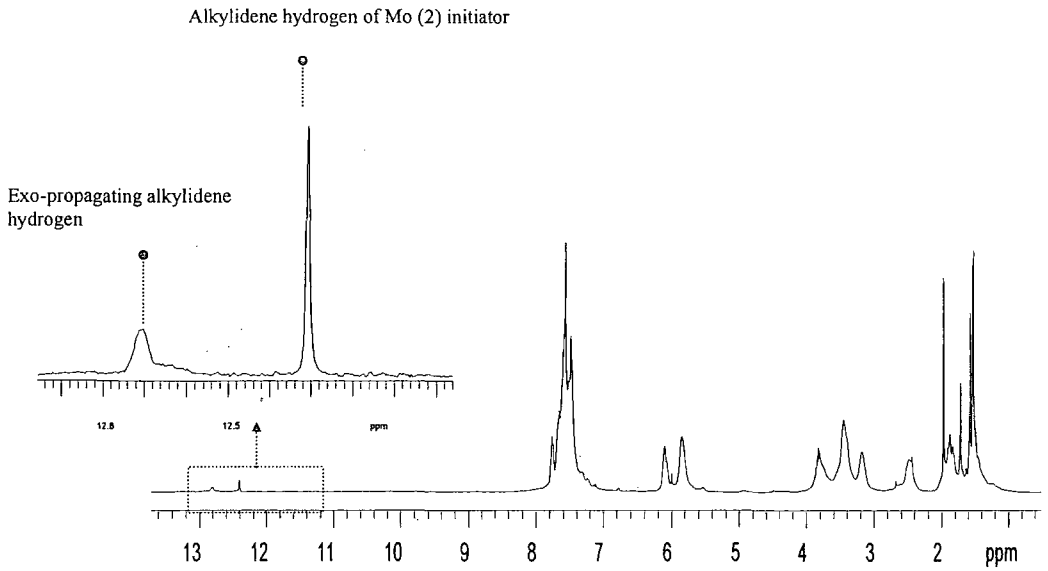


Figure 3.6: ^{1}H NMR spectra from polymerisation of exo-monomer by well-defined Mo (1) initiator.

3.2.4 Copolymerisation of exo-ethylphenyl norbornene dicarboxyimide and exo-hexyl norbornene dicarboxyimide

The alkyl norbornene dicarboxyimides prepared in the previous work were liquid and therefore it possible to carry out ROMP using well-defined ruthenium initiator in both solution and bulk. However, all the phenyl norbornene dicarboxyimide monomers in this work were solids. The exo-ethylphenyl norbornene dicarboxyimide (exo-PhC_2M) monomer was found to be soluble in exo-hexyl norbornene dicarboxyimide (exo-C_6M) monomer. The aim of this section was to test the possibility of carrying out ROMP on a mixture of monomers and obtain some information on the reactivity ratios of the monomers in the mixture. Three experiments were performed using the ruthenium initiator (10mg): the first polymerisation reaction contain 20 equivalents of exo-C_6M, the second polymerisation reaction contain 20 equivalents of exo-$PhC_2M$and the third polymerisation reaction contained a mixture of 20 equivalents of exo-C6M and exo-PhC_2M. All the experiments were analysed by ^{1}H NMR within the first ten minutes. All the monomers were consumed within the first ten minutes and no resonances due to the monomer could be found. It appears that in the case of the experiment using a mixture of two monomers both monomers are polymerising at a same rate. The alkylidene region in the NMR spectra of the homopolymerisation of the two monomers showed expected signals for initiator alkylidene and propagating alkylidene hydrogens. The polymerisation of the mixture is a random copolymerisation and we expect to see two

propagating alkylidene signals, see figure 3.7. The alkylidene region in the NMR spectrum showed a multiplet signal for the propagating alkylidene, which appears to be the results of overlapping of the two propagating signals characteristic of the two monomers. The ^{1}H NMR spectra for the three ROMP reactions are shown in figure 3.8.

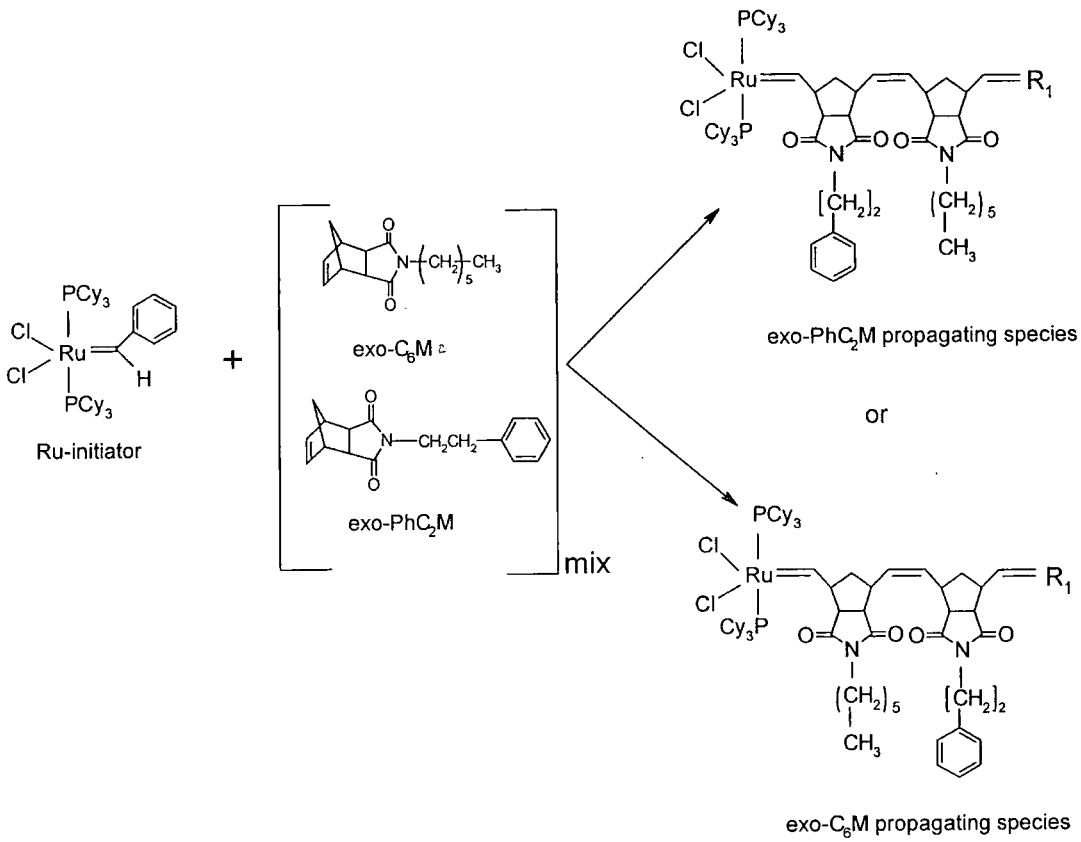


Figure 3.7: Expected propagation reaction in a mixture of exo-C_6M and exo-PhC_2M

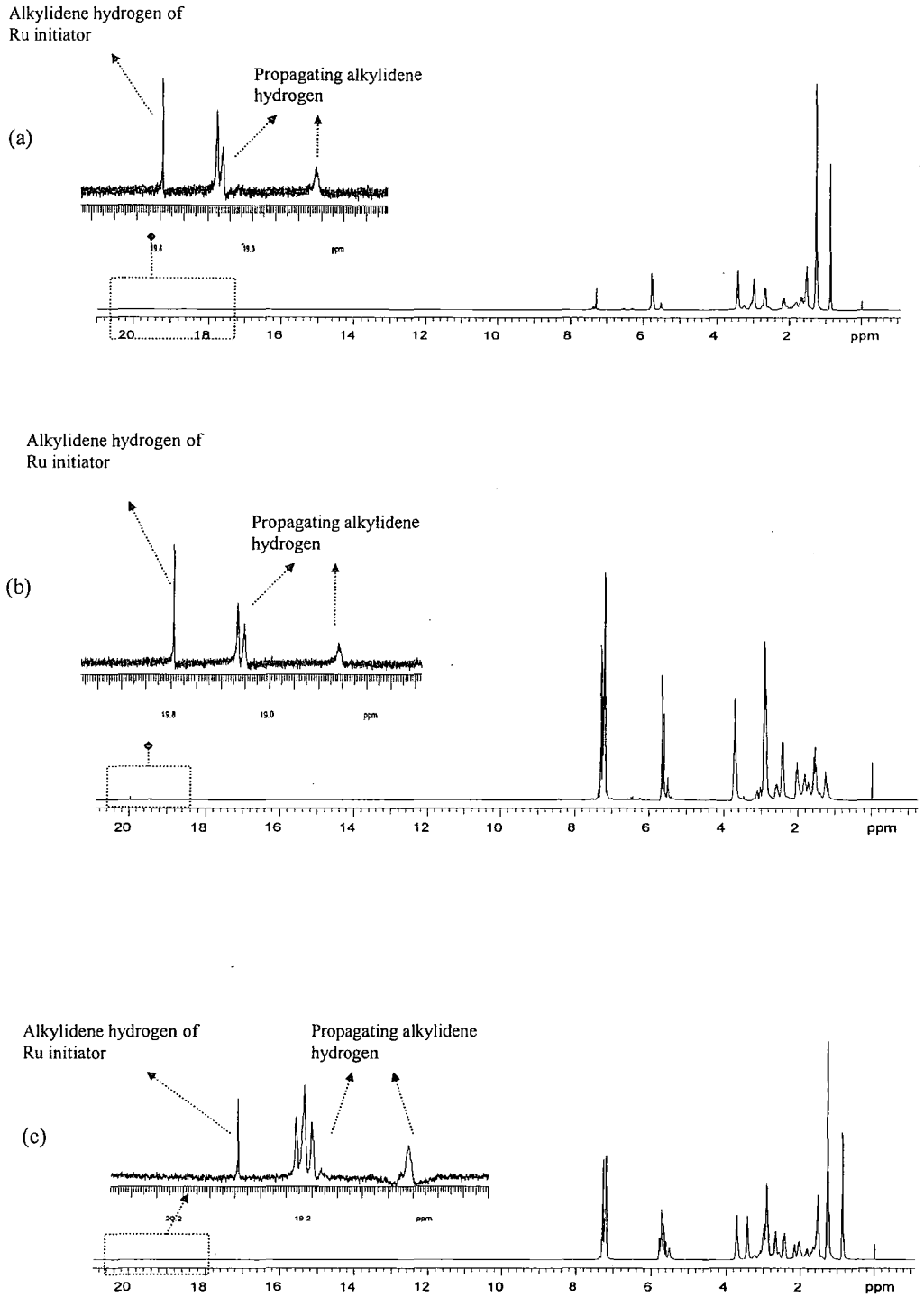


Figure 3.8: ^{1}H NMR spectra of the polymerisation of a mixture of exo-C6M and exo-PhC_2M.
(a) Exo-C6M spectra.
(b) Exo-PhC_2M
(c) Mixture of exo-C6M and exo-PhC_2M

3.2.5 Block copolymerisation of exo-phenyl norbornene dicarboxyimides and exo, endo-norbornene dimethylcarboxylate

To establish the living nature of the ROMP of exo-phenyl norbornene dicarboxyimides block copolymers were synthesised via sequential addition of monomers using exo, endo-norbornene dimethylcarboxylate as the co-monomer, see figure 3.9.

In a typical block copolymerisation reaction, ruthenium initiator (10mg) was dissolved in $CDCl_3$ and was added to exo-ethyl phenyl norbornene dicarboxyimide (100 equivalents) dissolved in $CDCl_3$. The reaction was stirred for 1 hr to allow all the monomer to be consumed in the reaction. Then exo, endo-norbornene dimethylcarboxylate (100 equivalents) dissolved in $CDCl_3$ was added to the reaction mixture. The reaction was allowed to stir for 1 hr and the reaction mixture was analysed by ^1H NMR. Figure 3.10 shows the ^1HNMR spectra of the living ROMP reaction for exo-ethyl phenyl norbornene dicarboxyimide (a), exo, endo-norbornene dimethylcarboxylate (b) and block copolymer (c). The alkylidene region in figure 3.10(c) shows that the resonances due the propagating alkylidene for exo-ethyl phenyl norbornene dicarboxyimide have disappeared and new set of resonances are appeared. Two sets of signals are observed in the alkylidene region for the homopolymerisation of exo, endo-norbornene dimethylcarboxylate figure 3.10(b), one at 19.35ppm and 19.12ppm and the other at 18.65ppm and 18.45ppm probably due to cis and trans vinylene contents although not absolute certain. The alkylidene region for the block copolymer shows only one set of signals at 18.64ppm and 18.43ppm, figure 3.10(c). This suggests that a block copolymer have been formed. It appears that the propagating ends in poly(exo-ethyl phenyl norbornene dicarboxyimide) polymerise exo, endo-norbornene dimethylcarboxylate in a different fashion to that of the initiator.

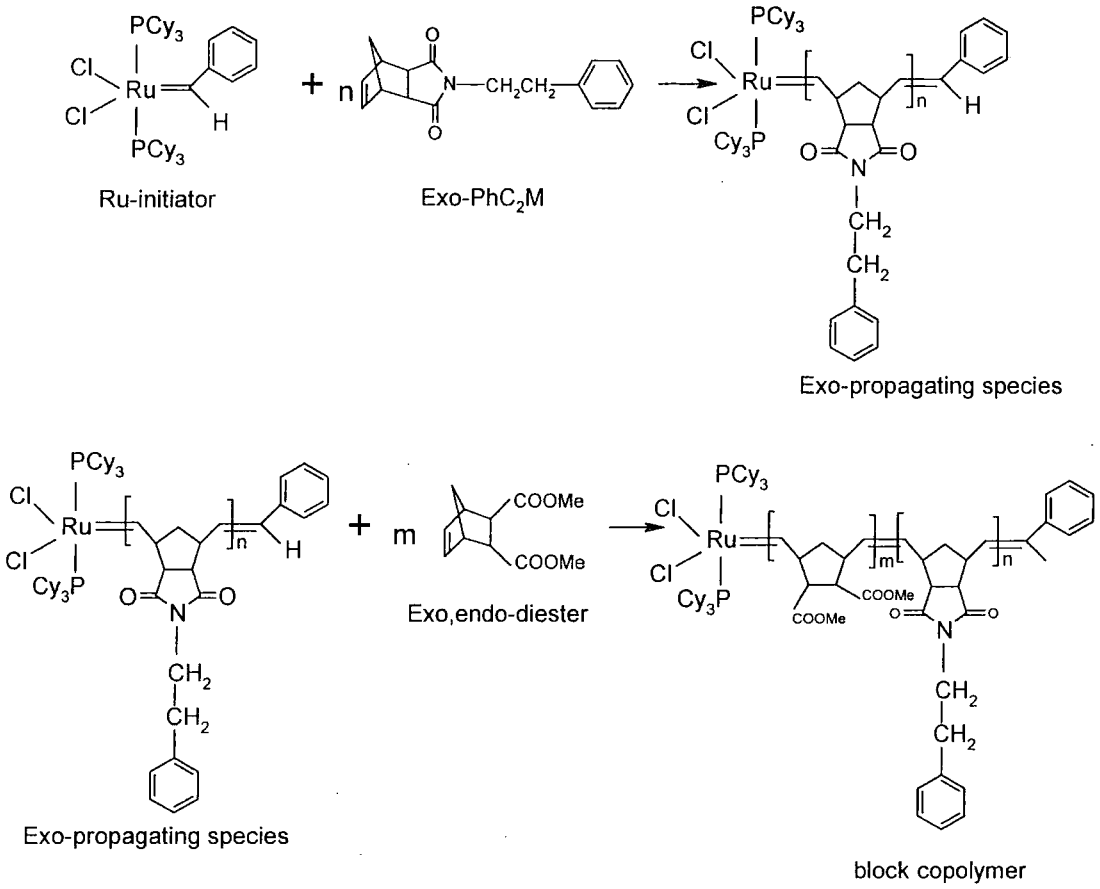


Figure 3.9: Outline of the polymerisation reaction between exo, endo-diester and exo-PhC_2M

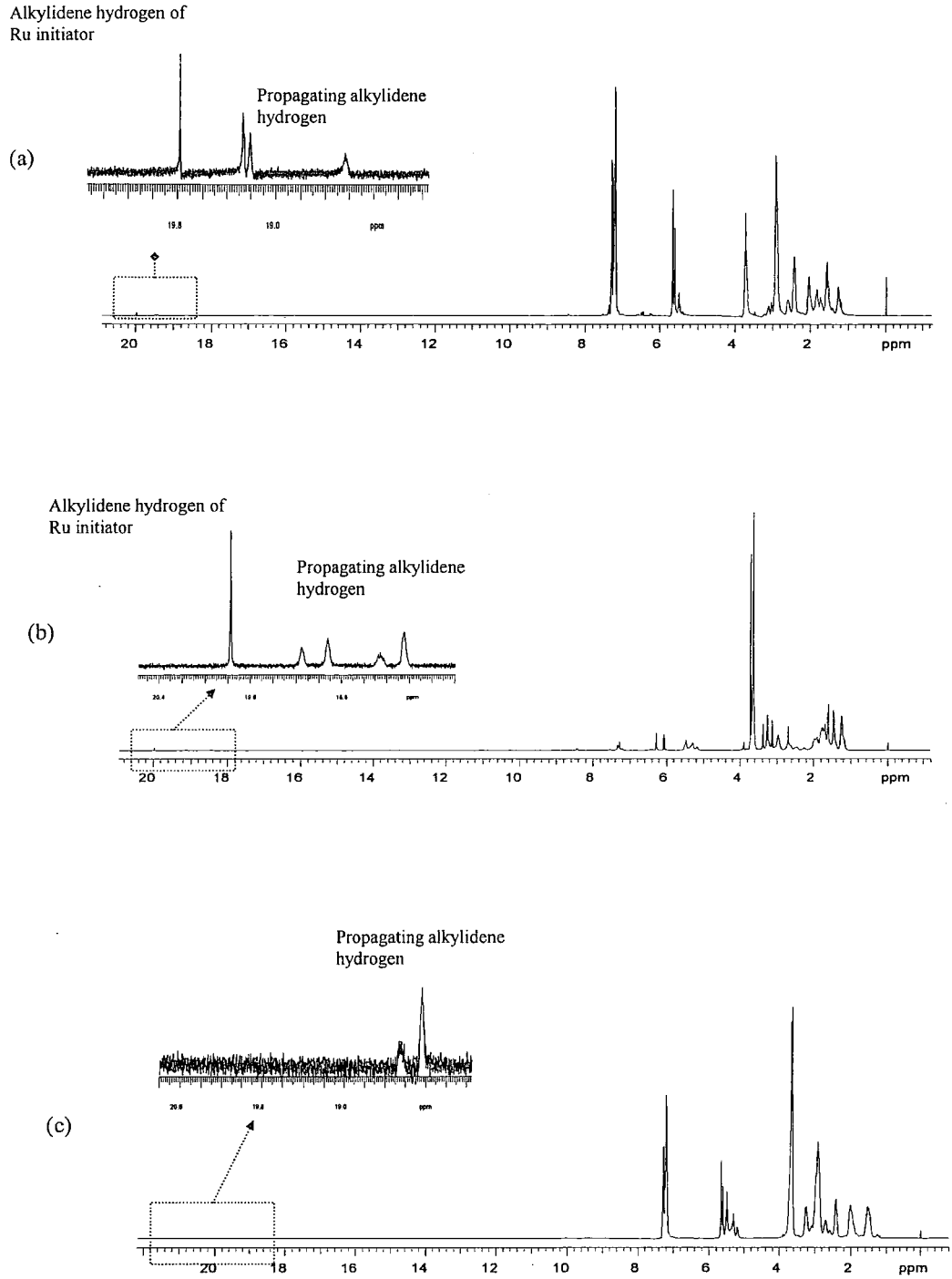


Figure 3.10: ^{1}H NMR spectra of the polymerisation of copolymer of exo-PhC_2M and a diester.

(a) Exo-PhC_2M
(b) Diester
(c) Diblock copolymer.

3.3 Scale up polymerisation reaction

The ROMP reactions of exo-phenyl norbornene dicarboxyimides using well-defined initiators were scaled up to provide polymer samples for ^{1}H NMR, ^{13}C NMR, and elemental analysis, the molecular weight measurement by GPC and thermal properties evaluation by DSC (differential Scanning Calorimetry) and DMTA (dynamic mechanical thermal analysis).

The polymerisation reaction schemes and the termination reaction for exo-phenyl norbornene dicarboxyimide using ruthenium initiator is shown in figure 3.11 and for using molybdenum initiator (Mo (1) or (2)) in figure 3.12. The terminating reagents for ROMP using ruthenium and molybdenum initiators are ethyl vinyl ether and benzaldehyde respectively.

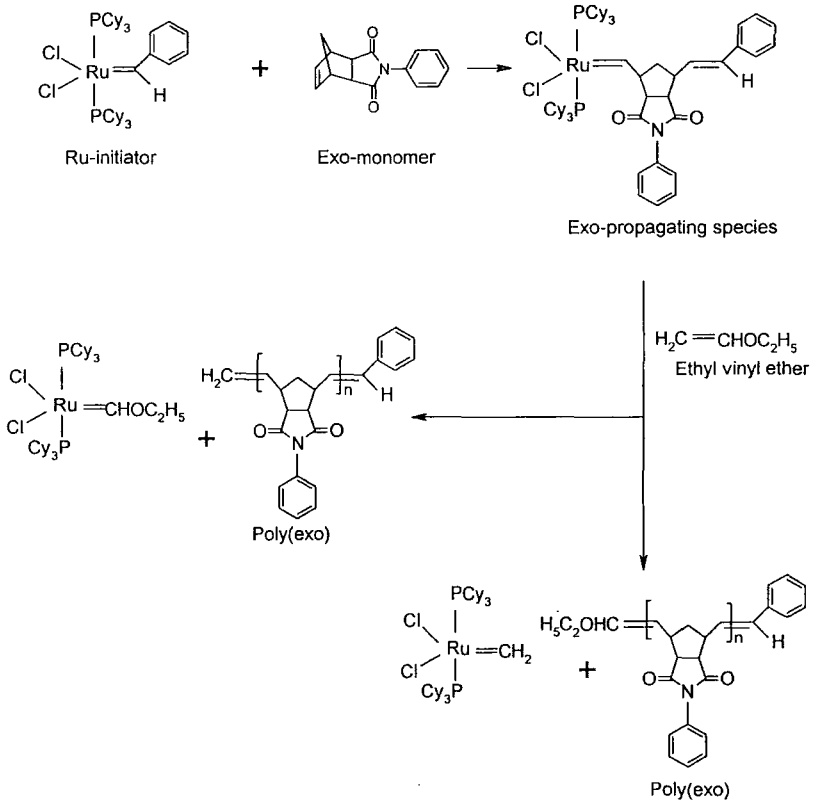


Figure 3.11: Outline of the synthesis and termination route for ROMP using ruthenium initiator

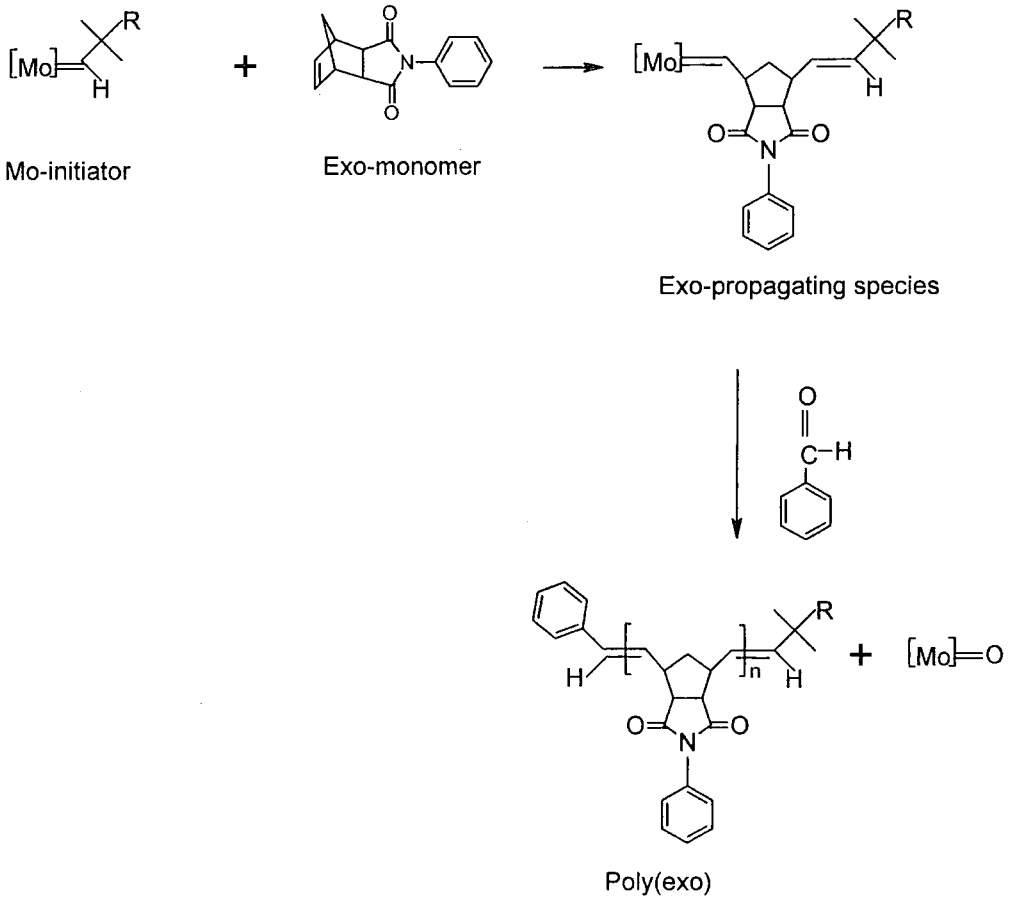


Figure 3.12: Outline of the polymerisation and termination route for ROMP using Mo (1) or Mo (2) initiator

For ruthenium initiator, 0.75 g and for both molybdenum initiators, 0.5g of each monomer was used. The ratio of monomer to initiator was 150:1. The polymerisation reactions were carried out in the glove box (Braun) at room temperature. Both initiator and monomer were dissolved in separate vials in dichloromethane and stirred for few minutes. The monomer solution was added to the initiator solution and the reaction mixture was stirred overnight. The polymerisation reaction was terminated by the addition of the terminating reagent. The polymers were recovered by precipitation twice in methanol and dried under vacuum resulting in white solids. All the polymers were film forming. The polymers formed from ruthenium initiator were soluble in THF, chloroform, dichloromethane and DMF.

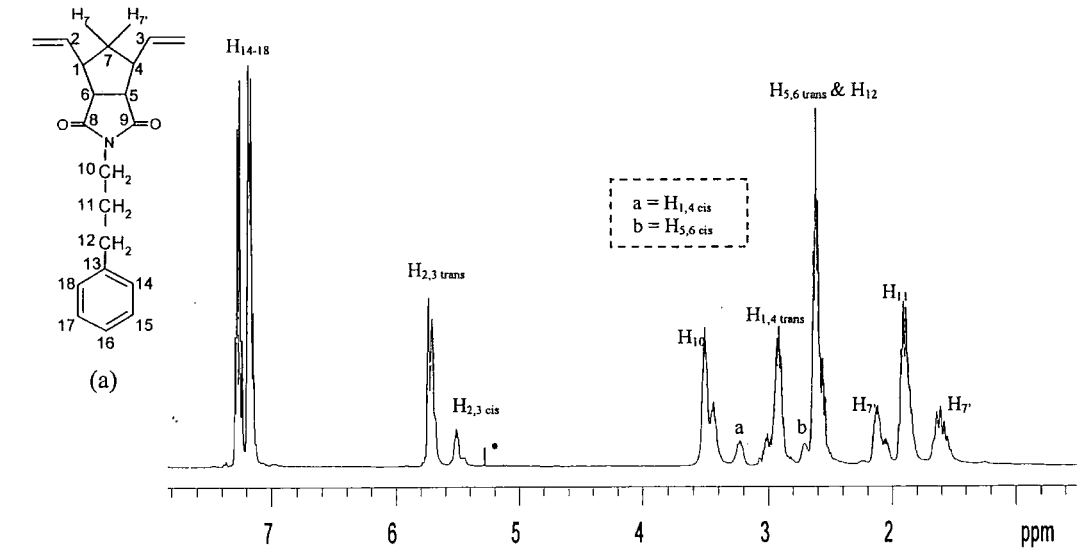
3.3.1 Polymer characterisation using ^{1}H and ^{13}C NMR spectroscopy

The cis / trans contents of the polymers are readily determined from the ^{1}H NMR spectrum from the integration of the resonance attributable to cis and trans olefinic hydrogen ($H_{2,3}$). The resonances due to trans and cis vinylenes for the polymers obtained by the well defined initiators are similar and for the trans vinylenes appears at 5.74ppm and for the cis vinylenes at 5.51ppm., see figures 3.13-3. Table 3.1 shows the cis and trans vinylene content of polymers prepared by each initiator. Generally the trans vinylene content for polymers prepared by ruthenium initiator is about 83%, for the polymers prepared by t-butoxy molybdenum initiator is about 97% and for the polymers prepared by hexafluoro-t-butoxy molybdenum initiator is about 31%. These results are consistent with the previous result[49] that ruthenium initiator give polymers with 80% trans content and that t-butoxy molybdenum initiator give polymers with high trans content while hexafluoro-t-butoxy molybdenum initiator give polymers with high cis content.

Polymer	M]/[I]	Initiator	^{1}H NMR	
			% Trans	% Cis
Poly(exo-PhM)	150	**Ru**	**83**	**17**
	150	Mo (1)	99	1
Poly(exo-PhCM)	150	**Ru**	**83**	**17**
	150	Mo (1)	97	3
	150	Mo (2)	30	70
Poly(exo-PhC_2M)	150	**Ru**	**83**	**17**
	150	Mo (1)	94	6
Poly(exo-PhC_3M)	150	**Ru**	**82**	**18**
	150	Mo (1)	94	6
Poly(exo-PhC_4M)	150	**Ru**	**83**	**17**
Poly(exo-C_4PhM)	150	**Ru**	**83**	**17**
	150	Mo (1)	97	3
	150	Mo (2)	32	68
Poly(exo-C_5PhM)	150	**Ru**	**84**	**16**
	150	Mo (1)	92	8
	150	Mo (2)	30	70
Poly(exo-C_6PhM)	150	**Ru**	**85**	**15**
	150	Mo (1)	96	4

Table 3.1: cis / trans distribution of the polymers produced by the three initiators

The ^{1}H and ^{13}C NMR spectra of the polymers obtained from ROMP of alkyl norbornene dicarboxyimides have been assigned in details in previous studies. The ^{1}H and ^{13}C NMR spectra of the polymers prepared from ROMP of phenyl norbornene dicarboxyimides were assigned in a similar manner. A typical ^{1}H and ^{13}C NMR spectra for the polymers obtained by ruthenium initiator, t-butoxy molybdenum, and hexofluoro t-butoxy molybdenum initiators are shown in figures 3.13-3.15, respectively. The assignment of the ^{1}H and ^{13}C NMR spectra for the polymers obtained by ruthenium initiator, t-butoxy molybdenum, and hexofluoro t-butoxy molybdenum initiators are very similar and are tabulated in tables 3.2-3.4, respectively.



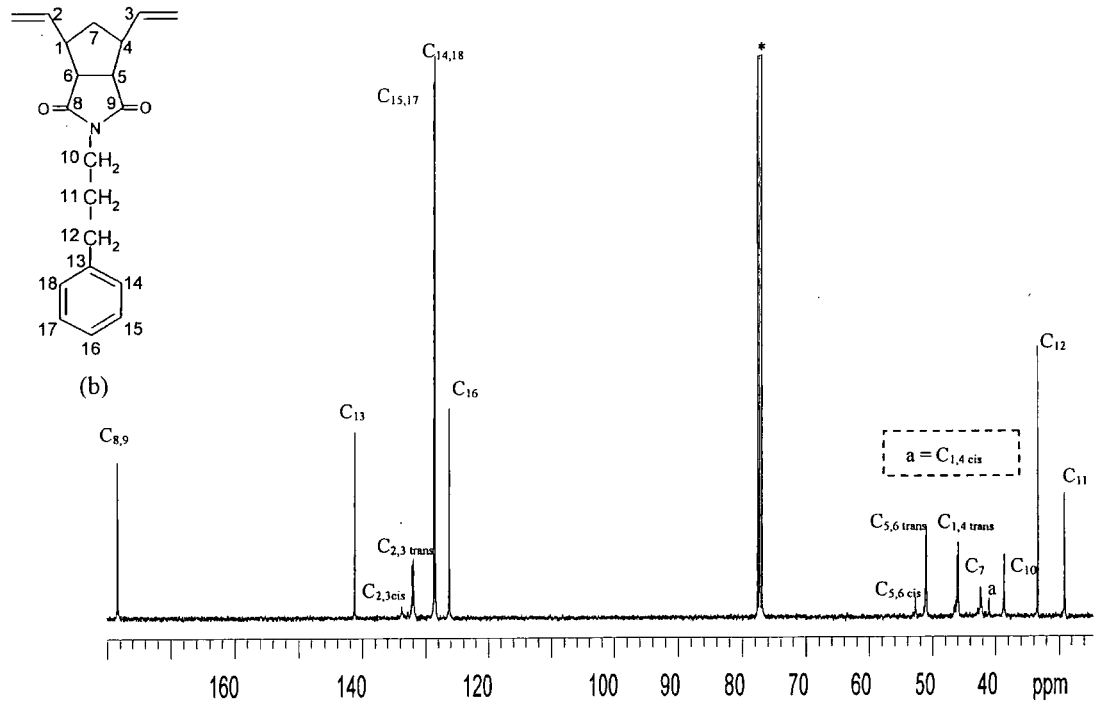


Figure 3.13: (a) ^{1}H NMR spectrum of poly (exo-PhC_3M) using Ru initiator in $CDCl_3$
(b) ^{13}C NMR spectrum of poly (exo-PhC_3M) using Ru initiator in $CDCl_3$
* Residual hydrogen in $CDCl_3$
• Solvent CH_2Cl_2

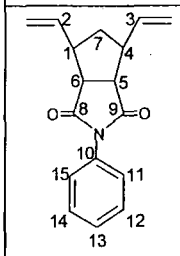
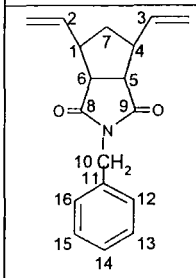
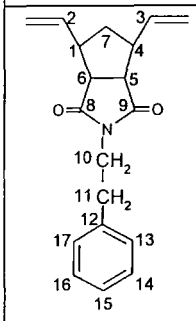
Polymer Ru	^{1}Hnmr		^{13}Cnmr	
	Hydrogen	Chemical shift (ppm)	Carbon	Chemical shift (ppm)
 Poly (exo-PhM)	$H_{12,14}$	7.44	$C_{8,9}$	177.45
	H_{13} / $H_{11,15}$	7.36 / 7.26	$C_{2,3}$	134.12 (cis), 132.05 (trans)
	$H_{2,3}$	5.78 (trans), 5.56(cis)	$C_{12,14}$ / C_{10}	129.33 / 128.73
	$H_{1,4}$	3.51 (cis), 3.13 (trans)	C_{13} / $C_{11,15}$	126.93 / 126.63
	$H_{5,6}$	2.86 (trans)	$C_{5,6}$	52.98 (cis), 51.17 (trans)
	H_7 / $H_{7'}$	2.19 / 1.68	$C_{1,4}$	46.37 (trans), 41.14 (cis)
			C_7	41.87
 Poly (exo-PhCM)	$H_{12\text{-}16}$	7.30 (m, 7.2-7.4)	$C_{8,9}$	178.14
	$H_{2,3}$	5.73 (trans), 5.50 (cis)	C_{11}	136.16
	H_{10}	4.58	$C_{2,3}$	133.70(cis), 131.98 (trans)
	$H_{1,4}$	3.21 (cis), 2.99 (trans)	$C_{12,16}$	128.93
	$H_{5,6}$	2.72 (cis), 2.64 (trans)	$C_{13,15}$ / C_{14}	128.87 / 128.16
	H_7 / $H_{7'}$	2.10 / 1.61	$C_{5,6}$	52.81 (cis), 51.09 (trans)
			$C_{1,4}$	45.89 (trans), 41.12 (cis)
			C_7 / C_{10}	42.41
 Poly (exo-PhC$_2$M)	$H_{14,16}$	7.30	$C_{8,9}$	178.31
	$H_{13,17}$ / C_{15}	7.22 (m, 7.18-7.26)	C_{12}	137.83
	$H_{2,3}$	5.66 (trans), 5.50 (cis)	$C_{2,3}$	133.64 (cis), 131.89 (trans)
	H_{10}	3.73	$C_{13,17}$	129.33
	$H_{1,4}$	3.10 (cis), 2.91 (trans)	$C_{14,16}$ / C_{15}	128.73 / 126.99
	H_{11}	2.91	$C_{5,6}$	52.63 (cis), 50.94 (trans)
	$H_{5,6}$	2.60 (cis), 2.42 (trans)	$C_{1,4}$	45.92 (trans), 41.19 (cis)
	H_7 / $H_{7'}$	2.03 / 1.55	C_7	42.29
			C_{10}/ C_{11}	39.37 / 33.44

Table 3.2: Summary of ^{1}H NMR assignment exo-monomers catalysed by well-defined ruthenium carbene initiator

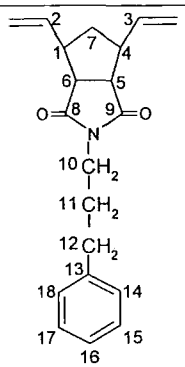
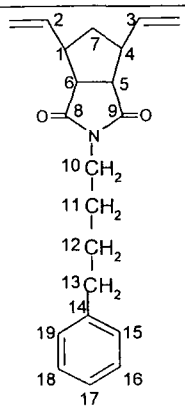
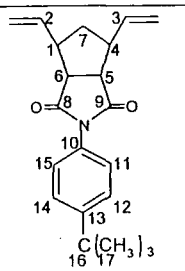
Polymer Ru	^{1}Hnmr		^{13}Cnmr	
	Hydrogen	Chemical shift (ppm)	Carbon	Chemical shift (ppm)
 Poly (exo-PhC_3M)	$H_{15,17}$	7.27	$C_{8,9}$	178.50
	$H_{14,18}$ / C_{16}	7.18 / 7.17	C_{13}	141.21
	$H_{2,3}$	5.74 (trans), 5.51 (cis)	$C_{2,3}$	133.79 (cis), 132.00 (trans)
	H_{10}	3.51	$C_{15,17}$	128.68
	$H_{1,4}$	3.22 (cis), 2.92 (trans)	$C_{14,18}$ / C_{16}	128.52 / 126.30
	$H_{5,6}$	2.71 (cis), 2.62 (trans)	$C_{5,6}$	52.78 (cis), 51.03 (trans)
	H_{12}	2.62	$C_{1,4}$	45.94 (trans), 41.04 (cis)
	H_7 / $H_{7'}$	2.11 / 1.61	C_7	42.37
	H_{11}	1.91	C_{10}/ C_{12}	38.68 / 33.43
			C_{11}	29.13
 Poly (exo-PhC_4M)	$H_{16,18}$	7.26	$C_{8,9}$	178.54
	H_{17} / $C_{15,19}$	7.16	C_{14}	142.21
	$H_{2,3}$	5.75 (trans), 5.52 (cis)	$C_{2,3}$	133.82 (cis), 132.01 (trans)
	H_{10}	3.46	$C_{15,19}$	128.68
	$H_{1,4}$	3.24 (cis), 2.97 (trans)	$C_{16.18}$ / C_{17}	128.62 / 126.11
	$H_{5,6}$	2.75 (cis), 2.62 (trans)	$C_{5,6}$	52.83 (cis), 51.08 (trans)
	H_{13}	2.62	$C_{1,4}$	46.10 (trans), 41.13 (cis)
	H_7 / $H_{7'}$	2.13 / 1.65	C_7	42.44
	$H_{11,12}$	1.59	C_{10}/ C_{13}	38.51 / 35.57
			C_{11}/ C_{12}	28.87 / 27.53
 Poly (exo-C_4PhM)	$H_{11,15}$	7.45	$C_{8,9}$	177.62
	$H_{12,14}$	7.18	C_{10}	151.69
	$H_{2,3}$	5.81 (trans), 5.56 (cis)	$C_{2,3}$	134.27 (cis), 132.45 (trans)
	$H_{1,4}$	3.55 (cis), 3.15 (trans)	C_{13}	129.33
	$H_{5,6}$	2.86 (trans)	$C_{11,15}$ / $C_{12.14}$	126.35 / 126.05
	H_7 / $H_{7'}$	2.19 / 1.70	$C_{5,6}$	53.04 (cis), 51.16 (trans)
	H_{17}	1.31	$C_{1,4}$	46.42 (trans), 41.12 (cis)
			C_7	42.23
			C_{16} / C_{17}	34.97 / 31.53

Table 3.2: Summary continued....

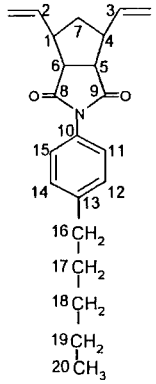
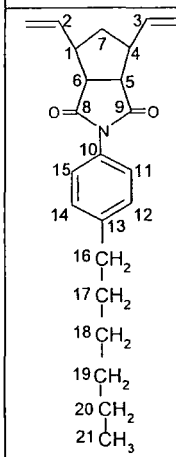
Polymer Ru	^{1}Hnmr		^{13}Cnmr	
	Hydrogen	Chemical shift (ppm)	Carbon	Chemical shift (ppm)
 Poly (exo-C_5PhM)	$H_{11,15}$	7.24	$C_{8,9}$	177.65
	$H_{12,16}$	7.15	C_{10}	143.64
	$H_{2,3}$	5.81 (trans), 5.56 (cis)	$C_{2,3}$	134.26 (cis), 132.32 (trans)
	$H_{1,4}$	3.53 (cis), 3.12 (trans)	C_{13}	129.52
	$H_{5,6}$	2.86 (trans)	$C_{11,15}$ / $C_{12,14}$	129.30 / 126.34
	H_{16}	2.60	$C_{5,6}$	53.02 (cis), 51.13 (trans)
	H_7 / $H_{7'}$	2.19 / 1.68	$C_{1,4}$	46.40 (trans), 41.12 (cis)
	H_{17}	1.60	C_7	41.91
	$H_{18\text{-}19}$	1.31	C_{16} / C_{17}	35.84 / 31.67
	H_{20}	0.88	C_{18} / C_{19}	31.22/ 22.76
			C_{20}	14.28
 Poly (exo-C_6PhM)	$H_{11.15}$	7.24	$C_{8,9}$	177.57
	$H_{12.14}$	7.15	C_{10}	143.64
	$H_{2,3}$	5.81 (trans), 5.56 (cis)	$C_{2,3}$	134.22 (cis), 132.31 (trans)
	$H_{1,4}$	3.53 (cis), 3.12 (trans)	C_{13}	129.51
	$H_{5,6}$	2.85 (trans)	$C_{11,15}$/ $C_{12,14}$	129.29 / 126.34
	H_{16}	2.61	$C_{5,6}$	53.02 (cis), 51.13 (trans)
	H_7 / $H_{7'}$	2.19 / 1.69	$C_{1,4}$	46.40 (trans), 41.11 (cis)
	H_{17}	1.59	C_7	41.91
	$H_{18\text{-}20}$	1.29	C_{16} / C_{17}	35.88 / 31.94
	H_{21}	0.88	C_{18} / C_{19}	31.51/ 29.20
			C_{20} / C_{21}	22.85 / 14.37

Table 3.2: Summary continued....

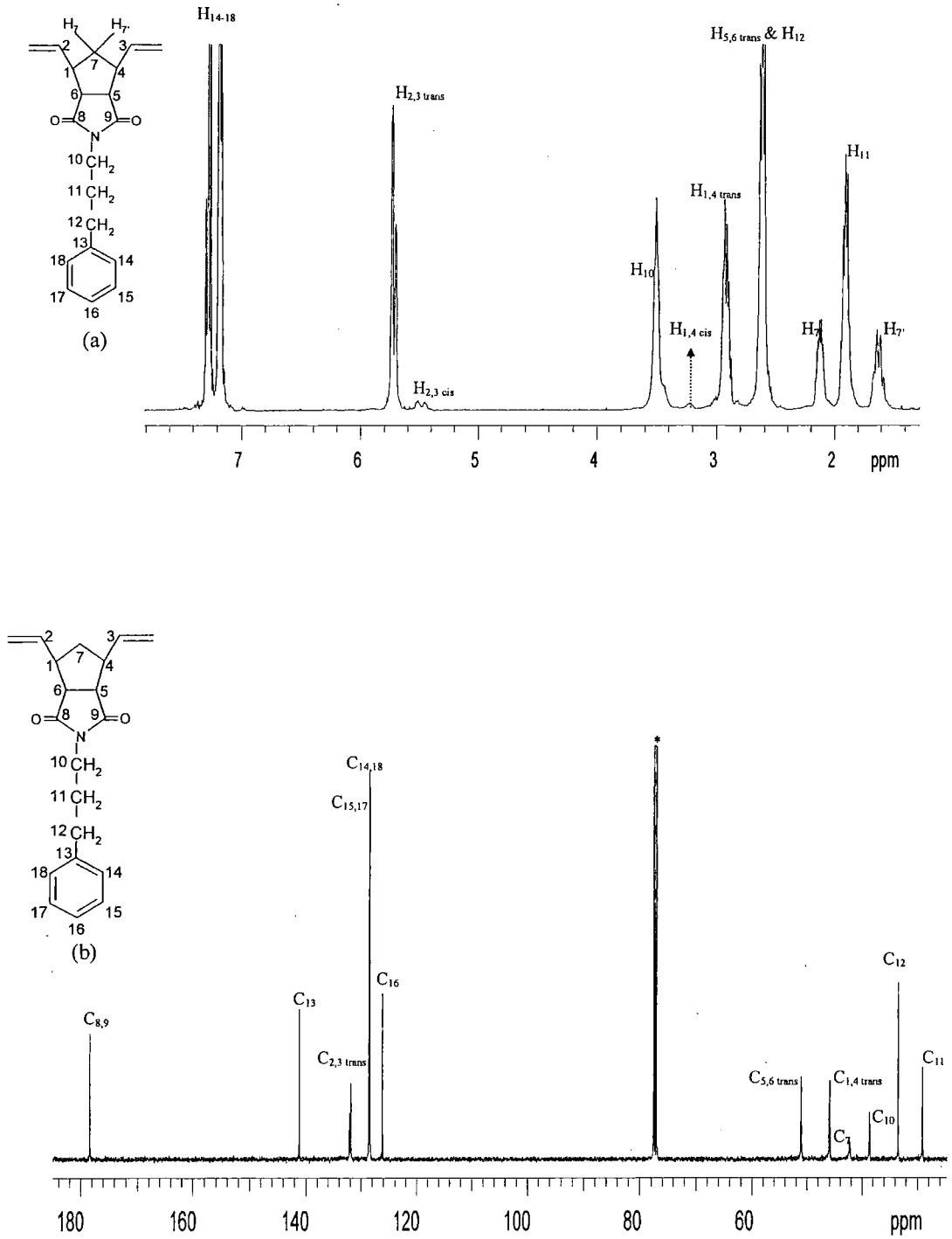


Figure 3.14: (a) ^1H NMR spectrum of poly (exo-PhC_3M) using Mo (1) initiator in $CDCl_3$
(b) ^{13}C NMR spectrum of poly (exo-PhC_3M) using Mo (1) initiator in $CDCl_3$
* Residual hydrogen in $CDCl_3$

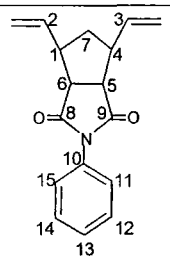
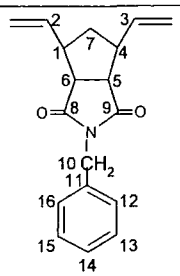
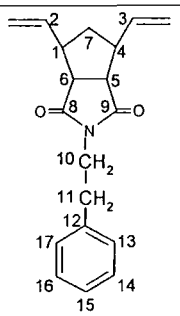
Polymer Mo (1)	^{1}Hnmr		^{13}Cnmr	
	Hydrogen	Chemical shift (ppm)	Carbon	Chemical shift (ppm)
 Poly (exo-PhM)	$H_{12,14}$	7.44	$C_{8,9}$	177.53
	H_{13} / $H_{11,15}$	7.36 / 7.26	$C_{2,3}$	132.37 (trans)
	$H_{2,3}$	5.80 (trans), 5.57(cis)	C_{10} / $C_{12,14}$	132.11 / 129.30
	$H_{1,4}$	3.51 (cis), 3.16 (trans)	C_{13} / $C_{11,15}$	128.71 / 126.63
	$H_{5,6}$	2.87 (trans)	$C_{5,6}$	51.19 (trans)
	H_7 / $H_{7'}$	2.19 / 1.70	$C_{1,4}$	46.42 (trans), 41.21(cis)
			C_7	42.08
 Poly (exo-PhCM)	$H_{12\text{-}16}$	7.30 (m, 7.24-7.34)	$C_{8,9}$	178.13
	$H_{2,3}$	5.74 (trans), 5.50 (cis)	C_{11}	136.19
	H_{10}	4.58	$C_{2,3}$	132.03 (trans)
	$H_{1,4}$	3.20 (cis), 2.99 (trans)	$C_{12,16}$	128.92
	$H_{5,6}$	2.65 (trans)	$C_{13,15}$ / C_{14}	128.84 / 128.14
	H_7 / $H_{7'}$	2.11 / 1.62	$C_{5,6}$	51.13 (trans)
			$C_{1,4}$	45.90 (trans)
			C_7 / C_{10}	42.30
 Poly (exo-PhC$_2$M)	$H_{14,16}$	7.30	$C_{8,9}$	178.34
	$H_{13,17}$ / C_{15}	7.23 (m, 7.18-7.26)	C_{12}	137.83
	$H_{2,3}$	5.65 (trans), 5.50 (cis)	$C_{2,3}$	131.92 (trans)
	H_{10}	3.73	$C_{13,17}$	129.33
	$H_{1,4}$	3.11 (cis), 2.92 (trans)	$C_{14,16}$ / C_{15}	128.73 / 126.98
	H_{11}	2.92	$C_{5,6}$	52.62 (cis), 50.94 (trans)
	$H_{5,6}$	2.60 (cis), 2.42 (trans)	$C_{1,4}$	45.93 (trans), 41.15 (cis)
	H_7 / $H_{7'}$	2.04 / 1.57	C_7	42.16
			C_{10}/ C_{11}	39.38 / 33.44

Table 3.3: Summary of ^{1}H NMR assignment exo-monomers catalysed by t-butoxy substituted molybdenum initiator

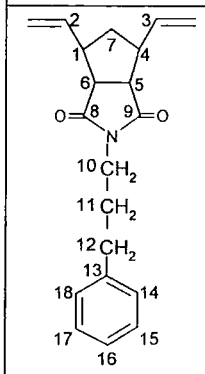
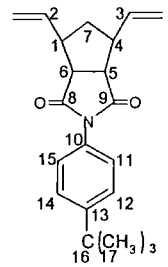
Polymer Mo (1)	^{1}Hnmr		^{13}Cnmr	
	Hydrogen	Chemical shift (ppm)	Carbon	Chemical shift (ppm)
 Poly (exo-PhC$_3$M)	$H_{15,17}$	7.28	$C_{8,9}$	178.51
	$H_{14,18}$ / C_{16}	7.18	C_{13}	141.21
	$H_{2,3}$	5.73 (trans), 5.51 (cis)	$C_{2,3}$	132.01 (trans)
	H_{10}	3.51	$C_{15,17}$	128.68
	$H_{1,4}$	3.22 (cis), 2.92 (trans)	$C_{14,18}$ / C_{16}	128.52 / 126.29
	$H_{5,6}$	2.62 (trans)	$C_{5,6}$	51.03 (trans)
	H_{12}	2.62	$C_{1,4}$	45.96 (trans), 41.05 (cis)
	H_7 / $H_{7'}$	2.12 / 1.62	C_7	42.39
	H_{11}	1:91	C_{10}/ C_{11}	38.68 / 33.43
			C_{12}	29.12
 Poly (exo-C$_4$PhM)	$H_{11,15}$	7.45	$C_{8,9}$	177.66
	$H_{12,14}$	7.18	C_{10}	151.68
	$H_{2,3}$	5.81 (trans), 5.56 (cis)	$C_{2,3}$	132.32 (trans)
	$H_{1,4}$	3.56 (cis), 3.15 (trans)	C_{13}	129.36
	$H_{5,6}$	2.87 (trans)	$C_{11,15}$ / $C_{12.14}$	126.30 / 126.03
	H_7 / $H_{7'}$	2.19 / 1.70	$C_{5,6}$	51.17 (trans)
	H_{17}	1.31	$C_{1,4}$	46.46 (trans)
			C_7	42.07
			C_{16} / C_{17}	34.94 / 31.50

Table 3.3: Summary continued....

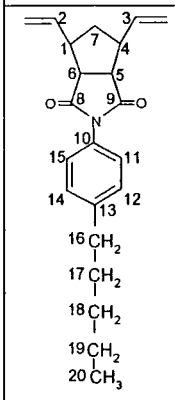
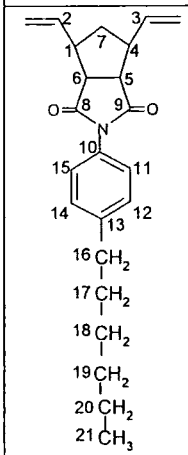
Polymer Mo (1)	^{1}Hnmr		^{13}Cnmr	
	Hydrogen	Chemical shift (ppm)	Carbon	Chemical shift (ppm)
 Poly (exo-C_5PhM)	$H_{11,15}$	7.24	$C_{8,9}$	177.61
	$H_{12,16}$	7.15	C_{10}	143.61
	$H_{2,3}$	5.81 (trans), 5.57 (cis)	$C_{2,3}$	132.31 (trans)
	$H_{1,4}$	3.53 (cis), 3.12 (trans)	C_{13}	129.59
	$H_{5,6}$	2.86 (trans)	$C_{11,15}$ / $C_{12,14}$	129.25 / 126.33
	H_{16}	2.60	$C_{5,6}$	51.17 (trans)
	H_7 / $H_{7'}$	2.19 / 1.70	$C_{1,4}$	46.43 (trans)
	H_{17}	1.60	C_7	42.08
	$H_{18\text{-}19}$	1.32	C_{16} / C_{17}	35.82 / 31.66
	H_{20}	0.88	C_{18} / C_{19}	31.15 / 22.72
			C_{20}	14.22
 Poly (exo-C_6PhM)	$H_{11.15}$	7.24	$C_{8,9}$	177.65
	$H_{12.14}$	7.15	C_{10}	143.65
	$H_{2,3}$	5.81 (trans), 5.56 (cis)	$C_{2,3}$	132.27 (trans)
	$H_{1,4}$	3.53 (cis), 3.16 (trans)	C_{13}	129.50
	$H_{5,6}$	2.85(trans)	$C_{11,15}$/ $C_{12,14}$	129.28 / 126.33
	H_{16}	2.61	$C_{5,6}$	51.13 (trans)
	H_7 / $H_{7'}$	2.19 / 1.69	$C_{1,4}$	46.40 (trans)
	H_{17}	1.59	C_7	41.94
	$H_{18\text{-}20}$	1.29	C_{16} / C_{17}	35.88 / 31.94
	H_{21}	0.88	C_{18} / C_{19}	31.51/ 29.20
			C_{20} / C_{21}	22.84 / 14.37

Table 3.3: Summary continued....

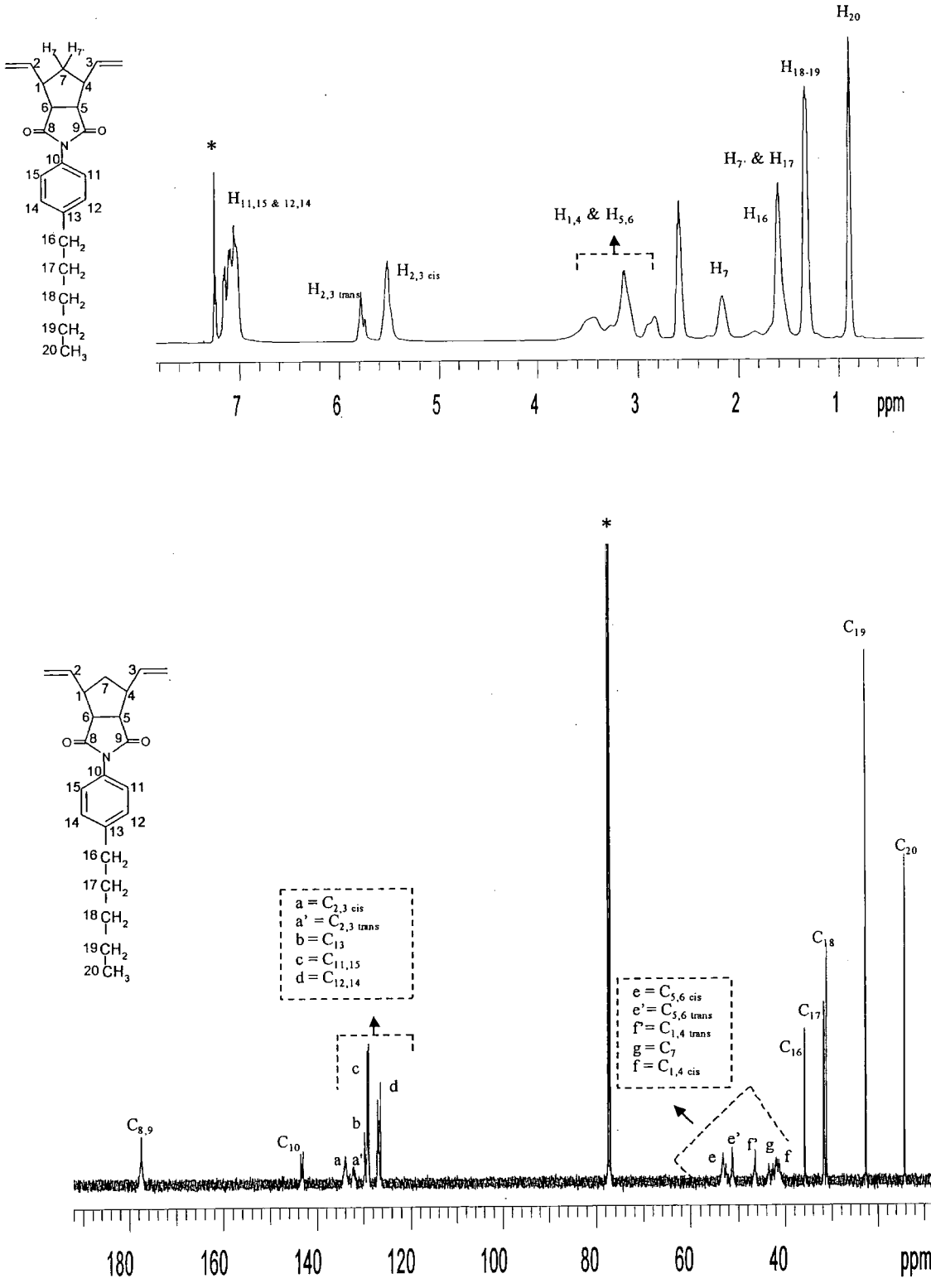


Figure 3.14 : (a) ^{1}H NMR spectrum of poly (exo-C$_5$PhM) using Mo (2) initiator in CDCl$_3$
(b) ^{13}C NMR spectrum of poly (exo-C$_5$PhM) using Mo (2) initiator in CDCl$_3$
* Residual hydrogen in CDCl$_3$

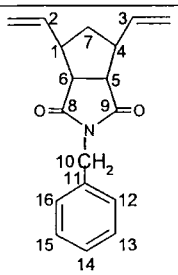
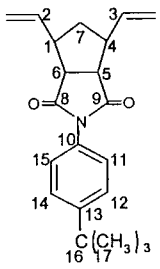
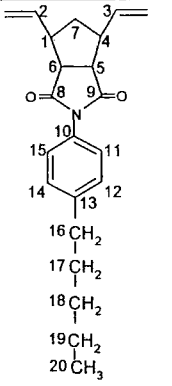
Polymer Mo (2)	^{1}Hnmr		^{13}Cnmr	
	Hydrogen	Chemical shift (ppm)	Carbon	Chemical shift (ppm)
 Poly (exo-PhCM)	$H_{12\text{-}16}$	7.23 (m, 7.12-7.33)	$C_{8,9}$	178.13
	$H_{2,3}$	5.71 (trans), 5.48 (cis)	C_{11}	136.41
	H_{10}	4.51	$C_{2,3}$	133.80 (cis), 131.99 (trans)
	$H_{1,4}$ / $H_{5,6}$	3.06 (m)	$C_{12,16}$	128.92
	H_7 / $H_{7'}$	2.04 / 1.48	$C_{13,15}$ / C_{14}	128.75 / 127.93
			$C_{5,6}$	53.22 (cis), 51.22 (trans)
			$C_{1,4}$	45.89 (trans), 41.28 (cis)
			C_7 / C_{10}	43.15 / 42.64
 Poly (exo-C_4PhM)	$H_{11,15}$ / $C_{12,14}$	7.28 (m, 7.11-7.47)	$C_{8,9}$	177.56
	$H_{2,3}$	5.76 (trans), 5.52 (cis)	C_{10}	151.31
	$H_{1,4}$ / $H_{5,6}$	3.13 (m)	$C_{2,3}$	134.14 (cis), 132.39 (trans)
	H_7 / $H_{7'}$	2.17 / 1.69	C_{13}	129.68
	H_{17}	1.29	$C_{11,15}$ / $C_{12.14}$	126.12 (m)
			$C_{5,6}$	53.31 (cis), 51.33 (trans)
			$C_{1,4}$	46.48(trans), 42.09 (cis)
			C_7	43.59
			C_{16} / C_{17}	34.93 / 31.54
 Poly (exo-C_5PhM)	$H_{11,15}$ / $C_{12,16}$	7.09 (m, 7.04-7.16)	$C_{8,9}$	177.55
	$H_{2,3}$	5.78 (trans), 5.52 (cis)	C_{10}	143.06
	$H_{1,4}$ / $H_{5,6}$	3.14 (m)	$C_{2,3}$	134.06 (cis), 132.24 (trans)
	H_{16}	2.59	C_{13}	129.86
	H_7 / $H_{7'}$	2.16 / 1.60	$C_{11,15}$ / $C_{12,14}$	128.89 / 126.38
	H_{17}	1.60	$C_{5,6}$	53.28 (cis), 51.31 (trans)
	$H_{18\text{-}19}$	1.33	$C_{1,4}$	46.41 (trans), 41.97 (cis)
	H_{20}	0.89	C_7	43.12
			C_{16} / C_{17}	35.83 / 31.75
			C_{18} / C_{19}	31.24 / 22.77
			C_{20}	14.26

Table 3.4: Summary of ^{1}H NMR assignment exo-monomers catalysed by hexafluoro-t-butoxy substituted molybdenum initiator

3.3.2 Polymer characterisation by elemental analysis

The polymers obtained from ROMP of exo-phenyl norbornene dicarboxyimide derivatives using the well-defined initiators were characterised by elemental analysis. The results are tabulated in table 3.5. Generally a good agreement between the calculated and found values has been obtained for all the polymer samples.

Polymer	Initiator	Calculated(found) in %		
Poly(exo-PhM)	Ru	**C = 75.30(73.84)**	**H = 5.48(5.54)**	**N = 5.85(5.82)**
	Mo (1)	C = (72.86)	H = (5.30)	N = (5.58)
Poly(exo-PhCM)	Ru	**C = 75.87(74.30)**	**H =5.97 (5.86)**	**N =5.53 (6.15)**
	Mo (1)	C = (74.76)	H = (5.84)	N = (5.52)
	Mo (2)	C = (74.46)	H = (5.79)	N = (5.20)
Poly(exo-PhC_2M)	Ru	**C =76.38(75.33)**	**H =6.41(6.32)**	**N = 5.24(5.22)**
	Mo (1)	C = (75.91)	H = (6.54)	N = (6.25)
Poly(exo-PhC_3M)	Ru	**C = 76.84(75.59)**	**H = 6.81(6.71)**	**N = 4.98(4.94)**
	Mo (1)	C = (76.33)	H = (6.87)	N = (6.13)
Poly(exo-PhC_4M)	Ru	**C = 77.26(76.56)**	**H = 7.17(7.14)**	**N = 4.74(5.86)**
Poly(exo-C_4PhM)	Ru	**C = 77.26(77.07)**	**H = 7.17(7.25)**	**N = 4.74(4.57)**
	Mo (1)	C = (75.89)	H = (6.99)	N = (4.60)
	Mo (2)	C = (75.89)	H = (7.05)	N = (4.50)
Poly(exo-C_5PhM)	Ru	**C = 77.64(76.45)**	**H = 7.49(7.43)**	**N = 4.53(5.41)**
	Mo (1)	C = (76.45)	H = (7.38)	N = (4.36)
	Mo (2)	C = (76.52)	H = (7.34)	N = (4.13)
Poly(exo-C_6PhM)	Ru	**C = 77.99(78.81)**	**H = 7.79(7.96)**	**N = 4.33(4.96)**
	Mo (1)	C = (77.06)	H = (7.74)	N = (5.49)

Table 3.5: Elemental analysis results of the polymers

3.3.3 Polymer characterisation by GPC

The polymers obtained from ROMP of phenyl norbornene dicarboxyimide derivatives using the well-defined initiators were subjected to Gel Permeation Chromatography (GPC) to determine their molecular weights and Polydispersity Indices (PDI). The results are tabulated in table 3.6. It can be seen that the t-butoxy molybdenum initiator produced polymers with narrow PDI compared to hexafluoro-t-butoxy molybdenum and ruthenium initiators. This is an indication of a well-controlled living polymerisation reaction. The hexafluoro-t-butoxy molybdenum initiator produced polymers with broader PDI. This can be attributed to due to the secondary metathesis reactions[50] or to the rate of propagation being faster than the rate of initiation. Polymers obtained by ruthenium initiator also gave polymers with broader PDI due to secondary metathesis reaction. Similar trend have bee previous been observed.[4]

Polymer	Initiator	GPC			
		[M]/[I]	Mn	Mw	PDI
Poly(exo-PhM)	**Ru**	**150**	**62,400**	**83,200**	**1.3**
	Mo (1)	150	11,400	11,700	1.03
Poly(exo-PhCM)	**Ru**	**150**	**46,500**	**61,600**	**1.3**
	Mo (1)	150	39,400	45,500	1.1
	Mo (2)	150	18,600	31,000	1.7
Poly(exo-PhC_2M)	**Ru**	**150**	**44,300**	**56,900**	**1.3**
	Mo (1)	150	35,800	47,200	1.1
Poly(exo-PhC_3M)	**Ru**	**150**	**48,800**	**59,000**	**1.2**
	Mo (1)	150	42,400	53,000	1.2
Poly(exo-PhC_4M)	**Ru**	**150**	**53,000**	**54,600**	**1.03**
Poly(exo-C_4PhM)	**Ru**	**150**	**51,000**	**64,600**	**1.3**
	Mo (1)	150	59,700	66,500	1.1
	Mo (2)	150	45,000	94,500	2.1
Poly(exo-C_5PhM)	**Ru**	**150**	**47,800**	**59,000**	**1.2**
	Mo (1)	150	35,800	41,000	1.1
	Mo (2)	150	19,400	47,600	1.7
Poly(exo-C_6PhM)	**Ru**	**150**	**45,700**	**55,300**	**1.2**
	Mo (1)	150	45,100	54,000	1.2

Table 3.6: GPC results of the polymers

3.3.4 Polymer characterisation using DSC

The glass transition temperatures, Tgs, for all the polymers have been obtained by DSC analysis and the results are shown in table 3.7. It can be seen that the Tgs for the polymers prepared by t-butoxy molybdenum initiator were about 15°C higher than the polymers produced using hexafluoro-t-butoxy molybdenum and the ruthenium initiators. The results suggest that for the systems studied the higher the trans content of the polymer, the higher the glass transition temperature. It was also found that the longer the alkyl chain in the polymer, entry 1-5 and 6-8, the lower the glass transition temperatures. This is consistent with the previous result by Feast[52] *et al* and earlier work by Hoff that followed the same trend.[53]

Entry	Polymer	Initiator	DSC		
			[M]/[I]	Mn	Tg (°C)
1	Poly(exo-PhM)	**Ru**	**150**	**62,400**	**223**
		Mo (1)	150	11,400	241
2	Poly(exo-PhCM)	**Ru**	**150**	**46,500**	**143**
		Mo (1)	150	39,400	161
		Mo (2)	150	18,600	148
3	Poly(exo-PhC_2M)	**Ru**	**150**	**44,300**	**103**
		Mo (1)	150	35,800	121
4	Poly(exo-PhC_3M)	**Ru**	**150**	**48,800**	**88**
		Mo (1)	150	42,400	98
5	Poly(exo-PhC_4M)	**Ru**	**150**	**53,000**	**69**
6	Poly(exo-C_4PhM)	**Ru**	**150**	**51,000**	**245**
		Mo (1)	150	59,700	260
		Mo (2)	150	45,000	242
7	Poly(exo-C_5PhM)	**Ru**	**150**	**47,800**	**162**
		Mo (1)	150	35,800	175
		Mo (2)	150	19,400	173
8	Poly(exo-C_6PhM)	**Ru**	**150**	**45,700**	**142**
		Mo (1)	150	45,100	148

Table 3.7: DSC results showing Tg of the polymers

The results also show that the Tg for the polymers prepared from ROMP of exo-phenyl norbornene dicarboxyimides are generally a lot higher than the polymers obtained from exo-alkyl norbornene dicarboxyimides studied previously.

Chapter 4

Overall conclusion and proposal for future work

4.1 Overall conclusion

The work described in this thesis illustrates that a series of exo-phenyl norbornene dicarboxyimide derivatives are synthesised and characterised using several spectroscopic methods. It also demonstrates that polymeric material can be prepared from phenylnorbornene d icarboxyimide derivatives using ROMP. Three well-defined initiators, ruthenium $Cl_2[(C_6H_{11})_3P]_2Ru{=}CHC_6H_5$, t-butoxy molybdenum $Mo[CHC(CH_3)_3][C_{10}H_{17}N][OC(CH_3)_3]_2$, Mo (1), and hexafluoro-t-butoxy molybdenum $Mo[CHC(CH3)_2C_6H_5][C_{10}H_{17}N][OC(CF_3)_2CH_3]_2$, Mo (2), were used.
The polymers prepared were fully characterised using 1H NMR, 13CNMR, elemental analysis, GPC and DSC.

The cis / trans contents of the polymers are readily determined from the ^1H NMR spectrum from the integration of the resonance attributable to cis and trans olefinic hydrogen. Generally the trans vinylene content for polymers prepared by ruthenium initiator is about 83%, for the polymers prepared by t-butoxy molybdenum initiator is about 97% and for the polymers prepared by hexafluoro-t-butoxy molybdenum initiator is about 31%.

The t-butoxy molybdenum initiator produced polymers with narrow PDI compared to hexafluoro-t-butoxy molybdenum a nd r uthenium i nitiators. This is a n i ndication of a well-controlled living polymerisation reaction. The hexafluoro-t-butoxy molybdenum initiator produced polymers with broader PDI. This can be attributed to due to the secondary metathesis reactions or to the rate of propagation being faster than the rate of initiation. P olymers o btained b y ruthenium i nitiator a lso g ave p olymers w ith b roader PDI due to secondary metathesis reaction. Similar trend have bee previous been observed.

The elemental analysis of polymers showed a good agreement between the calculated and found values has been obtained for all the polymer samples.

The Tgs for the polymers prepared by t-butoxy molybdenum initiator were about 15°C higher than the polymers produced using hexafluoro-t-butoxy molybdenum and the ruthenium i nitiators, suggesting that the higher the trans content of the polymer, the higher the glass transition temperature. It was also found that the longer the alkyl chain in the polymer, the lower the glass transition temperatures. The results also showed that the Tg for the polymers prepared from ROMP of exo-phenyl norbornene

dicarboxyimides are generally a lot higher than the polymers obtained from exo-alkyl norbornene dicarboxyimides studied previously.

4.2 Proposal for future work

The previous work showed that exo-alkyl norbornene dicarboxyimides could successfully be subjected to ROMP using well-defined ruthenium initiator resulting in well-defined linear polymers in both solution and bulk. It was also demonstrated that the copolymerisation of exo-alkyl norbornene dicarboxyimides with exo-alkyl dinorbornene dicarboxyimides difunctional monomers results in a well-defined crosslinked materials, using resin transfer moulding process (RTM). However, the Tg of the crosslinked materials were lower than the commercial materials based on Poly(DCPD). The linear polymeric materials produced here from the ROMP of exo-phenyl norbornene dicarboxyimides exhibited higher Tgs than Poly(DCPD). The monomers were all solid but soluble in exo-alkyl norbornene dicarboxyimides. It will therefore be possible to carry out ROMP-RTM processing of the monomers to obtain linear materials and also well-defined crosslinked materials using exo-alkyl dinorbornene dicarboxyimides difunctional monomers with higher Tgs.

Appendix 1

Instrumentation and procedures for measurements

i. NMR spectroscopy: ^{1}H, ^{13}C, COSY, DEPT

The samples were analysed either on a VARIAN INOVA 500 NMR spectrometer at 499.78 (^{1}H) / 125.67 (^{13}C) MHz, or VARIAN MERCURY 400 NMR spectrometer at 399.96 (^{1}H) / 100.57 (^{13}C) MHz, or BRUKER AVANCE 400 NMR spectrometer at 400.13 (^{1}H). The solvents used were deuterated chloroform and deuterated acetone.

ii. GEL PERMEATION CHROMATOGRAPHY (GPC)

- The samples were dissolved in one of the solvents; chloroform ($CHCl_3$), dimethylformamide (DMF), and tetrahydrofuran (THF). The choice of solvent depends on the solubility of the polymer. Each solvent was run at a different instrument.

- **THF:** Viscotek 200 with refractive index, viscosity and light scattering detectors, and 2 x 300mm PLgel 5μm mixed C columns; THF was used as the eluent with a flow rate of 1.0ml/min and a constant temperature of 30°C. Molecular weights were obtained using a conventional calibration curve generated from narrow molecular weight distribution PEG/PEO standards.
- **DMF:** Viscotek TDA 302 with refractive index detector, and 2 x 300mm PLgel 5μm mixed C columns; DMF was used as the eluent with a flow rate of 1.0ml/min and a constant temperature of 80°C. Molecular weight were obtained using triple detection, the detectors were calibrated with a single narrow molecular weight distribution polystyrene standard.
- **$CHCl_3$:** Viscotek TDA 301 with refractive index, viscosity and light scattering detectors, and 1 x 300mm PLgel 5μm mixed C columns; $CDCl_3$ was used as the eluent with a flow rate of 1.0ml/min and a constant temperature of 30°C. Molecular weight were obtained using triple detection, the detectors were calibrated with a single narrow molecular weight distribution polystyrene standard.

iii. MASS SPECROSCOPY

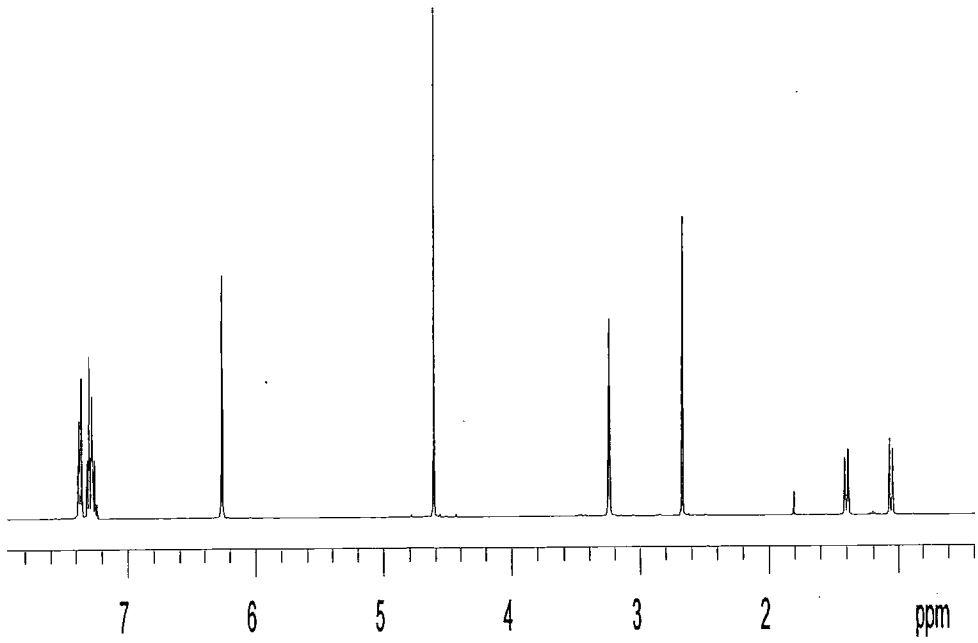
The samples were analysed on an EXETER ANALYTICAL, Inc CE-440 elemental analyser.

iv. DIFFERENTIAL SCANNING CALORIMETER (DSC)

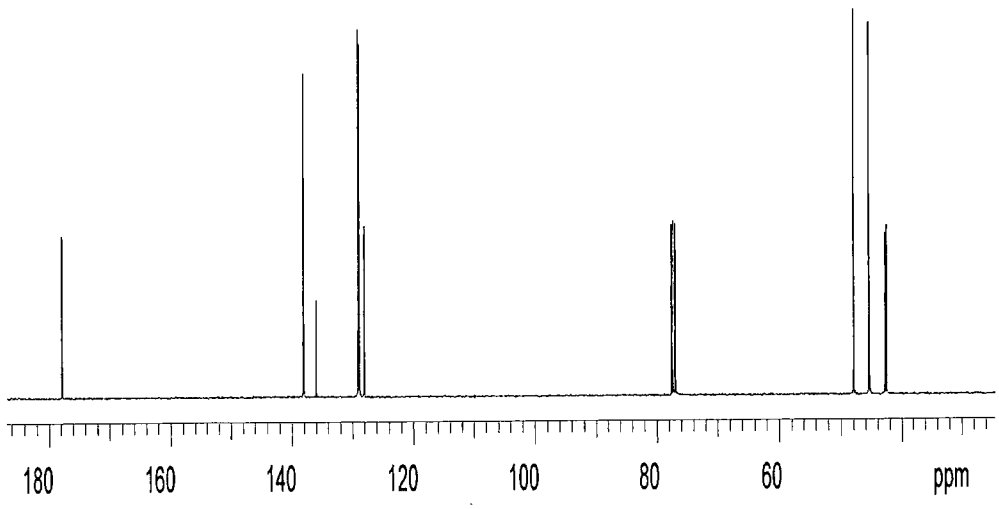
The samples were analysed on a Perkin Elmer DSC 7 or a Pyris 1 differential scanning calorimeter at a ramp rate of 10°C/min.

Appendix 2

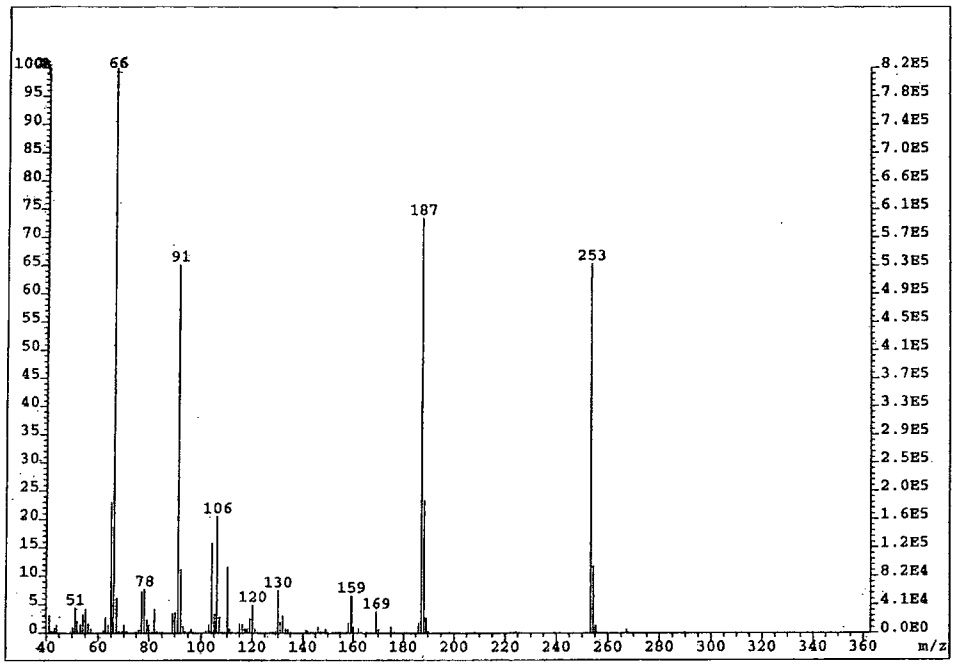
Analytical data for chapter 2



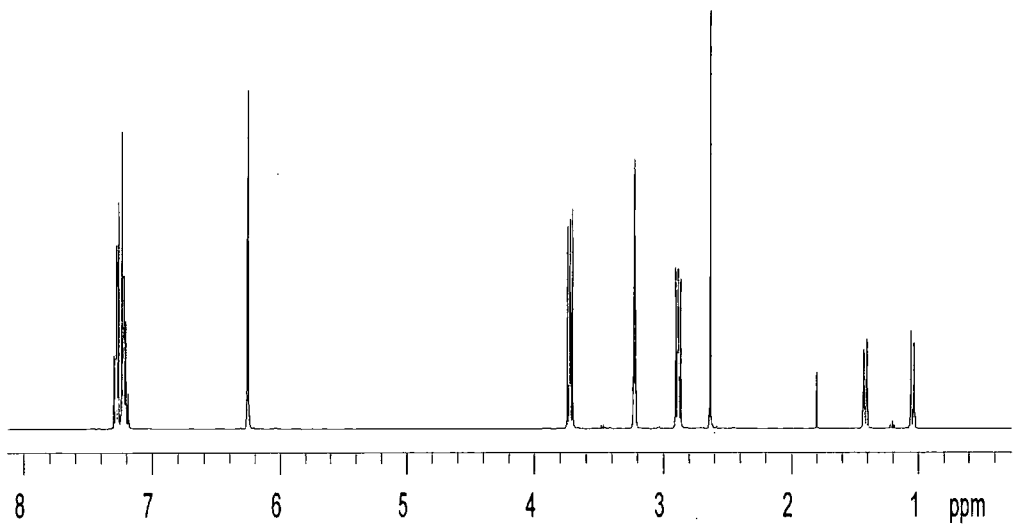
Appendix 2.1: ^{1}H NMR spectrum of exo-PhCM



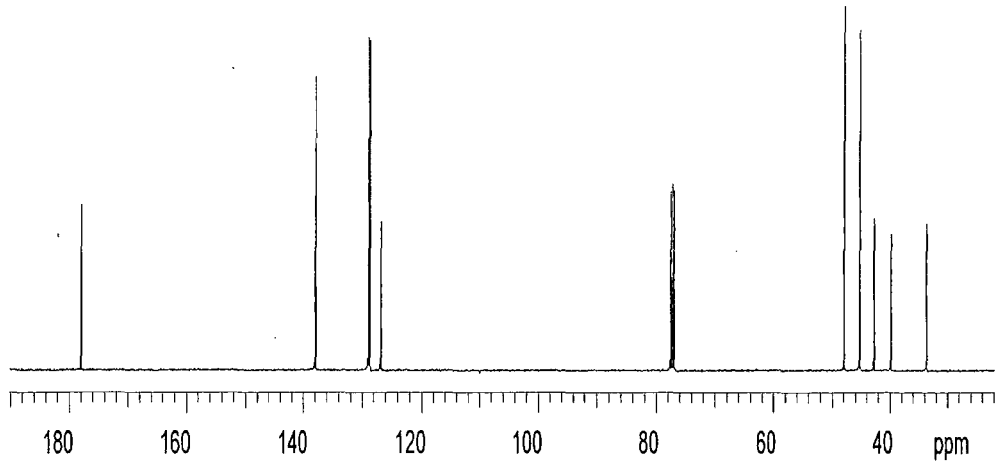
Appendix 2.2: ^{13}C NMR spectrum of exo-PhCM



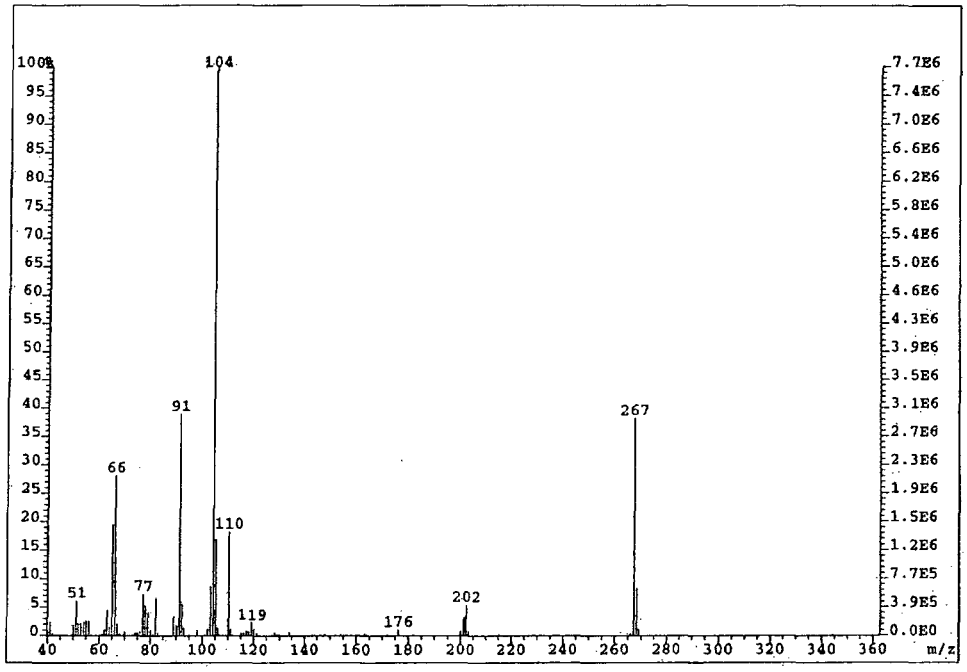
Appendix 2.3: Mass spectrum of exo-PhCM



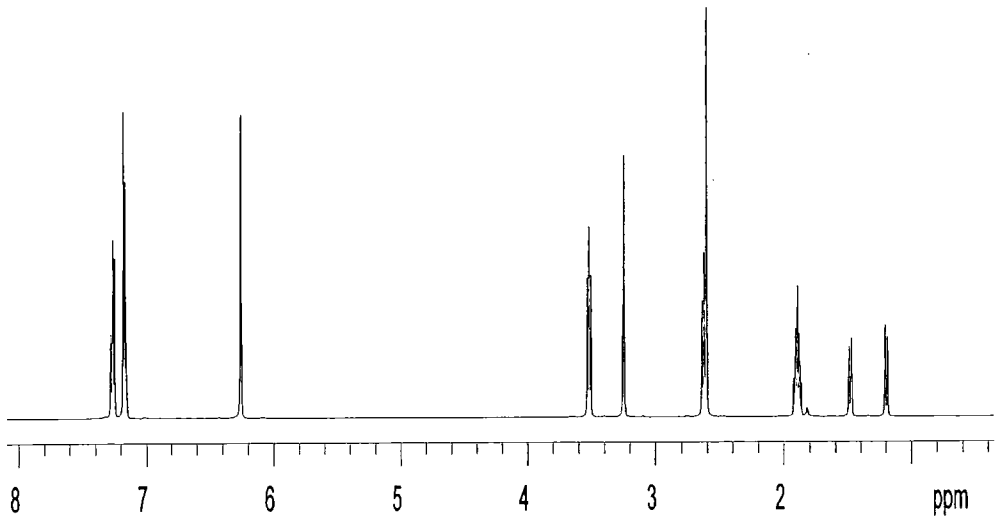
Appendix 2.4: ^{1}H NMR spectrum of exo-PhC_2M



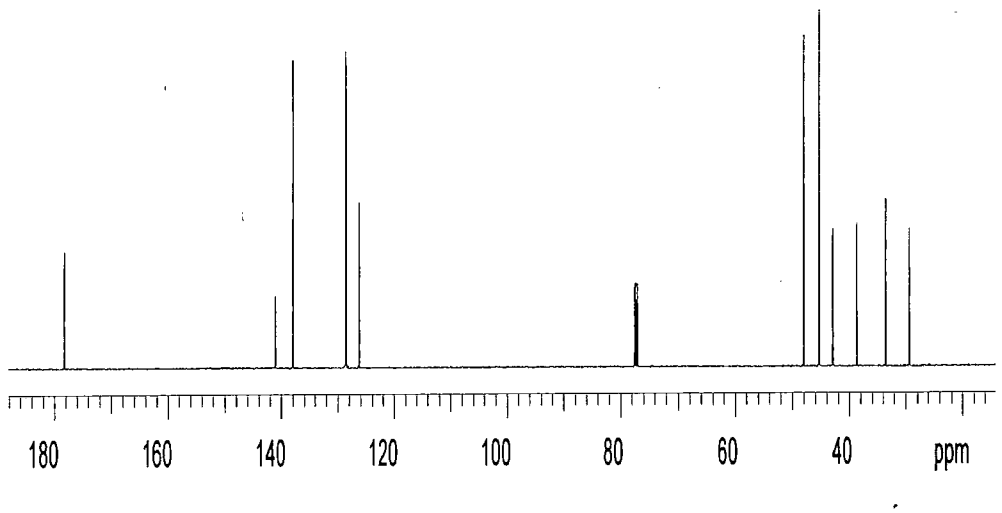
Appendix 2.5: ^{13}C NMR spectrum of exo-PhC_2M



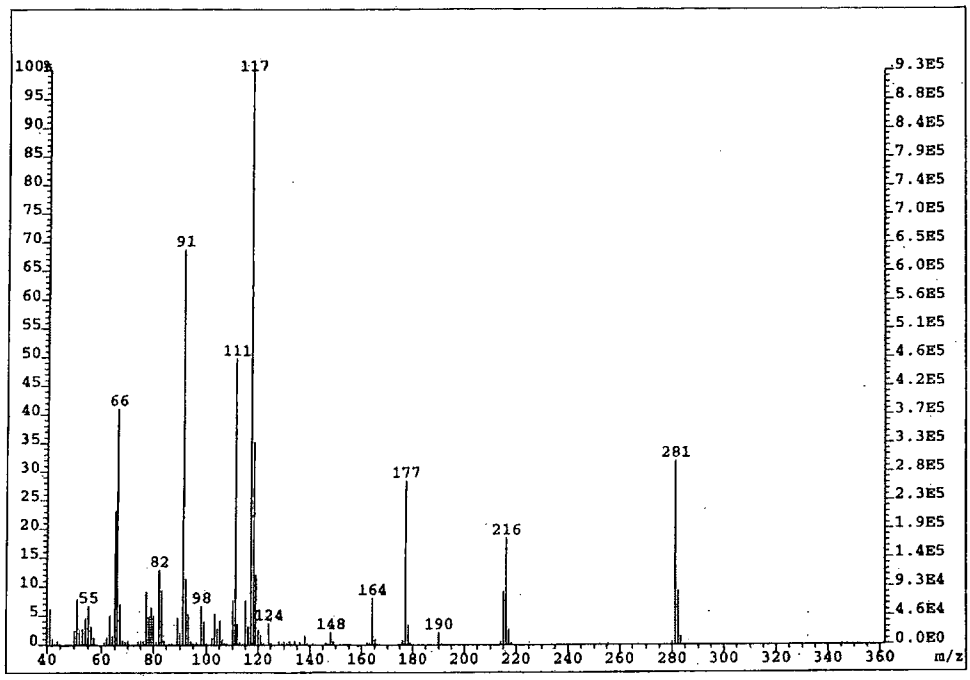
Appendix 2.6: Mass spectrum of exo-PhC_2M



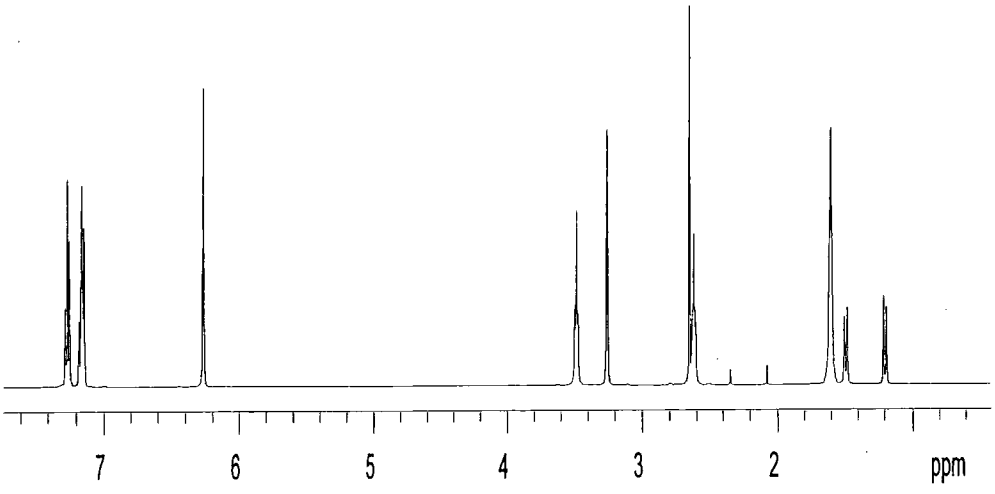
Appendix 2.7: ^{1}H NMR spectrum of exo-PhC_3M



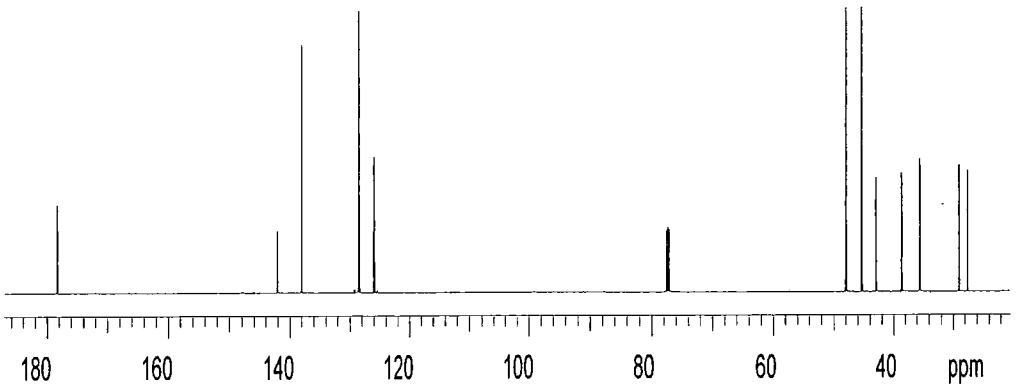
Appendix 2.8: ^{13}C NMR spectrum of exo-PhC_3M



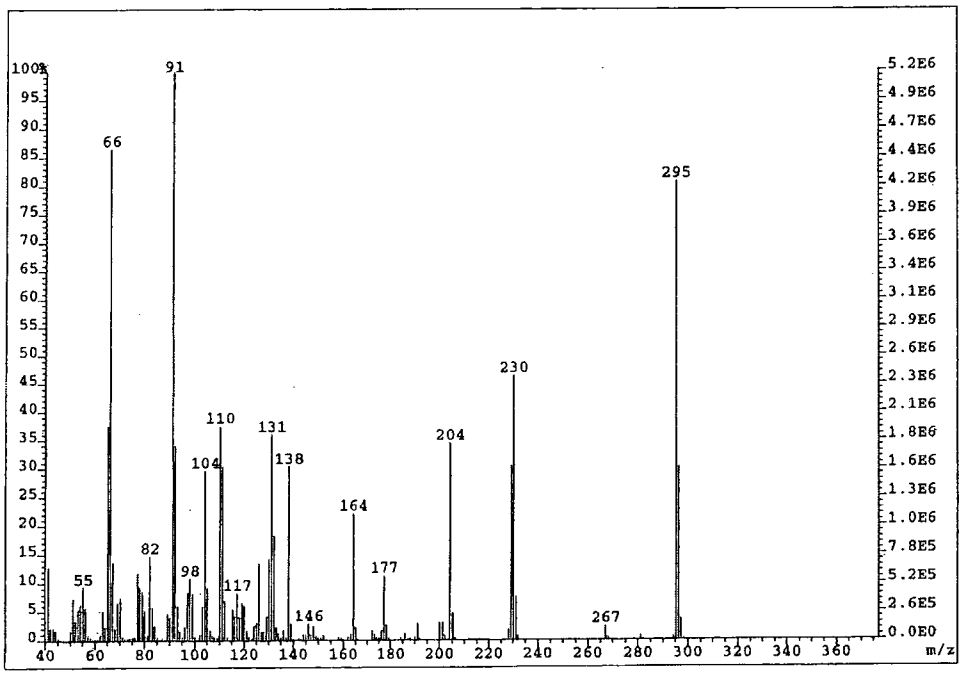
Appendix 2.9: Mass spectrum of exo-PhC_3M



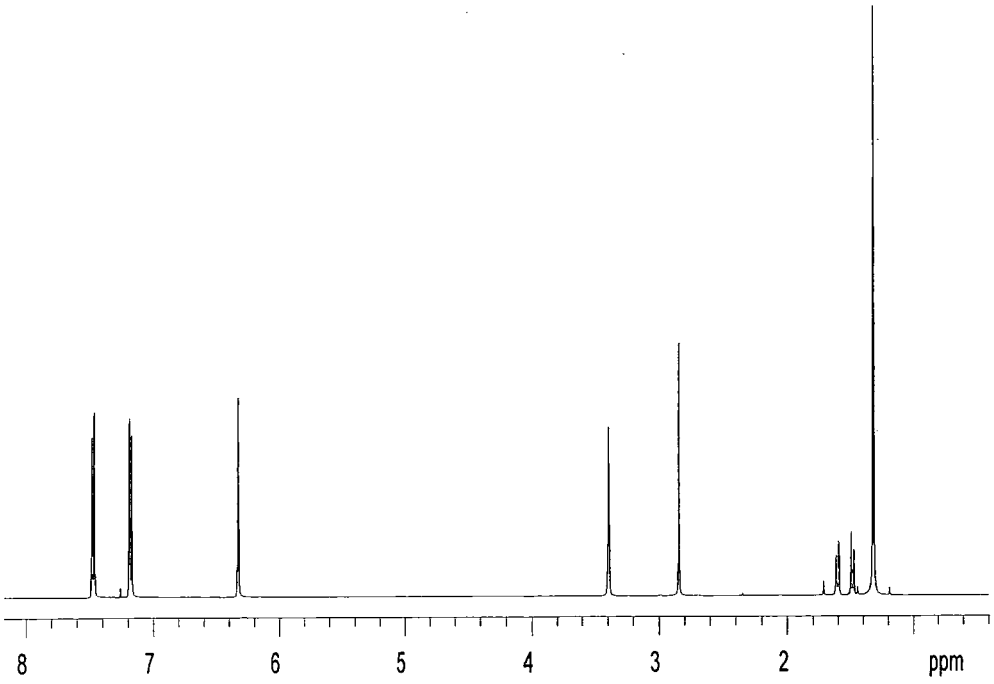
Appendix 2.10: ^1H NMR spectrum of exo-PhC_4M



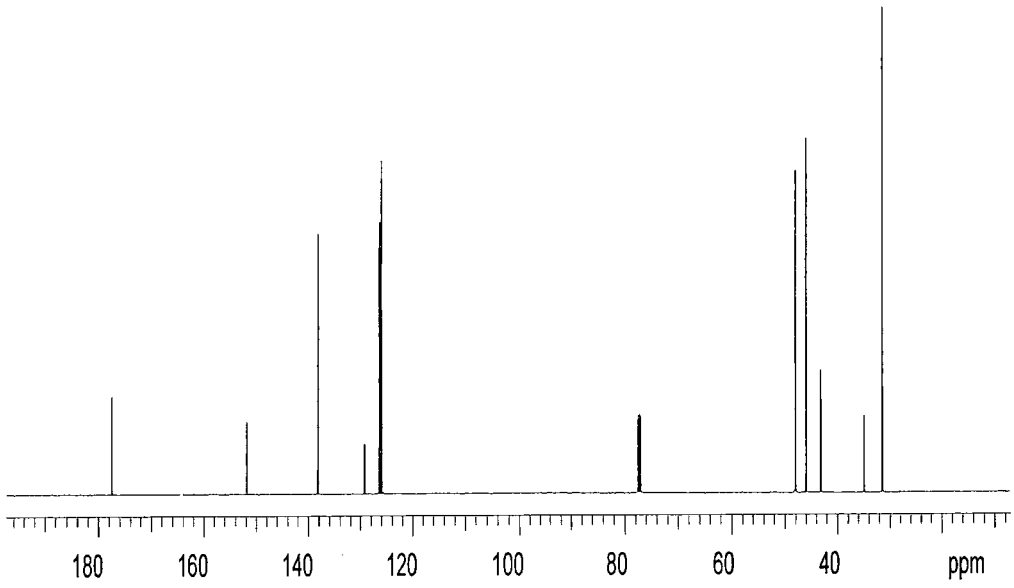
Appendix 2.11: ^{13}C NMR spectrum of exo-PhC_4M



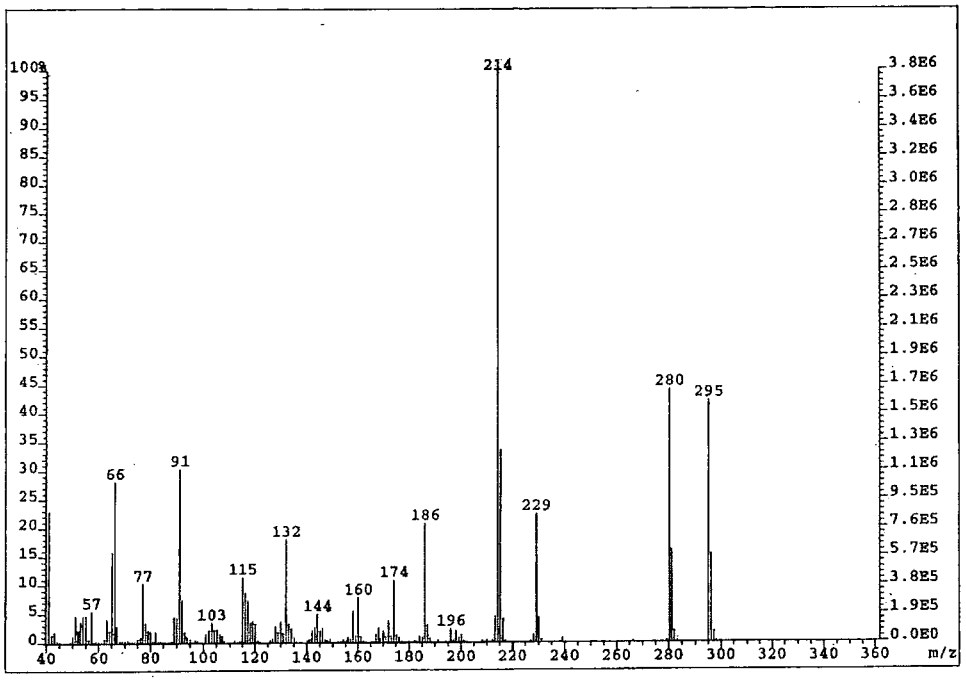
Appendix 2.12: Mass spectrum of exo-PhC_4M



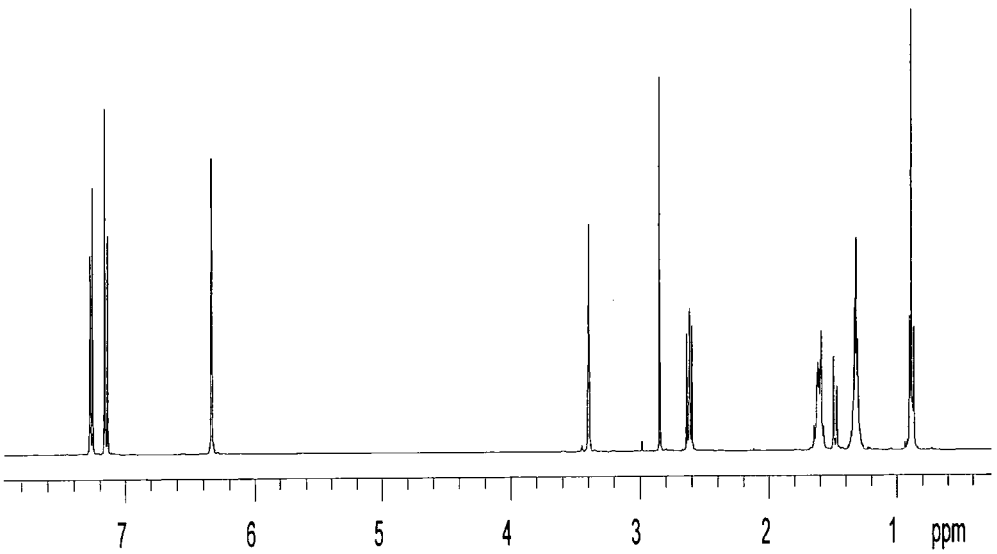
Appendix 2.13: ^{1}H NMR spectrum of exo-C_4PhM



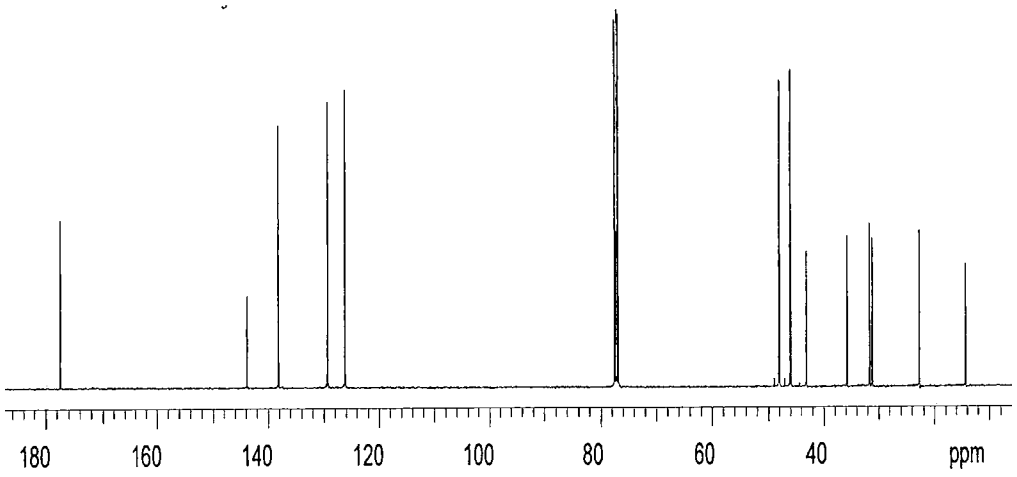
Appendix 2.14: ^{13}C NMR spectrum of exo-C_4PhM



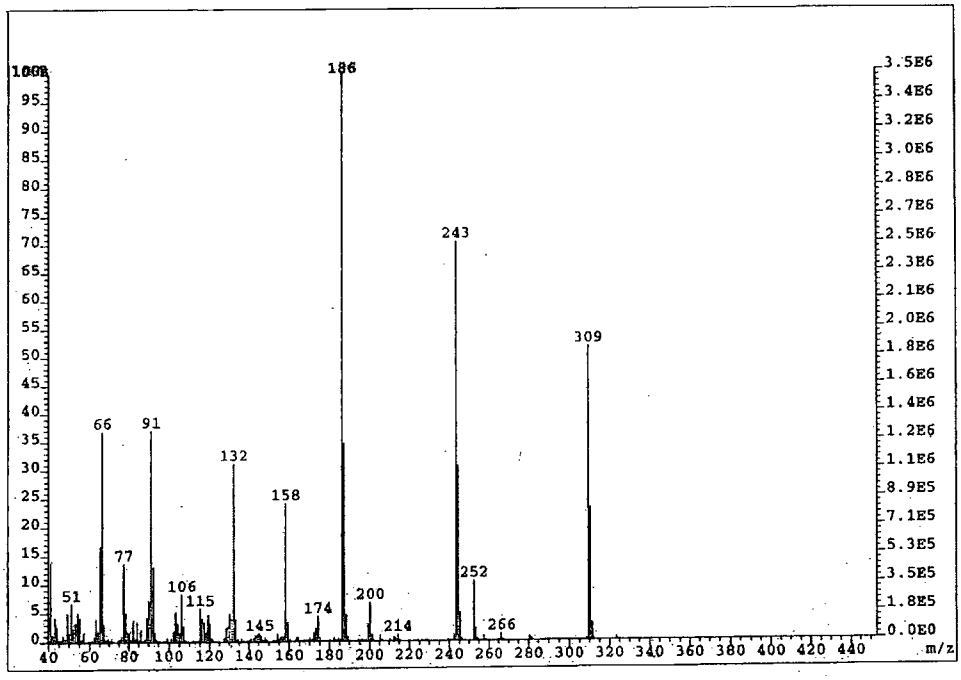
Appendix 2.15: Mass spectrum of exo-C_4PhM



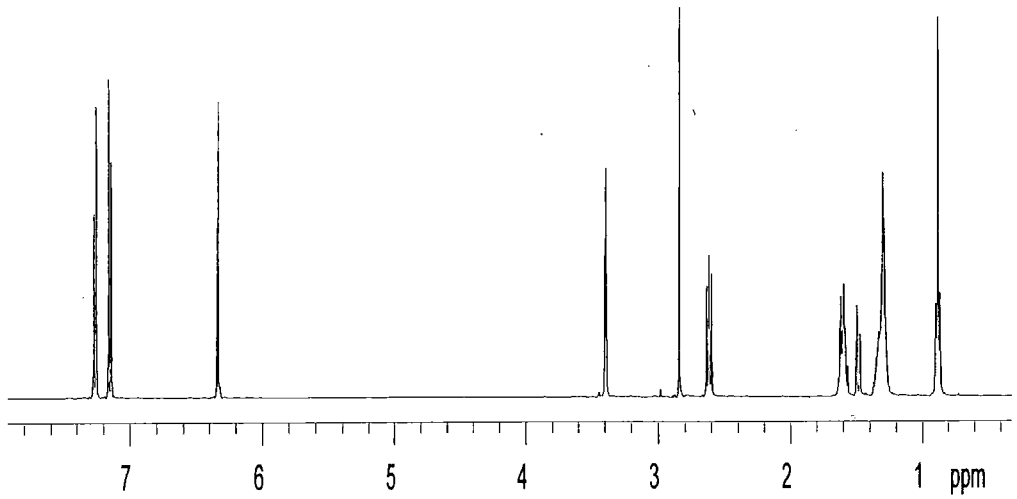
Appendix 2.16: ^{1}H NMR spectrum of exo-C_5PhM



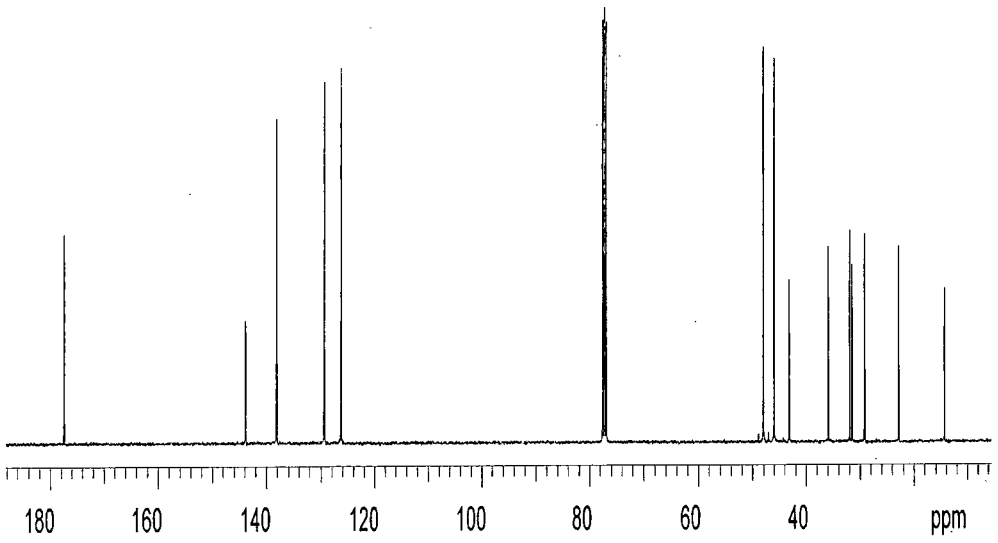
Appendix 2.17: ^{13}C NMR spectrum of exo-C_5PhM



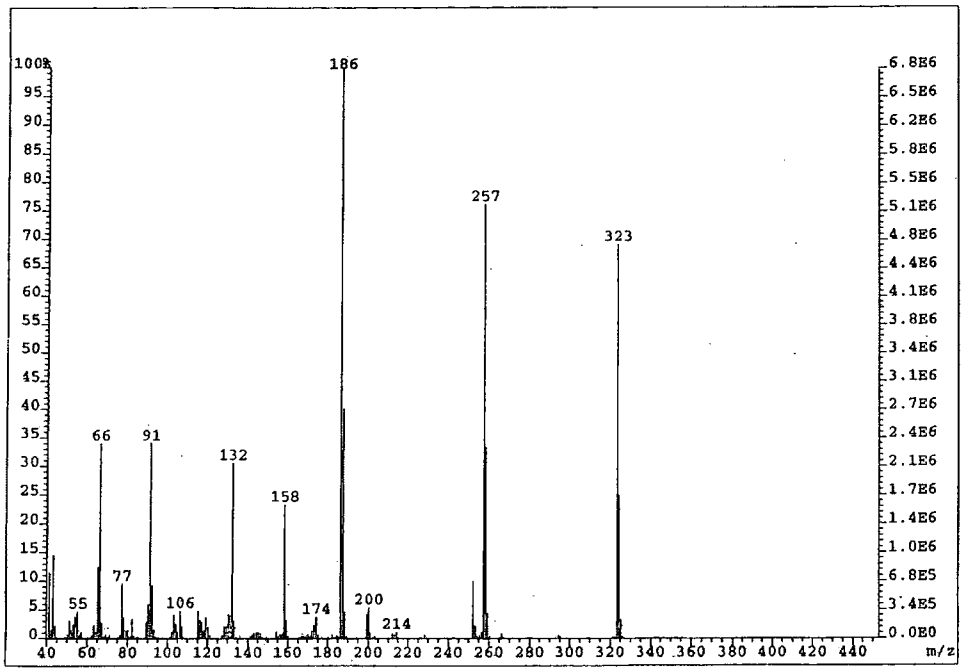
Appendix 2.18: Mass spectrum of exo-C_5PhM



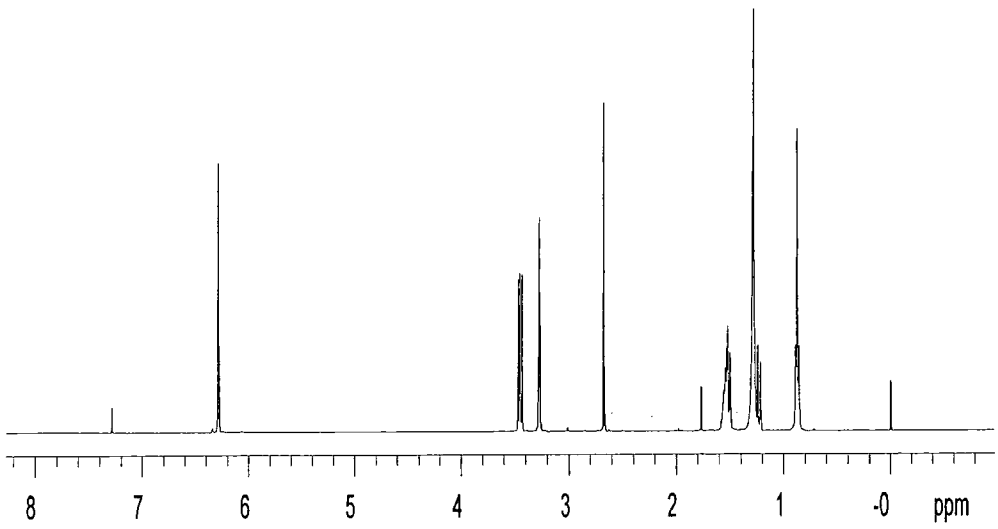
Appendix 2.19: ^{1}H NMR spectrum of exo-C_6PhM



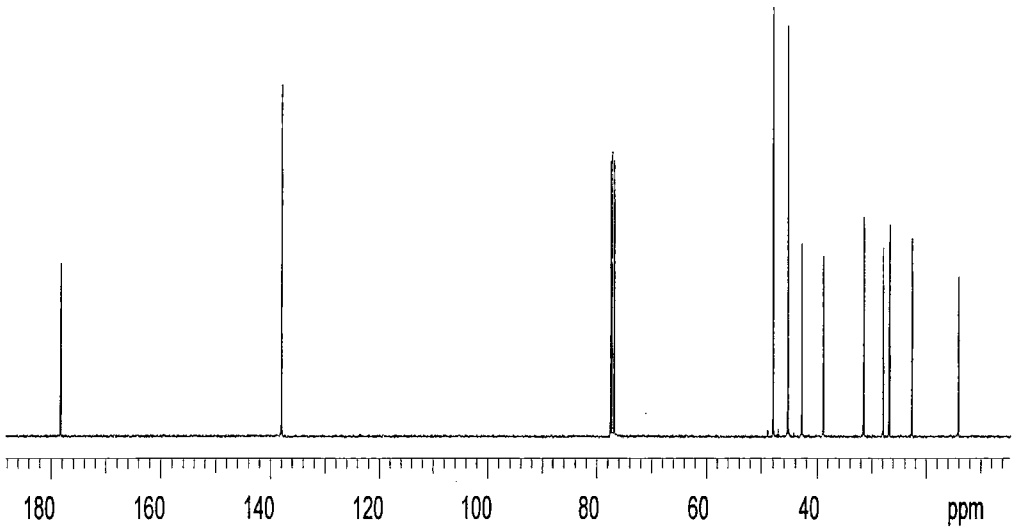
Appendix 2.20: ^{13}C NMR spectrum of exo-C_6PhM



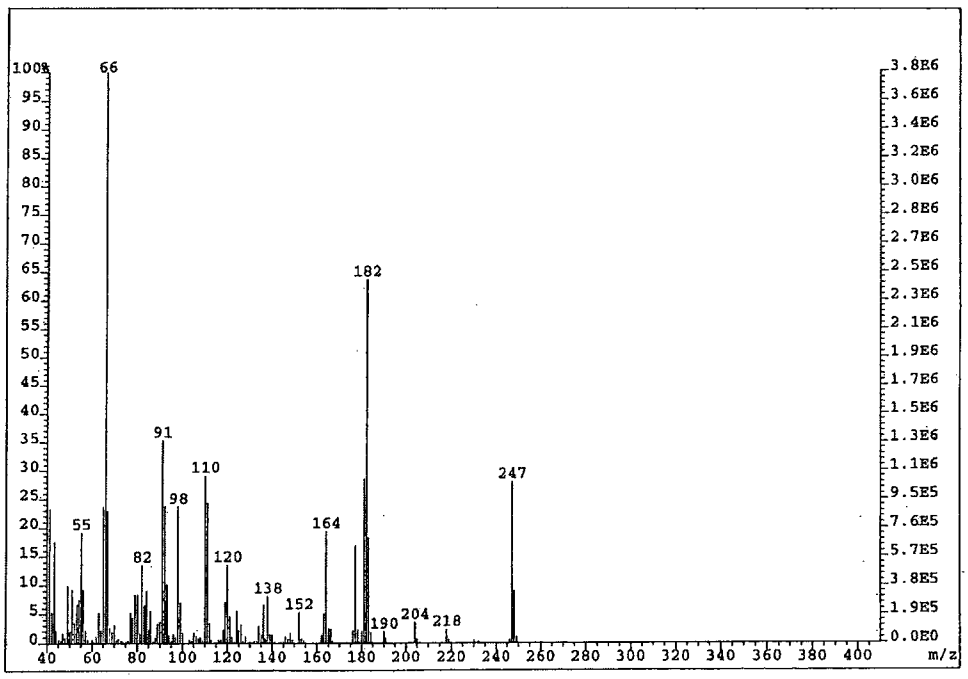
Appendix 2.21: Mass spectrum of exo-C_6PhM



Appendix 2.22: ^{1}H NMR spectrum of exo-C6M



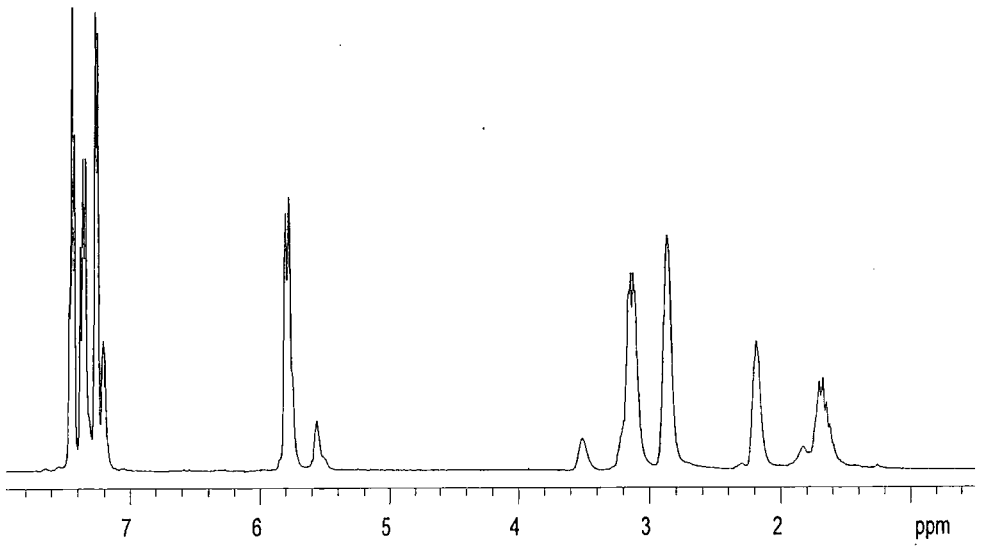
Appendix 2.23: ^{13}C NMR spectrum of exo-C6M



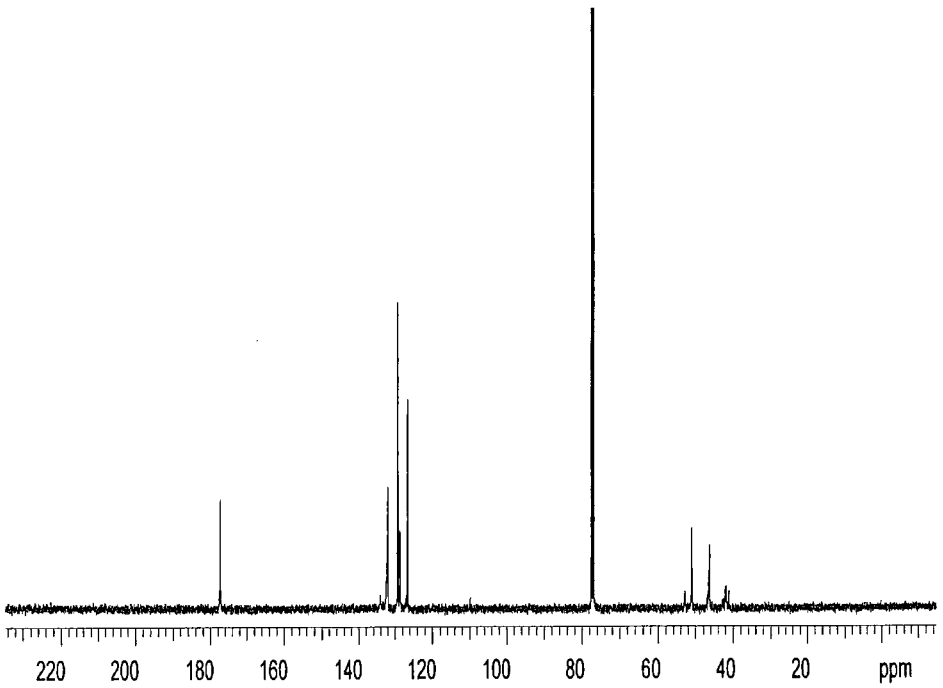
Appendix 2.24: Mass spectrum of exo-C6M

Appendix 3

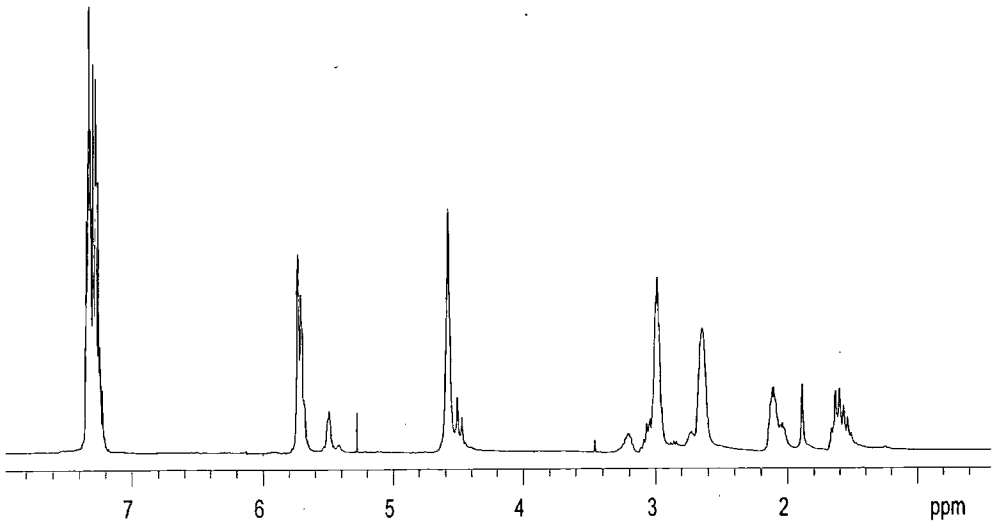
Analytical data for chapter 3



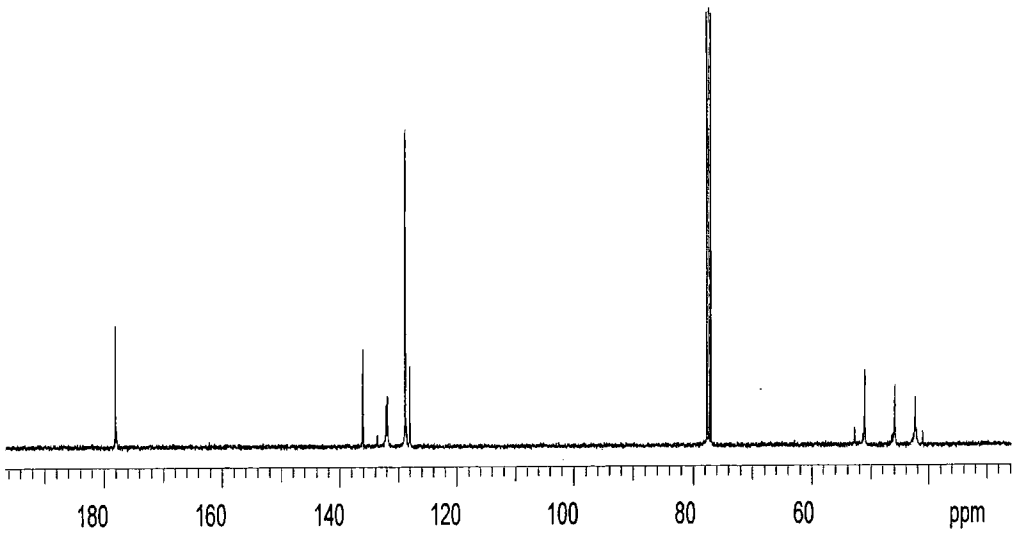
Appendix 3.1: ^{1}H NMR spectrum poly(exo-PhM) - Ru



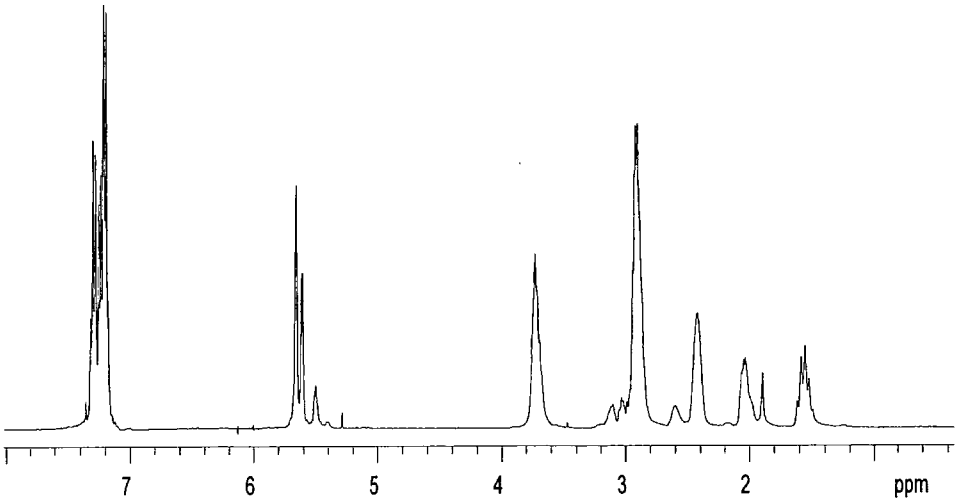
Appendix 3.2: ^{13}C NMR spectrum poly(exo-PhM) - Ru



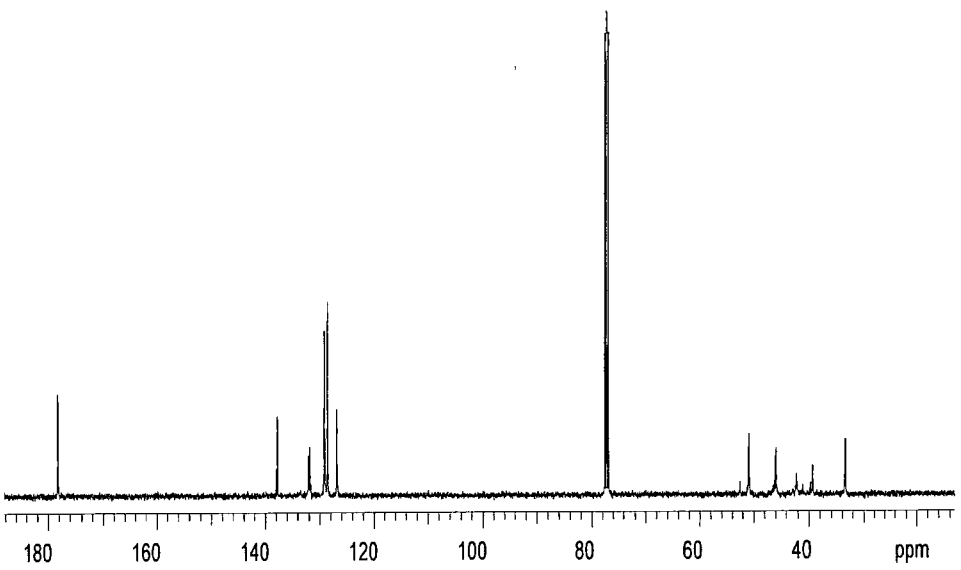
Appendix 3.3: ^{1}H NMR spectrum poly(exo-PhCM) - Ru



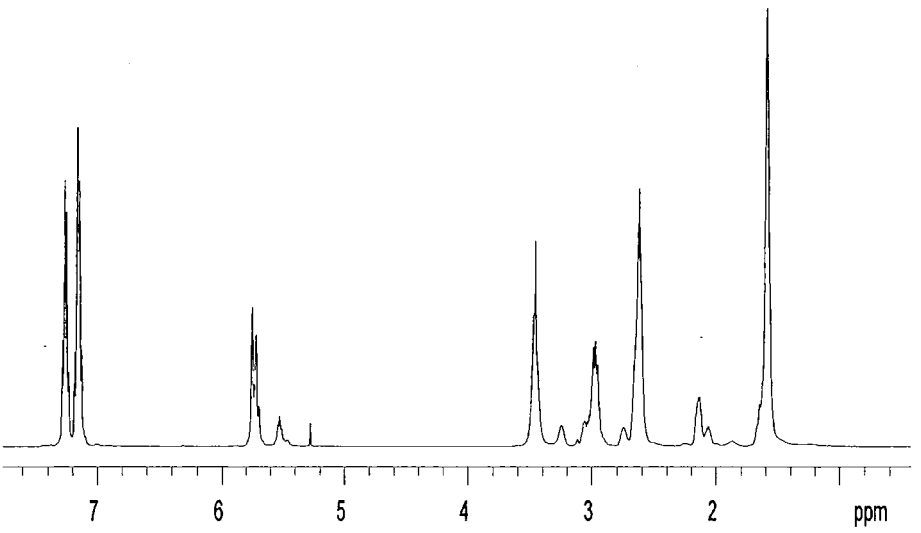
Appendix 3.4: ^{13}C NMR spectrum poly(exo-PhCM) - Ru



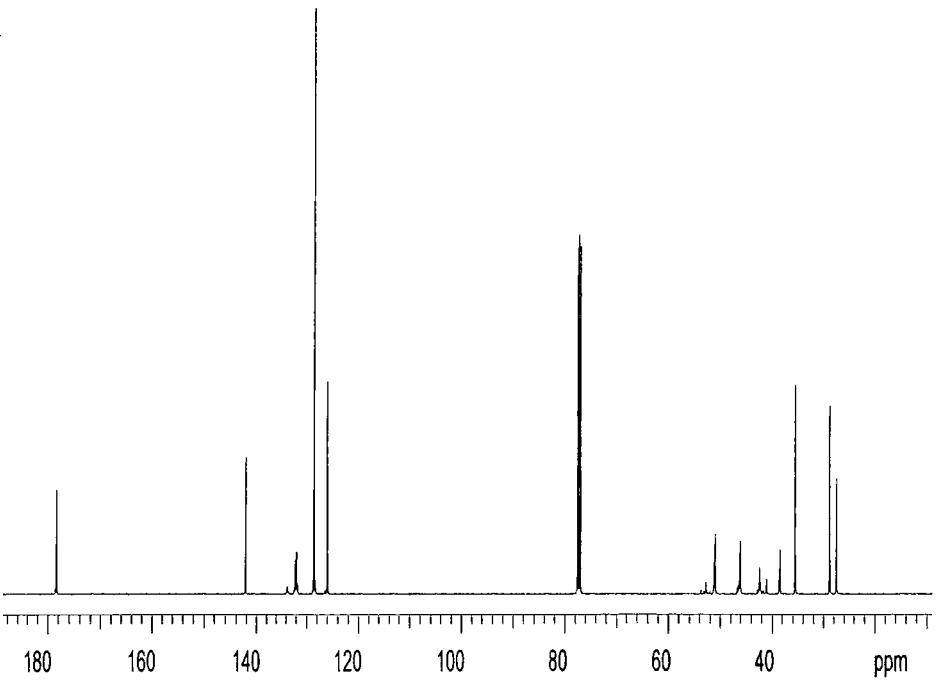
Appendix 3.5: ^{1}H NMR spectrum poly(exo-PhC_2M) - Ru



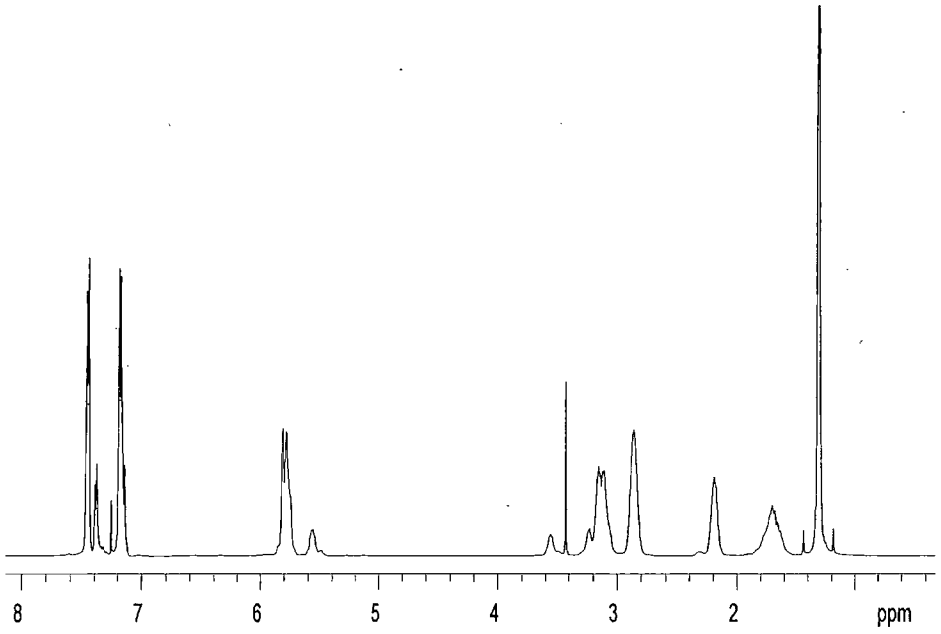
Appendix 3.6: ^{13}C NMR spectrum poly(exo-PhC_2M) - Ru



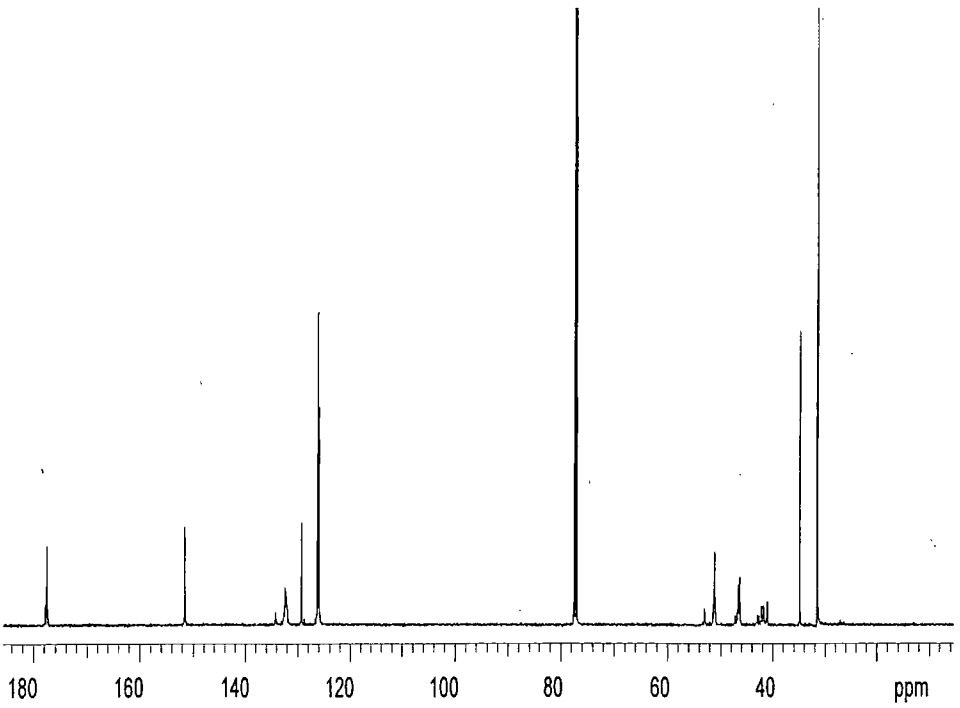
Appendix 3.7: ^{1}H NMR spectrum poly(exo-PhC_4M) - Ru



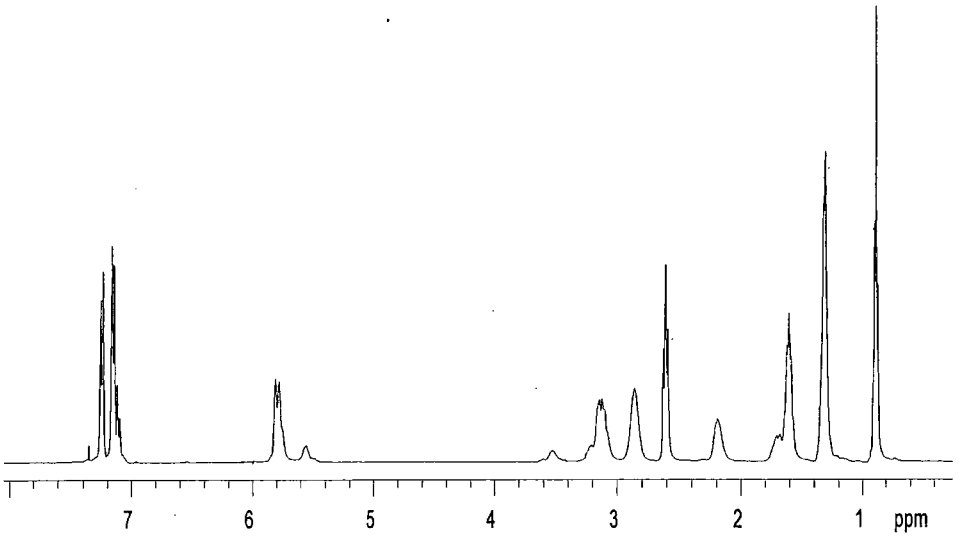
Appendix 3.8: ^{13}C NMR spectrum poly(exo-PhC_4M) - Ru



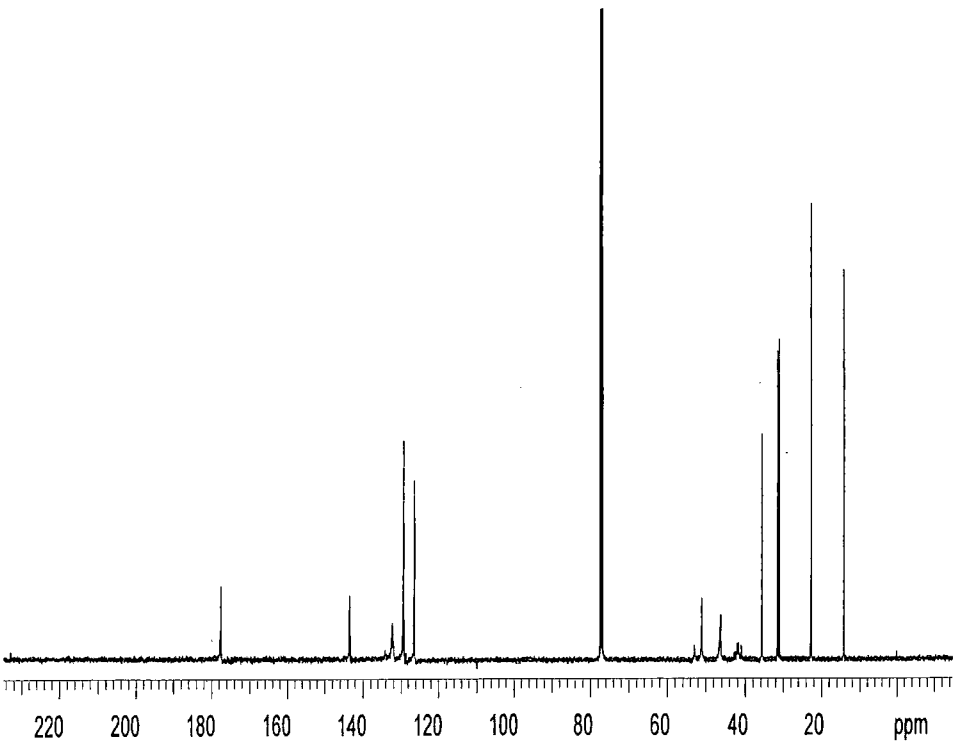
Appendix 3.9: ^{1}H NMR spectrum poly(exo-C_4PhM) - Ru



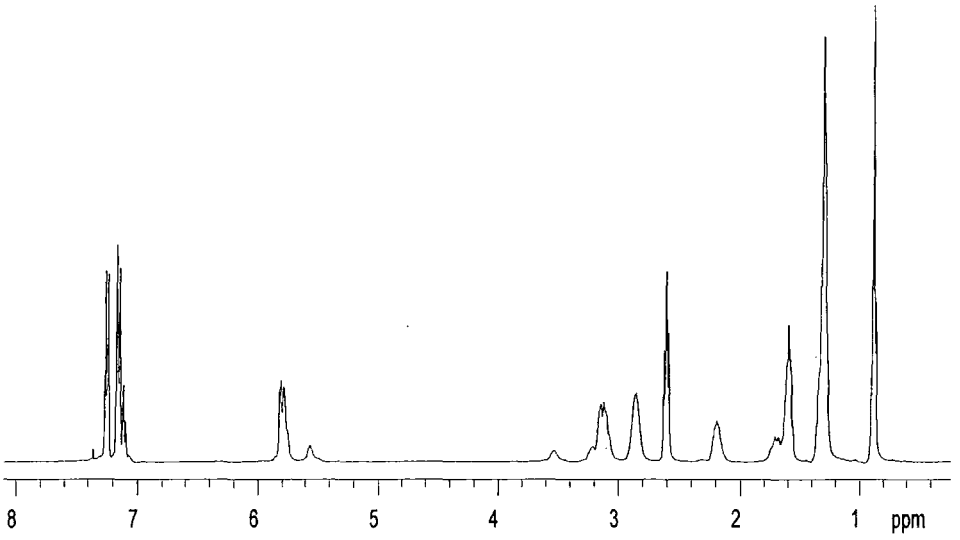
Appendix 3.10: ^{13}C NMR spectrum poly(exo-C_4PhM) - Ru



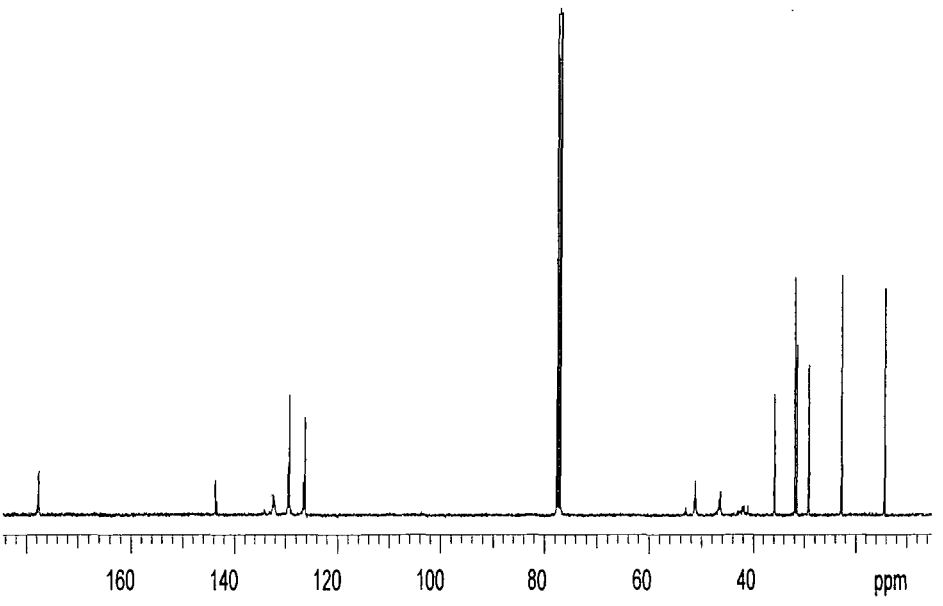
Appendix 3.11: ^{1}H NMR spectrum poly(exo-C_5PhM) - Ru



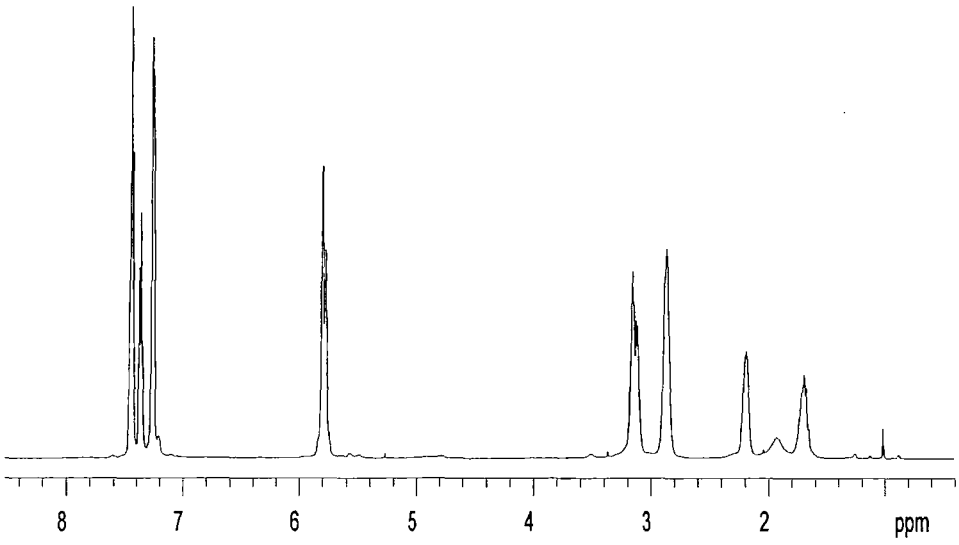
Appendix 3.12: ^{13}C NMR spectrum poly(exo-C_5PhM) - Ru



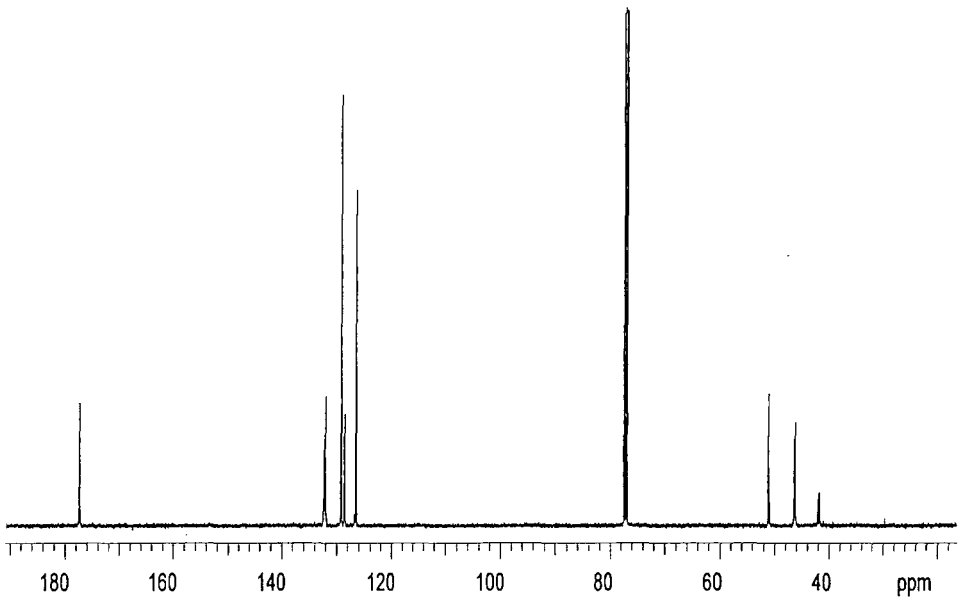
Appendix 3.13: ^{1}H NMR spectrum poly(exo-C_6PhM) - Ru



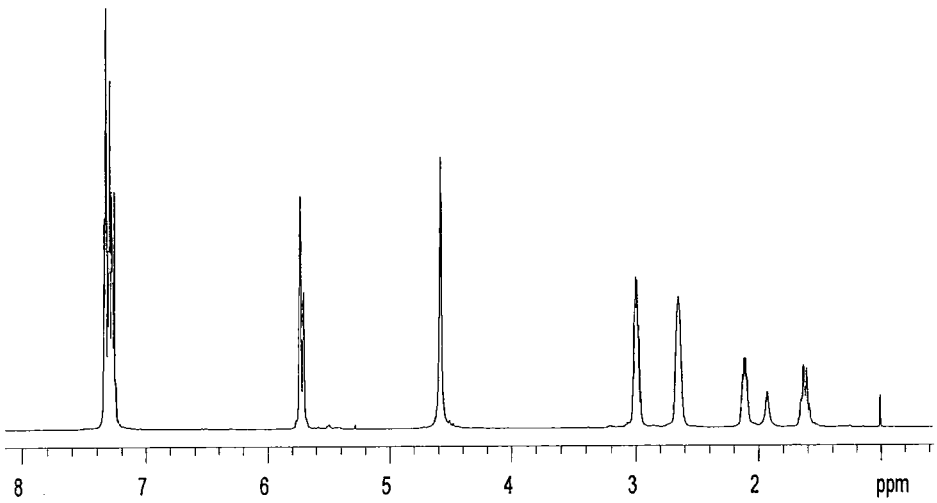
Appendix 3.14: ^{13}C NMR spectrum poly(exo-C_6PhM) - Ru



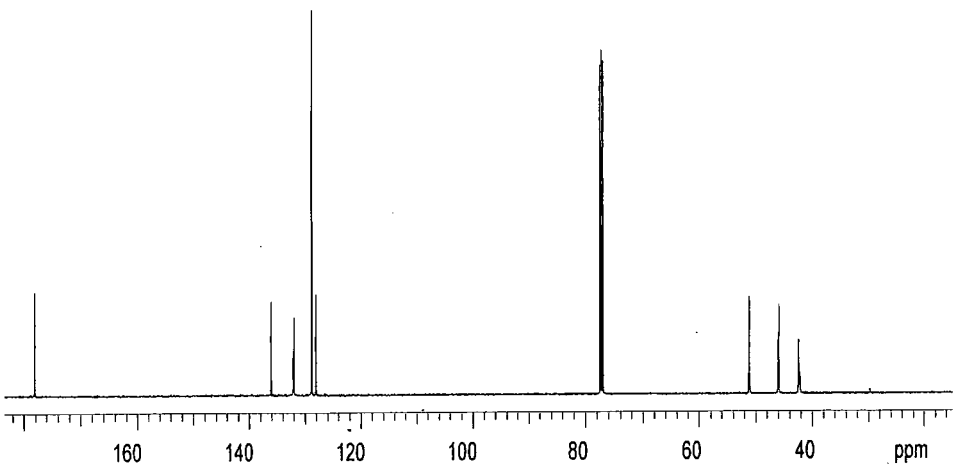
Appendix 3.15: ^{1}H NMR spectrum poly(exo-PhM) – Mo (1)



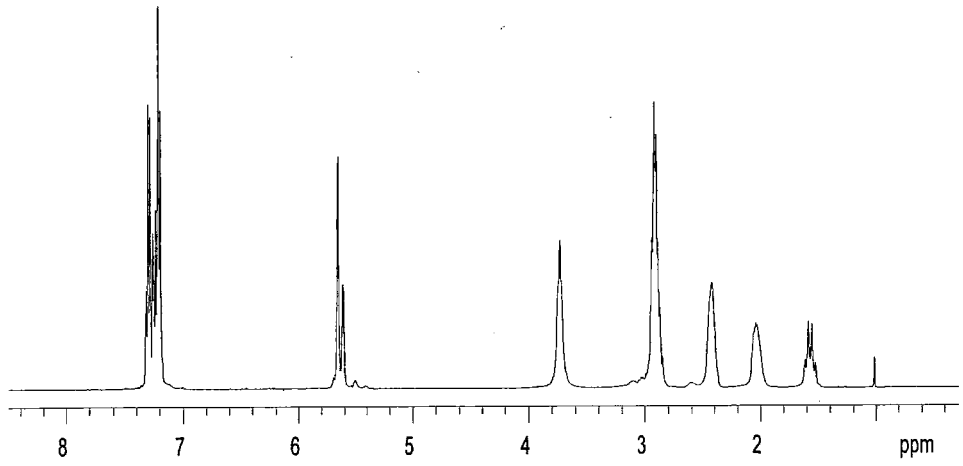
Appendix 3.16: ^{13}C NMR spectrum poly(exo-PhM) – Mo (1)



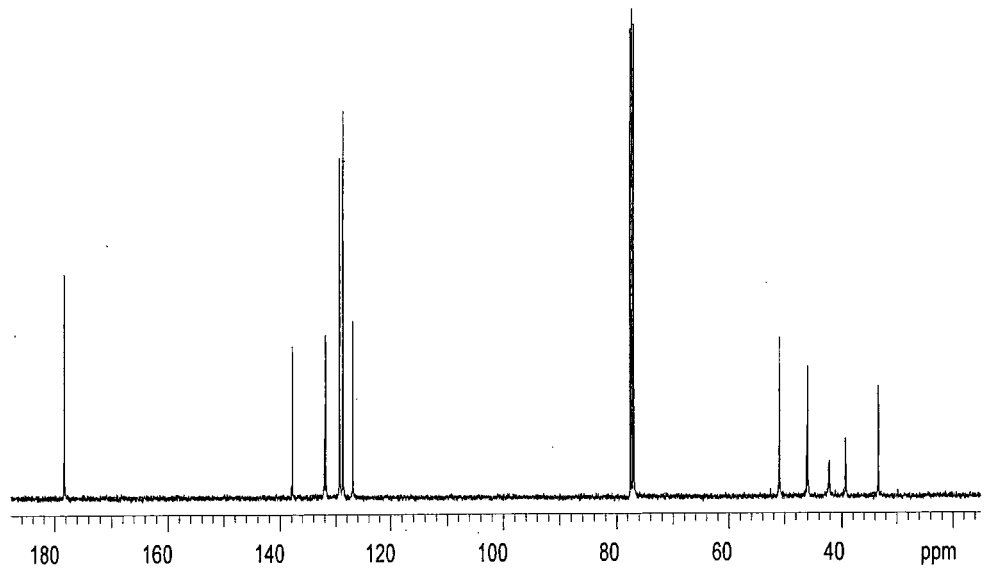
Appendix 3.17: ^{1}H NMR spectrum poly(exo-PhCM) – Mo (1)



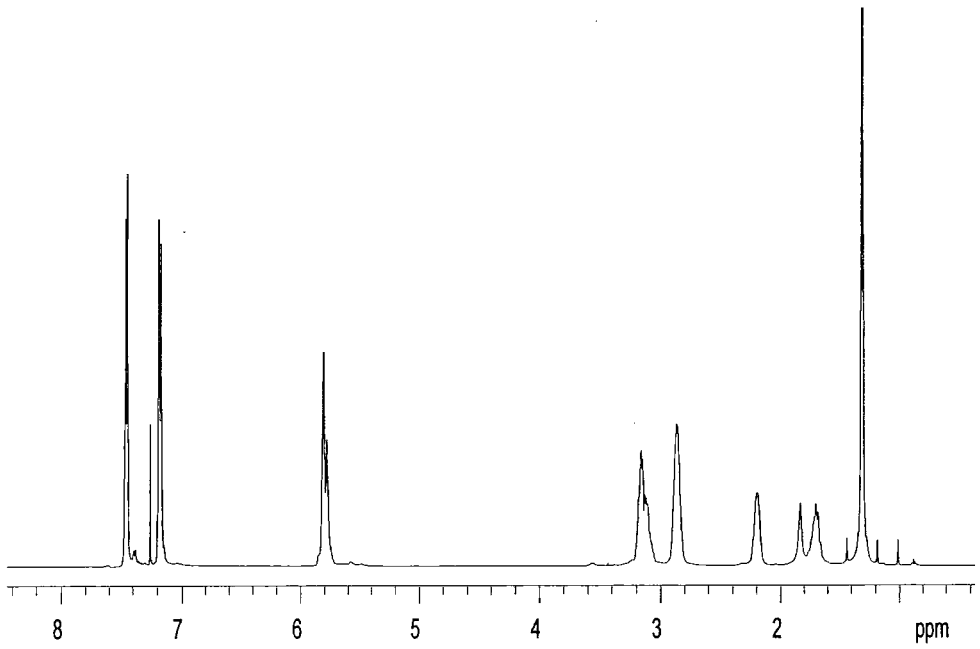
Appendix 3.18: ^{13}C NMR spectrum poly(exo-PhM) – Mo (1)



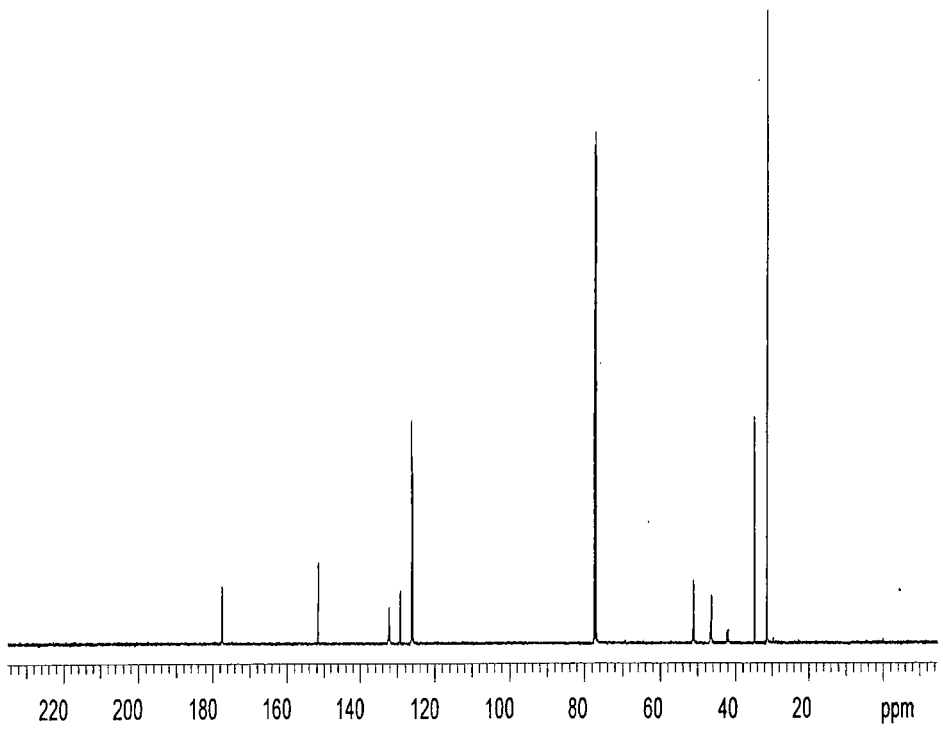
Appendix 3.19: ^{1}H NMR spectrum poly(exo-PhC_2M) – Mo (1)



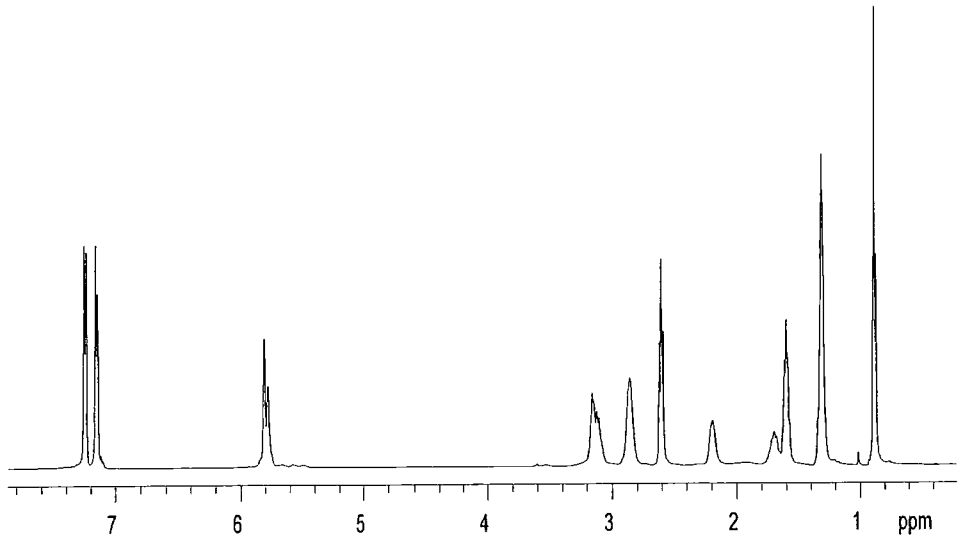
Appendix 3.20: ^{13}C NMR spectrum poly(exo-PhC_2M) – Mo (1)



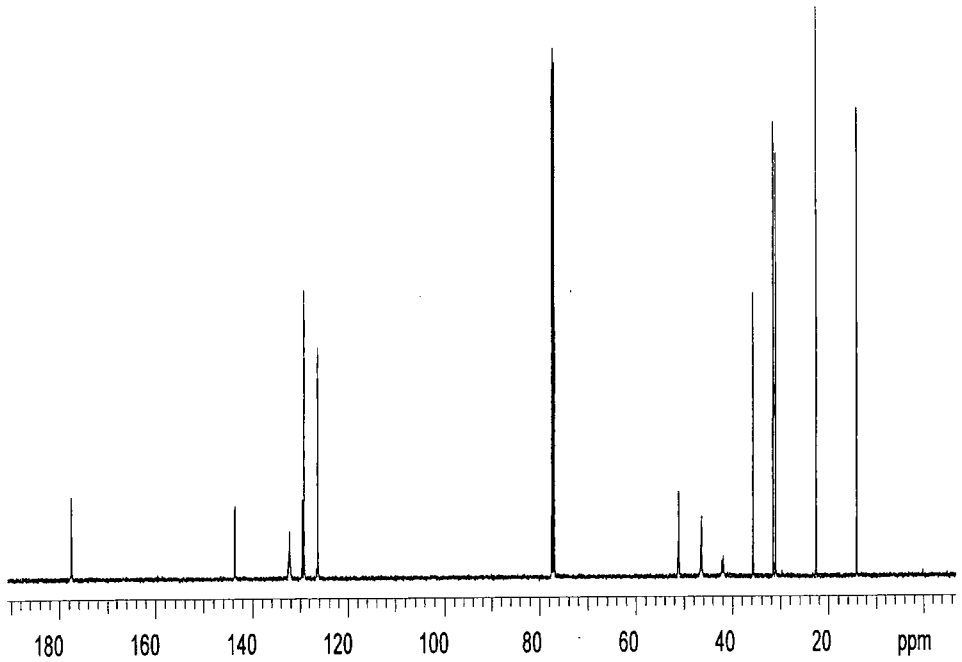
Appendix 3.21: ^{1}H NMR spectrum poly(exo-C_4PhM) – Mo (1)



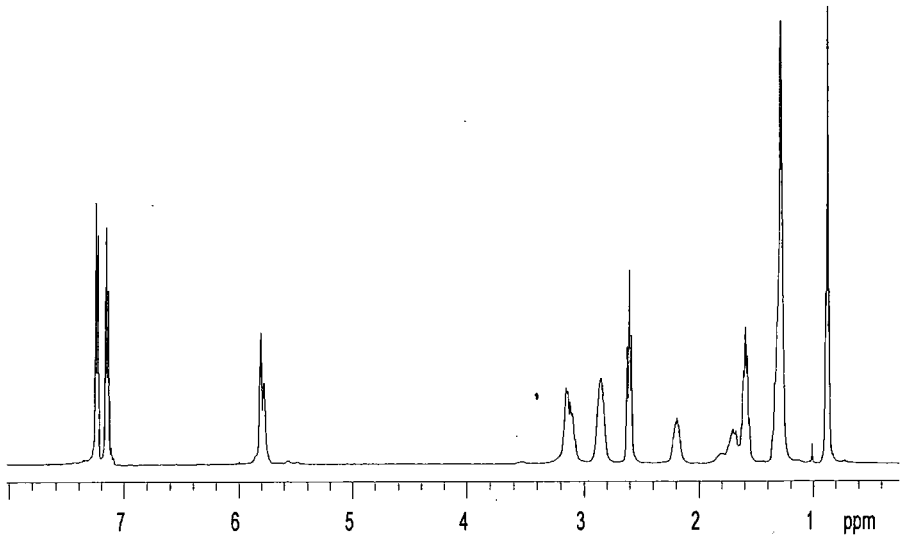
Appendix 3.22: ^{13}C NMR spectrum poly(exo-C_4PhM) – Mo (1)



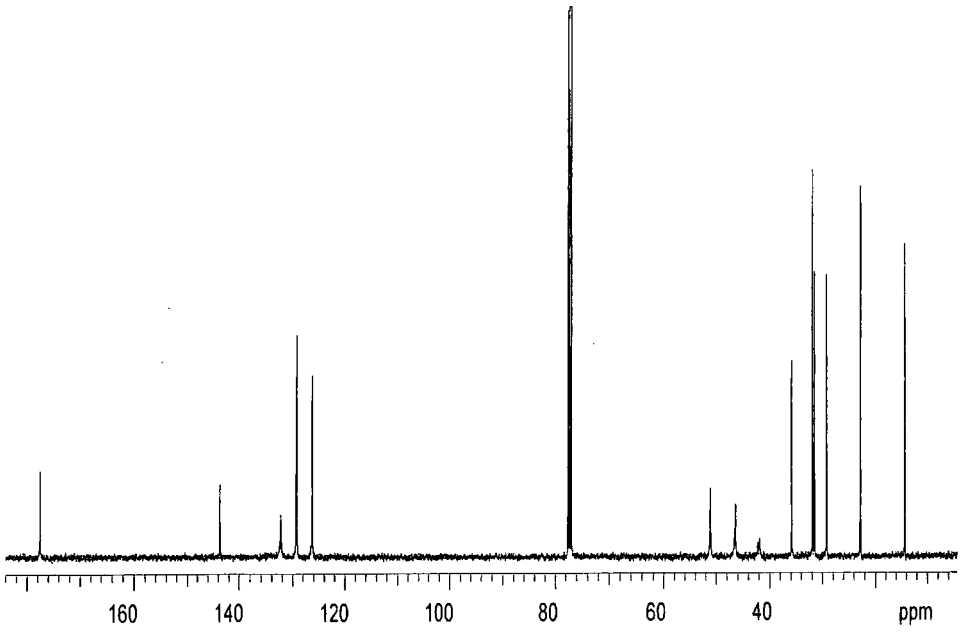
Appendix 3.23: ^{1}H NMR spectrum poly(exo-C_5PhM) – Mo (1)



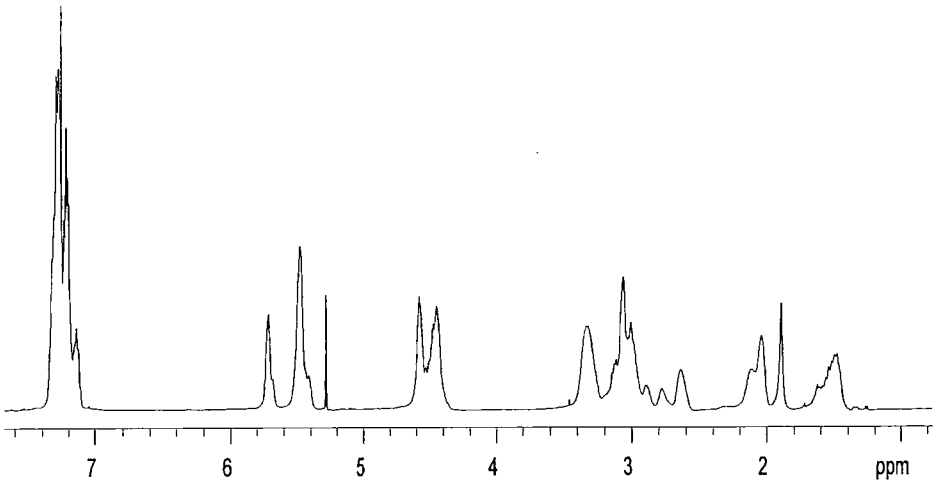
Appendix 3.24: ^{13}C NMR spectrum poly(exo-C_5PhM) – Mo (1)



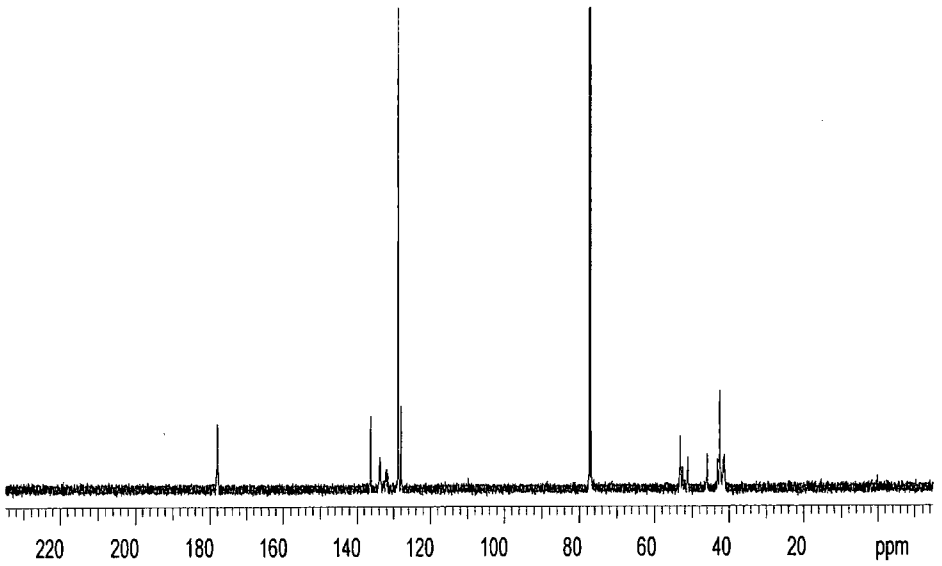
Appendix 3.25: ^{1}H NMR spectrum poly(exo-C_6PhM) – Mo (1)



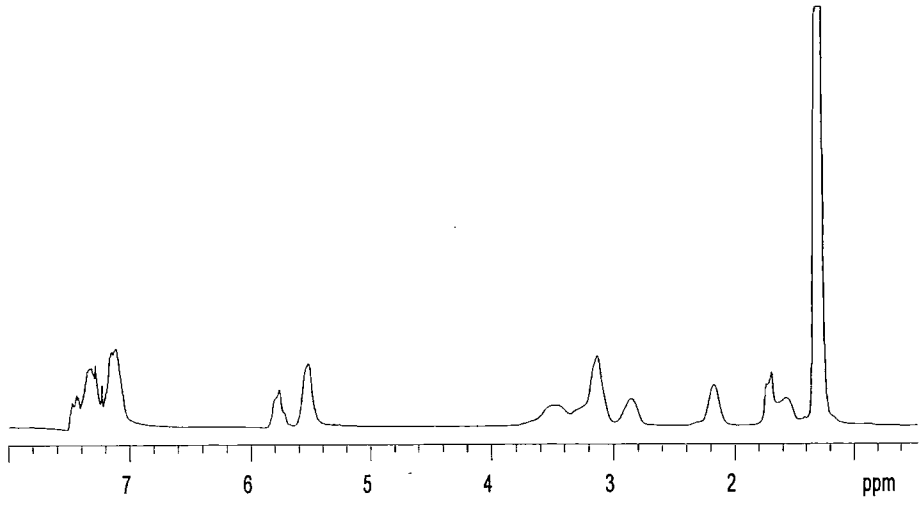
Appendix 3.26: ^{13}C NMR spectrum poly(exo-C_6PhM) – Mo (1)



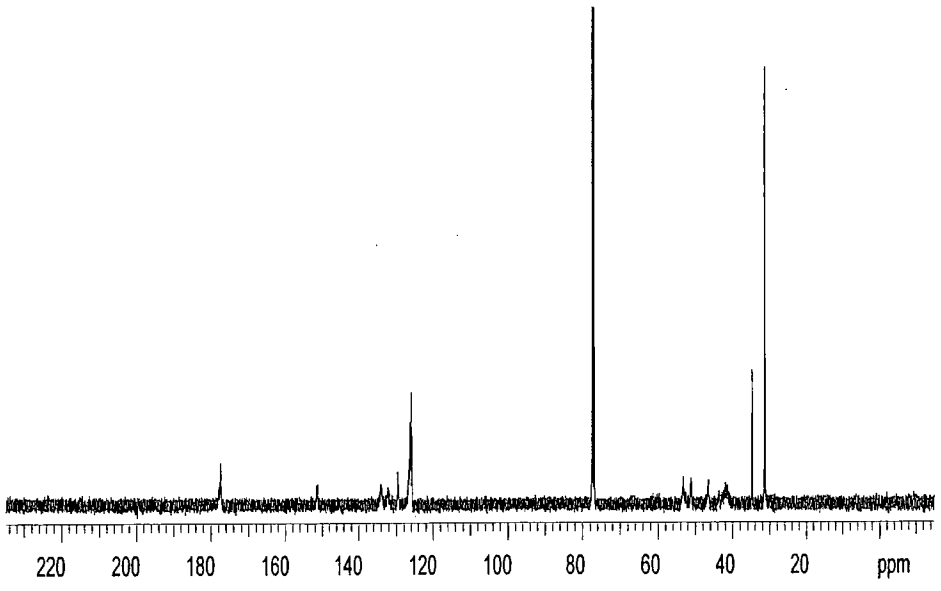
Appendix 3.27: ^{1}H NMR spectrum poly(exo-PhCM) – Mo (2)



Appendix 3.28: ^{13}C NMR spectrum poly(exo-PhCM) – Mo (2)



Appendix 3.29: ^{1}H NMR spectrum poly(exo-C_4PhM) – Mo (2)



Appendix 3.30: ^{1}H NMR spectrum poly(exo-C_4PhM) – Mo (2)

Appendix 4

Conferences and seminar attended

CONFERENCES AND SEMINARS ATTENDED

- **Prof Marcetta Darensbourg: Dept of Chemistry, Texas A&M University**
  Functioning Catalyst Inspired by Active Sites in Bio-organometallic Chemistry: Thew Hydrogenases (23rd October2002).
- **Prof Geoffrey Lawrance: Newcastle University, Australia**
  Designer Ligands: Macrocyclic and alicyclic molecules for metal complexation and biocatalysis (13th November 2002).
- **Dr David Procter: Dept of Chemistry, University of Glasgow**
  New Strategies and Methods for Organic Synthesis (22nd January 2003).
- **Prof Paul Raithby: Dept of Chemistry, University of Bath**
  Adventures in Organometallic Polymer chemistry (12th February 2003).
- **Prof Kingsley Cavell: University of Cardiff**
  (26th February 2003).
- **Prof Kevin Shakesheff: The Pharmacy school, University of Nottingham**
  Polymer materials in tissue engineering (19th March 2003).
- **Prof Joe Keddie: Dept of Physics, University of Surrey.**
  The sticky Business of Waterborne Pressure-Sensitive Adhesives (26th March 2003).
- **Royal Society of Chemistry: Dalton division, One day symposium**
  Metal Mediated Polymerisation (11th November 2002).

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