NEW CATALYSTS IN OLEFIN METATHESIS AND THEIR ELECTROCHEMISTRY

OLEFİN METATEZDE YENİ KATALİZÖRLER VE ELEKTROKİMYALARI

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for degree of **Doctor of Philosophy** in **Chemistry**.

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Okan Dereli

ABSTRACT

In this work, the activation of some transition metal halides such as $MoCl_5$, $ReCl_5$ and the synthesized aryloxide tungsten complexes *via* electrochemical or classical method and their applications on all types of metathesis reactions (olefin metathesis (OM), ring-opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET) polymerization and ring-closing metathesis (RCM) reaction), were first investigated.

In both electrochemical and classical catalyst systems, optimum conditions for metathetic reaction such as the olefin/catalyst ratio, cocatalyst/catalyst ratio, reaction time, electrolysis time, activation time and reaction temperature were studied. The metathetic products obtained were characterized by ^1H and ^{13}C NMR, GC-MS, IR and gel permeation chromatography (GPC) techniques.

The electrochemically generated Mo-based catalyst appears not as effective as the classical systems for the other metathesis-related reactions. On the other hand, it appears as a more effective catalyst than the classical catalyst systems for the ROMP of bicyclic olefins such as dicyclopentadiene, norbornadiene and norbornene in terms of olefin/catalyst ratio, reaction time and yield.

The two-component classical catalyst systems consisting of aryloxide-tungsten catalysts, $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ or $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$, and a cocatalyst were succesfully applied on all types of metathesis reactions. The $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ catalyst appears to be a very useful and effective catalyst since it is highly active even in air atmosphere.

Keywords: metathesis, catalyst, electrocatalysis, WCl_6, olefin, cyclic olefin, diene.

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ÖZET

Bu çalışmada, $MoCl_5$, $ReCl_5$ gibi bazı geçiş metal halojenürlerinin ve sentezlenen ariloksi tungsten komplekslerinin ‘elektrokimyasal’ veya ‘klasik’ metod yoluyla aktivasyonu ve metatez tepkimelerinin tüm çeşitlerine (olefin metatez (OM), halka açılımı metatez polimerizasyonu (ROMP), asiklik dien metatez (ADMET) polimerizasyonu ve halka kapanması metatez (RCM) tepkimesi) uygulamaları ilk kez gerçekleştirilmiştir.

Elektrokimyasal ve klasik katalizör sistemlerinin her ikisi için, olefin/katalizör oranı, kokatalizör/katalizör oranı, reaksiyon süresi, elektroliz süresi, aktivasyon süresi ve reaksiyon sıcaklığı gibi metatez tepkimelerinin optimum koşulları araştırılmıştır. Elde edilen metatetik ürünler ^1H ve ^{13}C NMR, GC-MS, IR ve GPC teknikleri ile karakterize edilmiştir.

Elektrokimyasal olarak üretilen Mo-bazlı katalizör, diğer metatez reaksiyonları için klasik sistemler kadar etkin gözükmezken, disiklopentadien, norbornadien ve norbornen gibi bisiklik olefinlerin halka açılımı metatez polimerizasyonu için klasik katalizör sistemlerine göre; olefin/katalizör oranı, reaksiyon süresi ve verim bakımından daha etkin olduğu ortaya çıkmıştır.

Ariloksi-tungsten katalizörleri $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ veya $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ ve bir kokatalizörden oluşan iki komponentli klasik katalizör sistemleri metatez tepkimelerinin tüm çeşitlerine başarıyla uygulanmıştır. $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ katalizörü hava atmosferinde bile yüksek aktivite gösterebilmesinden dolayı gayet etkin ve kullanışlı bir katalizör olarak ortaya çıkmaktadır.

Anahtar Kelimeler: metatez, katalizör, elektrokataliz, WCl_6, olefin, siklik olefin, dien.

Danışman: Prof. Dr. Yavuz İMAMOĞLU, Hacettepe Üniversitesi, Fen Fakültesi, Kimya Bölümü, İnorganik Kimya Anabilim Dalı

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CONTENTS

ABBREVIATIONS

ADMET	Acyclic diene metathesis
AM	Acetylene metathesis
Ar	Aryl
Boc	*t*-butoxycarbonyl
Bu	Butyl
COD	1,5-cyclooctadiene
COE	Cyclooctene
CPE, Cp	Cyclopentene
DCPD	Dicyclopentadiene
DM	Degradative metatesis
DME	1,2-dimethoxyethane
Et	Ethyl
FTIR	Fourier-transform infrared
Me	Methyl
Mes	Mesitylene
Mt	Metal
MW	Molecular weight
NBD	Norbornadiene
NBE	Norbornene
NMR	Nuclear magnetic resonance
Np	Neopentyl
OM	Olefin metathesis
Ph	Phenyl
Pr	Pyridine
RCM	Ring-closing metathesis
RIM	Reaction injection moulding
ROMP	Ring-opening metathesis polymerization
ROP	Ring-opening polymerization
$TBABF_4$	Tetra-n-butylammonium tetrafluoroborate
TBDMS	*t*-butyldimethylsilyl
THF	Tetrahydrofuran

FIGURES

TABLES

1. INTRODUCTION

One of the most attractive transition metal-catalyzed processes available to today's chemist is olefin metathesis. Modern synthesis strategies of specialty polymers, fine chemicals, natural products, and even protein mimics reported in the last decade are just some representative examples of the fields in which olefin metathesis is finding its applications.

Olefin metathesis has been investigated for over 50 years as one of the most motivating discoveries in organometallic chemistry, widely used in both academic and industrial settings. In 2005 professors Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock were awarded the Nobel Prize in Chemistry "for the development of the metathesis method in organic synthesis."

It was not until 1967 that the phrase olefin metathesis was used. Prior to this time, this transformation was actually present in two chemical processes that were believed to be mechanistically different. The first one was referred as a disproportionation (or dismutation) reaction and leads to the formation of substituted olefins and ethylene from propylene using supported oxide catalyst at elevated temperatures. The second one was identified as a ring-opening polymerization process when an unusual unsaturated polymer was obtained upon polymerization of the cyclic norbornene olefin with a traditional Ziegler-Natta 1,2-olefin catalyst at room temperature. The similarity of the overall reaction was not obvious as different catalysts and reactions conditions were involved. The connection between those two overall similar reactions was made by Calderon in 1967 with the discovery that the sytem WCl_6/$EtAlCl_2$/EtOH (1/4/1) was effective for the ring-opening metathesis polymerization of cyclooctene and 1,5-cyclooctadiene, and would also promote the cross-metathesis (disproportionation) of 2-pentene at room temperature. The finding that a unique catalytic system could provide those two dissimilar reactions suggested that there was one olefin metathesis process (Calderon, 1967). Henceforward the reaction became known as 'olefin metathesis', a term that applies to the reactions of both cycylic and acyclic olefins.

A large number of transition metals are known to catalyze olefin metathesis. The catalyst systems most commonly used are based on the metals W, Mo, Ru and Re. The use of catalysts with their selective and effective transformation properties in olefin metathesis and polymerization systems is a growing interest. There has been great effort and competition in developing the novel active catalysts. This interest and competition has been spurred by the development of commercially available transition metal alkylidene catalysts for the olefin metathesis reaction (Schrock et al., 1990; Schrock and Hoveyda, 2003; Nguyen et al., 1992; Schwab et al., 1995; Trnka and Grubbs, 2001), notably the molybdenum or tungsten complexes of Schrock and the ruthenium complexes developed by Grubbs. Today, activity and stereochemistry of reaction can be controlled by using various derivates of well-defined stable carbene complexes.

When a catalyst is not a metal-alkylidene, a cocatalyst is added to generate a metalcarbene, known as the active species for metathesis. The homogeneous system WCl_6/SnR_4 is extensively studied in the literature and is appropriate for non-functionalized and fuctionalized olefins (Ivin, 1997).

In the contiuning efforts to develop new catalyst systems, the recent works have been focused on tungsten compounds supported by bulky aryloxide ligands. In early studies, a few tungsten complexes with aryloxide ligands have been tested as metathesis catalyst precursors, namely $W(OC_6H_5)_6$, $WO(OC_6H_5)_4$, $WCl_2(OAr)_4$, and related complexes (Natta et al., 1964; Maatschappij, 1972; Knoche, 1970; Höcker et al., 1973; Dodd and Rutt, 1982, 1985).

Basset and Quignard reported the synthesis of three families of aryloxide complexes of W(VI): $WCl_{6-x}(OAr)_x$ with x = 2, 3, and 4. The catalytic properties derived from these precursors have been described (Quignard et al., 1986, 1987). In a subsequent report, Bell described the preparation of also the oxo-chloro aryloxide complexes, $WOCl_{4-x}(OAr)_x$, in a similar manner, derived from $WOCl_4$ and its corresponding phenol (Bell, 1992).

These complexes are generally stable in air and known to provide very active metathesis catalysts for linear, cyclic and functionalised alkenes in the presence of a cocatalyst like $EtAlCl_2$, $Et_3Al_2Cl_3$ or R_4M (R = methyl or butyl, M = Sn or Pb) (Quignard et al., 1985; Dodd and Rutt, 1988; Vosloo et al., 1997; van Schalkwyk et al., 2002; Marvey et al., 2004).

Tungsten aryloxides are useful because they can be easily synthesized from WCl_6 and its corresponding phenol and offer good handling stability. Moreover, these compounds are very versatile, because their activity and stereoselectivity can be modified, by changing their ring substituents. Thus, electronegative groups increase the reduction potential of tungsten atoms, enhancing the catalytic activity of these compounds in metathesis. Furthermore, stereoselectivity can be achieved by placing bulky groups in 2,6 positions of the ring.

It has been already reported that the electrochemical reduction of transition metal salts, such as WCl_6, under controlled potential at a platinium cathode with an aluminium anode, results in the formation of stable and active olefin metathesis catalysts (Gilet et al., 1983; Düz, 1997). Until now, by using this catalytic system, olefin metathesis and the other related reactions were studied (Gilet et al., 1983; Düz, 1997; Melkuç, 2000; Dereli, 2001; Boz, 2003; Çetinkaya, 2003 and Karabulut, 2006).

The aim of this study is to apply the two-component classical catalyst systems containing a precatalyst and a cocatalyst and the electrochemically generated catalyst systems, which have not been studied before, to metathesis reactions.

In this work, the activation of some transition metal halides such as $MoCl_5$, $ReCl_5$ and the synthesized aryloxide tungsten complexes *via* electrochemical or classical method and their applications on all types of metathesis reactions (olefin metathesis (OM), ring-opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET) polymerization and ring-closing metathesis (RCM) reaction), were first investigated. For this purpose, few di- and tetrasubstituted aryloxide tungsten (VI) complexes ($W(OAr)_2Cl_4$ and $W(OAr)_4Cl_2$ type, respectively) were synthesized from WCl_6 and phenol derivatives by using the synthesis method of Quignard et al., and also an oxo-chloro aryloxide complex, $WOCl_3(OAr)$, in similar manner, was prepared as described by Bell.

2. GENERAL INFORMATION

2.1 Some Properties of Olefin Metathesis Reactions

The word metathesis comes from the Greek *meta* (change) and *tithemi* (place). In olefin chemistry it describes the interchange of carbon atoms between a pair of double bonds.

Olefin metathesis reactions do not occur spontaneously. The reactions are generally reversible and, with the right catalyst system, equilibrium can be attained in a matter of seconds, even with substrate/catalyst ratios of 10^4. Catalyst systems for olefin metathesis almost invariably contain a transition metal compound. These are sometimes effective by themselves (like some active metal carbene, metallacyclobutane or carbyne complexes) but often require the presence of a second compound called as cocatalyst, and sometimes a third (promoter). The systems most commonly used are based on the chlorides, oxides, oxychlorides, or olefin complexes of W, Mo, Re, Ru or Rh. Os or Ir compounds are sometimes used, and occasionally Ti, V, Cr, Co, Nb, or Ta compounds. Typical cocatalysts are $EtAlCl_2$, R_3Al and R_4Sn (R = Ph, Me, Et, Bu), while promoters often contain oxygen, e.g, O_2, EtOH, PhOH (Ivin, 1997).

The applications of the metathesis reactions can be classified in various groups. This process can be divided into three categories:

(a) Simple exchange reactions
  - metathesis reaction involving two equal olefins and
  - cross-metathesis (CM) reaction involving two different olefins.

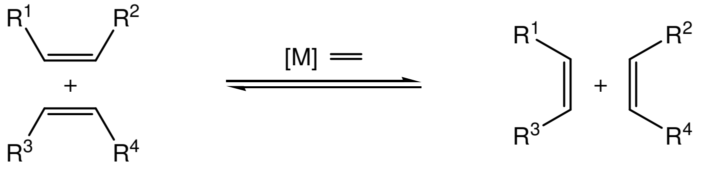
(b) Metathesis polymerizations
  - ring-opening metathesis polymerization (ROMP) and
  - acyclic diene metathesis polymerization (ADMET).

(c) Ring-closing metathesis (RCM).

2.2 Applications of Metathesis Reactions

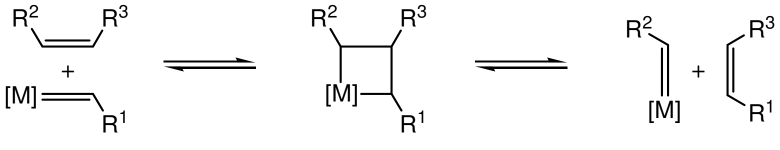
2.2.1 Olefin metathesis (OM)

Olefin metathesis reactions have been used in recent years as a well-established synthetic method in both industrial and laboratorial applications. The reaction consists of an alkene double bond cleavage, followed by a statistic redistribution of alkylidene fragments.



If one of the product alkenes is volatile (such as ethylene) or easily removed, then the reaction shown above can be driven completely to the right. Likewise, using a high pressure of ethylene, internal olefins can be converted to terminal olefins. This reaction allows for new olefins to be synthesized and used as raw materials in polymers, perfumes, drugs and agrochemical industrial products, also serving as the starting point for more complex organic molecules.

The mechanism, originally proposed by Chauvin in 1971, is generally accepted to involve the formation and subsequent cleavage of a metallacyclobutane intermediate (Herisson and Chauvin, 1971).



The cleavage can either occur in a productive fashion to afford a new olefin and a new metal carbene complex or a non-productive fashion to afford starting material. Generally, each step is reversible and the reaction is under thermodynamic control.

2.2.2 Ring-opening metathesis polymerization (ROMP)

Ring-opening metathesis polymerization (ROMP) is the conversion of cyclic olefins to unsaturared polyalkenamers. This reaction is a unique process in which the number of double bonds in the monomer is preserved. The general mechanism for this process is outlined in Figure 2.1. It is enthalpically driven by the release of ring-strain associated with the monomer. Thus, strained cycloalkenes such as norbornenes, cyclobutenes, and barrelenes have been successfully polymerized using a variety of metal alkylidenes. In contrast, monomers that possess a relatively low strain energy, such as cyclopentenes, are more difficult to polymerize and far fewer catalysts are known to be capable of polymerizing such monomers. Since ROMP is also under thermodynamic control and thus is an equilibrium controlled process, depolymerizations can occur where growing chains “back-bite” or chain transfer to form cyclic olefins and shorter polymeric chains.

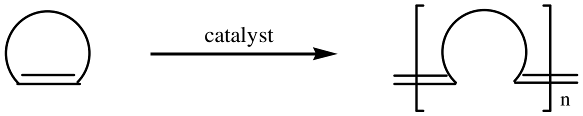


Figure 2.1 Ring-opening metathesis polymerization (ROMP).

ROMP reactions carry out under moderate conditions. The reaction is propagated by metal carbene complexes, resulting in linear high polymer as well as cyclic oligomers formed either concurrently or subsequently by intramolecular metathesis reactions. Low concentration of monomer favours the intramolecular reactions, which is an advantage in the preparation of the cyclic dimer of cyclooctene, an intermediate in the perfume industry.

At one time it seemed likely that the high-trans polymer of cyclopentene would find use as an all-purpose elastomer. Raw materials were cheap and the product had properties akin to those of natural rubber. However, its early promise has not been fulfilled. Other high-trans polymers, such as those formed from norbornene, and cyclooctene have found their way on to market as components of elastomeric products, and the ROMP of endo-dicyclopentadiene is being used to produce large objects by reaction injection moulding (RIM).

A major advantage of ROMP is that its characteristics can be tuned which allows unsurpassed control over of the polymer's size, shape, and functionality. Through careful catalyst selection, ROMP can be used as a living polymerization where chain transfer is absent and polymers with predictable molecular weights and low polydispersity can be synthesized. Block copolymers via the sequential addition of different monomers have been prepared using ROMP. Through appropriate functionalization, ROMP has also been used to prepare highly cross-linked, conducting, liquid-crystalline, water soluble, biologically active, and surface-bound polymers (Patton et al., 1986; Royappa et al., 1998; Ungerank et al., 1997; Lynn et al., 1998; Nomura and Schrock, 1996; Weck et al., 1999).

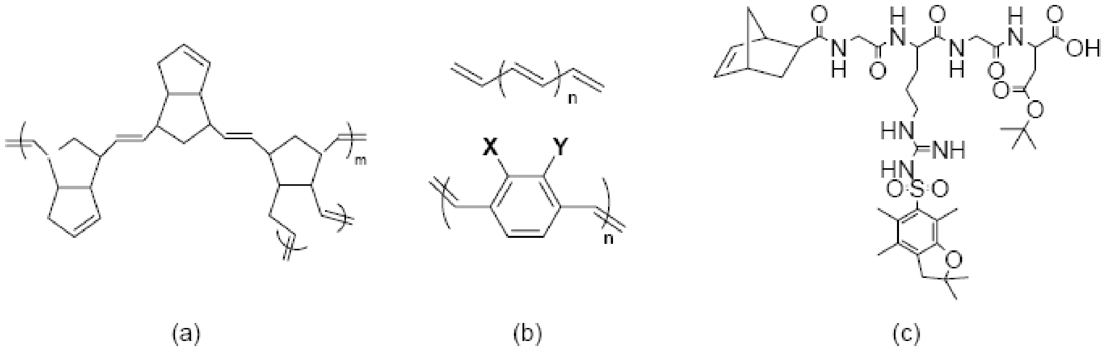


Figure 2.2 Represenative examples of polymers prepared using ROMP: (a) polyDCPD, which possesses high mechanical stability due to its cross-linked structure; (b) polyacetylene and polyphenylene, which are conducting organic polymers; (c) polynorbornene with a pendant bioactive peptide.

ROMP can also be used to prepare end-functionalized (telechelic) polymers, which have been traditionally difficult to prepare using other polymerization methods. Such polymers have application in chain extension processes, cross-linked polymeric networks, and reaction injection molding. One versatile approach involves the ROMP of a cyclic olefin monomer in the presence of an acyclic functionalized alkene that behaves as a chain transfer agent (CTA). Propagating polymer chains react with a CTA such that the functional group is effectively transferred to the active growing species. This results in a polymeric chain and a new metal carbene each containing a functional group from the CTA. The new metal carbene can then react with either monomer (producing a new polymer chain) or a preformed polymer chain (transferring the active species). The only polymer endgroups that do not contain functional groups originating from the CTA are those from the initiating metal carbene and the terminating agent, which in principle, can be chosen to match those of the CTA. In absence of any termination reactions, the number of active centers is preserved, and can lead to telechelic polymers with a number averaged degree of functionality (F_n) that approaches 2.0.

In olefin metathesis reactions, a cis reactant may yield all-cis products, or all-trans products, or a mixture of cis and trans, depending on the catalyst and substrate For example, in the ROMP of 5,5-dimethylnorbornene, $ReCl_5$-initiation gives an all-cis polymer, while $RuCl_3$-initiation gives an all-trans polymer (Grubbs, 1982; Ivin et al., 1982, 1997; Ho et al., 1982). Detailed studies, using ^{13}C NMR spectroscopy, on the microstructures of numerous ROMP polymers and copolymers have led to the development of theories, which provide a rationalization of the polymer's primary microstructural features, e.g., *cis*/*trans* double bond ratio and distribution, regiochemistry, copolymer ratios and tacticity (Ivin, 1997).

2.2.3 Acyclic diene metathesis (ADMET)

Acyclic diene metathesis is a step-growth condensation type polymerization that normally employs an α,ω-diene in conjunction with a metathesis catalyst to produce high molecular unsaturated polymer (Figure 2.3). The reaction is driven by removal of a small condensate, usually ethylene.

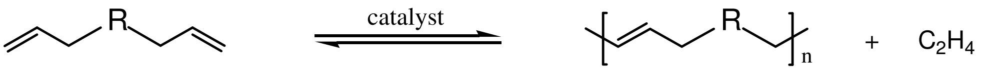


Figure 2.3 Acyclic diene metathesis (ADMET) polymerization.

Acyclic diene metathesis (ADMET) polymerization is another method that provides access to linear, unsaturated hydrocarbon polymers and materials containing a wide variety of functionalities along the polymer backbone. This class of polymerization reactions has been well established and comprehensively studied by the Wagener group.

The recent reviews provide a comprehensive view of the ADMET chemistry (Tindall et al.,1998; Davidson and Wagener, 1999; Schwendeman et al., 2002). In general, ADMET polymerization can be described as the condensation of terminal dienes into unsaturated polymers, yielding a molecule of ethylene in every propagation step. Based on this description, ADMET falls in the category of *step-propagation condensation-type* polymerization (Odian, 1991). ADMET follows the same rules as any other polycondensation reaction, meaning that high conversions (>99%) with no side reactions are necessary to produce high molecular weight polymers. This reaction, as in the case of any condensation polymerization, is an equilibrium process, which proceeds in a stepwise fashion to form dimer, trimer, tetramer, and so on to obtain high molecular polymer. The size of the polymer increases continuously with time (conversion) at relatively slow rate. High molecular weight polymer is obtained at the end of polymerization when the conversion of monomer is larger than that of 99%. Thus, a highly active catalytic system is required throughout the polymerization; most catalysts however, show higher activity towards terminal olefins for steric hindrance reasons, and so α,ω-diene monomers are often used in ADMET polymerization.

The study of hydrocarbon monomers, both aliphatic and aromatic, has led to the understanding of many features of ADMET chemistry. Pure hydrocarbon monomers such as 1,9-decadiene are readily available and have been used as the standard for reactivity and compatibility mainly because of the absence of basic functionalities and their ease of purification.

Polyoctenylene, the ADMET polymer produced from 1,9-decadiene, is a linear structure that contains a double bond every repeat unit separated from each other by six methylene groups. Hydrogenation of this polymer provides access to *perfectly linear polyethylene*. Structures of this type are step polymers that can be used to model polymers produced by chain chemistry.

Early investigations of polymerization of 1,5-hexadiene and 1,9-decadiene, by Wagener and co-workers in the mid-1980s, demonstrated that “classical” catalysts such as $WCl_6/EtAlCl_2$ can lead to both cationic vinyl addition chemistry and in addition to polycondensation chemistry (Lindmark-Hamberg and Wagener, 1987), thereby defining the need for active and well-defined catalysts for metathesis. Fortunately, in 1986, Schrock and co-workers successfully prepared the first well-defined, single site catalyst, a breakthrough in this field (Schaverien et al., 1986). This breakthrough led to more stable ruthenium based catalytic systems discovered by Grubbs.

Like many other polycondensation reactions, ADMET polymerization is best performed in the bulk (neat) to maximize the molar concentration of monomer (terminal olefins) and to promote a shift in the equilibrium of the reaction from monomer towards unsaturated polymer formation. Bulk polymerization also minimizes undesired cyclization, a well known concurrent reaction in polycondensation chemistry. Moreover, high vacuum is applied to remove the condensate ethylene, which further shifts the reaction towards polymer formation. The mechanism of the ADMET polymerization cycle has been well documented. Each step in this mechanism is in true chemical equilibrium, and the ultimate driving force for the reaction is removal of ethylene. The catalytic cycle starts with coordination of an olefin, followed by formation of a metallacyclobutane intermediate and productive cleavage that leads to the formation of the metathesis active alkylidene complex. These subsequent reactions produce a methylidene complex followed by the coordination of another monomer. Productive cleavage of another metallacyclobutane results in release of ethylene – one molecule for each “coupling” reaction.

The developments in the field of well-defined catalysts along with the clean mechanism of ADMET have become instrumental in the synthesis of novel polymers with controlled architectures. The design starts with the preparation of a α,ω-diene bearing the desired type of functionality or specific type of branching. The resultant polymer retains this functionality and a specific backbone sequence. ADMET has produced unsaturated polymers where the functionalities have been ethers, esters, carbonates, sulfides and many more functionalities (O’Gara et al., 1993; Schwendeman et al., 2002; Lehman and Wagener, 2003; Baughman and Wagener, 2005; Matloka and Wagener, 2006). Consequently, ADMET bypasses typical synthetic obstacles in the synthesis of polymers and copolymers, and allows creating polymer structures that cannot be prepared via other routes.

2.2.4 Ring-closing metathesis (RCM)

Ring-closing metathesis (RCM) of α,ω-dienes is used to form cyclic olefins (Figure 2.4). In contrast to ROMP, RCM is enthalpically disfavored. The reaction is entropically driven by the release of volatile small molecules (e.g., ethylene). However, ring formation is limited by the relative ring strain of the product; highly strained olefins such as norbornene cannot be synthesized using RCM.

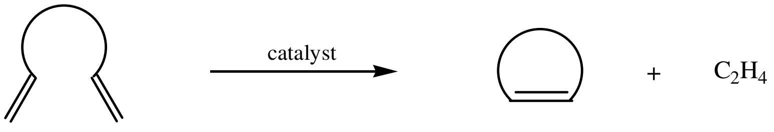


Figure 2.4 Ring-closing metathesis (RCM).

Although ring-closing metathesis (RCM) was used relatively early for synthetic purposes, for example by Tsuji (1980) and Villemin (1980), it has not became established as a method. Recently ring-closing metathesis (RCM) reactions has received a great deal of attention (Figure 2.5).

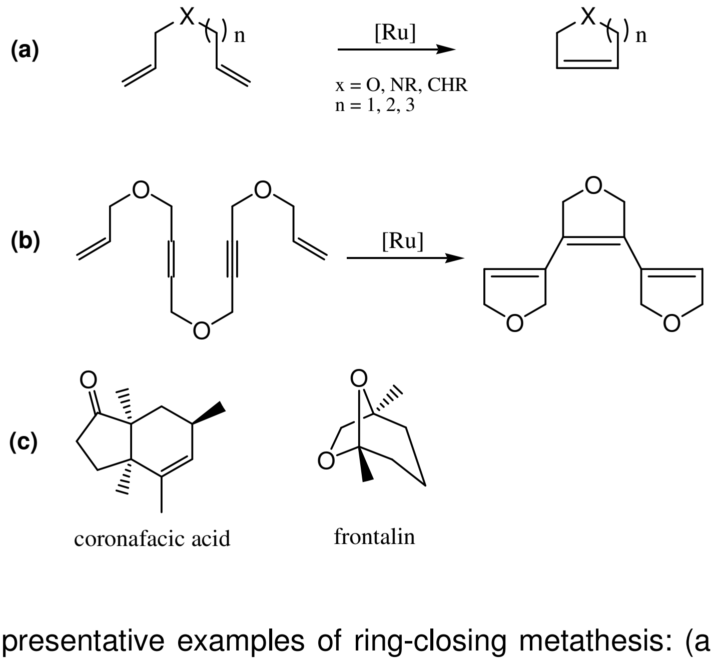


Figure 2.5 Representative examples of ring-closing metathesis: (a) RCM of α,ω-dienes to form 5, 6, and 7 membered rings; (b) tandem RCM to form a multi-cyclic substrate; (c) examples of natural products prepared using RCM.

The cyclization of a variety of medium-sized rings (6, 7, 8 membered) and larger ring systems have been reported (Miller et al., 1996; Fraser and Grubbs, 1995). Tri- and tetra-substituted cyclic olefins (Kirkland and Grubbs, 1997), bicyclic aza compounds (Dyatkin, 1997), and β-lactams (Barrett et al., 1997) have also been prepared using RCM. Tandem cyclizations where sequential RCM reactions have been used in the formation of multicyclic ring systems (Zuercher et al., 1996). Ring-closing metatheses have proven to be key steps in various total syntheses. A number of natural products including epothilone A, coronafacic acid, and frontalin have been synthesized using RCM as the key step (Scholl and Grubbs, 1999).

2.3 Metathesis Catalyst Systems

The number of catalyst systems that initiate olefin metathesis is very large indeed. A single compound is sometimes effective but more commonly the catalyst system contains two, three, or more components. The systems may be heterogeneous or homogeneous, though it is sometimes difficult to be sure whether a system is truly homogeneous and to know whether the catalytic activity resides in the homogeneous or the heterogeneous part.

The most common metathesis catalyst systems consist of compounds of the transition metals, which is shown in the Table 2.1.

Table 2.1 The active transition metals in metathesis catalyst systems.

IVB	VB	VIB	VIIB	VIIIB	
Ti	V	Cr			
Zr	Nb	**Mo**		Ru	Rh
Hf	Ta	**W**	**Re**	Os	Ir

The systems constituted from W, Mo and Re are generally those the most effective. Catalysis by compounds of non-transition elements is very much the exception. Rare examples appear to be Al_2O_3 and $EtAlCl_2$ (Isagulyants, 1969; Ivin, 1978), Me_4Sn/Al_2O_3 (Ahn et al., 1992) and $MgCl_2$ (Buchacher et al., 1996).

Half-lives for olefin metathesis can vary from a few seconds to several days. The activity of a particular catalyst system is dependent on a number of factors including: (i) the proportions of the components (there is frequently a maximum at some particular composition); (ii) pretreatment procedures, especially for catalysts supported on Al_2O_3 or SiO_2; (iii) the order in which the components are mixed; and (iv) in the case where the olefin is added last, the period of incubation before adding the olefin. Optimization of a given catalyst system by adjustment of the various parameters in turn can be quite a lengthy procedure.

Cocatalysts normally consist of an organometallic compound of a non-transition metal in groups I-IV. The most commonly used are BuLi, $EtAlCl_2$, R_3Al, and R_4Sn (R = Me, Bu, Ph, etc.). Their function may be several-fold. First, they may provide an alkyl ligand at the transition metal which can be subsequently converted into an alkylidene ligand by reductive elimination. Secondly, reduction of the transition metal opens up sites for the coordination of the reactant olefin. Thirdly, the cocatalyst itself may act as a ligand, attaching itself to the catalytic complex in some way, thereby modifying the electron density at the transition metal atom.

Third components, especially hydroxylic compounds, hydridic compounds, and hydrogen itself, may well assist the formation of Mt-H bonds, for which there is IR and NMR evidence in some systems (Laverty et al., 1976).

2.3.1 Classical catalyst systems

In classical catalyst systems, halogens, oxyhalogens, or olefin complexes of transition metal are used together with an organometallic compound of non-transition metal in groups I-IV (Ziegler-Natta type), or a metal halogen lacking of electron (Friedel-Crafts type). Such many homogenous catalyst systems are well known, e.g., $WCl_6/EtAlCl_2/EtOH$, $Mo(NO)_2L_2Cl_2/R_3Al_2Cl_3$ (L = Py, PPh_3; R = Me, Et) $WOCl_4/SnMe_4$, $MeReO_3/AlCl_3$, $Re(CO)_5Cl/EtAlCl_2$. The use of small amounts of oxygen containing compounds (called as promoter), e.g., O_2, EtOH, PhOH, leads to an increase in activity. Although the classical catalysts based on transition metal salts are easily obtained, there are poorly defined with respect to the actual active catalytic component, since only a part of the metal is directly involved in the catalytic process. Their activity is therefore controllable only to a certain extent, which complicates their specific application in organic sytnhesis.

Supported catalysts are frequently used for gas-phase olefin metathesis in flow systems at 0-400 °C. Supported catalysts are generally activated by pretreatment, usually at high temperature (550 °C), with gases such as H_2, O_2, CO or HCl. Various refractory materials have been tested as supports, in particular the oxides of Si, Al, Th, Zr, and Ti, of which SiO_2 and Al_2O_3 are the most commonly employed. The role of the support is seldom passive. In many cases there are indications of chemical interaction between the support and transition metal compounds, so it is always necessary to quote the support in defining the overall catalyst system. The surface area of the support is typically more than 200 m^2g^{-1} while the catalyst content is generally 1-20 % by weight. Examples of heterogeneous catalyst systems are Re_2O_7/Al_2O_3, $MoO_3/CoO/Al_2O_3$, WO_3/SiO_2, Mo/SiO_2 or Al_2O_3, $W(CO)_6/SiO_2$ or Al_2O_3 (Ivin, 1997).

2.3.2 Well-defined catalyst systems

Early homogeneous olefin-metathesis catalysts were prepared in a wide variety of ways from various types of starting materials in which the metal was in an oxidation state between 0 and VI. Although such catalytic systems were examined extensively by physical organic techniques, the oxidation state of the metal and the nature of the ligands were never determined. For this reason, and in contrast to “well-defined” catalysts (isolable and characterizable complexes that are essentially identical to intermediates in the catalytic reaction), early catalysts now may be considered “ill-defined.” Today, a metal-containing compound that provides catalytic activity, but is not directly related to the catalyst that is actually present in the reaction, would be called a “catalyst precursor” or a “precatalyst.”

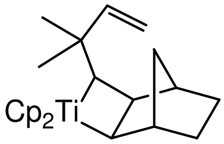
In virtually all ill-defined systems the percentage of metal that is active at any one time is thought to be small. This is one of the reasons why characterization of the active species in these circumstances has not been possible. Ill-defined catalysts often tend to produce side products, or are readily deactivated by common Lewis basic functional groups. As a consequence of these features, the activity of ill-defined catalysts, even if reproducible, cannot be controlled in a rational manner.

Complications observed in connection with the use of ill-defined catalysts, and the lack of a plausible mechanistic platform that would allow for an interpretation of selectivity and reactivity data, pointed to the preparation of well-defined catalysts as a compelling research objective. Well-defined metathesis catalysts are those that i) are essentially identical to the active species in terms of metal oxidation state and ligand coordination sphere, ii) react with olefins to yield observable new carbene complexes derived from those olefins, and iii) are stable enough to be characterized through spectroscopic means and preferably also X-ray structural analysis.

In 1964 Fischer and Maasböl reported the reaction of phenyl lithium with $W(CO)_6$ to give an anionic complex which contains an acyl ligand. Protonation followed by treatment with diazomethane yielded the first deliberately synthesized "metal carbene" complex, $(CO)_5W{=}CPh(OMe)$. The Fischer-type carbene complexes are low-valent and generally characterized by the presence of one or two heteroatoms (O, N, or S) bonded to the carbene carbon. Such complexes do not normally initiate the chain metathesis of olefins, since they are both coordinatively and electronically (18ē) saturated. However, they can sometimes be activated for metathesis by heating, or by reaction with a cocatalyst, or photochemically. Reports of hundreds of compounds that bear a heteroatom-stabilized carbene ligand soon followed.

In the 1970s several significant publications concerning the mechanism of olefin metathesis appeared. Chauvin and Herisson demonstrated convincingly that metal-catalyzed olefin metathesis is the result of a non-pair-wise exchange of alkylidene fragments. Herisson and Chauvin are given credit for first proposing in 1971 the now widely accepted mechanism. Casey et al. synthesized $(CO)_5W{=}CPh_2$ and showed that it reacts with certain olefins in a manner consistent with the metallacyclobutane mechanism (Casey and Burkhardt, 1973). In 1976, Katz reported a series of tungsten complexes $(CO)_5W{=}CPhR$, which were previously prepared by Casey and Fischer, that were found to catalyze the polymerization of a variety of cyclic olefins without the need for any cocatalyst. These investigations collectively provided strong evidence that metal carbene complexes are indeed intermediates in olefin metathesis reactions.

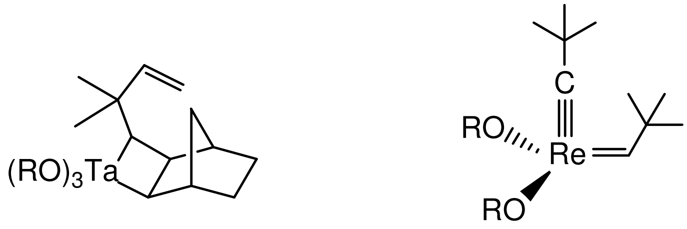
The Fischer carbenes, which are low oxidation state carbenes, were shown to be olefin metathesis catalysts of low activity. Although fragments of the initiation carbene were later observed as end groups on the polymers produced by such catalysts, the intermediates in the reaction could not be observed. The high oxidation state, late metal complexes of Tebbe, Schrock and Osborn provided the transition to the synthesis of well-defined catalysts. In contrast to ‘classical’ catalysts, well-defined catalysts are those were the propagating species can be observed and controlled. Such systems represent the transition to modern metathesis catalysis.



Gilliom's catalyst

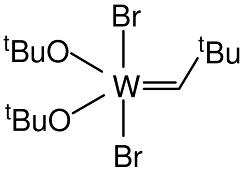
Fred Tebbe (1978) demonstrated that a titanium methylene complex would catalyze the non-productive metathesis exchange of the methylenes between two terminal olefins. Although the catalyst was not particularly active, it served as an excellent model system since the complex was very stable and the propagating methylidene could be observed and studied. These experiments established the metallacyclobutane as a viable intermediate in olefin metathesis. Utilizing the well-defined Tebbe system, additional mechanistic and synthetic studies were carried out. The titanocyclobutane complex was the first example of well-defined system that could be isolated. In a continuation of the Tebbe mechanistic studies, Gilliom found that the Tebbe complex would form a stable metallacycle with norbornene. When this complex was heated with more norbornene, a polymer was formed. The resulting polymer contained an active titanacyclobutane at the end of the polymer that could be reactivated on heating (Gilliom and Grubbs, 1986).

Single-component Ta and Re catalysts were developed shortly after and found to display similar activites in mediating olefin metathesis as the titanocyclobutane complex.



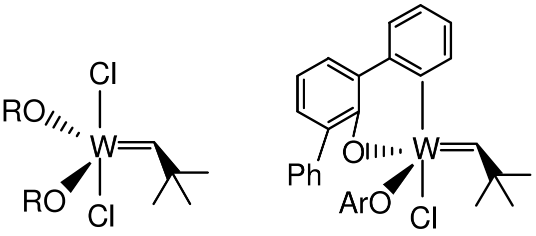
Schrock's catalysts

In 1982, Osborn reported and observed via NMR techniques the metathesis activity of the tungsten (VI) carbene $W(CH^tBu)(OCH_2{}^tBu)_2(X)_2$ (X = Cl, Br) activated by aluminium halides. Upon use of $GaBr_3$, the mechanism could be specified: the carbene complex can form an adduct with the Lewis acid that abstracts one halogen, and the generated cationic tungsten carbene is responsible for the metathesis activity (Kress et al., 1982; Kress and Osborn, 1983).



+ $AlCl_3$, $GaBr_3$

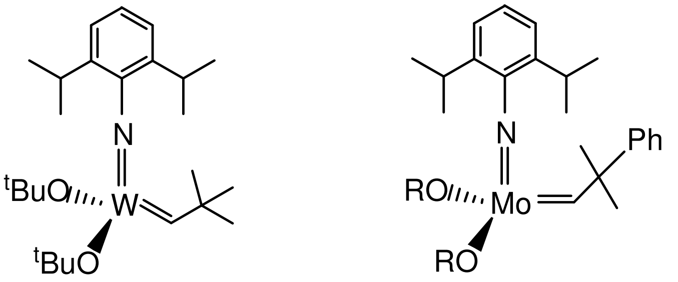
Osborn's catalyst



Basset's catalysts

In 1985, Basset and co-workers reported the synthesis of the first single component highly active tungsten carbene. With the chloro-aryloxide carbene $W(OAr)_2Cl(CHCMe_3)(OR_2)$ (Ar = 2,6-$(Ph)_2$-C_6H_3, R = Et, *i*Pr), norbornene and functionalized norbornenes (ester and nitrile groups) could be quantitatively polymerized in 10 s at room temperature. The bulky aryloxide ligands were considered as protecting groups with respect to carbene dimerization and coordination of functional groups (poisoning) (Quignard et al., 1985).

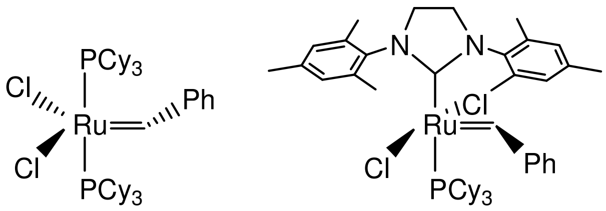
A variety of Mo and W catalysts were developed by Schrock and co-workers in the late 1980's and early 1990's. With appropriate ligand substitution, these catalysts were highly active in polymerizing a wide range of cyclic olefins. However, their viability is limitied by a low thermal stability and high sensitivity to oxygen, water, and functional groups such as alcohols and aldehydes. In addition, rigorously purified solvents and starting materials must be used to avoid premature catalyst decomposition (Schrock, 1990; Feldman and Schrock, 1991).



R = $C(CH_3)(CF_3)_2$; R = $C(CH_3)_3$

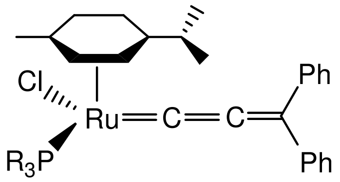
Schrock's catalysts

A new class of olefin metathesis catalysts based on Ru was reported by Grubbs in 1992. These catalysts were found to be stable to a wide range of functional group including alcohols, aldehydes, acids, air, and protic solvents (Nguyen et al., 1992).



First-generation catalyst Second-generation catalyst

Grubbs' catalysts



Furstner's catalyst

Subsequent efforts focused on facilitating their synthesis, tuning their initiation characteristics through carbene ligand modifications, and the development of chiral analogs (Chang et al., 1998; Fürstner et al., 1998). Although Ru catalysts are typically more functional group tolerant than their Mo counterparts, their activity is typically much lower. However, in 1999, another breakthrough occurred and another new class of Ru based catalysts was developed (Scholl et al., 1999).

2.3.3 Photochemically generated catalyst systems

Günther found the activity of $WCl_6/i\text{-}Bu_3Al$ as catalyst for the ROMP of cyclopentene could be enhanced if the WCl_6 was first, irradiated in CCl_4 solution at 100 ºC or in toluene solution at about 40 ºC (Günther et al., 1970). Since then, all types of olefin metathesis can be stimulated by photochemical means, normally using a mercury lamp as the source. Different results are sometimes obtained according to whether the olefin is present from the start (photoassisted reaction), or is added immediately after irradiation of the catalyst system (photocatalyzed reaction), or is added only after a period of incubation of the photochemical products (modified photocatalyzed reaction) (Taniélian et al., 1981).

There were many speculations about the structure of active species. The initiating species in the $W(CO)_6/CCl_4/h\nu$ system appear to depend on the substrate. It was supposed that active initiator is $W{=}CCl_2$ in the $W(CO)_6/CCl_4/h\nu$ system (Agapiou and McNelis, 1975). It was suggested that the initiating species has a dichlorocarbene ligand, $[W]{=}CCl_2$, since dichlorocarbene moiety has been identified in the products of reaction of preirradiated $W(CO)_6/CCl_4/h\nu$ with 1-ethoxynorbornene (Rudler, 1980). The overall reaction for the formation of the initial metal carbene appears to correspond to reaction below with intermediate formation of $W(CO)_5$, $W(CO)_5Cl$, $W(CO)_4Cl_2$ and CCl_3 (Garnier et al., 1980; Taniélian et al., 1981).

$$W(CO)_6 \quad + \quad CCl_4 \quad \xrightarrow{hV} \quad Cl_2C{=}WCl_2(CO)_3 \quad + \quad 3\,CO$$

However, in the reaction with 4-octene and 7-tetradecene, no $RCH{=}CCl_2$ is detected during cross-metathesis (Karan and İmamoğlu, 1989) and in the reaction with 2-pentene there is again no evidence for metathesis initiation by $[W]{=}CCl_2$ (Schilder et al., 1992). In the last case it appears that $[W]{=}CCl_2$ is destroyed before it can react with the substrate and the metathesis reaction is initiated from the surface of a precipitate; the nature of the initiating species is not clear. The other extensively used catalyst systems are $W(CO)_6/TiCl_4/h\nu$, $W(CO)_6/ZrCl_4/h\nu$ and $W(CO)_6/BF_3/h\nu$. The role of the halide in these systems has been investigated.

2.3.4 Electrochemically generated catalyst systems

The electrochemical behaviour of salts or complexes of transition metals have been the subject of many investigations, however, very few works have been devoted to the generation of catalytic species. The synthesis of electrohemically active catalytic species was first achieved by Lehmkuhl in 1973.

The treatment of salts or complexes of transition metals by a reducing reagent and a Lewis acid such as organoaluminium compounds leads to the synthesis of active catalytic species for the activation of unsaturated hydrocarbons. These catalytic species were also synthesized by electrochemical techniques, and they gave high yield metathetic products without isomerization (Gilet et al., 1979).

The number of electrons transferred can be easily checked by controlling the electrode potential, and the oxidation state of the metal can be stabilized in this electrochemical system. The reduction of salts of transition metal under the certain cathodic potential, such as WCl_6 and $MoCl_5$, leads to the formation of active species, such as $W{=}CR_2$ (R = H, alkyl). These homogenous catalysts proceed metathesis of alkenes effectively and selectively (Gilet et al., 1983). This type of catalyst also seems to be practical in the other organic reactions. Furthermore one of the most interesting aspects of the electrochemical technique is that the oxidation state of the reduced species can be stabilized at a controlled potential, and thus the further side reactions occuring when chemical reducing agents are used can be prevented.

Mechanism of formation of active carbene in the electrochemical system as proposed by Gilet et. al. (Gilet et al., 1983) is :

<u>Cathode:</u>

$$WCl_6 + e^- \longrightarrow WCl_6^-$$

Anode:

$$WCl_6^- + Al \longrightarrow AlCl + WCl_5 + e^-$$

$$WCl_6 + Al \longrightarrow WCl_5 + AlCl$$

$$AlCl + CH_2Cl_2 \longrightarrow Cl_2AlCH_2Cl \quad (I)$$

$$WCl_6 + 2\,(I) \longrightarrow CH_2{=}WCl_4 + 2\,AlCl_3 + CH_2Cl_2$$

$$2\,WCl_5 + (I) \longrightarrow CH_2{=}WCl_4 + AlCl_3 + WCl_6$$

Another mechanism suggested for the formation of carbene from WCl_6 in electrochemical system is that the active complex was produced after the reaction of any olefin added to the electrolized WCl_6 salt in dichloromethane (Düz, 1997). The reductive electrolysis at +0.9 V and the oxidative electrolysis at +1.6 V both produced the catalytically active species in the metathesis of olefins. The possible electrochemical reactions occuring at the cathode and anode are given below.

Reductive electrolysis (at +0.9 V)

Cathode:

$$WCl_6 + e^- \longrightarrow WCl_6^{\cdot-}$$

$$WCl_6^{\cdot-} \longrightarrow WCl_5^{\cdot} + Cl^-$$

Anode:

$$Cl^- \longrightarrow Cl^{\cdot} + e^-$$

$$Al + 3\,Cl^- \longrightarrow AlCl_3 + 3\,e^-$$

$$WCl_5^{\bullet} \longrightarrow WCl_5^+ + e^-$$

Oxidative electrolysis (at +1.6 V)

Anode:

$$WCl_6 \longrightarrow WCl_5^+ + Cl^\bullet + e^-$$

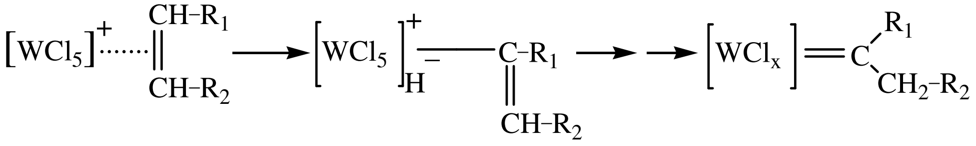
$$2\,Cl^\bullet \longrightarrow Cl_2$$

Cathode:

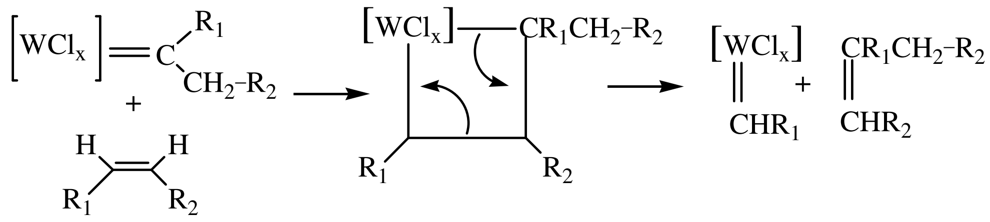
$$WCl_6 + e^- \longrightarrow WCl_5^\bullet + Cl^-$$

The only common species produced during either of these electrolysis experiments is WCl_5^+.

The accepted mechanism in literature for the catalysis in several olefin metathesis catalyst systems involve the initial formation of a metal-olefin complex intermediate via π-interaction which then gives a metal carbene structure by 1,2 hydride shift (Ivin, 1997).



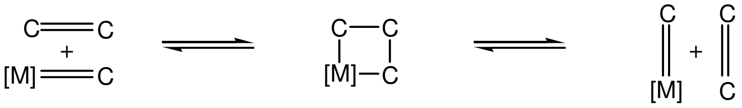
The olefin metathesis proceeds *via* this metal carbene compound according to the well-known following step (Ivin, 1997).



(R_1 = H, alkyl ; R_2 = alkyl)

2.4 Possible Routes to Metal Carbene Initiating Species

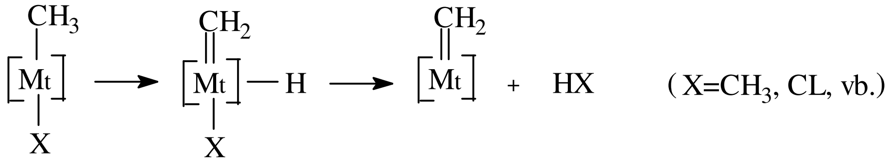
The carbene mechanism of olefin metathesis reaction is now extremely documented and accepted. It is assumed that olefin coordination to a metallocarbene leads to a metallacyclobutane which rearranges to a new olefin and a new metallocarbene. It is also well accepted that metathesis of cyclic or acyclic olefins also obeys the same mechanism which involves a carbene and a metallacyclobutane intermediate (Herisson and Chauvin, 1971).



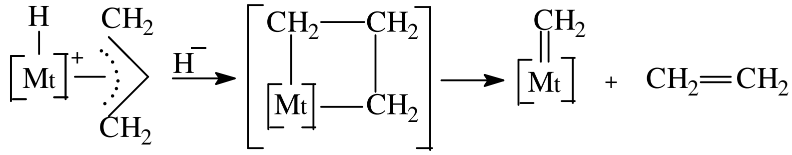
(Metal carbene mechanism)

The metal carbenes may be divided into three types: (i) Those consisting of an actual metal carbene, such as $W(=CPh_2)(CO)_5$; (ii) Those containing an alkyl or allyl group in one of the components, e.g. $EtAlCl_2$, from which a carbene ligand can readily be generated; (iii) Those having neither a performed carbene nor an alkyl group in any component. In the last case metal carbene can only be formed by interaction of the substrate olefin itself with the transition metal center. Some of the suggested mechanisms of formation of the active metal carbenes are shown in Figure 2.6.

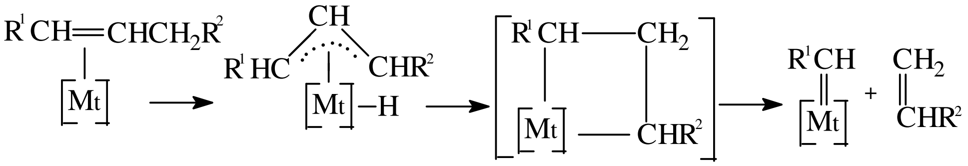
With every non-carbene catalyst system there is the question as to the nature of the initiating metal carbene complex and how it is formed from the catalyst/cocatalyst/olefin. When the cocatalyst contains an alkyl group, there is usually an obvious path whereby this becomes the source of the alkylidene group attached to the metal and there is much evidence from the initial products of reaction or from end groups in polymers formed by ROMP that can be brought to bear on this question (Ivin, 1983). When there is no cocatalyst the initiating metal carbene complex must result from a reaction between the catalyst and the substrate olefin (Gilet et al., 1983; Kazuta and Tanaka, 1987; Novak and Grubbs, 1988).



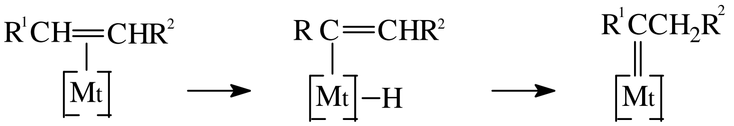
(a)



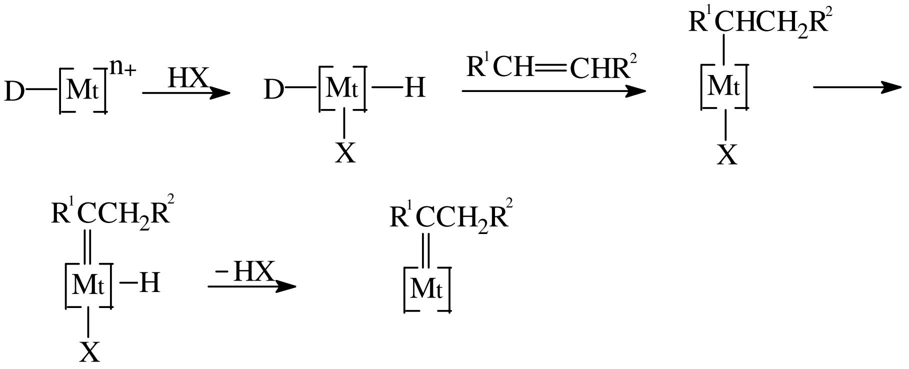
(b)



(c)

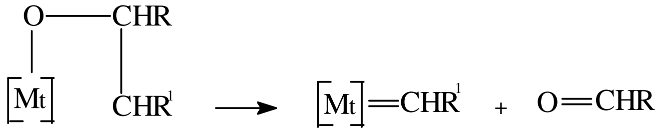


(d)



(e)

(Mt = metal and D = donor; HX = H_2O, ROH, PhOH, RCOOH, HCl, H_2, HO-Al(Si), e.g.)



(f)

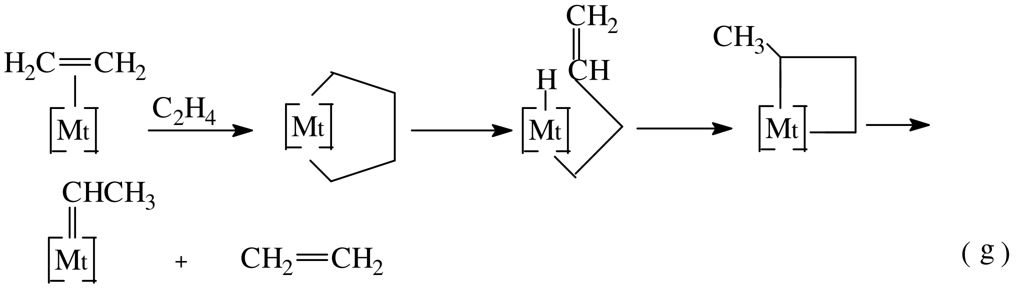


Figure 2.6 Possible routes to metal carbene initiating species in olefin metathesis.

The first, they may provide a alkyl ligand at the transition metal which can be subsequently converted into on alkylidene ligand by reductive elimination (Fig. 2.6, mechanism (a)). The presence of a cocatalyst or additive appears not always to be essential for activity on the only possible route to a metal carbene is then by direct interaction of the olefin with the transition metal site (Fig. 2.6, mechanisms (c), (d)). The π-allyl mechanism for formation of the initial metal carbene (Fig. 2.6, mechanism (b)). Hydroxilic compounds, hydridic compounds and hydrogen itself, may well assist the formation of Mt-H bonds, for which there is IR and NMR evidence in some systems. These in turn can provide a route to the formation of the initial metal-carbene (Fig 2.6, mechanism (e)).

2.5 Electrochemical Techniques

2.5.1 Cyclic voltammetry

In cyclic voltammetry, the sweep traces a triangular form; that is, the potential is first increased linearly to a peak and then decreased to its starting point at the same rate. Generally, the cycle is completed in a fraction of a second to a few seconds (Skoog,1985).

Figure 2.7 shows cyclic voltammetric curves for three reducible analytes. The solid curve is for reversible reactions. When the potential is first reversed (point B), the current remains positive and is largely due to the diffusion-controlled reduction of analyte. Ultimately, however, potential C is reached at which the analyte is no longer reduced; the current here is zero with further positive changes in the potential, oxidation of the previously reduced species begins and proceeds until its concentration reaches zero. The anodic peak D results.

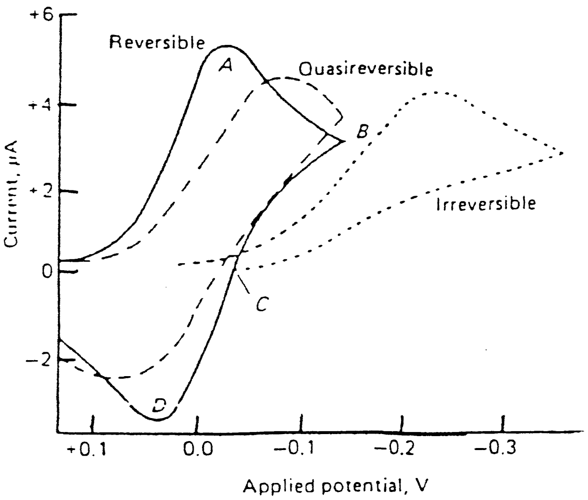


Figure 2.7 Cyclic voltammetric curves for three reducible analytes.

The curve labeled quasireversible is the voltammogram for an system in which the electron transfer process is not instantaneous. Here, the difference in potential between the cathodic and anodic peaks provides a measure of the relative rates of the reduction and oxidation reactions.

The third curve in figure 2.7 is a voltammogram for a irreversible electrode process. Here, only a cathodic peak is observed because the product formed in the initial reduction is not reoxidized at a significant rate.

Cyclic voltammetry, while not used for routine quantitative analyses, has become an important tool for the study of mechanisms and rates of oxidation-reduction processes, particularly in organic and metal organic systems. Often cyclic voltammograms will reveal the presence of intermediates in oxidation-reduction reactions. Usually platinum is used for fabrication of microelectrodes used with this technique.

2.5.2 Coulometric methods

Coulometric methods of analysis measure the quantity of electricity, that is, the number of coulombs, required to carry out a chemical reaction.

There are two general techniques used in coulometry. One, *the controlled-potential method,* maintain a constant electrode potential by continuously monitoring the potential of the working electrode as compared to a reference electrode. The current is adjusted continuously to maintain the desired potential. The other method, known as *constant-current coulometry*, maintains a constant current throughout the reaction period.

The quantity of electricity required is most commonly measured with an electronic integrator. The quantity of electricity or charge is measured in units of the coulomb (C) and the faraday (F). The coulomb is the quantity of charge that transported in one second by a constant current of one ampere.

If the current, *i*, remains constant as in constant-current coulometry, then the total number of coulombs is given by the product of current and time; thus

$$Q = i \times t$$

If, as in controlled- potential coulometry the current changes continuosly, then Q is given by the integration of time versus current ;

$$Q = \int_0^\infty I.dt$$

The faraday is the quantity of electricity that will produce one equivalent of chemical change at an electrode. Since the equivalent is an oxidation-reduction reaction corresponds to the change brought about by one mole of electrons, the faraday is equal to the charge of one mole of electrons. One faraday is equal to 96,487 C.

3. EXPERIMENTAL

3.1 Materials

3.1.1 Solvents

Purification of solvent is very important because the presence of water and organic impurities may cause exhaustion of products occuring during the electrochemical studies.

Dichlorometane (CH_2Cl_2) :

Dichloromethane was washed with concentrated H_2SO_4 until the acid is colourless, after taking of acidic phase, washed with water, and then with aqueous solution of Na_2CO_3, $NaHCO_3$ or NaOH (5%, w/w) and again with water, followed by drying over $CaCl_2$. It was then distilled over P_2O_5 under nitrogen, and kept under nitrogen. Dichloromethane, the dielectrical constant of which is 9.1, was purchased from Merck.

Carbon tetrachloride (CCl_4) :

Carbon tetrachloride was distilled, degassed and stored under nitrogen. It was purchased from Merck.

Chlorobenzene (C_6H_5Cl) :

Chlorobenzene (Aldrich) was dried over phosphorous (V) oxide and distilled under nitrogen.

Toluene ($C_6H_5CH_3$) :

Toluene was distilled, and stored under nitrogen. It was purchased from Merck.

Cyclohexane (C_6H_{12}) :

Cyclohexane was distilled, and stored under nitrogen. It was purchased from Merck.

Tetrahydrofuran (THF) :

Tetrahydrofuran required for dissolving the polymers was used as received (Merck).

Methanol (CH_3OH) :

Methanol required for quenching the reactions and precipitating the polymers was used as received (Merck).

Ethanol (C_2H_5OH) :

1 liter of absolute ethanol, which was purchased from Merck, in a 2 liters flask with 7g of clean dry sodium, and 25g of pure ethyl succinate was added and the mixture was refluxed for 2 hours in a system protected from moisture, and then the ethanol was distilled.

3.1.2 Olefins

All the olefins (Aldrich), except for norbornene (Aldrich, recieved as), were refluxed over KOH or Na metal and then distilled over CaH_2 under nitrogen atmosphere, and kept in dark bottles under nitrogen.

3.1.3 Phenols

The phenolic compounds (phenol, 4-*tert*-butylphenol, 2,4-di-*tert*-butylphenol, 2,6-dichlorophenol, 1-Naphthol) were used as obtained from the supplier (Aldrich).

3.1.4 Catalysts

$MoCl_5$ and $ReCl_5$ were supplied by Aldrich (99.9+%) and used as received. WCl_6 (Aldrich) was purified by sublimation to remove the more volatile impurities ($WOCl_2$ and $WClO_4$) under nitrogen atmosphere at 220 ºC, and kept under nitrogen atmosphere (Uchida et al., 1971). Chloro-aryloxide complexes of tungsten (VI), $W(OAr)_xCl_{6-x}$ (x = 2 or 4) were synthesized using WCl_6 and the appropriate phenol.

3.1.5 Cocatalysts

All cocatalysts, tetramethyltin ($SnMe_4$), tetraethyltin ($SnEt_4$), tetra-*n*-butyltin ($SnBu_4$), tetraphenyltin ($SnPh_4$), tetraphenyllead ($PbPh_4$), are commercial products obtained from Aldrich and were used as received.

3.2 Synthesis of Aryloxide Tungsten (VI) Complexes

The synthesis method of Quignard et al. was used to synthesise the tungsten (VI) aryloxide complexes (Quignard et al.1987). Treatment of WCl_6 with various unsubstituted and substituted phenols ArOH in toluene or carbontetrachloride solvents leads to chloro aryloxide complexes of tungsten, $W(OAr)_xCl_{6-x}$ (OAr = aryloxide; x = 2 or 4). All synthesis reactions were performed under nitrogen atmosphere. The complexes formed are stable in air at room temperature, and insoluble in pentane, hexane, and alcohols but are soluble in aromatic and chlorinated solvents. The oxo-chloro aryloxide complex, $WOCl_3(O\text{-}2,6\text{-}C_6H_3\text{-}Cl_2)$, in similar manner, was prepared as described by Bell (1992). The purity of complexes was tested by tin-layer cromatography.

3.2.1 Synthesis of dichlorotetrakis(aryloxy)tungsten(VI) complex ($W(O\text{-}C_6H_5)_4Cl_2$)

$$WCl_6 \quad + \quad 4\ C_6H_5OH \quad \xrightarrow[\text{reflux}]{CCl_4} \quad W(O\text{-}C_6H_5)_4Cl_2 \quad + \quad 4\ HCl$$

To tungsten hexachloride (WCl_6; 3.5g, 8.8 mmol) suspended in carbon tetrachloride (CCl_4; 20 mL) was added a solution of phenol (C_6H_5OH; 3.5g, 37 mmol) in carbon tetrachloride (CCl_4; 30 mL). The reaction mixture was stirred under reflux over one hour. The solvent of the resulting solution was evaporated. Removal of solvent followed by recrystallization from toluene/ethanol (1/2) at –5 ºC gave the pure product as black needles (3.9g, 70% yield). The product obtained was washed with ethanol, and dried under vacum for six hours and kept in dark bottles under nitrogen atmosphere.

3.2.2 Synthesis of dichlorotetrakis(4-*tert*-butylphenoxy)tungsten(VI) complex ($W(O\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu)_4Cl_2$)

$$WCl_6 \ + \ 4\ HO\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu \xrightarrow[\text{reflux}]{C_6H_5CH_3} W(O\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu)_4Cl_2 \ + \ 4\ HCl$$

To tungsten hexachloride (WCl_6; 2.985g, 7.5 mmol) suspended in toluene ($C_6H_5CH_3$; 20 mL) was added a solution of 4-*tert*-butylphenol ($HO\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu$; 4.5g, 30 mmol) in toluene ($C_6H_5CH_3$; 30 mL). The reaction mixture was stirred under reflux for six hours. Evaporation followed by recrystallization from toluene/ethanol (1/2) at –5 ºC gave the pure product as a black powder (3.8g, 60% yield). The product obtained was washed with ethanol, and dried under vacum for six hours and kept in dark bottles under nitrogen atmosphere.

3.2.3 Synthesis of dichlorotetrakis(2,4-di-*tert*-butylphenoxy)tungsten(VI) complex ($W(O\text{-}2,4\text{-}C_6H_3\text{-}t\text{-}Bu_2)_4Cl_2$)

$$WCl_6 \ + \ 4\ HO\text{-}2,4\text{-}C_6H_3\text{-}t\text{-}Bu_2 \xrightarrow[\text{reflux}]{C_6H_5CH_3} W(O\text{-}2,4\text{-}C_6H_3\text{-}t\text{-}Bu_2)_4Cl_2 + 4\ HCl$$

To tungsten hexachloride (WCl_6; 2.985g, 7.5 mmol) suspended in toluene ($C_6H_5CH_3$; 20 mL) was added a solution of 2,4-di-*tert*-butylphenol ($HO\text{-}2,4\text{-}C_6H_3\text{-}t\text{-}Bu_2$; 6.18g, 30 mmol) in toluene ($C_6H_5CH_3$; 30 mL). The reaction mixture was stirred under reflux over six hours. The solvent of the resulting solution was evaporated. The residue obtained was washed with ethanol, and dried under vacum for six hours. The product formed as a black powder (5.2g, 65% yield) was kept in dark bottles under nitrogen atmosphere.

3.2.4 Synthesis of tetrachlorobis(2,6-dichlorophenoxy)tungsten(VI) complex ($W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$)

$$WCl_6 + 2\ HO\text{-}2,6\text{-}C_6H_3Cl_2 \xrightarrow[\text{reflux}]{CCl_4} W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 + 2\ HCl$$

To tungsten hexachloride (WCl_6; 1.02g, 2.56 mmol) suspended in carbon tetrachloride (CCl_4; 20 mL) was added a solution of 2,6-dichlorophenol ($HO\text{-}2,6\text{-}C_6H_3Cl_2$; 0.83g, 5.1 mmol) in carbon tetrachloride (CCl_4; 20 mL). The reaction mixture was stirred under reflux for four hours. Removal of solvent followed by washing with ethanol gave the pure product as black microcrystals with green luster (1.3g, 80% yield). The product obtained was dried under vacum for six hours and kept in dark bottles under nitrogen atmosphere.

3.2.5 Synthesis of dichlorotetrakis(1-naphtoxy)tungsten(VI) complex ($W(O\text{-}1\text{-}C_{10}H_7)_4Cl_2$)

$$WCl_6 + 4\ HO\text{-}1\text{-}C_{10}H_7 \xrightarrow[\text{reflux}]{C_6H_5CH_3} W(O\text{-}1\text{-}C_{10}H_7)_4Cl_2 + 4\ HCl$$

To tungsten hexachloride (WCl_6; 1.0g, 2.5 mmol) suspended in toluene ($C_6H_5CH_3$; 20 mL) was added a solution of 1-naphtol ($HO\text{-}1\text{-}C_{10}H_7$; 1.44 g, 10 mmol) in toluene ($C_6H_5CH_3$; 30 mL). The reaction mixture was stirred under reflux over four hours. The solvent of the resulting solution was evaporated. The residue obtained was washed with ethanol, and dried under vacum for six hours. The product formed as a black powder (1.5g, 70% yield) was kept in dark bottles under nitrogen atmosphere.

3.2.6 Synthesis of oxotrichloro(2,6-dichlorophenoxy)tungsten(VI) complex ($WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$)

$$WOCl_4 \quad + \quad HO\text{-}2,6\text{-}C_6H_3Cl_2 \quad \xrightarrow{C_6H_{12}} \quad WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2) \quad + \quad HCl$$

To a quantity of tungsten oxytetrachloride ($WOCl_4$; 3.79g, 11.1 mmol) stirred in cyclohexane (C_6H_{12}; 50 mL) was added dropwise a solution of 2,6-dichlorophenol ($HO\text{-}2,6\text{-}C_6H_3Cl_2$; 1.18g, 11.1 mmol) in cyclohexane (C_6H_{12}; 25 mL). The dropwise addition of the phenolic solution was accomplished over a period of 30 min. During the phenol addition, the solution changed from orange to deep red and purple crystals precipitated from the reaction solution. The reaction mixture was stirred at room temperature for two hours. After this time, the reaction mixture was filtered to remove the dark red-purple crystalline product $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$, and the collected solids were washed with cyclohexane (10 mL) and dried under vacum; (4.2g, 81% yield).

3.3 Electronic Instrumentation

The electrochemical instrumentation consisted of a POS Model 88 potentiostat and EVI 80 Model voltage integrator (coulometer). The measurements were carried out under a nitrogen atmosphere in a three-electrode cell having a jacket through which water from a constant-temperature bath was circulated. In cyclic voltammetric experiments, a polished Pt disc electrode with a diameter of 0.10 cm, inlaid in a glass capillary of 0.80 cm was used as a working electrode and a Pt wire (2 cm^2) immersed in CH_2Cl_2/ 0.1 M tetra-*n*-butyl ammonium tetrafluoroborate ($TBABF_4$) separated from the electrolysis solution by a sintered glass disc was used as a counter-electrode. The reference electrode consisted of AgCl coated on a silver wire in CH_2Cl_2/ 0.1 M $TBABF_4$, which was also separated from the electrolysis solution by a sintered glass disc. Exhaustive controlled-potential experiments were carried out in an undivided cell with a macro working platinum foil electrode (2.0 cm^2) and an aluminum foil (2.0 cm^2) counter electrode. Electrolysis was carried out without the supporting electrolyte due to its deleterious effect on the catalyst system. For this reason, the distance between platinum working and aluminum counter electrode was kept constant and as small as possible (i.e. 2.0 mm) in order to keep the solution resistance to a minimum.

3.3.1 Preparation of electrochemical cell

The medium, where the electrochemical behavior of any substance is investigated in nonaqueous electrochemical studies is to be refined from O_2 and water. Thus, all electrochemical experiments were carried out under pure and dry nitrogen. A special electrochemical cell was used in the experiments, as shown in Figure 3.1. The cell was washed with basic $KMnO_4$, concentrated HCl, acidic $K_2Cr_2O_7$, distilled water and alcohol, before use. Then it was dried at 120 ºC, and cooled under nitrogen atmosphere and becomes ready to use for electrochemical experiments.

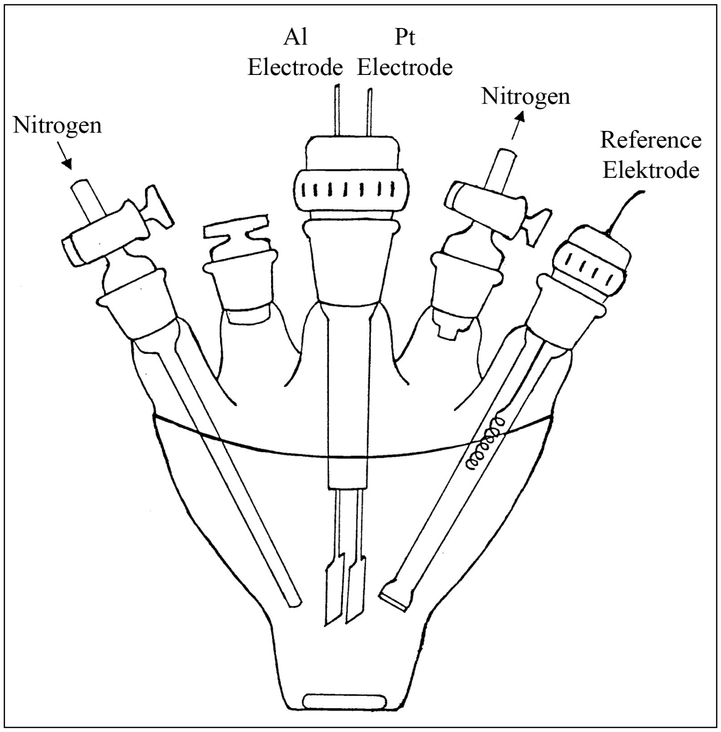


Figure 3.1 The electrochemical cell.

3.3.2 Activation of catalyst in electrochemical catalyst system

All the reactions were carried out under nitrogen atmosphere and at ambient temperature. All electrolysis processes were conducted for 3 hours, except for those performed for the effect of electrolysis time on conversion. Before adding the dichloromethane and catalyst to cell, nitrogen was passed through the empty cell for a while. $MoCl_5$ (0.15 g, 0.55 mmol) was introduced into the electrochemical cell containing CH_2Cl_2 (20 ml) and a red solution was observed. The electrodes were put into the cell, and connected with cables to potentiostat. Reductive electrolysis at +0.7 V (at first reduction potential) was applied to the red solution for 3 h. The color of the solution darkened progressively. Aliquots from this catalytic solution were used in polymerization reactions.

3.3.3 Polymerization reactions in electrochemical catalyst system

All reactions were initiated in the solution, at room temperature and under dry nitrogen atmosphere. To optimize the reaction conditions, a series of experiments were performed by varying the olefin/catalyst ratio, reaction time and electrolysis time. A typical reaction was as follows: 1ml of the catalytic solution was taken with an automatic pipette from the cell and added to norbornene (0.30 g, in 1 ml of dichloromethane) in a Schlenk tube containing a magnetic stir bar. A rapid gelation was observed and stirring was continued until prevented by the viscosity increase. The reaction was quenched by methanol addition after 30 min. The polymers formed were washed with methanol, dissolved in THF and reprecipitated with methanol to remove the catalytic residues, dried and weighed. Polymerization yield (%) was defined by comparing the weight of the polymer with the weight of the monomer used.

3.4 Catalytic Reactions in Classical Catalyst System

All catalytic reactions were performed in an inert atmosphere with Schlenk techniques under nitrogen. A typical reaction was as follows: the aryloxide tungsten based procatalyst (5×10^{-5} mol) was placed in the reaction vessel under nitrogen, and the solvent chlorobenzene (2.5 mL) added. The mixture was then heated to 85 ºC after which the cocatalyst (1.5×10^{-4} mol) was added. 1-octene (2.5×10^{-3} mol) was added to the reaction mixture after an activation period of 10 min at 85 ºC and the reaction mixture was stirred for 5 h. The reaction was quenched by methanol addition and an internal standard for GC analysis i.e., hexadecane was added to the reaction mixture. All polymerization reactions were also carried out in a solution in a similar manner to metathesis reaction of 1-octene as described above. In the metathesis copolymerization experiments, a mixture of equimolar of cyclic olefins was introduced to the reaction medium. The polymers formed were washed with methanol, dissolved in THF and reprecipitated with methanol to remove the catalytic residues, dried and weighed. Polymerization yield (%) was defined by comparing the weight of the polymer with the weight of the monomer used.

3.5 Analysis

The product mixtures obtained from the metathesis reactions of acyclic olefins were analysed by GC-MS (gas chromatography-mass spectrometry) technique. Gas chromatographic analyses were performed on a Shimadzu GCMS-QP5050*A* using an optima column, 5-1.0 µm (50 m × 0.32 mm), in a temperature range of 50-250 ºC (8 ºC $\min^{-1}$) and the carrier gas was helium at 1 ml $\min^{-1}$. The temperatures of injection and detector were 275 ºC and 280 ºC respectively.

3.6 Calculations

The internal standard method (with *n*-hexadecane) was used for the quantitative determinations of the products. Relative response factors were determined for authentic samples. The relation between peak areas and concentration;

$$A_i = f_i \times G_i \tag{1}$$

A_i : the area of the component *i*
f_i : the response factor for component *i*
G_i : the amount of component *i*

The response factors for each component are calculated relative to standard. The number of moles of each product can be calculated by using equation (2).

$$n_i = (f_i / f_{st}) \times (A_i / MW_i) \times (MW_{st} / A_{st}) \times n_{st} \qquad (2)$$

Products are given according to their carbon numbers and symbolized as C_n.

In the olefin metahesis and ring-closing metahesis reactions, the total conversion of the products at the end of the reaction, according to number of moles was calculated.

For metathesis product;

$$\text{Conversion (\%)} = \frac{\text{converted olefin (mmol)}}{\text{initial olefin (mmol)}} \times 100$$

In the metathesis polymerization reactions, polymerization yield (%) was defined by comparing the weight of the polymer with the weight of the monomer used (but, for copolymerization reactions, the ‘total’ monomer used).

For the resulting polymer;

$$\text{Yield (\%)} = \frac{\text{weight}_{\text{polymer}}}{\text{weight}_{\text{monomer used}}} \times 100$$

3.7 Characterization of Polymers

^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker GmBH 400 MHz high-performance digital FT-NMR Spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as the reference. IR spectra of polymers were obtained from KBr pellets. Infrared analyses were performed using a Mattson 1000 Model FT-IR spectrophotometer.

The following symbols are used for the metathesis copolymerization reactions:
f_1, f_2 : mole fractions of monomers, M_1, M_2, respectively in the feed.
F_1, F_2 : mole fractions of M_1, M_2 units, respectively in the copolymer.
σ_c (M_1M_1) : fraction of cis double bonds in M_1M_1 dyads; likewise for M_1M_2, M_2M_2.

Gel permeation chromatography (GPC) data were obtained using a Shimadzu LC-10AD*VP* liquid chromatograph equipped with a Shimadzu SPD-10A*VP* UV detector, relative to polystyrene standards. Samples were prepared in THF (0.5 % w/v) as eluent and passed through a µ-styragel column. A constant flow rate of 1 ml min^{-1} was maintained at 25 ºC.

4. RESULTS AND DISCUSSION

4.1 An Investigation of Applications of Classical and Electrochemical Catalyst Systems on Olefin Metathesis Reactions

Olefin metathesis is of great value in organic and polymer synthesis. The reactions do not ocur spontaneously. They all require the presence of a catalyst system containing a transition metal compound (precursor), frequently in conjuction with a second compound (cocatalyst) and sometimes a third (promoter). Over the years, many homogeneous catalytic systems were developed for the olefin metathesis reactions. Transition metal halides such as WCl_6, $MoCl_5$, $ReCl_5$, $RuCl_3$, etc. are known as precursors in the metathesis reactions. The search for the ideal homogeneous catalytic system for the alkene metathesis has led to inter alia the discovery of the particular catalytic activity of tungsten (VI) aryloxide complexes of the type $W(OAr)_xCl_{6-x}$ (OAr = unsubstituted or substituted phenoxides; x = 2 or 4). These complexes are generally stable in air and known to provide very active metathesis catalysts for linear, cyclic and functionalised alkenes in the presence of a cocatalyst like R_xAlCl_{3-x}, R_4M (M = Sn, Pb). Aryloxide ligands offer some advantages in that their electron-withdrawing properties can be varied by changing the substituents on the ring and their steric effect on tungsten can be modified by varying the bulkiness of the substituents on the *o,o'*-position on the aryloxide.

In this study, the activation of some transition metal halides and the synthesized aryloxide tungsten complexes *via* electrochemical or classical method and their applications on olefin metathesis reactions were first investigated. For this purpose, few di- and tetrasubstituted aryloxide tungsten (VI) complexes ($W(OAr)_2Cl_4$ and $W(OAr)_4Cl_2$ type respectively) were synthesized from WCl_6 and phenol derivatives by using the synthesis method of Quignard et al., and also an oxo-chloro aryloxide complex, $WOCl_3(OAr)$, in similar manner, was prepared as described by Bell.

4.1.1 The Electrochemical behavior and activation of catalyst precursors

The generation of active moieties for metathesis of alkenes from WCl_6 via electrohemical technique was first studied by Gilet et al. and the electroreduction of this salt at a platinum cathode with an aluminum anode under controlled potential was reported to produce an active species for the metathesis of alkenes under mild conditions (Gilet et al., 1978, 1983). One of the most interesting aspects of the electrochemical technique is that the oxidation state of the reduced species can be stabilized at a controlled potential. Furthermore the absence of cocatalyst avoids the side reactions such as izomerization, alkylation of the substrates occuring when chemical reducing agents are used. For these reasons, electrochemistry seems to be a useful tool for the synthesis of catalytic moieties. A recent report for the electrochemically generation of an alkene metathesis catalyst from methylene chloride solution of WCl_6 was described by Düz et al. (2003).

For the synthesis of new catalytic species generated electrochemically as metathesis catalyst, the electrochemical behaviours of some metal halides such as $MoCl_5$, $ReCl_5$ and some aryloxide tungsten (VI) complexes such as $W(O\text{-}C_6H_5)_4Cl_2$, $W(O\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu)_4Cl_2$, $W(O\text{-}2,4\text{-}C_6H_3\text{-}t\text{-}Bu_2)_4Cl_2$, $W(O\text{-}1\text{-}C_{10}H_7)_4Cl_2$, $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$, $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ were first studied.

For this reason, firstly, a series of cyclic voltammetric experiments was performed. The electrochemical behaviours of these catalyst precursors at a platinum disc electrode in a solution of 0.01 M of methylene chloride (CH_2Cl_2) as a solvent were studied in order to obtain the cyclic voltammetric curves. Tetra-*n*-butyl ammonium tetrafluoroborate ($TBABF_4$, 0.01 M) was used as a supporting electrolyte. Cyclic voltammetric data for the compounds reported here summarized in Table 4.1. As shown in Table 4.1, the reduction potentials for these catalyst precursors, especially for aryloxide tungsten complexes, are generally negative potentials.

Table 4.1 Electrochemical data in methylene chloride for the studied compounds.[a]

Compound		**$E°$ (CH_2Cl_2)** [b,c]	
$MoCl_5$	+1.10 V	–0.30 V	–1.10 V
$ReCl_5$	+0.07 V	–0.90 V	–1.50 V
$W(O\text{-}C_6H_5)_4Cl_2$	–0.83 V		
$W(O\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu)_4Cl_2$	–0.54 V	–1.66 V	
$W(O\text{-}2,4\text{-}C_6H_3\text{-}t\text{-}Bu_2)_4Cl_2$	–0.10 V	–1.64 V	
$W(O\text{-}1\text{-}C_{10}H_7)_4Cl_2$	+0.80 V	–0.59 V	–1.59 V
$W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$	+0.35 V	–1.00 V	
$WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$	+0.50 V		

[a] All measurements were recorded under N_2 with 0.01 M $TBABF_4$ as supporting electrolyte.
[b] All potentials are referenced to Ag/AgCl in CH_2Cl_2.
[c] The scan range was –2.0 to +2.0 V. The scan rate was 100 mV s^{-1}.

For all catalyst precursors, all constant potential electrolysis processes were carried out at more negative potentials than the reduction peak values that were determined from their cyclic voltammograms. These electrolysis experiments resulted that only $MoCl_5$ precursor could be activated *via* electrochemical technique for olefin metathesis reactions. With the other catalyst precursors, $ReCl_5$ and W-based complexes, to obtain metathetically active species for olefin metathesis reactions *via* ‘electrogeneration’, couldn’t be achieved.

This presented work first examines the activity of the species obtained from $MoCl_5$ *via* electroreduction in the metathesis and the other related reactions as an investigation of electrochemical catalyst systems.

4.1.2 The classical activation of catalyst precursors

Even though there are few studies on metathesis and the related reactions initiated by aryloxide tungsten (VI) based catalyst systems, much scientific work has been done on the metathesis reactions carried out by $MoCl_5$ and $ReCl_5$ based 'classical catalyst systems'.

With this purpose, the 'classsical activations' of the synthesized aryloxide tungsten (VI) complexes in the presence of a cocatalyst like MR_4 (M = Sn, Pb; R = Me, Et, Bu and Ph) were studied. No metathesis activity was observed by tetra-substituted aryloxide tungsten complexes, $W(O\text{-}C_6H_5)_4Cl_2$, $W(O\text{-}4\text{-}C_6H_4\text{-}t\text{-}Bu)_4Cl_2$, $W(O\text{-}2,4\text{-}C_6H_3\text{-}t\text{-}Bu_2)_4Cl_2$, $W(O\text{-}1\text{-}C_{10}H_7)_4Cl_2$ when they were associated with Sn-based cocatalysts and Pb-based cocatalyst, *via* classical method.

As to di-substitued complex, $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$, and oxo-chloro aryloxide complex, $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$, the two-component classsical systems containing these aryloxide complexes and a cocatalyst were active metathesis catalysts towards the olefin metathesis (OM), ring-opening metathesis polymerization (ROMP), acyclic diene (ADMET) metathesis poymerization and ring-closing metathesis (RCM) reactions.

In the light of all of this, the applications of electrochemically generated $MoCl_5$ based catalyst system and these two-component classical systems, containing these aryloxide complexes and a cocatalyst on metathesis and related reactions, were investigated in detail in this study.

4.2 Electrochemical Behavior of $MoCl_5$ in Methylene Chloride

The reduction potentials of the $MoCl_5$ were determined by cyclic voltammetric method. The voltammogram of $MoCl_5$ in methylene chloride-0.01 M tetra-*n*-butyl ammonium tetrafluoroborate ($TBABF_4$) at a platinum disc electrode is shown in Figure 4.1 (b).

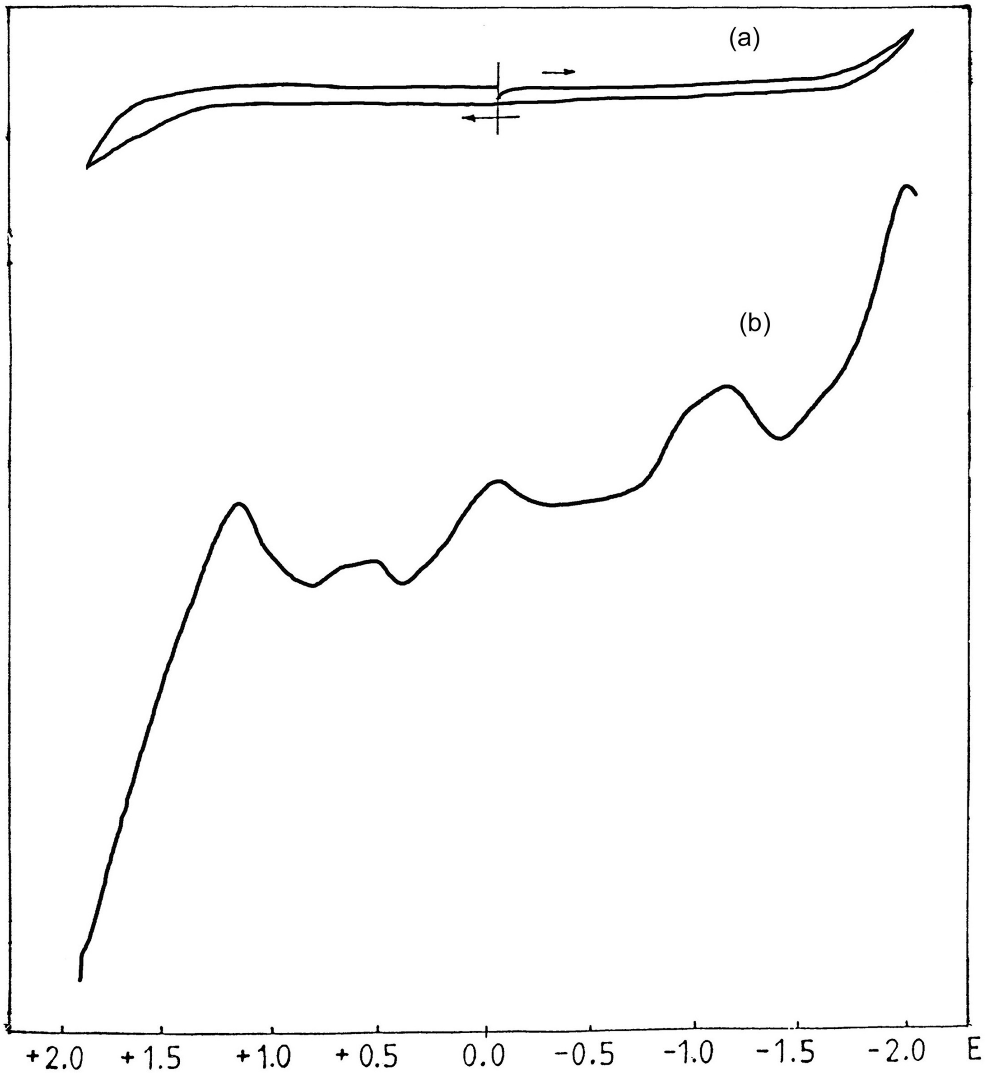


Figure 4.1 **(a)** The cyclic voltammogram of dichloromethane-0.01M $TBABF_4$.
(b) The voltammogram of $MoCl_5$ in dichloromethane-0.01M $TBABF_4$.

Figure 4.1 (a) shows the cyclic voltammogram of the blank solution of the $TBABF_4$ (0.01 M) in CH_2Cl_2, between –2.0 V and +2.0 V potentials at the scan rate of 100 mV/s. As seen in Figure 4.1 (a), no electrochemical response was seen at blank solution of the $TBABF_4$ (0.01 M) between –2.0 V and +2.0 V potentials.

It has been difficult to obtain voltammetric curves, as $MoCl_5$ reacts almost immediately with the supporting electrolytes. For this reason, the cycle was not completed. As seen the voltammogram of $MoCl_5$ in Figure 4.1 (b), there are three half-wave potentials of reduction. The first, second and third reductions are easily observed with a peak potential of +1.10 V, –0.30 V and –1.10 V, respectively. It is also considered that the observed peak between first and second reductions appears due to chemical degradation.

The reductive electrolysis studies at +0.7 V, which is more negative potential than the first reduction peak value, produced catalytically active species. All reductive electrolyses were done at +0.7 V for 3 hours.

4.3 ROMP Reactions by Electrochemically Generated $MoCl_5$-Based Catalyst

Polymerization of cycloolefins can proceed via two main pathways: either via the opening of C=C double bonds with the formation of saturated polymers with cyclic units in the main chain or via the ring opening leading to unsaturated linear polymers. Addition polymerization, cis- and trans- content, and the other properties depend on the catalyst chosen. The ring-opening metathesis polymerization is quite different as compared to the other polymerization prosesses. The double bond is preserved during the ring opening, and the reaction has high stereospecifity (polymerization of mono- and bicyclic olefins), and occurs under moderate conditions. Except for a few cases, (for example cyclohexene) the reaction may provide polyalkenamer. From these polyalkenamers, some alkenamers such as polypentenamer and polyoctenamer have properties as rubber. Polynorbornene and its derivatives show properties like plastic (Nicolescu, 1985).

In this study, ring-opening metathesis polymerization (ROMP) of some bicyclic olefins, such as norbornadiene, dicyclopentadiene and norbornene by electrochemically generated $MoCl_5$-based catalyst system were first experimented.

4.3.1 ROMP of dicyclopentadiene

Ring-opening metathesis polymerization of dicyclopentadiene (DCPD) can take place by two different pathways: in the first, the reaction occurs with opening of the norbornene unit leading to linear polydicyclopentadiene while in the second both the norbornene and cyclopentene rings are successively opened forming a cross-linked polymer. The homopolymerization of dicyclopentadiene (DCPD) has been studied using various metathesis catalyst systems which are typically composed of a transition metal halide and a non-transition metal cocatalyst. The structure of the resulting polymer depends upon the identity of both catalyst componenets, ranging from a highly cross-linked, insoluble polymer to one that is linear and completely soluble. The formation of polydicyclopentadiene is thought to occur as illustrated in Figure 4.2, through the ring-opening metathesis polymerization (ROMP) of the strained norbornene ring. The olefin present in the cyclopentene ring is also assumed to undergo a ROMP reaction leading to cross-linked polymer. This reasonable assumption has been accepted for more than 35 years, primarily due to the difficulty associated with characterizing cross-linked polymers.

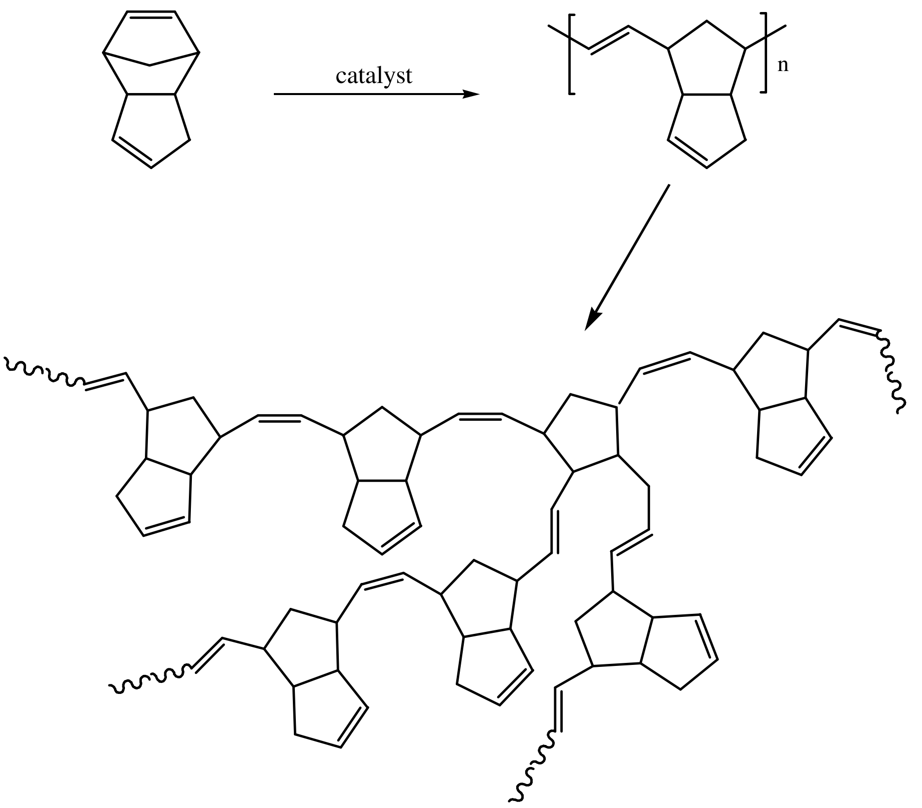


Figure 4.2 Currently accepted mechanism for the polymerization of dicyclopentadiene (DCPD).

ROMP of dicyclopentadiene by electrochemically generated $MoCl_5$-based catalyst system produced ‘cross-linked’ polymers of DCPD. The obtained polymers were insoluble in common solvents. IR spectrum of the polymer is shown in Figure 4.3. The spectrum indicates that the polymer has high-trans content by the high ratio of the intensity of the 970 cm^{-1} (trans-bond) peak to that of the 740 cm^{-1} (cis-bond) peak. The spectrum of the polymer indicates that the product obtained is a metathetic polymer, which forms via ring-opening. In addition, the presence of the bands around 1650 cm^{-1} (C=C vibrations) also supports that the double bonds are retained in the polymer.

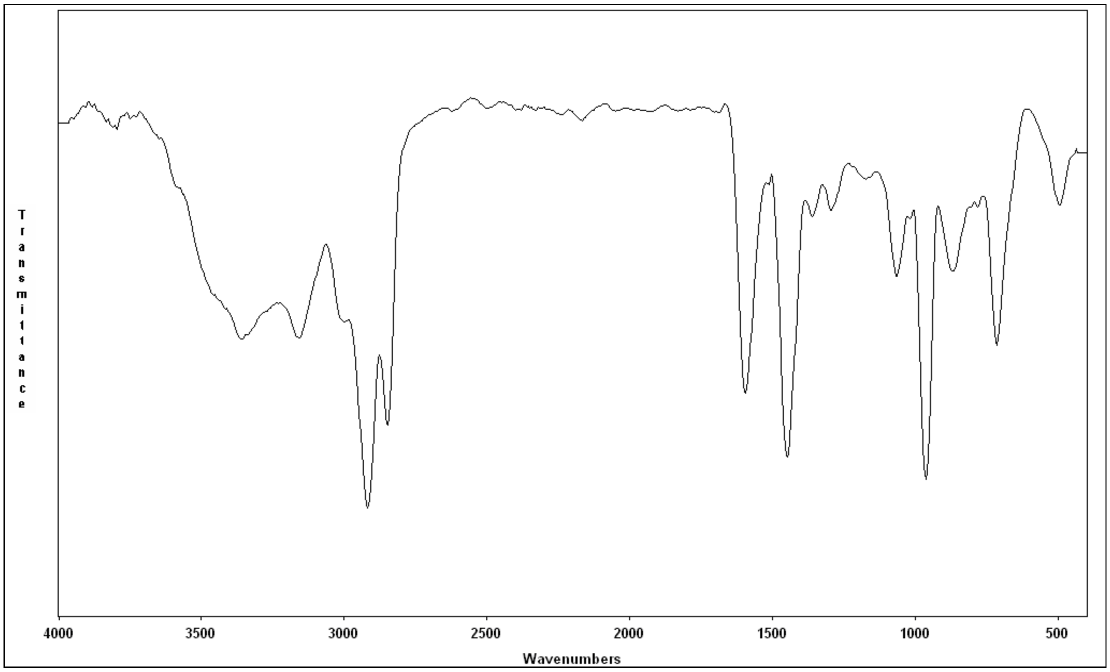


Figure 4.3 FT-IR spectrum of poly(DCPD) made using $MoCl_5$-ē-Al-CH_2Cl_2 catalyst system.

With electrochemically generated $MoCl_5$-based catalyst system, optimum parameters for polymerization conditions such as olefin/catalyst ratio, reaction time were determined.

4.3.1.1 Effect of olefin / catalyst ratio on ROMP of dicyclopentadiene

With this purpose, 0.0275 mmol of catalyst was added to different amounts of olefin. Polymerizations were carried out at ambient temperature, for 24 hours. The polymers obtained were weighed, and the percentage yields were calculated.

Figure 4.4 shows the effect of olefin / catalyst ratio on the yield of poly(DCPD). As clearly seen from the figure, the polymerization yield increases with the amount of olefin used, and reaches a maximum at a certain olefin / catalyst ratio which is around 300.

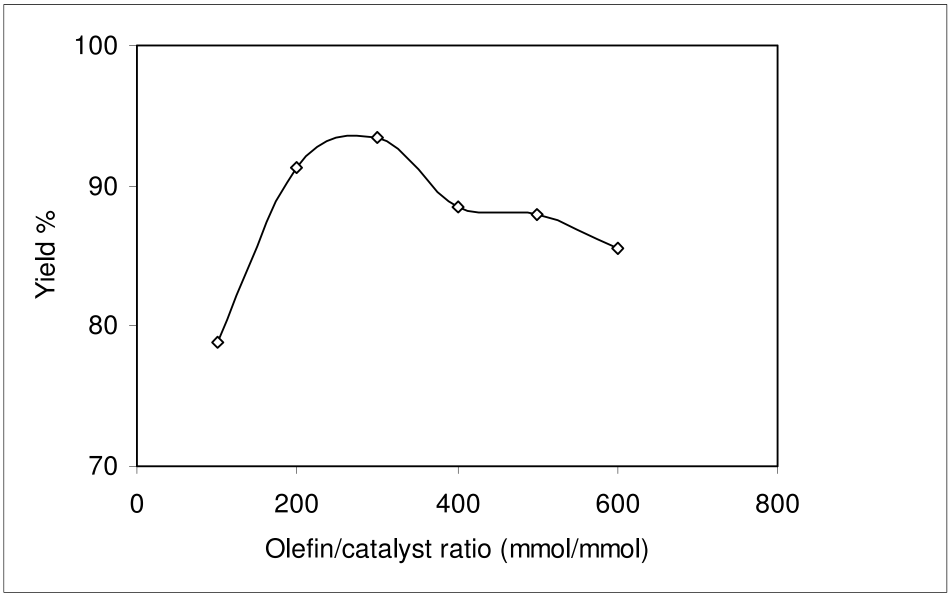


Figure 4.4 The effect of olefin / catalyst ratio on the yield of poly(DCPD).

4.3.1.2 Effect of reaction time on ROMP of dicyclopentadiene

At this stage, the effect of the reaction time on conversion of DCPD was examined. The olefin / catalyst ratio was kept at 300, and reaction was quenched by the addition of methanol after 0,5, 1, 2, 4, 8, and 16 minutes from the start of reaction. The percentage conversions to the polymers obtained were calculated.

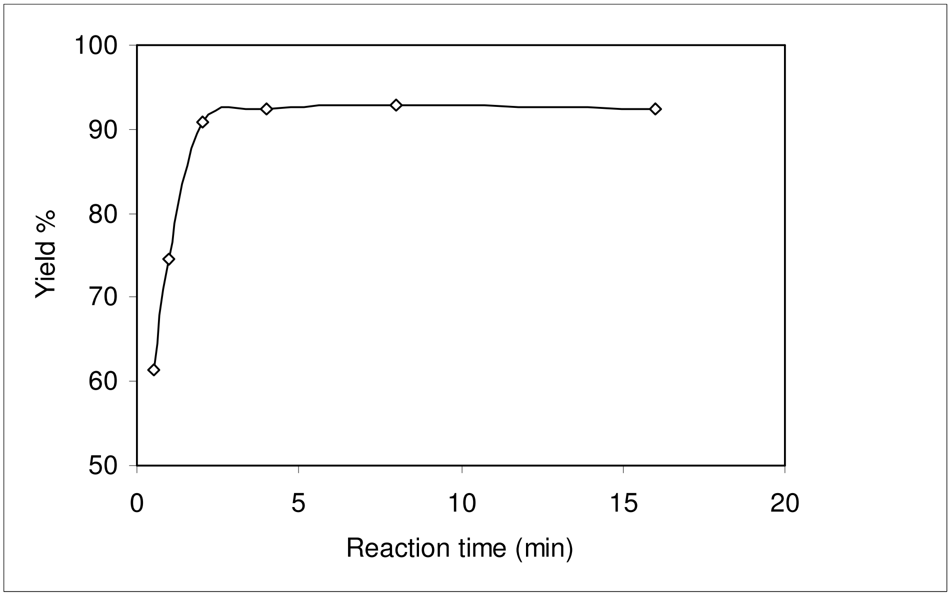


Figure 4.5 The effect of reaction time on the yield of poly(DCPD).

Conversion increases with reaction time, and reaches a maximum in about 4 minutes, as seen in Figure 4.5.

4.3.2 ROMP of norbornadiene

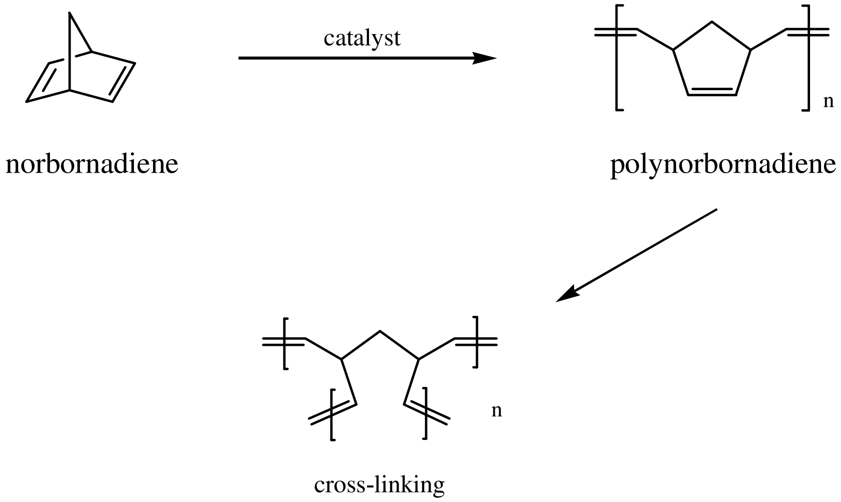


Figure 4.6 The metathesis polymerization of norbornadiene (NBD).

The ring-opening metathesis polymerization of norbornadiene (NBD) is shown as illustrated in Figure 4.6. Polymers obtained from norbornadiene were observed not to dissolve in organic solvents due to cross-linking. IR spectrum of the polymer exhibited the same characteristics as observed for poly(DCPD) indicating that the product is a metathetic polymer (Figure 4.8).

4.3.2.1 Effect of olefin / catalyst ratio on ROMP of norbornadiene

At this stage, by adding 0.0275 mmol of catalyst to different amounts of olefin, optimum olefin / catalyst ratio was determined. Polymerizations were carried out at ambient temperature, for 24 hours. The polymers obtained were weighed, and the percentage conversions were calculated.

Figure 4.7 shows the effect of olefin / catalyst ratio on the conversion of norbornadiene. As seen from the figure, conversion to the polymer increases with the amount of olefin used, and passes through a maximum at a certain olefin / catalyst ratio which is around 200.

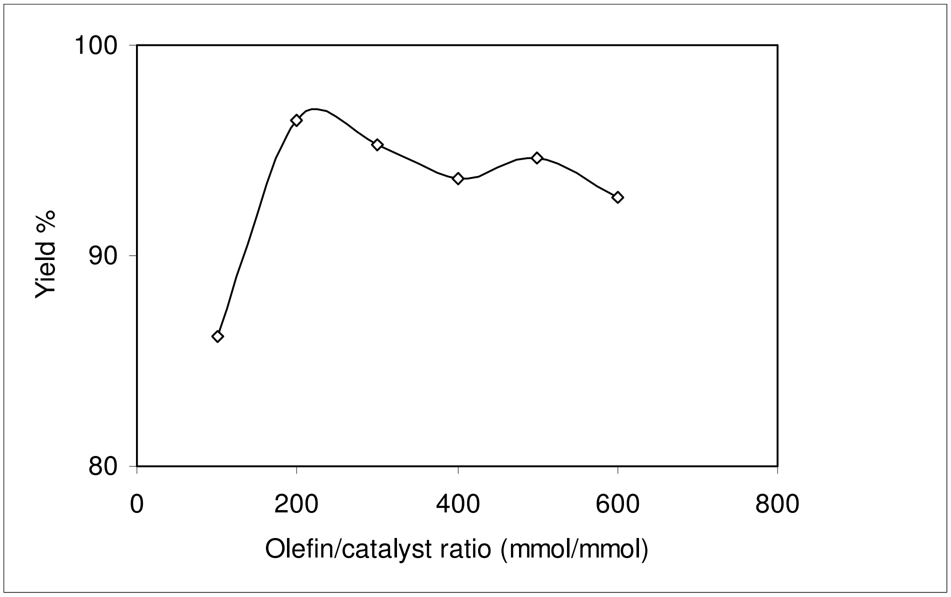


Figure 4.7 The effect of olefin / catalyst ratio on the yield of poly(NBD).

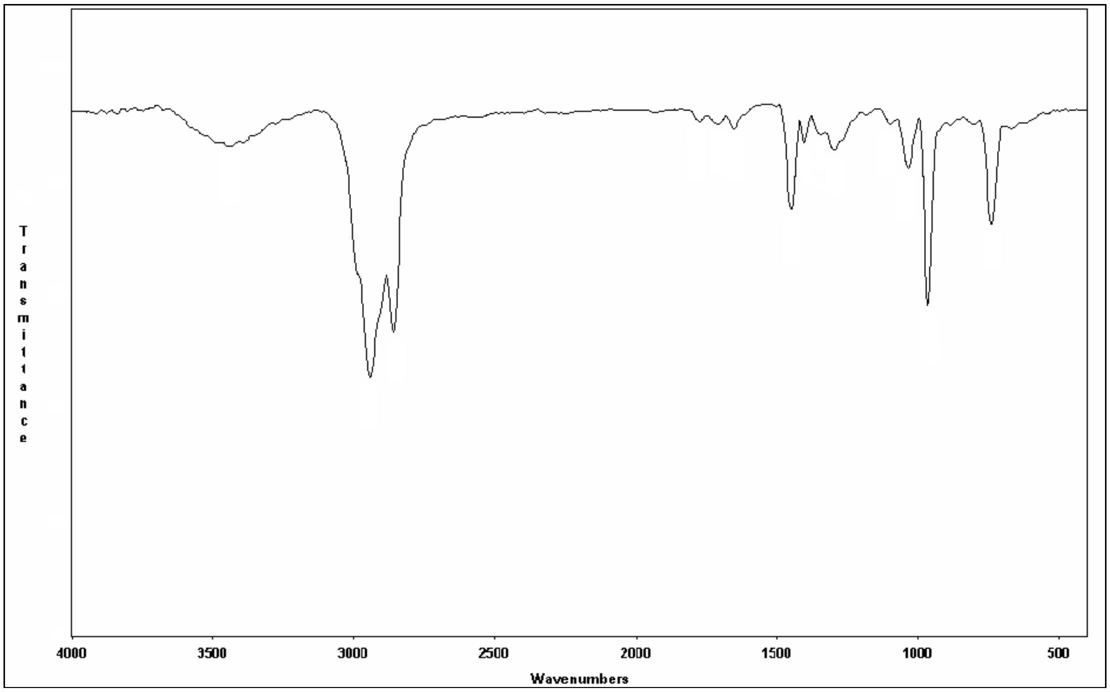


Figure 4.8 FT-IR spectrum of poly(NBD) made using $MoCl_5$-ē-Al-CH_2Cl_2 catalyst system.

4.3.3 ROMP of norbornene

The polymerization of norbornene is an important area of research because the microstructure of polynorbornene can provide useful insight into the mechanism of ROMP reactions. There are numerous studies involving the applications of a wide range of different catalyst systems in the ROMP of norbornene and its derivatives. In the present study, the application of the electrochemically generated molybdenum-based catalyst system $MoCl_5$-ē-Al-CH_2Cl_2 to ring-opening metathesis polymerization of bicyclo[2.2.1]hept-2-ene (norbornene) is described. The polymer product has been characterized by ^1H and ^{13}C NMR, IR and gel-permeation chromatography techniques. In addition, the influence of reaction parameters, e.g., reaction time, electrolysis time and catalyst aging time, on conversion has been analysed in detail. The results are compared, in terms of the reaction conditions and polymer microstructure with those obtained by the WCl_6-ē-Al-CH_2Cl_2 system.

All reactions were initiated in the solution, at room temperature and under dry nitrogen atmosphere. A series of polymerizations was conducted at ambient temperature in order to estimate the polymer yield quantitatively. At first, a set of experiments was performed by varying the olefin / catalyst ratio from 40:1 to 400:1. Conversion to polymer was obtained in maximum yield when the olefin / catalyst ratio was 160. This ratio has been found as 125 for the tungsten-based catalyst system.

The ring-opening polymerization of norbornene by olefin metathesis catalysts leads to a polymer, with chains containing 1,3-disubstituted cyclopentane rings (Figure 4.9).

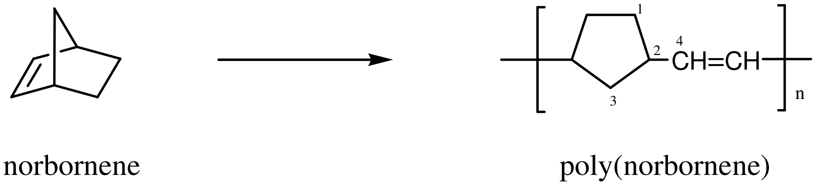


Figure 4.9 Ring-opening metathesis polymerization (ROMP) of norbornene.

The polymers obtained were characterized by ^1H and ^{13}C NMR and GPC techniques. GPC performed in THF allowed determination of $\overline{M}_w = 130000$ and polydispersity index PDI = 2.15 (Table 4.2). The resulting polynorbornenes are completely soluble in common organic solvents. As shown in Table 4.2, the electrochemical molybdenum-based system leads to polymers of higher molecular weight and lower polydispersity in comparison with the electrochemical tungsten-based system.

^1H and ^{13}C NMR spectroscopic data for the resulting polymer obtained in the presence of the $MoCl_5$-ē-Al-CH_2Cl_2 system are consistent with the data previously reported for the polymers of norbornene prepared via ROMP by other catalyst systems (Ivin, 1983, Dragutan et al., 1985, Ivin and Mol, 1997).

The geometric structure of polynorbornene was determined from ^1H and ^{13}C NMR spectra according to Ivin and co-workers (Ivin et al., 1977; 1978 and 1979, Greene et al., 1986). The ^{13}C NMR spectrum (Fig. 4.10) consists of a group of olefinic carbon peaks (δ = 130–135 ppm), and a group of upfield peaks (δ = 30–50 ppm) due to the ring-carbon atoms. The cis- and trans-ethylenic carbon atoms give two multiplets, related to C^4 carbon, centered respectively at 133.88 ppm and 133.02 ppm. A comparison of these two peaks corresponding to C^4 carbon allows estimation of the trans stereoselectivity of this catalyst system. Since the C^2, C^1 and C^3 chemical shifts in the polymer are sensitive to the cis or trans configuration of the two nearest double bonds, a detailed analysis of the ^{13}C NMR spectrum provides a rich source of information concerning the microstructure of the polymer chain (Ivin et al., 1977; 1978 and 1979, Greene et al., 1986). Table 4.3 gives the peak assignments of polymer obtained in the presence of the $MoCl_5$-ē-Al-CH_2Cl_2 system. The relative proportions of double-bond sequences, represented as trans-cis (tc), trans-trans (tt), cis-cis (cc) and cis-trans (ct) units, were determined from the four methine carbon (C^2) signals at δ_c 43.44 (tc), 43.15 (tt), 38.66 (cc) and 38.42 (ct). Here, the chain carbon atoms that are located between two double bonds are labelled as cc, ct, tc or tt. The first letter denotes the cis or trans structure at the nearest double bond; the second letter, at the next nearest double bond.

In this way, the reactivity ratios, r_t = tt / tc and r_c = cc / ct, were calculated as r_t = 2.32 and r_c = 0.62, giving an $r_t r_c$ value of 1.44. The fraction of cis double bonds σ_c was estimated as 0.41 (average of four values derived from C^4, C^2, C^1 and C^3 signals) (Fig. 4.11). The σ_c and $r_t r_c$ values thus obtained characterize a highly trans polymer with a slightly blocky distribution of cis and trans structures. Ivin et al. (1979) reported that polynorbornenes with a fraction of cis-double bond σ_c up to 0.35 showed a 'random' distribution of cis and trans structures ($r_t r_c$ = 1), whereas polymers having σ_c = 0.35–0.85 showed a 'blocky' distribution ($r_t r_c > 1$) with $r_t r_c > 5$ in some cases. Also, an increase of σ_c increases and reduces the r_c and r_t values respectively (Ivin et al., 1979, Bokaris and Kosmass, 2003). A comparison of the fraction of cis double bonds σ_c, the reactivity ratios r_c and r_t, and $r_t r_c$ values ($r_t r_c > 1$ related to blocky distributions of cis and trans double bonds) in the polymerization of norbornene with the electrochemical molybdenum- and tungsten-based catalyst systems are shown in Table 4.2. It is remarkable that the $MoCl_5$-ē-Al-CH_2Cl_2 catalyst system gave a polynorbornene of a high trans content (ca 60% trans), whereas the WCl_6-ē-Al-CH_2Cl_2 catalyst system produced a polymer with a high cis content (ca 60% cis), exhibiting similar stereochemical characteristics seen in the previous ROMP systems based on $MoCl_5$ and WCl_6. The results correlate well with the literature, that the polymers produced from WCl_6-based systems are of intermediate cis-content (Ivin et al., 1979, Bokaris and Kosmass, 2003, Dimonie et al., 1992, Dragutan et al., 1998). According to Ivin et al. (1979), steric interactions around the active center and the higher oxidation state of the metal favour the formation of cis double bonds. The mechanism proposed in the WCl_6-ē-Al-CH_2Cl_2 catalyst system involves the initial formation of the olefin adduct with the WCl_5^+ species (Düz et al., 2003). The observed higher cis fraction of the polymer obtained with WCl_6-ē-Al-CH_2Cl_2 catalyst system conforms with the suggested mechanism that the olefin entering the cage around tungsten (VI) prefers the cis orientation, leading to cis double bonds in the polymer.

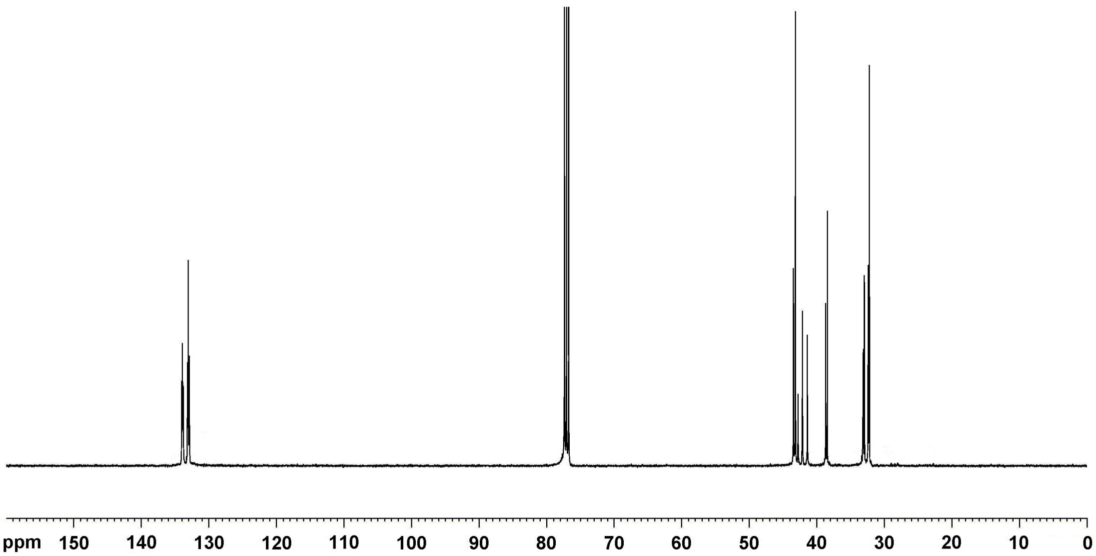


Figure 4.10 ^{13}C NMR spectrum of polynorbornene made using $MoCl_5$-ē-Al-CH_2Cl_2 catalyst system (in $CDCl_3$).

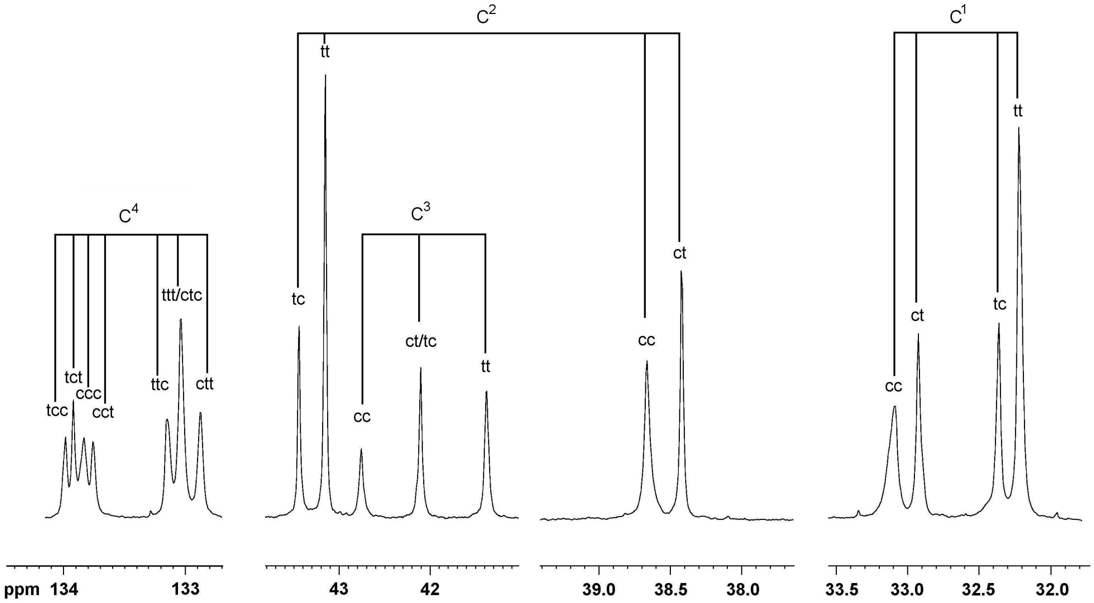


Figure 4.11 Expanded ^{13}C NMR spectrum of polynorbornene made using $MoCl_5$-ē-Al-CH_2Cl_2 catalyst system (in $CDCl_3$).

Table 4.2 A comparison of ROMP of norbornene by the $MoCl_5$-ē-Al-CH_2Cl_2 and WCl_6-ē-Al-CH_2Cl_2 catalyst systems.

Catalyst	$\overline{M}_n$	$\overline{M}_w$	PDI	σ_c	r_t	r_c	$r_t r_c$	Type of distribution	Reference
$MoCl_5$-ē-Al-CH_2Cl_2	60480	130000	2.15	0.41	2.32	0.62	1.44	slightly blocky	Dereli, 2005
WCl_6-ē-Al-CH_2Cl_2	15160	47600	3.14	0.61	1.33	2.53	3.37	blocky	Dereli, 2004

The trans stereoselectivity determined by ^{13}C NMR is in good agreement with that obtained from the ^{1}H NMR spectrum as shown in Figure 4.12. The spectrum shows signals in both the olefinic region (δ = 5.0–6.0 ppm) and in the alkyl region (δ = 1.0–3.0 ppm). The fact that the polymer is mainly trans may also be seen from its ^{1}H NMR spectrum, when the two signals at 5.23 ppm and 5.36 ppm, respectively demonstrating the cis and trans olefinic protons attached to the C^4 carbon atom, were considered. The cis percentage of polymer (ca. 40 %) estimated from the ^{1}H NMR spectrum agrees well with that obtained from ^{13}C NMR. Furthermore, the fraction of cis double bonds (σ_c = 0.41) calculated from the integrals of the signals at δ_H = 2.81 (HC^2, *cis*-polynorbornene) and at δ_H = 2.45 (HC^2, *trans*-polynorbornene) confirms the same cis content of the polymer.

Table 4.3 ^{13}C NMR peak assignments (ppm from TMS) of polynorbornene produced by the electrochemical Mo-based catalyst system.

Chemical shift δ (ppm)	Asssignment	Chemical shift δ (ppm)	Asssignment
32.22	1 tt	43.15	2 tt
32.36	1 tc	43.44	2 tc
32.92	1 ct	132.88	4 ctt
33.09	1 cc	133.04	4ctc ≡ 4 ttt
38.42	2 ct	133.15	4 ttc
38.66	2 cc	133.76	4 cct
41.38	3 tt	133.83	4 ccc
42.10	3 tc ≡ 3 ct	133.92	4 tct
42.76	3 cc	133.99	4 tcc

So, the NMR spectra confirm that there is no loss of C=C double bond during polymerization and indicate the formation of a mainly trans compound with one acyclic C=C double bond and one cyclopentane unit.

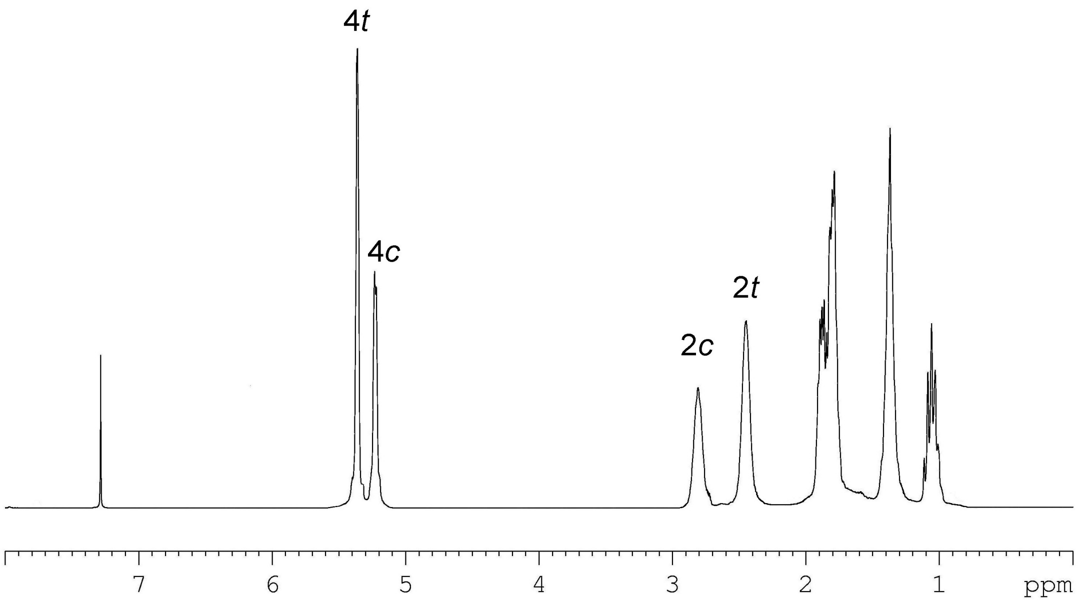


Figure 4.12 ^{1}H NMR spectrum of polynorbornene made using $MoCl_5$-ē-Al-CH_2Cl_2 catalyst system (in $CDCl_3$).

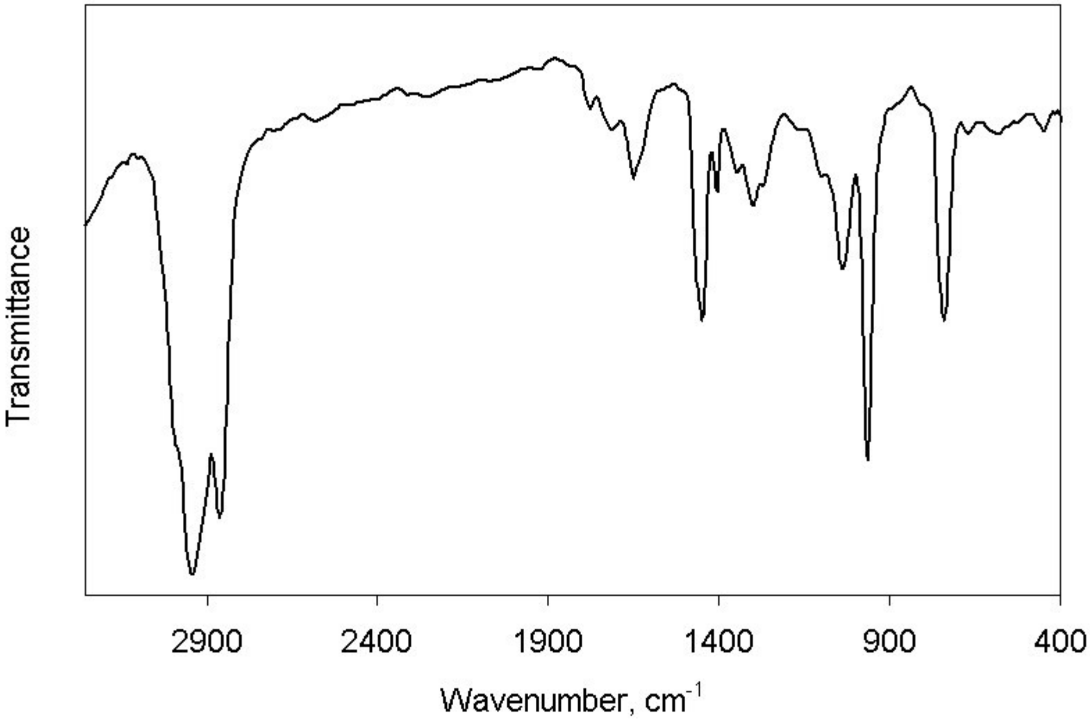


Figure 4.13 FT-IR spectrum of polynorbornene made using $MoCl_5$-ē-Al-CH_2Cl_2 catalyst system.

Here, it is particularly important to note that no evidence of the addition chemistry is apparent in the NMR spectra except for the retention of the C=C double bonds during polymerization. IR spectroscopy was also used to support the retention of unsaturation in the polymer and high trans stereochemistry was assigned. Figure 4.13 illustrates the FTIR spectrum of the polymer. The trans content of the polymer is confirmed by the stronger absorption of the trans C=CH out-of-plane bending at 966 cm^{-1} with respect to the absorption at 742 cm^{-1} arising from the cis C=CH out-of-plane bending. The absorption at 1649 cm^{-1}, belonging to the C=C stretching, indicates the retention of the double bonds in the polymer obtained via the ROMP mechanism.

Consequently, the $MoCl_5$-ē-Al-CH_2Cl_2 system appears to be an efficient catalyst system for the ROMP of bicyclic olefins such as norbornene. The electrochemical molybdenum-based system leads to a mainly trans product ($\sigma_c = 0.41$), in contrast to the mainly cis polymer ($\sigma_c = 0.61$) obtained with the tungsten-based analogue in the production of polynorbornene, which exhibits similar stereochemical characteristics to those seen in the other ROMP systems based on $MoCl_5$ and WCl_6. The polynorbornene produced is slightly blocky, with a higher cis composition ($\sigma_c = 0.41$) when compared with the random commercial polymer 'Norsorex' ($\sigma_c = 0.21$). The catalytic activity is retained for about 32 h under nitrogen atmosphere. A comparison with some catalyst systems applied in the ROMP of norbornene in terms of polymerization conditions, polymer yield and molecular weight is given in Table 4.4. The electrochemically generated molybdenum- and tungsten-based catalysts both seem to be more active than the other catalyst systems in the ROMP of norbornene due to higher polymerization yields and shorter reaction periods.

Table 4.4 A comparison of results of metathesis polymerization of norbornene using various catalyst systems.

Catalyst	Olefin / Catalyst	Reaction time	Temp.[k] (ºC)	Yield (%)	$\overline{M}_w$	Reference
$MoCl_5$-ē-Al-CH_2Cl_2[a]	160	4 min	25	87	130000[l]	Dereli, 2005
Molybdenum (VI) salt[b]	—	—	rt	52	57100[l]	McCann, 1996
Molybdenum complex[c]	300	16 h	40	68	2253000[l]	Yeung, 1999
Molybdenum alkylidene[d]	400	1 h	rt	>98	119000[l]	Nomura, 2000
Molybdenum (II) complex[e]	100	24 h	25	45	16000[l]	Petasis, 1993
Molybdenum-nitrosyl complex[f]	100	10 min	rt	75	236000[l]	Aime, 2001
Ruthenium alkylidene[g]	100	1 h	rt	99	46530[m]	Schwab, 1996
Tungsten alkylidene[h]	25	10 min	rt	90	68000[m]	Czelusniak, 2002
Titanium initiator[i]	100	8 h	70	—	23875[m]	Keller, 2002
Osmium complex[j]	50	2 h	rt	95	433600[l]	VanderLende, 1994

[a] Generated after 3 h of electrolysis time.
[b] (cin-H_4)[Mo_8O_{26}(cin)$_2$].
[c] [Mo(η-C_7H_7)(MeCN)I_2].
[d] Mo($CHMe_2Ph$)(*N*-2,6-$^{i}Pr_2C_6H_3$)($O^{t}Bu$)$_2$.
[e] [$(CO)_4$Mo(μ-Cl_3)]Mo($SnCl_3$)$(CO)_3$].
[f] [$Mo(NO)_2Cl_2(MeCN)_2$]Cl.
[g] $RuCl_2$(=CHPh)(PPh_3)$_2$.
[h] W(NPh)($CHCMe_3$)(PMe_3)[($NSiMe_3$)$_2C_6H_4$].
[i] Dimethyltitanocene.
[j] (μ-H)$_2Os_3(CO)_{10}$.
[k] rt: room temperature.
[l] Determined by GPC (calibration with polystyrene standards).
[m] Calculated from the original $\overline{M}_n$ values determined by GPC.

4.3.3.1 Effect of reaction time on ROMP of norbornene

At this stage, the effect of the reaction time on conversion of norbornene was examined. The olefin / catalyst ratios were kept at 160 and 125 for electrochemical molybdenum- and tungsten-based systems respectively, and reaction was quenched by the addition of methanol after 0,5, 1, 2, 4, 8, and 16 minutes from the start of reaction. The percentage conversions to the polymers obtained were calculated.

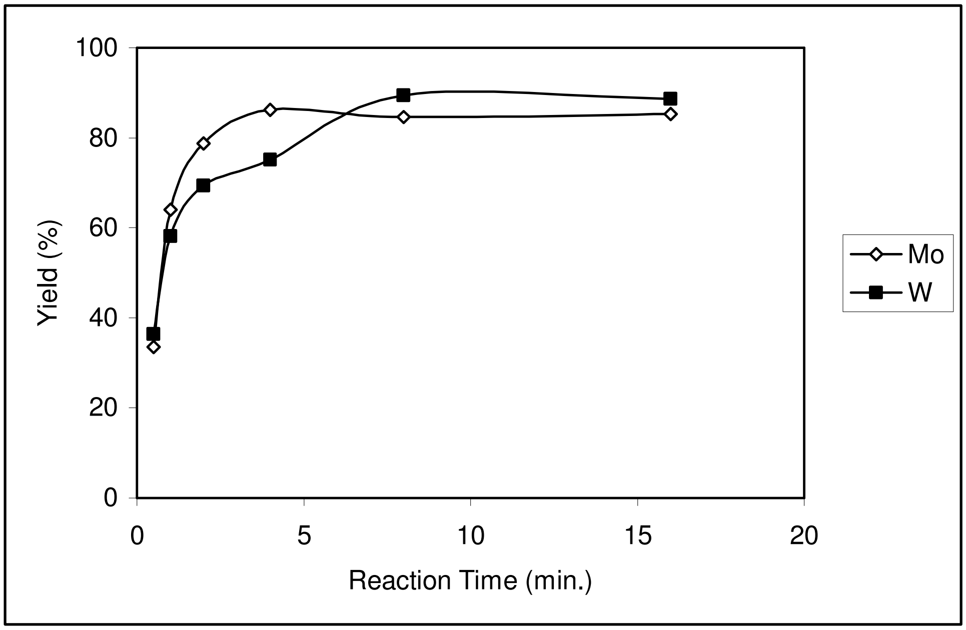


Figure 4.14 The influence of reaction time on the conversion of ROMP of norbornene in CH_2Cl_2 at room temperature (olefin / Mo = 160; olefin / W = 125; catalyst = 0.025 mmol).

Figure 4.14 shows the influence of different reaction times on the amount of polynorbornene for electrochemical molybdenum- and tungsten-based systems, comparetively. Polymerization conversion first increased with reaction time and reached a plateau value at around 4 min. Both molybdenum- and tungsten-based systems conducted the polymerization of norbornene with high conversions and at short periods, as also shown in Fig. 4.14.

4.3.3.2 Effect of electrolysis time on ROMP of norbornene

At this step, the effect of the electrolysis time on conversion of norbornene was studied. The olefin/catalyst ratios were kept at 160 and 125 for electrochemical molybdenum- and tungsten-based systems respectively, and active catalyst obtained in different electrolysis times (30, 60, 90, 120, 150, and 180 minutes) was added to the olefin. Polymerizations were quenched by the addition of methanol. The percentage conversions to the polymers obtained were calculated.

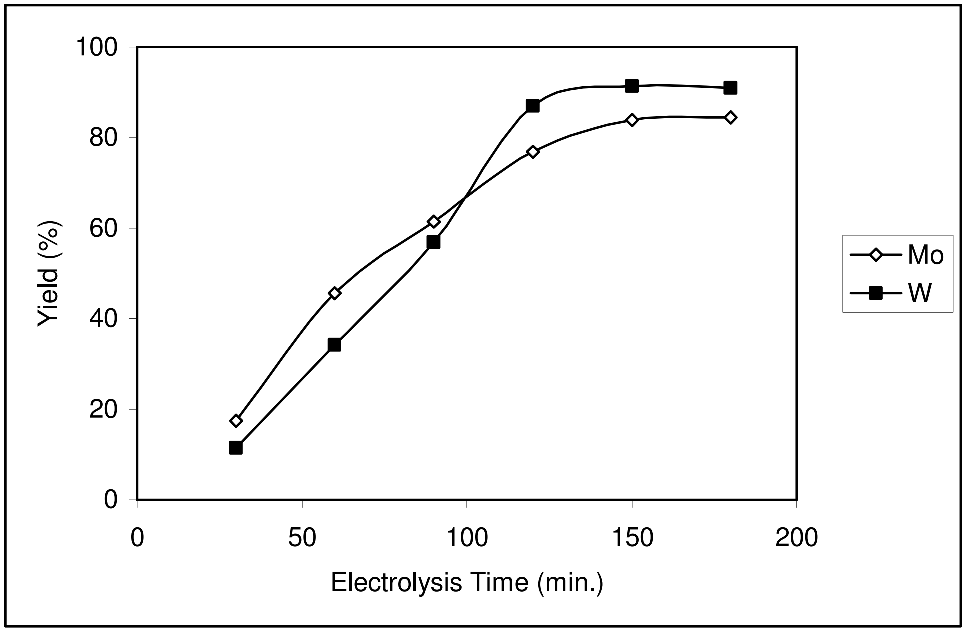


Figure 4.15 The influence of electrolysis time on the conversion of ROMP of norbornene in CH_2Cl_2 at room temperature (olefin/Mo = 160; olefin/W = 125; current range: 200-400 μA; $E_{cathodic}$ = + 700 mV and + 900 mV vs. Ag/AgCl for $MoCl_5$ and WCl_6, respectively).

Figure 4.15 shows the influence of different electrolysis times on the amount of polynorbornene for electrochemical molybdenum- and tungsten-based systems. With prolonged electrolysis time, the concentration of the active catalyst formed during the electrolysis and conversion to the polymer increased, and the maximum conversion was obtained approximately in 2.5-3 h of electrolysis time for both catalyst systems (Fig. 4.15).

4.3.3.3 Effect of catalyst aging on ROMP of norbornene

At this stage, the effect of catalyst aging on norbornene conversion was examined. The metathesis polymerization of norbornene catalyzed by electrochemically produced fresh molybdenum- and tungsten-based catalysts, resulted in metathesis product, polynorbornene. To investigate the stability of the catalysts with time, catalysts were aged under nitrogen atmosphere. They were used after certain periods in the same catalytic reaction. The percentage conversions to the polymers obtained were calculated.

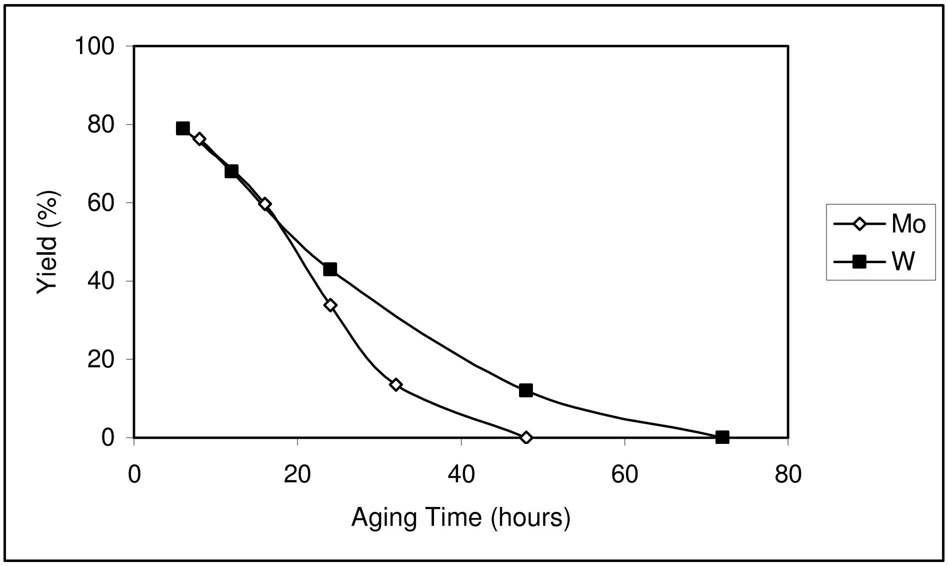


Figure 4.16 The influence of catalyst aging on the conversion of ROMP of norbornene in CH_2Cl_2 at room temperature (olefin / Mo = 160; olefin / W = 125).

The effect of catalyst aging on norbornene conversion is given in Figure 4.16. It was found that the catalytically active species formed from WCl_6 during electrolysis retain their activity for nearly 2 days when kept under nitrogen atmosphere. With the $MoCl_5$-ē-Al-CH_2Cl_2 system, this period was shorter than for the tungsten-based system (Fig. 4.16). The activity towards ROMP of norbornene slowly diminished and was completely lost after 2 days. The average rate of decrease in the polymerization yield is 2.3 % for every 1 h passing for catalyst aging, which also indirectly indicates the rate of the catalyst decay.

4.4 Applications of Metathesis Reactions by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ Catalyst

In recent years, the use of derivatives of WCl_6 with oxygen-containing ligands has shown growing interest. Several tungsten (VI) phenoxide complexes have been employed in different types of metathesis reactions, such as olefin metathesis (OM), ring-opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET) polymerization, ring-closing metathesis (RCM) (Balcar et al., 1992; Nakayama et al., 1993; Vosloo et al., 1997; Gomez et al., 1998; Schalkwyk et al., 2002; Marvey et al., 2004). Aryloxide alkylidene complexes of tungsten obtained from $W(OAr)_xCl_{6-x}$ are known to be very efficient in several types of metathesis reactions in the presence of a cocatalyst like R_xAlCl_{3-x}, R_4M (M = Sn, Pb).

In this study, tungsten compound with aryloxo ligand, $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$, was investigated as catalyst for the first time for all types of metathesis reactions mentioned above.

4.4.1 Olefin metathesis (OM) reactions by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ catalyst

Olefin metathesis reactions of 1-octene were studied by using the two-component systems containing $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ precatalyst and an Sn- or Pb-based compound as a cocatalyst (Figure 4.17).

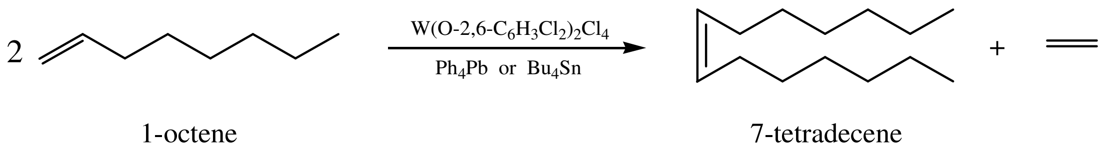


Figure 4.17 Olefin metathesis reaction of 1-octene.

Gas chromatographic analyses of the reaction mixtures indicated the formation of metahtesis products. Olefin metathesis of 1-octene in the presence of these two-component systems resulted in the formation of the metathesis product 7-tetradecene. The products observed are given in the Table 4.5 with respect to their retention times. GC-MS spectra of the products formed in the olefin metathesis of 1-octene are given in Figure 4.18 and Figure 4.19. The main product of the reaction is 7-tetradecene. The other peaks belong to unreacted olefin, solvent and internal standard.

Table 4.5 The products in the olefin metathesis of 1-octene.

Retention time (min)	Product	Molecular formula	Molecular weight
7.0	1-Octene	C_8H_{16}	112
8.6	Chlorobenzene	C_6H_5Cl	112
20.1	7-Tetradecene	$C_{14}H_{28}$	196
23.8	n-Hexadecane	$C_{16}H_{34}$	226

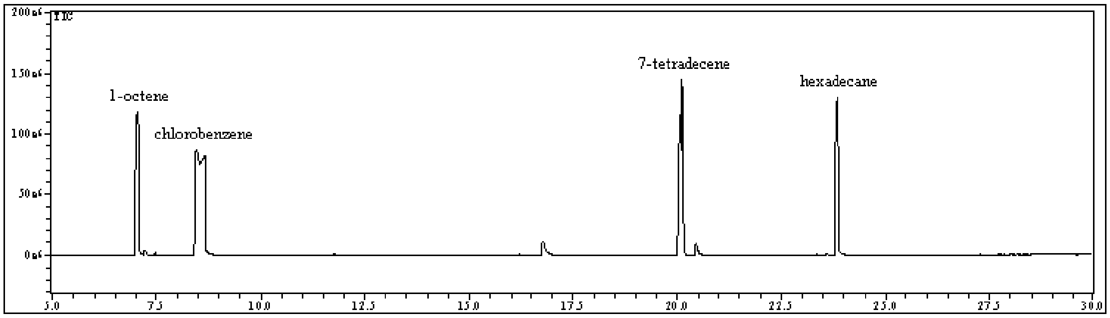
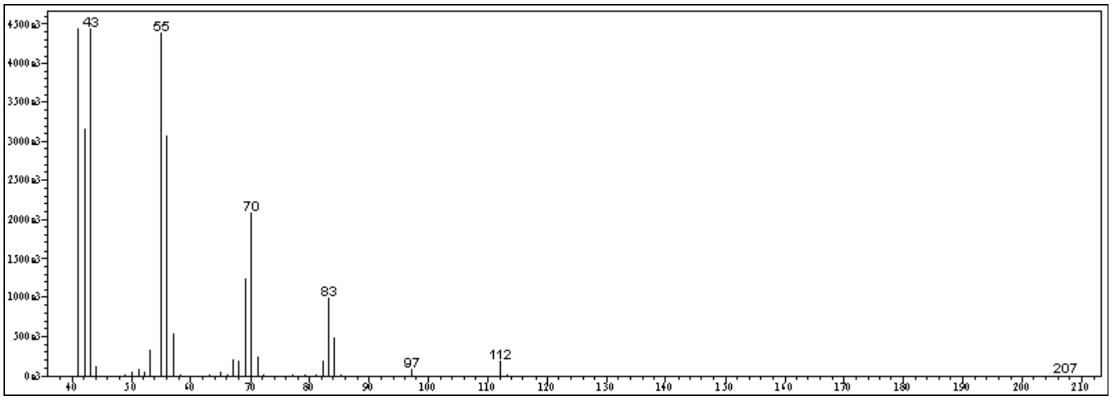
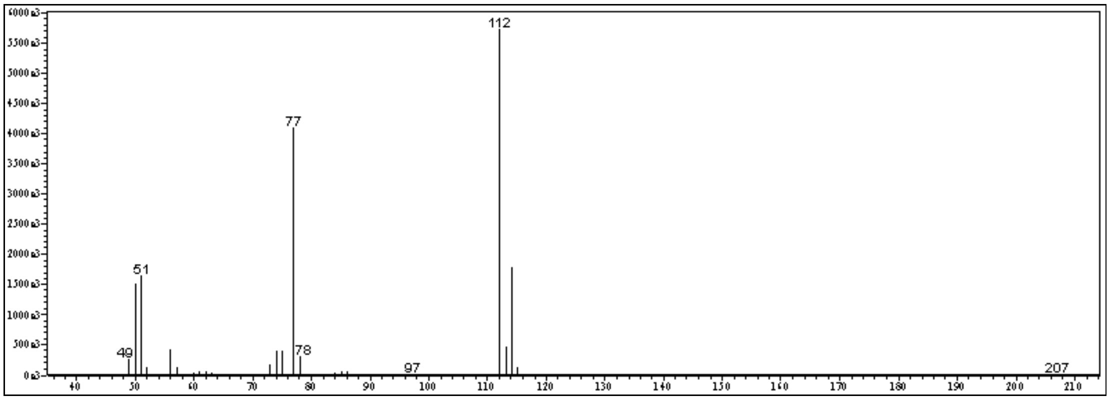


Figure 4.18 Gas chromatogram of the olefin metathesis products of 1-octene.

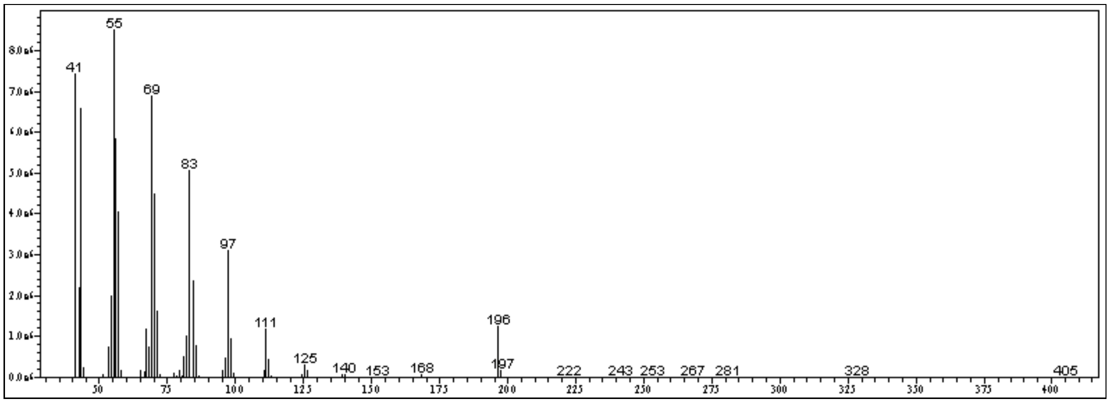
Name: 1-octene **Ret. Time:** 7.0



Name: chlorobenzene **Ret. Time:** 8.6



Name: 7-tetradecene **Ret. Time:** 20.1



Name: hexadecane **Ret. Time:** 23.8

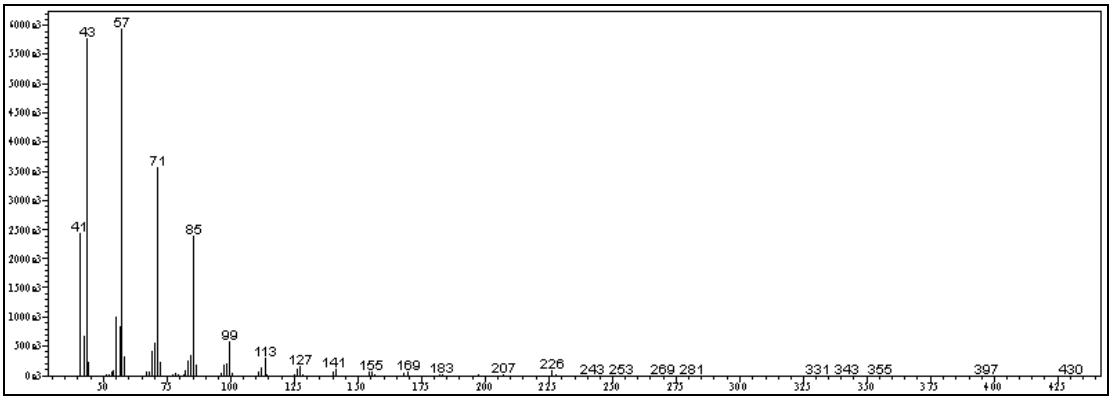


Figure 4.19 Mass spectra of the olefin metathesis products of 1-octene.

4.4.1.1 Influence of cocatalyst / W molar ratios

The activity of a particular catalyst system is dependent on a number of factors including: (i) the proportions of the components; (ii) pretreatment procedures; (iii) the order in which the components are mixed; (iv) in the cases where the olefin is added last, the period of incubation before adding the olefin and (V) reaction time and reaction temperature. Optimization of a given catalyst systems by adjustment of the various parameters inturn can be quite a lengthy procedure.

Various cocatalysts and cocatalyst / W molar ratios are well known to be effective with $W(OAr)_xCl_{6-x}$ complexes for the metathesis of alkenes. The effect of cocatalyst / W molar ratio on the catalytic activity of $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ precatalyst towards the metathesis of 1-octene was investigated by varying the cocatalyst / W molar ratio (1 to 6). The results of the investigation with cocatalysts Ph_4Pb and Bu_4Sn at different cocatalyst / W molar ratios are given in Fig. 4.20.

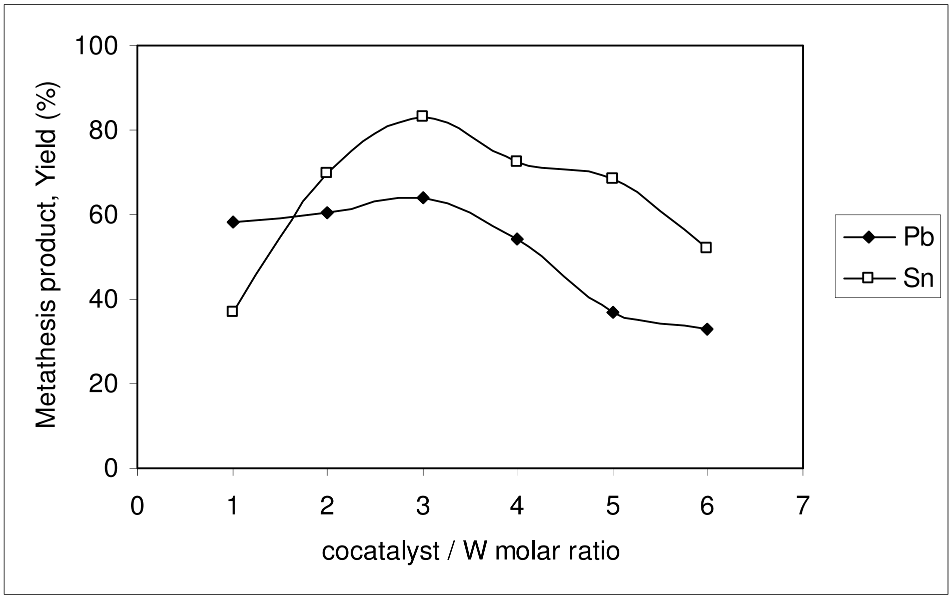


Figure 4.20 Influence of the cocatalyst / W molar ratio on the metathesis activity of the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / R_4M (M = Sn, Pb) catalytic system (temperature = 85 ºC; time = 2 h).

In both cases an increase in metathesis product yield was observed with an increase in the cocatalyst / W molar ratio, although the increase in yields is more gradual for Pb cocatalyst. A maximum yield of metathesis products is obtained at cocatalyst / W molar ratios of 1 to 3 and 2 to 5, respectively, for Pb and Sn cocatalysts. The yields generally decrease at higher cocatalyst / W molar ratios. From the results obtained, the optimal value for both the Pb / W and the Sn / W ratio appears to be 3.

4.4.1.2 Influence of interaction time

At this stage, the effect of the interaction time on metathesis activity of W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ precatalyst was investigated. Interaction time is defined as the period before the 1-octene is added to a mixture of the catalyst and cocatalyst in chlorobenzene. The metathesis product yields at various interaction times ranging from 0 to 30 min is given in Figure 4.21.

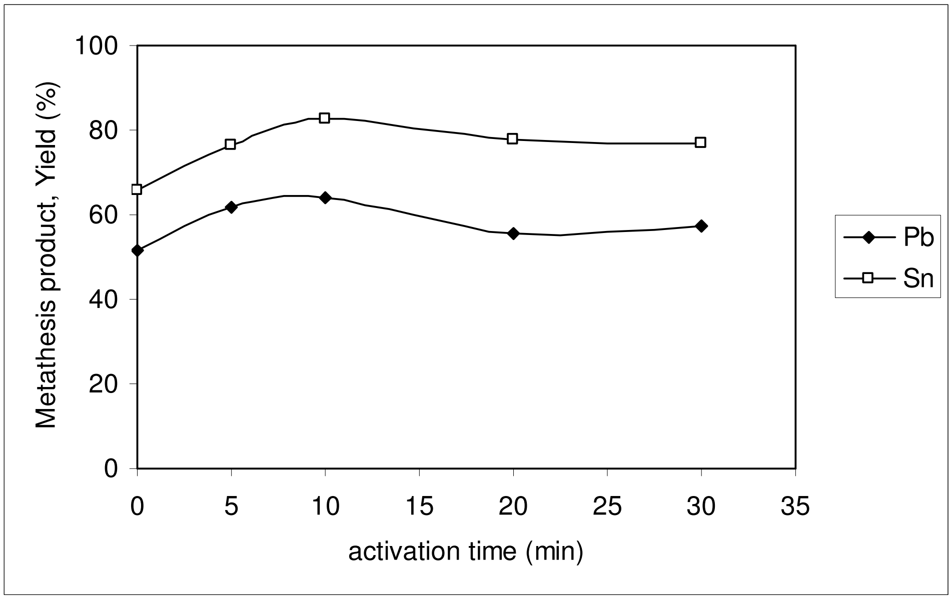


Figure 4.21 Influence of the interaction time on the metathesis activity of the W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ / R_4M (M = Sn, Pb) catalytic system (temperature = 85 ºC; cocatalyst / W molar ratio = 3).

In this experiment, cocatalyst / W molar ratio was kept as 3. As it is seen clearly from Figure 4.21, in both cases a slight increase is observed with an increase in interaction time from 0 to 10 min. A decrease in metahesis product yield is observed at interaction times greater than about 10 min. From these results, it can be seen that the maximum yield of metathesis product is obtained after interaction time of 10 min between catalyst and cocatalyst.

4.4.1.3 Influence of reaction temperature

At this step, the effect of reaction temperature on metathesis activity of W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ precatalyst was studied. The cocatalyst / W molar ratio and interaction time were kept as 3 and 10 min, respectively. Figure 4.22 shows the influences of different reaction temperatures on the metathesis product yield.

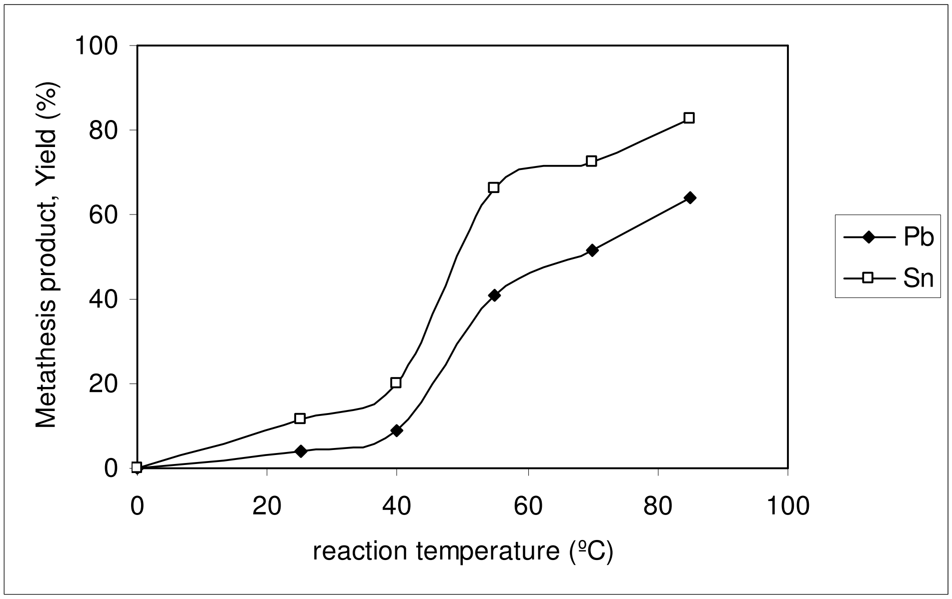


Figure 4.22 Influence of the reaction temperature on the metathesis activity of the W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ / R_4M (M = Sn, Pb) catalytic system (cocatalyst / W molar ratio = 3; activation time = 10 min).

The influence of the reaction temperature on the yield of metathesis products indicates that temperatures greater than about 55 ºC are needed to activate the system. As it is seen clearly from Figure 4.22, very little metathesis is observed in both cocatalyst systems from 0 to 40 ºC. A drastic increase in metathesis products is observed from 55 to 85 ºC. A maximum yield of metathesis products is obtained at 85 ºC.

4.4.1.4 Influence of reaction time

At this stage, the effect of reaction time on the yield of metathesis products was examined. The cocatalyst / W molar ratio, interaction time and reaction temperature were kept as 3, 10 min and 85 ºC, respectively. The kinetic profile of the metathesis reactions of 1-octene is illustrated in Figure 4.23. An example of gas chromatograms of olefin metathesis reaction mixtures of 1-octene catalyzed by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Ph_4Pb catalyst system at different reaction times is also given in Figure 4.24.

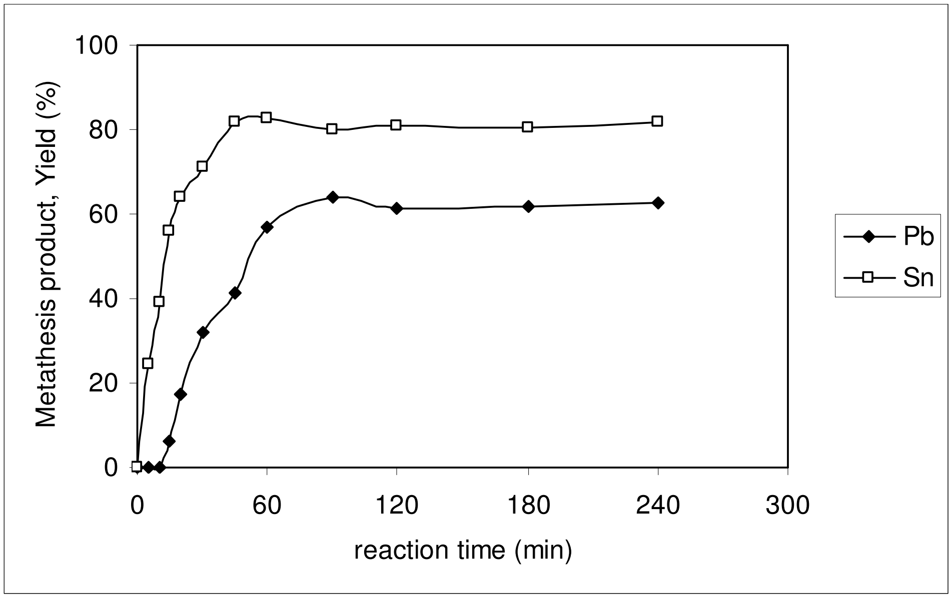


Figure 4.23 Influence of the reaction time on the metathesis activity of the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / R_4M (M = Sn, Pb) catalytic system (temperature = 85 ºC; cocatalyst / W molar ratio = 3; activation time = 10 min).

Figure 4.23 and 4.24 demonstrate that the changes in yield of metathesis product, 7-tetradecene during the course of reaction. The metathesis yield increases with time, and then tends to a constant value as a consequence of a significant decrease of the reaction rate. With Pb cocatalyst, the reaction proceeds slower than those conducted with Sn cocatalyst. As illustrated in Figure 4.15, it is evident from these results that while the metathesis equilibrium is reached within about 45 min with Sn cocatalyst, this period is 90 min for Pb cocatalyst and that the equlibrium is truly established after about 4 h.

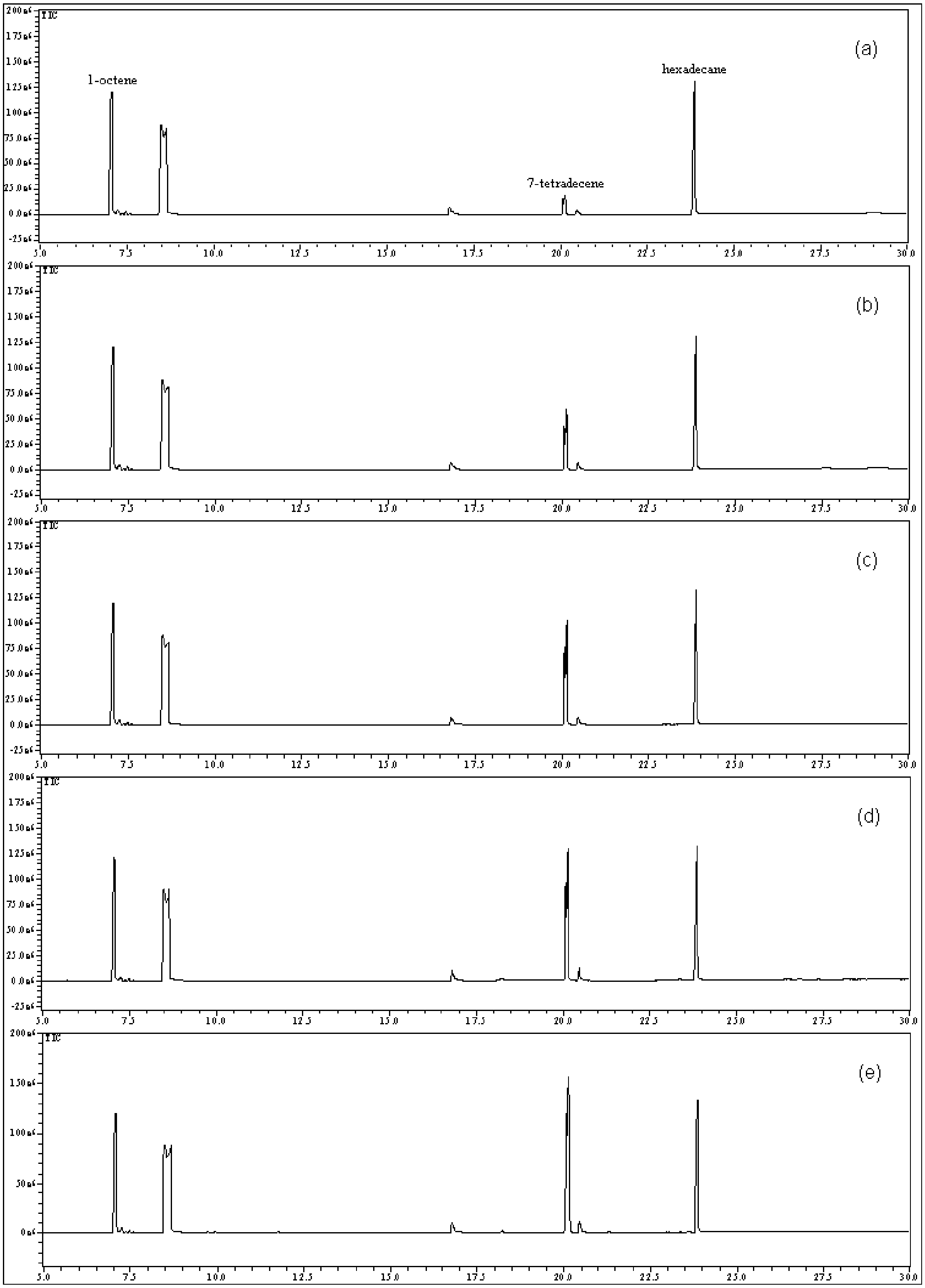


Figure 4.24 Gas chromatograms of olefin metathesis reaction mixtures of 1-octene; after (a) 15 min, (b) 20 min, (c) 30 min, (d) 45min, (e) 60 min.

4.4.1.5 Influence of olefin / catalyst molar ratio and air atmosphere

In this study, the effect of the olefin / catalyst molar ratio and the air atmosphere on the catalytic activity of W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ precatalyst was studied. For this purpose, a series of experiments was performed by varying the olefin / catalyst molar ratio (50:1 to 500:1). The results obtained are given in Figure 4.25.

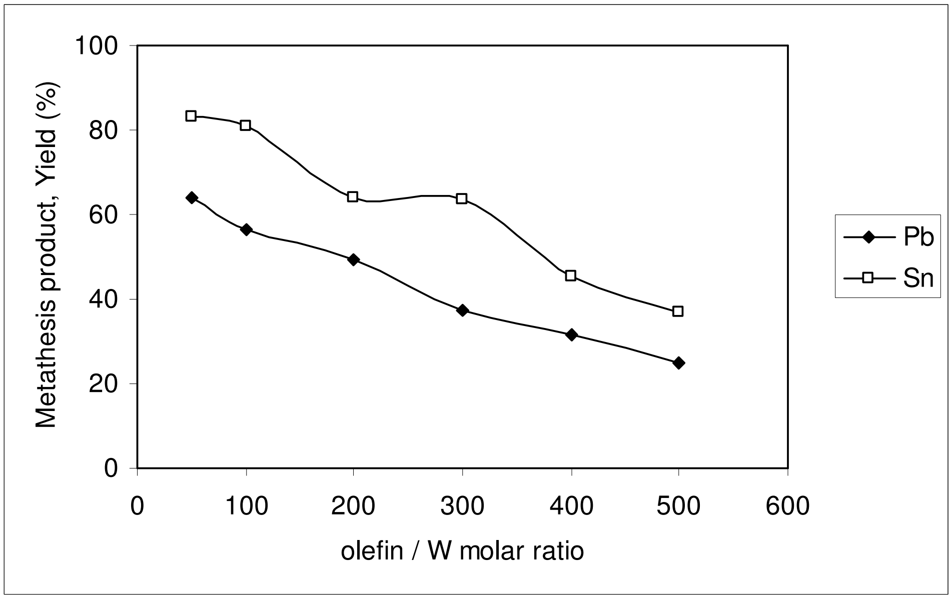


Figure 4.25 Influence of the olefin / catalyst molar ratio on the metathesis activity of the W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ / R_4M (M = Sn, Pb) catalytic system (temperature = 85 ºC; cocatalyst / W molar ratio = 3; activation time = 10 min).

Figure 4.25 shows that in both Sn and Pb catalyst systems the metathesis yield decreases when the olefin / catalyst molar ratio is increased from 50:1 to 500:1.

The metathesis activity of both the catalytic systems were also investigated in air atmosphere. The results are illustrated in Table 4.6.

Table 4.6 Influence of an air atmosphere on the reactions of 1-octene in the presence of $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / R_4M (M = Sn, Pb) catalytic systems.

Cocatalyst	**in N_2 atmosphere (yield %)**	**in air atmosphere (yield %)**
Sn	83.2	74.5
Pb	64.1	59.8

Very little deactivation of both the catalytic systems was found for metathesis reactions of 1-octene. Therefore, the results indicated that both aryloxide catalyst systems are highly active even in air atmosphere.

4.4.2 ROMP reactions by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ catalyst

Ring-opening metathesis polymerization (ROMP) of cyclic olefins by transition metal catalysts is a unique process of olefin metathesis, which leads to unsaturated linear homopolymers and copolymers (Figure 4.26). This type of polymerization reactions has been the subject of many investigations since norbornene had been polymerized with titanium-based catalysts by Anderson and Merckling (1955) to an unsaturated polymer and later cyclopentene by Eleuterio (1957) with a heterogeneous molybdena/alumina catalyst. Since then, huge efforts have been devoted to the development of new catalytic systems for polymerization of olefins, the ultimate aim being the discovery of catalysts which allow control over the structure, molecular weight and physical / chemical properties of the polymers. Several industrial processes involving ROMP have been developed and brought into practice, such as the ROMP of cyclooctene, norbornene and dicyclopentadiene, leading to useful polymers, baceuse these monomers are quite cheap and readily available. The properties of the resulting polymers depend on the monomer structure, the initiating system and the reaction conditions.

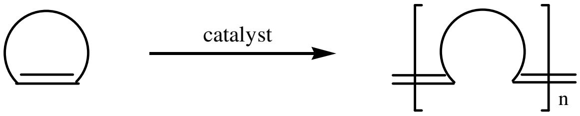
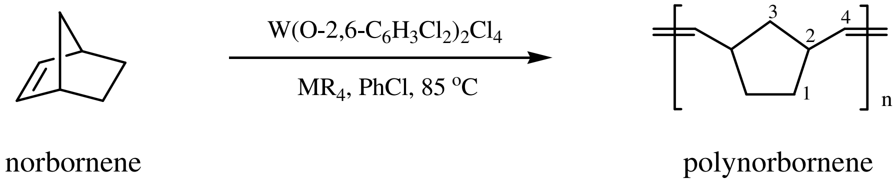


Figure 4.26 Ring-opening metathesis polymerization (ROMP) process.

In this study, ring-opening metathesis homopolymerization and copolymerizations (*via* ROMP) of some mono- and bicyclic olefins, such as norbornene, cyclooctene and 1,5-cyclooctadiene by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalytic system were first experimented. All reactions were initiated in the bulk, at 85 ºC and under nitrogen atmosphere. The results obtained revealed that the tungsten (VI) complex $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ is also highly active catalyst for ROMP reactions of cyclic olefins in the presence of Bu_4Sn compound as cocatalyst. The polymers obtained were characterized by ^1H and ^{13}C NMR, IR and GPC techniques. Because the geometric structures of polymers are sensitive to the catalyst system used, the microstructures of polymers have been analysed in detail.

4.4.2.1 ROMP of norbornene by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ catalyst

The ring-opening polymerization of bicyclo[2.2.1]hept-2-ene (norbornene, NBE) is readily brought about by olefin metathesis catalysts, to give a polymer, whose chains contain 1,3-disubstituted cyclopentane rings. The geometric structure of polynorbornene was determined from ^1H and ^{13}C NMR spectra according to Ivin et al. (1977, 1978, 1979, 1986). All these values are in good agreement with various literature data related to polynorbornene prepared via ROMP (Fig. 4.27, 4.28 and 4.29).



The carbon atoms in the poly-NBE are numbered from 1 to 4. ^{13}C NMR spectrum of poly-NBE consists of a group of olefinic carbon peaks, and a group of upfield peaks due to the ring-carbons. The two multiplets corresponding to C^4 carbon centered at 133.84 and 133.03 ppm refer to *cis*- and *trans*-vinylic carbon atoms, respectively. A comparison of these two peaks related to C^4 carbon allows estimation of the trans stereoselectivity of the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system. Since the C^2, C^1 and C^3 chemical shifts in the polymer are sensitive to the cis or trans configuration of the two nearest double bonds, a detailed analysis of the ^{13}C NMR spectrum provides a rich source of information concerning the microstructure of the polymer chain. Table 4.7 gives the peak assignments of polymer obtained in the presence of $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system. The relative proportions of double bond sequences, represented as trans-cis (tc), trans-trans (tt), cis-cis (cc) and cis-trans (ct) units were determined from the four methine carbon (C^2) signals at δ_c 43.42 (tc), 43.13 (tt), 38.66 (cc) and 38.41 (ct). Here, the chain carbons that are located between two double bonds are labelled as cc, ct, tc or tt. The first letter denotes the cis or trans structure at the nearest double bond; the second letter, at the next nearest double bond. In this way, the reactivity ratios, r_t = tt/tc and r_c = cc/ct, were calculated as r_t = 1.97 and r_c = 0.59, giving the $r_t r_c$ value of 1.154. The fraction of cis-double bonds (σ_c), was estimated as 0.43 (Fig. 4.28). The σ_c and $r_t r_c$ values thus obtained characterize a mainly trans polymer with a slightly blocky distribution of cis and trans structures.

Table 4.7 ^{13}C NMR peak assignments (ppm from TMS) of polynorbornene produced by the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system.

Carbon	Position and asssignment			
C^4	133.99 (tcc)	133.93 (tct)	133.84 (ccc)	133.76 (cct)
	133.15 (ttc)	133.03 (ctc ≡ ttt)	132.87 (ctt)	
C^2	43.42 (tc)	43.13 (tt)	38.66 (cc)	38.41 (ct)
C^1	33.11 (cc)	32.93 (ct)	32.37 (tc)	32.21 (tt)
C^3	42.76 (cc)	42.09 (tc ≡ ct)	41.37 (tt)	

The results obtained by ^{13}C NMR are consistent with the ^1H NMR spectrum shown in Figure 4.29. The spectrum shows signals in both the olefinic region and in the alkyl region. The fact that the polymer is mainly trans may also be visualized from its ^1H NMR spectrum, when the resonances at 5.23 ppm and 5.37 ppm, assigned respectively to the cis and trans ethylenic protons, were considered. The σ_c (ca 41%) calculated from the ^1H NMR spectrum agrees well with that obtained from the ^{13}C NMR. Additionally, the relative integrated peak areas of the two signals at 2.81 and 2.45 ppm, demonstrating the cis and trans protons atteched to C^2 carbon in the cyclopentane ring, indicate a similar trans-content of the polymer.

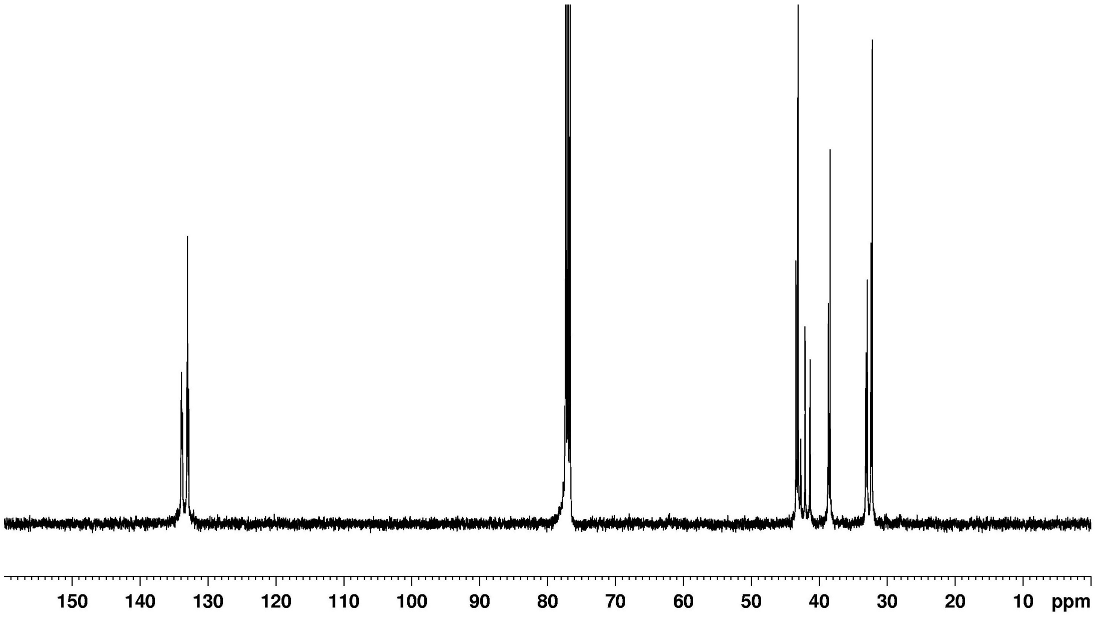


Figure 4.27 ^{13}C NMR spectrum (400 MHz, CDCl$_3$) of poly-NBE obtained with the W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$ / Bu$_4$Sn catalyst system.

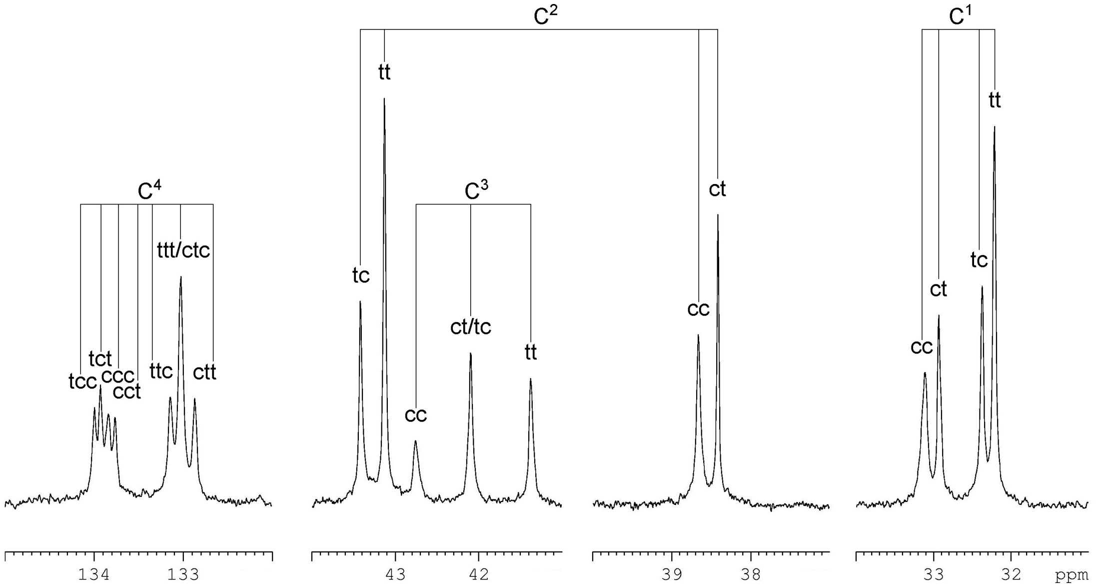


Figure 4.28 Expanded ^{13}C NMR spectrum (400 MHz, CDCl$_3$) of poly-NBE obtained with the W(O-2,6-C$_6$H$_3$Cl$_2$)$_2$Cl$_4$ / Bu$_4$Sn catalyst system.

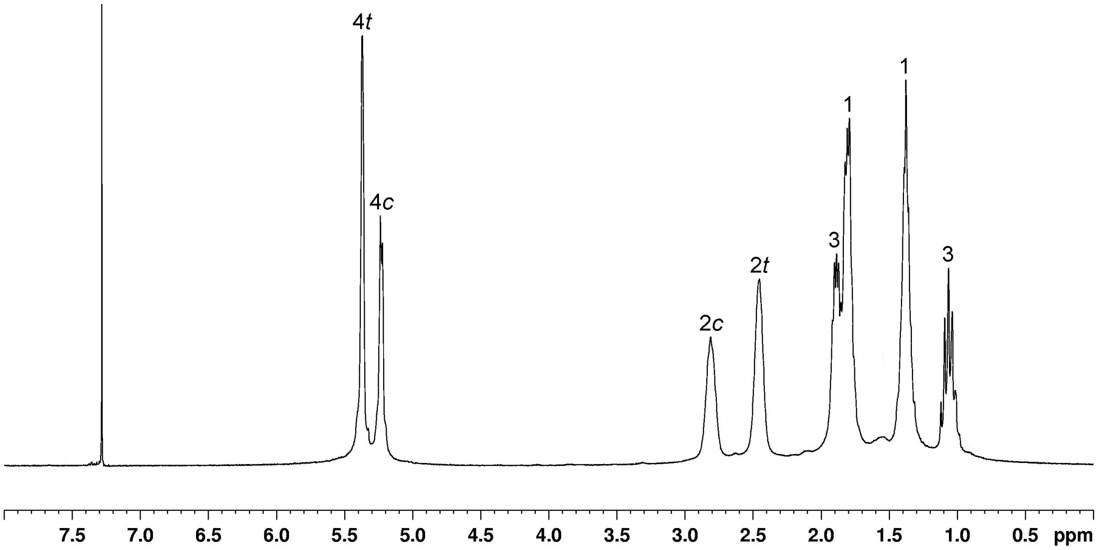


Figure 4.29 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of poly-NBE obtained with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system.

The metathesis polymerization activity and polymer stereoselectivity with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system were also investigated in an air atmosphere. The results are illustrated in Table 4.8. A small increase in cis-content of polymer is observed while polymerization yield decreases when the catalytic reaction is carried out in air atmosphere.

Table 4.8 Influence of an air atmosphere on ROMP of norbornene by the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system.

	σ_c	r_t	r_c	$r_t r_c$	Type of distribution	Yield %
in N_2 atm	0.43	1.97	0.59	1.154	slightly blocky	96.8
in air atm	0.48	1.62	0.77	1.255	slightly blocky	65.8

The metatesis polymerization reactions of norbornene were carried out with the various cocatalysts. Table 4.9 gives the obtained results.

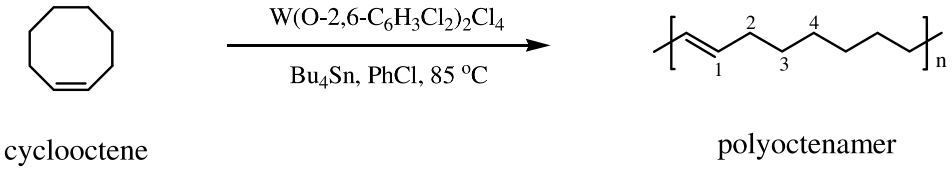
Table 4.9 Influence of various cocatalysts on ROMP of norbornene by the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 / R_4M$ catalyst system.

cocatalyst	σ_c	r_t	r_c	r_tr_c	Type of distribution	Yield %
Et_4Sn	0.28	3.46	0.35	1.205	slightly blocky	67.4
Me_4Sn	0.32	2.53	0.43	1.088	random	84.8
Bu_4Sn	0.43	1.97	0.59	1.154	slightly blocky	96.8
Ph_4Sn	0.43	2.02	0.69	1.398	slightly blocky	88.5
Ph_4Pb	0.49	2.02	0.73	1.486	slightly blocky	96.2

The cis content of polymers (σ_c) prepared using the various cocatalysts varied from about 0.28 to 0.49. As shown in Table 4.9, an increase of σ_c increases the r_c values while generally reduces the r_t values. In all cases, almost, a slightly blocky distributions of cis and trans double bonds were observed in the polymerization of norbornene with the cocatalysts used.

4.4.2.2 ROMP of cyclooctene by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ catalyst

With $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 / Bu_4Sn$ classical catalytic system, the ring-opening polymerization of cyclooctene leads to the high-*trans* polyoctenamer.



The carbon atoms in the polyoctenamer are numbered from 1 to 4. The microstructure of the resulting polyoctenamer was deduced from the ^{13}C NMR spectra (Table 4.10, Fig. 4.30 and 4.31).

The ^{13}C NMR spectrum shows three resolved signals for both the cis and trans olefinic carbon atoms. Adjacent double bonds in the polyoctenamer chain are close enough to affect each other and triad splitting of the cis and trans olefinic signals is observed. The assignment of these peaks is based on the observation that the splitting pattern for this effect generally appears to consist of one intense peak and two smaller peaks of equal intensity on either side, for both the cis and trans signals. Assignments of the C^3 to the double bonds indicates that the polyoctenamer was highly blocky and the more intense peak is assigned as trans, trans, trans (*ttt*) or cis, cis, cis (*ccc*). The *ttc* (or *cct*) and *ctt* (or *tcc*) peaks should have the same intensities since the presence of a *ttc* carbon requires the presence of a *ctt* carbon. The *ctc* and *tct* peaks should be relatively low intensity and be overlapped by the *ttt* and *ccc* peaks respectively (Dounis et al., 1995). The C^2 and C^3 atoms are only subjected to the effect of the nearest double bond, giving one peak for both cis and trans with C^2c upfield from C^2t by 5.38 ppm and C^3t upfield from C^3c by 0.11 ppm. The C^4 shows a four-line splitting pattern in the *cc*, *ct*, *tc* and *tt* sequence of environments.

The *cis* olefinic carbon appears at 129.88 ppm, and the *trans* olefinic carbon appears at 130.34 ppm. The carbon atom adjacent to the olefinic carbon also has two different resonances, i.e., the *cis* carbon at 27.22 ppm and the *trans* carbon at 32.60 ppm. The relative intensities of cis and trans olefinic peaks at the C^1 region and of the cis and trans non-olefinic peaks at the C^2 region give similar trans-contents of the polyoctenamer, i.e. 84%.

The results obtained by ^{13}C NMR agree well with the ^1H NMR spectrum. The ^1H NMR spectrum of the polyoctenamer has olefinic proton signals at 5.37 ppm and 5.40 ppm corresponding to cis and trans peaks respectively and non-olefinic proton signals between 2.2 ppm and 1.0 ppm (Fig. 4.32). The relative intensities of the olefinic peaks at 5.37 and 5.40 ppm give a cis/trans ratio of 18/82. Moreover, the relative integrated peak areas of the two signals at 2.07 and 1.99 ppm reveal a similar trans-content of the polymer.

Table 4.10 ^{13}C NMR peak assignments (ppm from TMS) of polyoctenamer produced by the W(O-2,6-$C_6H_3Cl_2$)$_2$$Cl_4$ / Bu_4Sn catalyst system.

Carbon	Position and asssignment			
C^1	130.34 (ttt)	129.88 (ccc)		
C^2	32.60 (t)	27.22 (c)		
C^3	29.75 (c)	29.64 (t)		
C^4	29.23 (cc)	29.18 (ct)	29.10 (tc)	29.04 (tt)

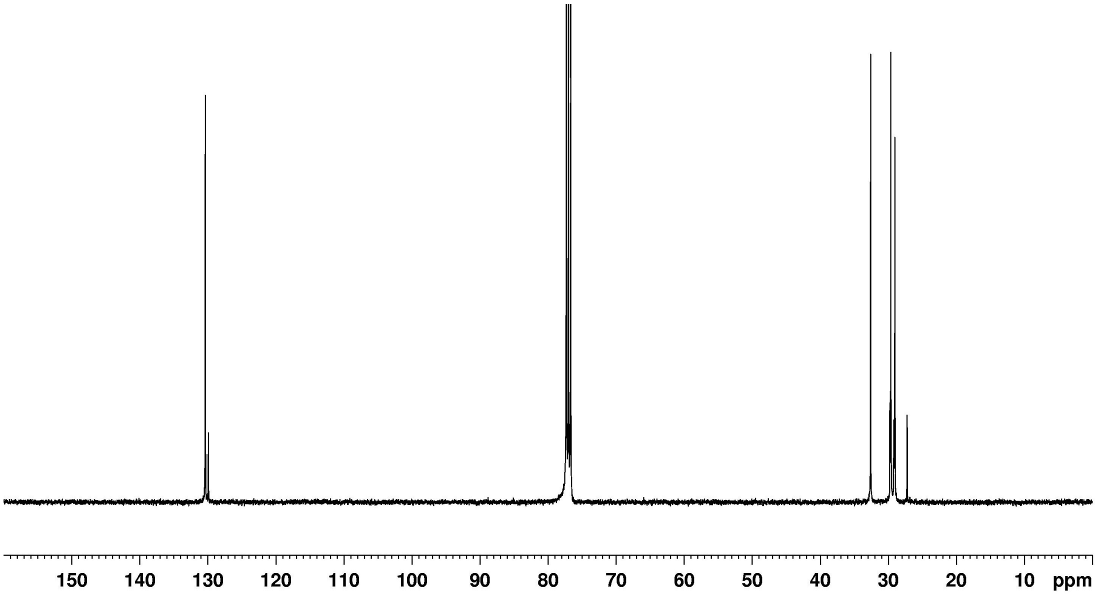


Figure 4.30 ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polyoctenamer obtained with the W(O-2,6-$C_6H_3Cl_2$)$_2$$Cl_4$ / Bu_4Sn catalyst system.

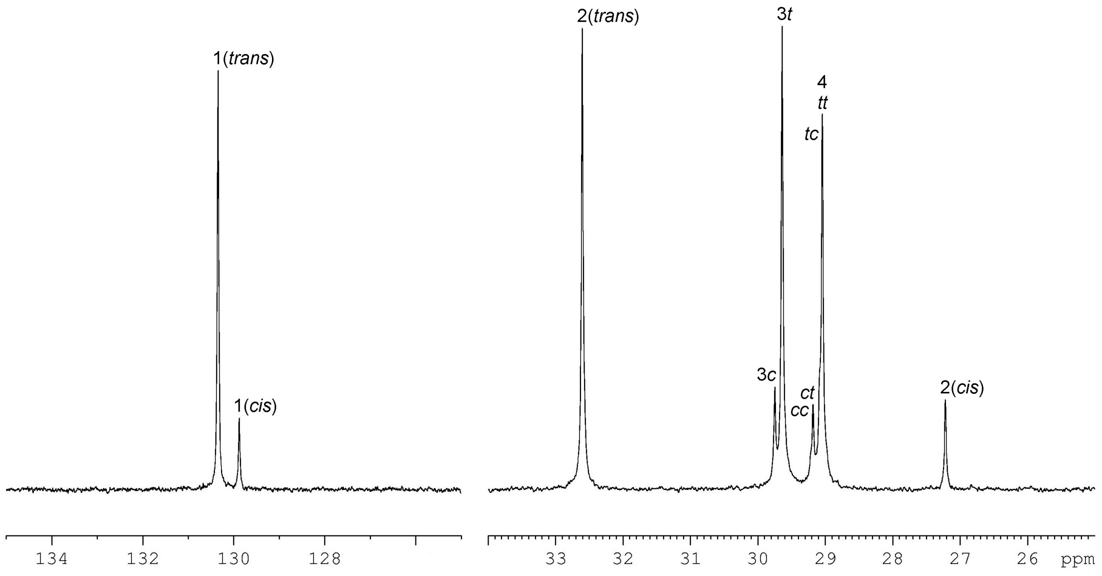


Figure 4.31 Expanded ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polyoctenamer obtained with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system.

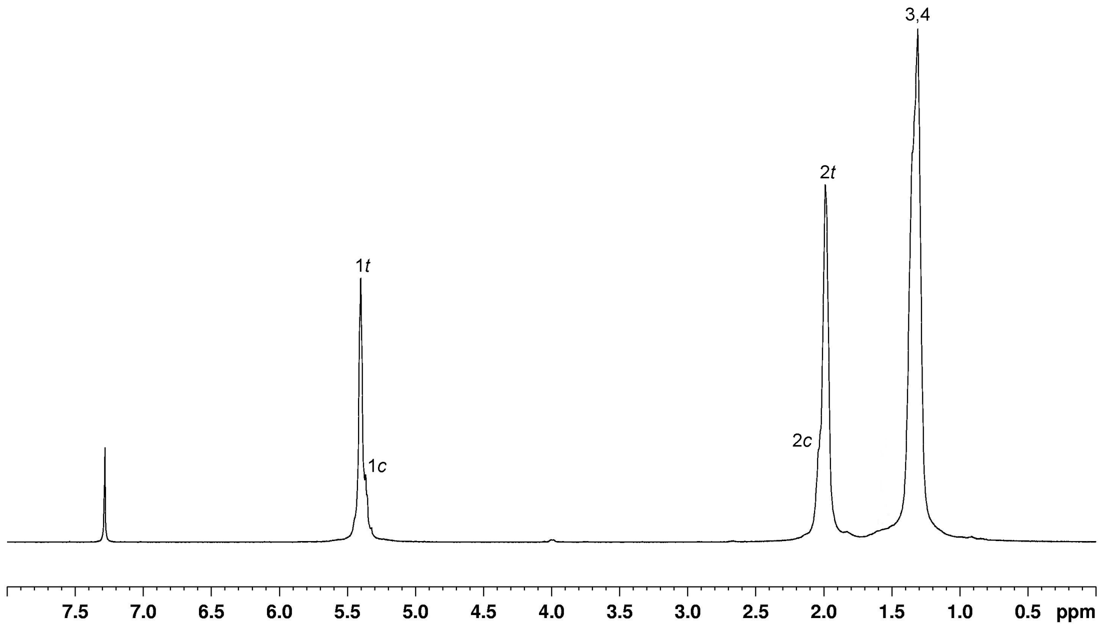
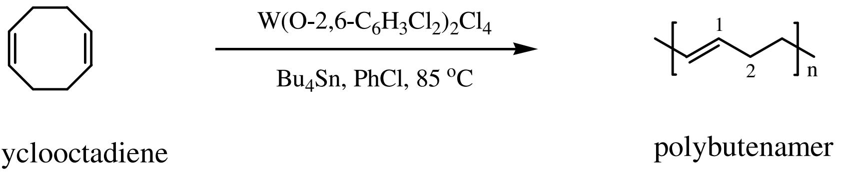


Figure 4.32 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polyoctenamer obtained with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system.

4.4.2.3 ROMP of 1,5-cyclooctadiene by W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ catalyst

Investigation of the stereochemistry of the ROMP reaction of 1,5-cyclooctadiene was made by ^{13}C and ^{1}H NMR. The microstructure of the resulting polybutenamer was deduced from the ^{13}C NMR spectrum (Fig. 4.33 and 4.34). The carbon atoms in the polybutenamer are numbered as 1 and 2, as indicated below and Table 4.11.



The W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system produced high-*trans* polybutenamer. ^{13}C NMR spectrum of polybutadiene has resonances in both the olefinic region and in the alkyl region. A comparison of the *cis* and *trans* olefinic peaks related to C^1 carbon gave *trans* stereoselectivity (69 %) of polybutenamer produced by this catalyst system. The C^2 carbons show signals for the *tt* and *tc* environments, with the signals for C^2*tt* separated from that for C^2*tc* by 0.05 ppm, while the signal for the *cis* configuration at 27.42 ppm occurs as an unresolved singlet. The signal for the olefinic carbons shows four peaks assigned as shown in the table; these peaks are further split possibly due to triad and even pentad effects.

Table 4.11 ^{13}C NMR peak assignments (ppm from TMS) of polybutenamer produced by the W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system.

Carbon	Position and asssignment			
C^1	130.15 (tc)	130.02 (tt)	129.63 (cc)	129.44 (ct)
C^2	32.73 (tt)	32.68 (tc)	27.42 (cc ≡ ct)	

The results obtained by ^{1}H NMR agrees with that estimated from the ^{13}C NMR spectrum. In the ^{1}H NMR spectrum of the polybutadiene there are two groups of peaks: one group corresponds to non-olefinic proton signals, and the second group of peaks is related to the olefinic proton signals (Fig. 4.35). The relative intensities of the cis and trans olefinic peaks at 5.40 ppm and 5.44 ppm respectively give a cis/trans ratio of 29/71. Additionally, the relative integrated peak areas of the two signals at 2.11 and 2.06 ppm indicate a similar trans-content of the polymer.

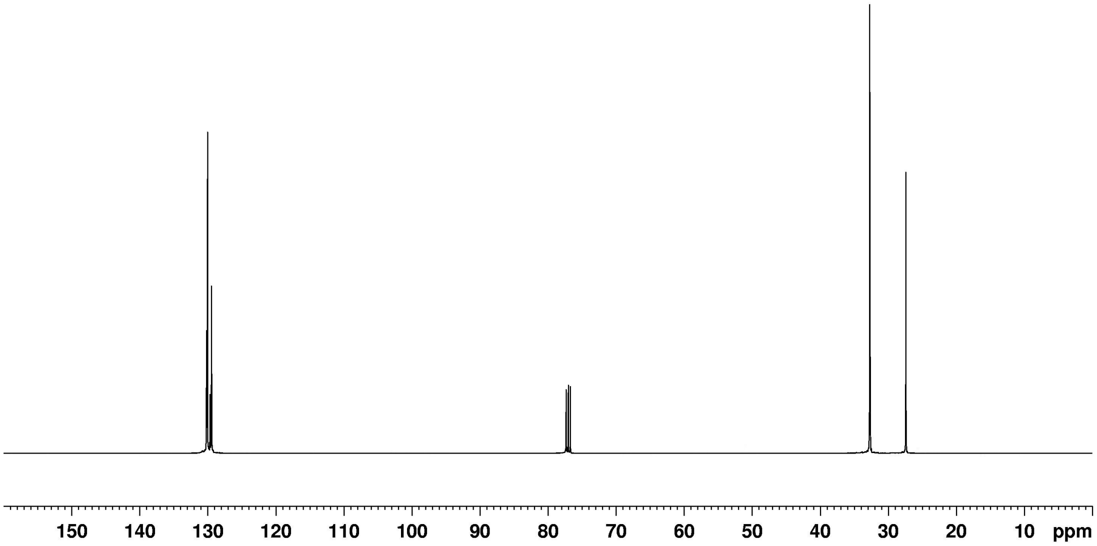


Figure 4.33 ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polybutenamer obtained with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system.

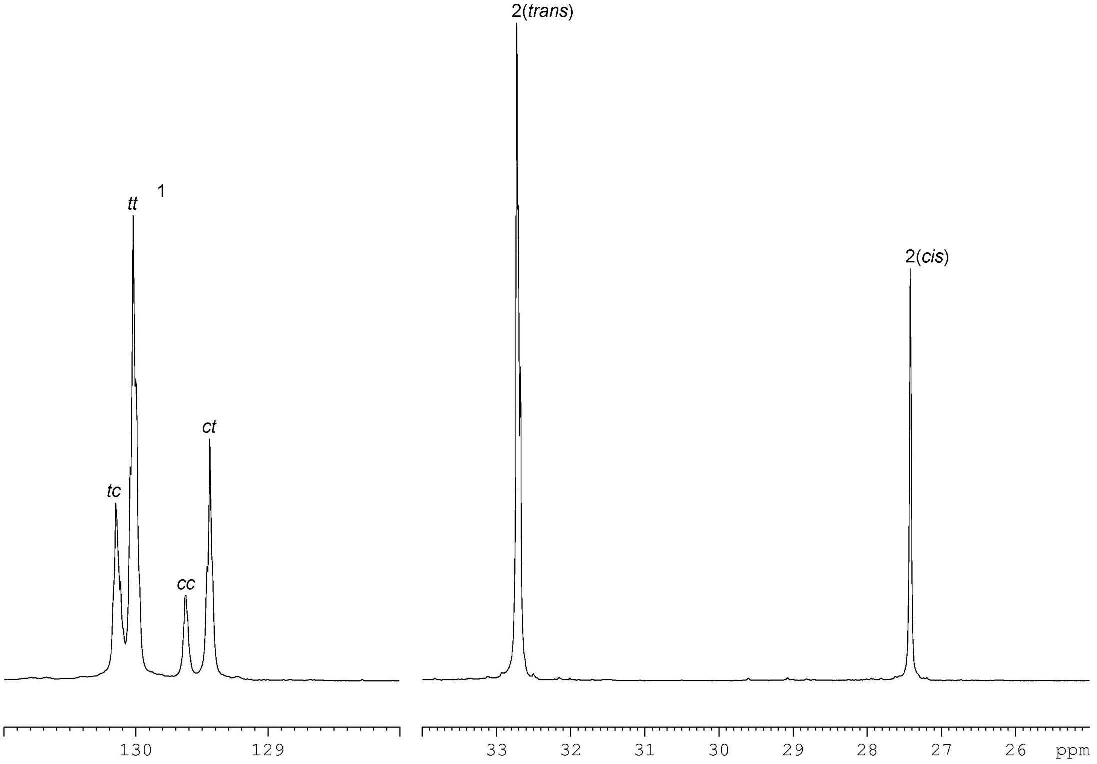


Figure 4.34 Expanded ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polybutenamer obtained with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system.

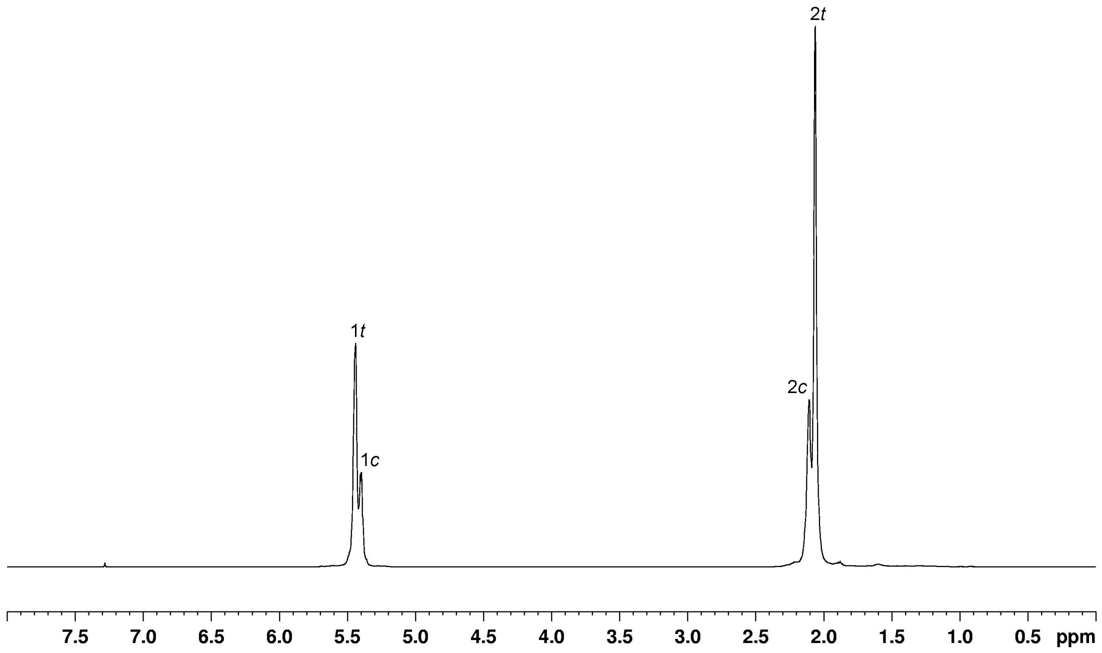


Figure 4.35 ^1H NMR spectrum (400 MHz, $CDCl_3$) of polybutenamer obtained with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system.

4.4.3 Metathesis reactions between cyclic alkenes by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ catalyst

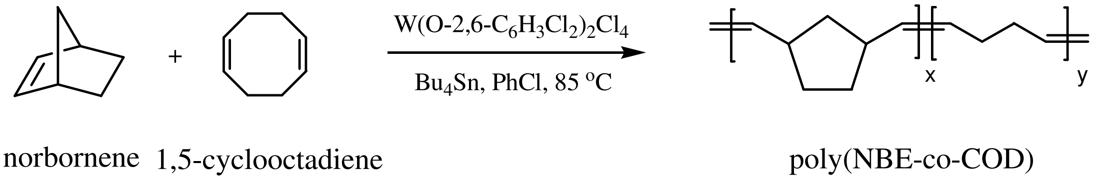
Copolymerization is an aspect of polymer chemistry that continues to attract widespread interest, not only because it affords the opportunity to prepare and study polymers with a wide variety of main chain architectures but also because of the mechanistic insights which may be gained from a detailed analysis of the microstructure of such materials. Copolymers can be synthesized by various polymerization methods. Metathesis reactions between two different cyclic olefins lead to formation of copolymers by ring-opening metathesis reactions.

The chemical industry is using metathesis catalysts to produce increasing amounts of plastic material with special properties since ROMP methodology allows the preparation of new kinds of homo- and co-polymers and elastomers. However, copolymerization of monomer mixtures by ring-opening metathesis polymerization (ROMP) is rare. Also, much of this scientific work has been done on the homopolymerization of cycloolefins, and only very few publications have been devoted to the copolymerization of these cycloolefins. Detailed studies, using ^{13}C NMR spectroscopy, on the microstructures of numerous ROMP polymers and copolymers have led to the development of theories, which provide a rationalization of the polymer's primary microstructural features, e.g., *cis*/*trans* double bond ratio and distribution, regiochemistry, copolymer ratios and tacticity.

In this work, ring-opening copolymerization studies were made on the systems 1,5-cyclooctadiene (COD)/norbornene (NBE), cyclopentene (CPE)/norbornene, cyclooctene (COE)/norbornene by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 / Bu_4Sn$ catalyst system. All reactions were initiated in the bulk, at 85 ºC and under nitrogen atmosphere. The structures of copolymers obtained were characterized by ^{1}H and ^{13}C NMR, and GPC techniques. Since the copolymer composition is sensitive to the catalyst system used, the microstructures of copolymers have been analysed in detail.

4.4.3.1 Metathesis reaction of 1,5-cyclooctadiene with norbornene

In this work, metathesis reaction of 1,5-cyclooctadiene with norbornene was examined. Metathesis reaction of 1,5-cyclooctadiene with norbornene resulted in the formation of co-COD-NBE polymers as illustrated below.



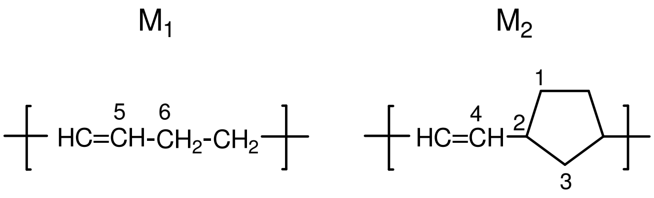
Homopolymerization reaction results of 1,5-cyclooctadiene and norbornene were also compared with those obtained from copolymerization reactions. Gel permeation chromatographic analyses show only one peak for copolymer, confirming the formation and purity of copolymer. A summary of the polymerization results is given in Table 4.12.

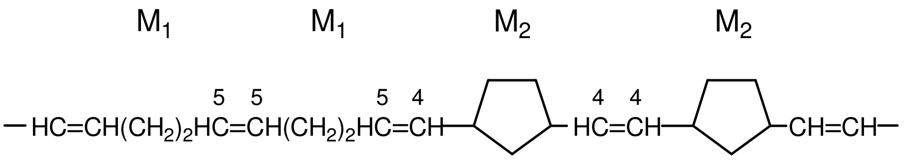
The geometric structures of copolymers were determined from ^{13}C and ^{1}H NMR spectra according to Ivin et al. (1979 and 1982). A detailed interpretation of the ^{13}C NMR spectrum of the ring-opened copolymers of 1,5-cyclooctadiene (M_1) and norbornene (M_2) concerning copolymer composition, reactivity ratios, homo and heterodyad distribution, cis/trans ratio and distribution for each dyad are given.

Table 4.12 Characterization of polymers obtained by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 / Bu_4Sn$ (COD/NBE/cocatalyst/catalyst = 50:50:3:1; activation time:10 min; at 85 ºC).

Monomer	Properties of polymers	
1,5-cyclooctadiene (COD)	σ_c	0.31
	$\overline{M}_w$	4900
	PDI	2.12
	Yield (%)	35.6
Norbornene (NBE)	σ_c	0.43
	$\overline{M}_w$	27400
	PDI	2.84
	Yield (%)	96.8
1,5-cyclooctadiene:Norbornene (1:1)	σ_c	0.32 (M_1M_1); 0.56 (M_2M_2)
	$\overline{M}_w$	10800
	PDI	2.19
	Yield (%)	60.2

In copolymers of two monomers, M_1 (1,5-cyclooctadiene) and M_2 (norbornene), the compositional dyads may be M_1M_1, M_1M_2, M_2M_1 or M_2M_2.





The carbon atoms in M_2 unit are numbered 1, 2, 3, 4, and the carbon atoms in M_1 unit are numbered 5, 6 as indicated. In every region of the ^{13}C NMR spectrum of the ring-opened copolymer there are peaks additional to those present in the spectra of homopolymers. The spectrum of the olefinic carbons is shown in expanded form in Fig.4.36. The peaks fall into four distinct groups which, from downfield to upfield, are readily assigned to the dyad structures shown in Table 4.13.

Table 4.13 Assignment of C^4 and C^5 lines in the ^{13}C NMR spectrum of 1,5-cyclooctadiene (M_1) / norbornene (M_2) copolymers produced by the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm
4c (M_2M_1)	135.48 135.32
4t (M_2M_1)	135.20 135.07
4c (M_2M_2)	133.99 133.90 133.82 133.76
4t (M_2M_2)	133.11 133.02 132.88
5tc (M_1M_1) 5tt (M_1M_1) 5cc (M_1M_1) 5ct (M_1M_1)	130.13 130.00 129.60 129.41
5c/t (M_1M_2)	127.90 127.81

The peaks in the middle two groups (M_1M_1 and M_2M_2) are identical in position with those found in the spectra of the two homopolymers. In the olefinic region of the copolymer of 1,5-cyclooctadiene and norbornene, M_1M_2 and M_2M_1 heterodyads occured as well as M_1M_1 and M_2M_2 homodyads. The 4 *c/t* M_2M_1 and 5 *c/t* M_1M_2 peaks indicate the formation of 1,5-cyclooctadiene/norbornene copolymers. The mole fraction of the butadiene units in the copolymer, F_1, was calculated from the area of the two upfield groups of peaks divided by the total are as 0.69. The fraction of double bonds having cis configuration, σ_c, was calculated from the C^4 and C^5 peak intensities for both M_1M_1 and M_2M_2 dyads. The cis contents of M_1M_1 and that of M_2M_2 in the copolymer are 32% and 56%, respectively. The *c/t* line order for M_2M_2 is the reverse of that for M_1M_1 (Table 4.13) so that the line orders for both types of olefinic carbons in M_1M_2 is uncertain.

Table 4.14 Assignment of C^1, C^2, C^3 and C^6 lines in the ^{13}C NMR spectrum of 1,5-cyclooctadiene (M_1) / norbornene (M_2) copolymers produced by the W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm	Designation and assignment	Peak position in ppm
1cc (MM_2)	33.08	3cc ($M_2M_2M_2$)	42.72
1ct (MM_2)	32.91	3cc ($M_1M_2M_2$)	42.39
1tc (MM_2)	32.34	3cc ($M_1M_2M_1$)	42.04
1tt (MM_2)	32.17	3ct ($M_1M_2M_2$)	
		3ct ($M_2M_2M_2$)	
2tc (M_2M_2M)	43.39	3ct ($M_1M_2M_1$)	41.71
2tt (M_2M_2M)	43.13	3tc ($M_1M_2M_2$)	41.64
2cc (M_2M_2M)	38.63	3tt ($M_1M_2M_1$)	41.37
2ct (M_2M_2M)	38.39	3tt ($M_1M_2M_2$)	41.30
		3tt ($M_2M_2M_2$)	41.24
2tc (M_1M_2M)	43.47	6t (M_1M_2)	32.81
2tt (M_1M_2M)	43.22	6t (M_1M_1)	32.69
2cc (M_1M_2M)	38.28	6c (M_1M_2)	27.62
2ct (M_1M_2M)	38.03	6c (M_1M_1)	27.38

The double bond pair distribution on both M_2M_2M and M_1M_2M triads is alternating with respect to *cis* and *trans* strucures. The peak positions and assignments for the non-olefinic region of co-COD-NBE polymers are listed in Table 4.14.

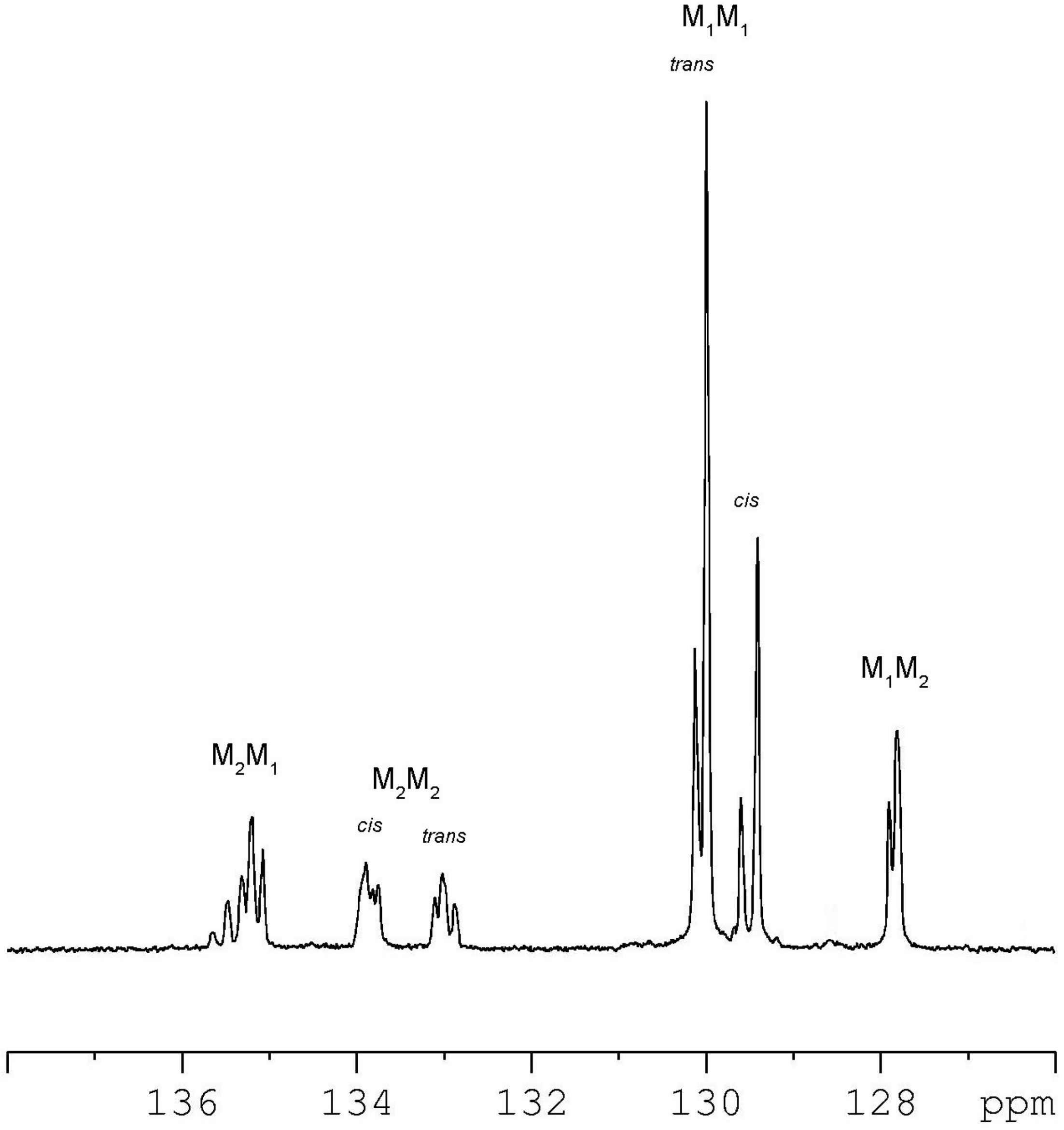


Figure 4.36 Olefinic region of the ^{13}C NMR spectrum (400 MHz, in $CDCl_3$) of copolymer prepared from 1,5-cyclooctadiene (M_1) and norbornene (M_2) using $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn as catalyst.

The ^{1}H NMR spectrum of 1,5-cyclooctadiene/norbornene copolymer was measured in $CDCl_3$ (Figure 4.37). For the poly(NBE-co-COD), signals were seen in both the olefinic region and in the alkyl region. ^{1}H NMR spectrum of poly(NBE-co-COD) had olefinic proton signals at 5.14–5.49 ppm, the *cis* and *trans* proton signals attached to C^2 carbon in the cyclopentane ring at 2.79 and 2.45 ppm and the other proton signals at 0.94–2.16 ppm. ^{1}H NMR and ^{13}C NMR spectroscopic data for copolymers obtained by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ are consistent with data previously reported for NBE/COD copolymers prepared via ROMP (Ivin et al., 1982).

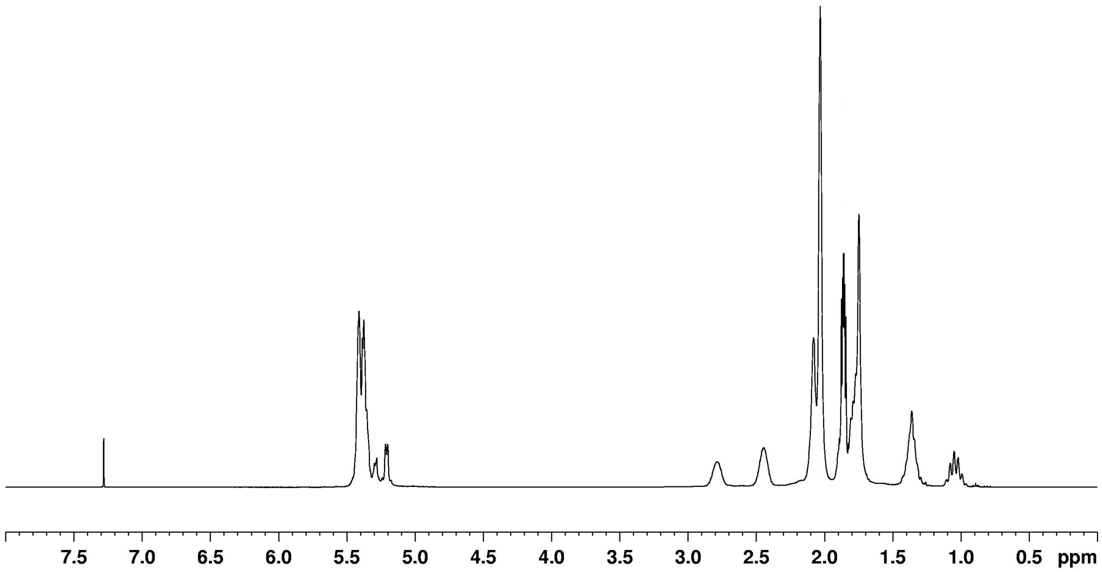
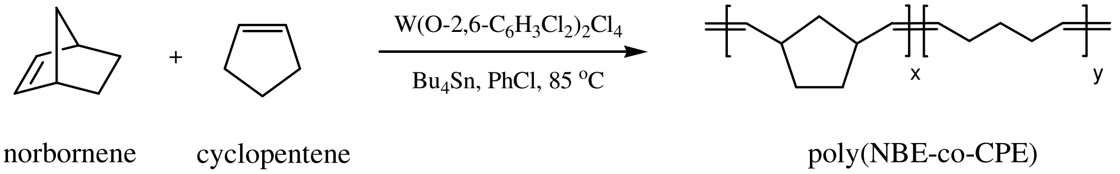


Figure 4.37 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$) of copolymer prepared from 1,5-cyclooctadiene (M_1) and norbornene (M_2) using $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4/Bu_4Sn$ as catalyst.

4.4.3.2 Metathesis reaction of cyclopentene with norbornene

In this work, metathesis copolymerization reaction of cyclopentene with norbornene was investigated. The $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalytic system produced the ring-opened copolymers of cyclopentene and norbornene.

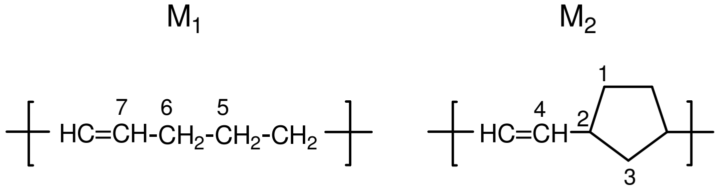


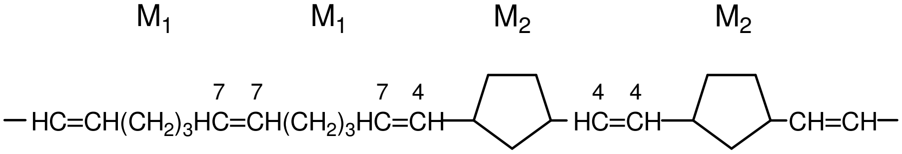
The copolymerization results are presented in the Table 4.15. A single peak was observed in the GPC, which illustrates the product is a copolymer and not a blend of homopolymers.

Table 4.15 Characterization of polymers obtained by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn (CPE/NBE/cocatalyst/catalyst = 50:50:3:1; activation time:10 min; at 85 ºC).

Monomer	Properties of polymer	
Cyclopentene:Norbornene (1:1)	σ_c	0.14 (M_1M_1); 0.30 (M_2M_2)
	$\overline{M}_w$	19500
	PDI	2.33
	Yield (%)	68.4

^1H and ^{13}C NMR spectra of copolymer produced by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst are good agreement with those previously reported for cyclopentene and norbornene copolymers in literature (Ivin et al., 1979, 1982; Manivannan et al., 2000). The peak positions and assignments are recorded in Tables 4.16 and 4.17. In every region of the spectrum there are peaks additional to those present in the spectra of homopolymers. The olefinic region of the ^{13}C NMR spectrum of the copolymer is shown Figure 4.38. The carbon atoms in M_2 unit are numbered 1, 2, 3, 4, and the carbon atoms in M_1 unit are numbered 5, 6, 7 as indicated. The peaks in the middle groups (M_1M_1 and M_2M_2) are identical in position with those found in the spectra of the two homopolymers. As shown in the olefinic region of the ^{13}C NMR spectrum, M_1M_2 and M_2M_1 heterodyads occured as well as M_1M_1 and M_2M_2 homodyads. The peaks concerning 4 *c/t* M_2M_1 and 7 *c/t* M_1M_2 showed the formation of cyclopentene/norbornene copolymers.





The ^{13}C NMR analysis revealed that the copolymer obtained by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 / Bu_4Sn$ catalyst system contains 24 mole % M_1 units, 1-pentenylene, and 76 mole % M_2 units, 1,3-cyclopentylenevinylene. The fractions of *cis* double bonds (σ_c) in M_1M_1 and M_2M_2 dyads were estimated as 0.14 and 0.30, respectively. For M_2M_2M triads, the cis/trans reactivity ratios, r_t = tt / tc and r_c = cc / ct, were calculated as $r_t = 3.105$ and $r_c = 0.290$, giving an r_tr_c value of 0.900. In a similar way, for M_1M_2M triads, these values were found as $r_t = 2.759$, $r_c = 0.308$, and $r_tr_c = 0.849$. The r_tr_c values thus obtained characterize a copolymer with an alternating distribution of *cis/trans* double bond pair sequences for both M_2M_2M and M_1M_2M triads. The *c/t* line order for M_2M_2 is the reverse of that for M_1M_1 (Table 4.16) so that the line orders for both types of olefinic carbons in M_1M_2 is uncertain.

Table 4.16 Assignment of C^4 and C^7 lines in the ^{13}C NMR spectrum of cyclopentene (M_1) / norbornene (M_2) copolymers produced by the W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm
4c/t (M_2M_1)	135.53 135.42 135.19 135.03
4c (M_2M_2)	133.98 133.92 133.83 133.76
4t (M_2M_2)	133.13 133.02 132.86
7t (M_1M_1)	130.32
7c (M_1M_1)	129.81
7c/t (M_1M_2)	128.29 128.17

The ^1H NMR spectrum of cyclopentene/norbornene copolymer is given in Figure 4.39. The spectrum shows signals in both the olefinic region and in the alkyl region. ^1H NMR spectrum of poly(NBE-co-CPE) had olefinic proton signals at 5.15–5.48 ppm, the *cis* and *trans* proton signals attached to C^2 carbon in the cyclopentane ring at 2.80 and 2.45 ppm and the other proton signals at 0.95–2.09 ppm. ^1H NMR spectroscopic data for copolymers obtained by W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system are good agreement with data previously reported for NBE/CPE copolymers prepared via ROMP (Manivannan et al., 2000).

Table 4.17 Assignment of C^1, C^2, C^3, C^5 and C^6 lines in the ^{13}C NMR spectrum of cyclopentene (M_1) / norbornene (M_2) copolymers produced by the W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm
2tc (M_2M_2M)	43.41
2tt (M_2M_2M)	43.12
2cc (M_2M_2M)	38.66
2ct (M_2M_2M)	38.41
2tc (M_1M_2M)	43.52
2tt (M_1M_2M)	43.24
2cc (M_1M_2M)	38.28
2ct (M_1M_2M)	38.02
3 ($M_2M_2M_2$)	42.76
3 ($M_1M_2M_2$), ($M_2M_2M_2$) or ($M_1M_2M_1$)	42.09
3 ($M_1M_2M_2$), ($M_2M_2M_2$) or ($M_1M_2M_1$)	41.35
1cc (M_2M_2)	33.10
1ct (M_2M_2)	32.93
1cc (M_1M_2)	32.84
1ct (M_1M_2)	32.65
1tc (M_2M_2 / M_1M_2)	32.37
1tt (M_2M_2 / M_1M_2)	32.21
6tc (MM_1M_1 / MM_1M_2)	32.04
6tt (MM_1M_1 / MM_1M_2)	31.95
5cc ($M_1M_1M_1$)	29.84
5tc ($M_1M_1M_2$)	
5ct/tc ($M_2M_1M_2$)	
5ct/tc ($M_1M_1M_1$)	29.67
5ct ($M_1M_1M_2$)	
5tt ($M_1M_1M_1$ / $M_1M_1M_2$ / $M_2M_1M_2$)	29.51
6cc (MM_1M_2)	27.16
6ct (MM_1M_2)	26.92
6cc (MM_1M_1)	26.83
6ct (MM_1M_1)	26.70

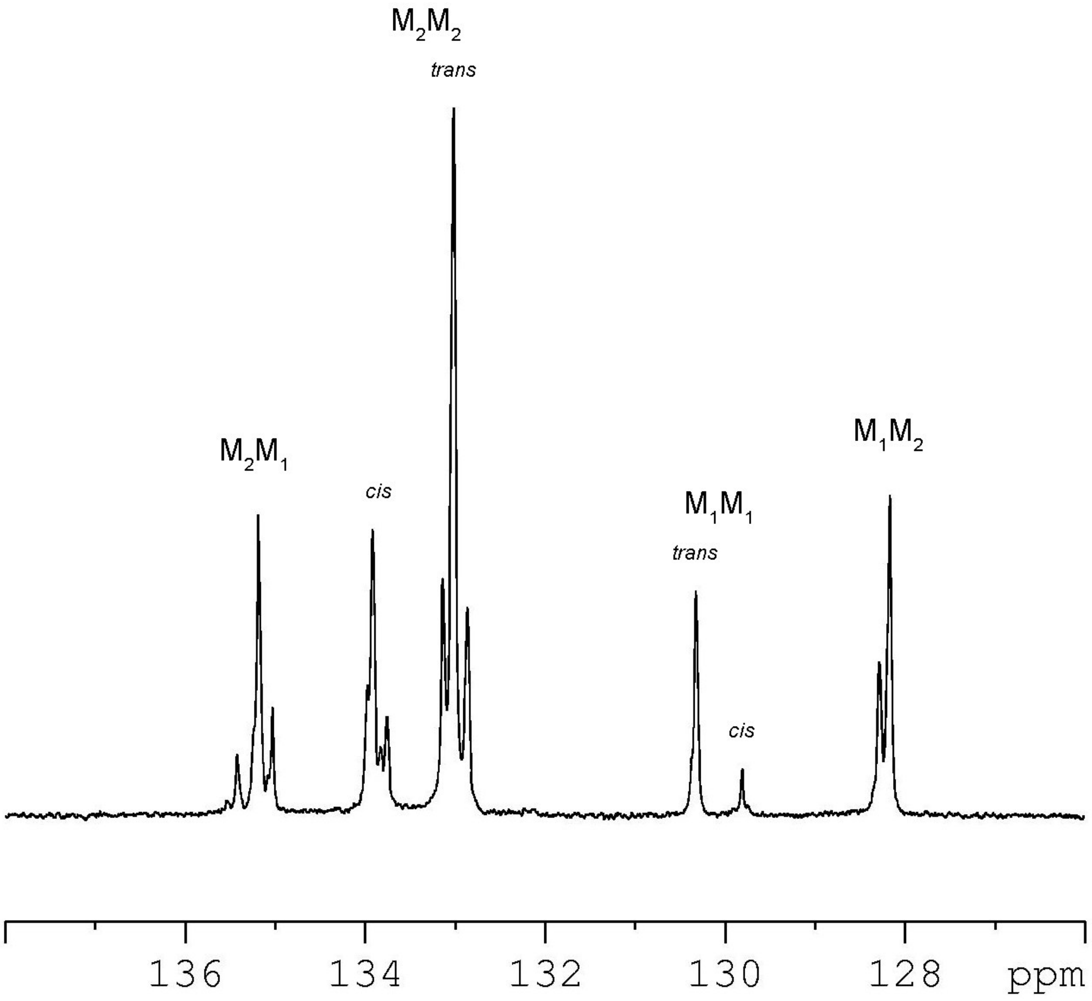


Figure 4.38 Olefinic region of the ^{13}C NMR spectrum (400 MHz, in $CDCl_3$) of copolymer prepared from cyclopentene (M_1) and norbornene (M_2) using $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn as catalyst.

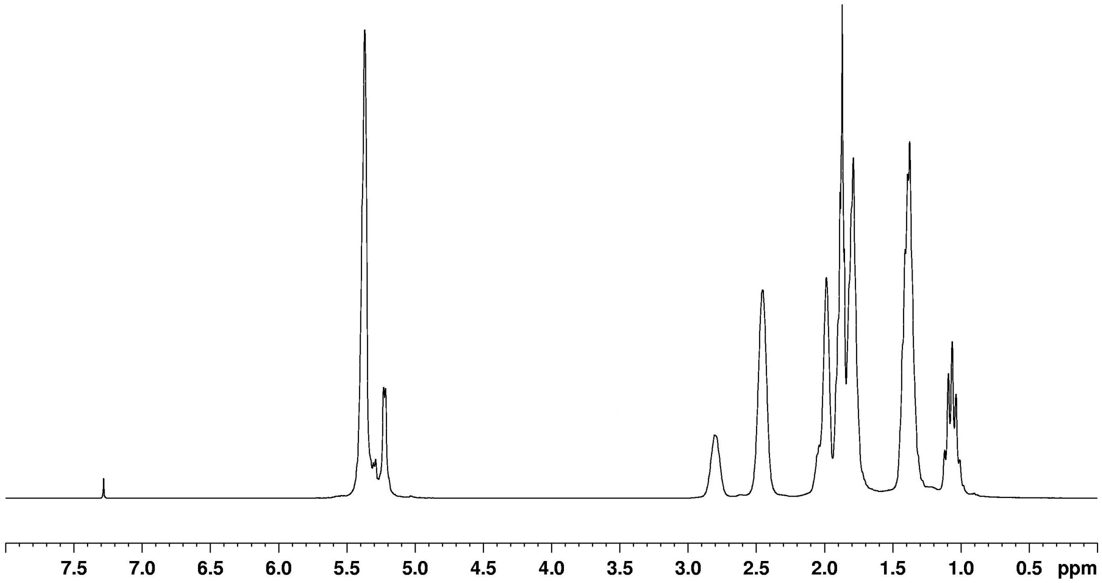
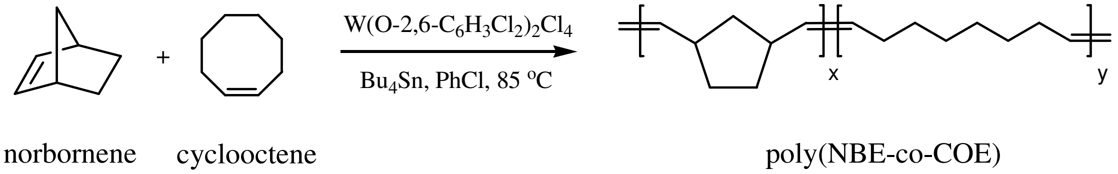


Figure 4.39 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$) of copolymer prepared from cyclopentene (M_1) and norbornene (M_2) using $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn as catalyst.

4.4.3.3 Metathesis reaction of cyclooctene with norbornene

In this work, metathesis copolymerization reaction of cyclooctene with norbornene was investigated. The $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn system catalyzed the reaction to give the ring-opened copolymers of cyclooctene and norbornene.

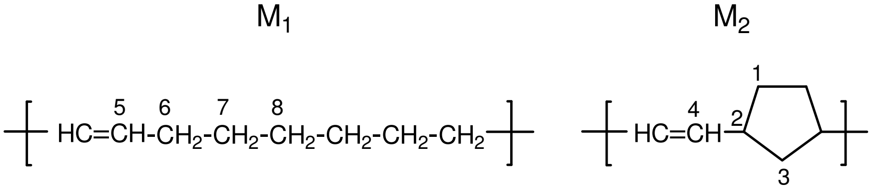


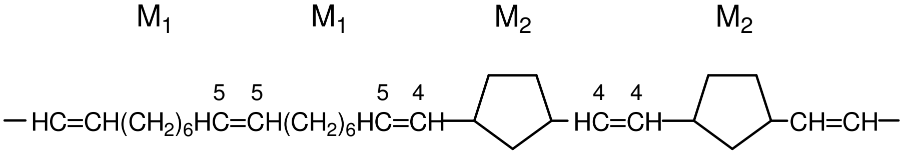
A comparison of the results of homopolymerization and copolymerization reactions of cyclooctene and norbornene was given in Table 4.18. The microstructure of the copolymer obtained was determined by ^{1}H and ^{13}C NMR spectroscopy.

Table 4.18 Characterization of polymers obtained by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn (COE/NBE/cocatalyst/catalyst = 50:50:3:1; activation time:10 min; at 85 ºC).

Monomer	Properties of polymers	
Cyclooctene (COE)	σ_c	0.16
	$\bar{M}_w$	16800
	PDI	1.81
	Yield (%)	83.8
Norbornene (NBE)	σ_c	0.43
	$\bar{M}_w$	27400
	PDI	2.84
	Yield (%)	96.8
Cyclooctene:Norbornene (1:1)	σ_c	0.32 (M_1M_1); 0.45 (M_2M_2)
	$\bar{M}_w$	20300
	PDI	1.95
	Yield (%)	89.1

The carbon atoms in M_2 unit are numbered 1, 2, 3, 4, and the carbon atoms in M_1 unit are numbered 5, 6, 7, 8 as indicated below.





The peak positions for the olefinic region of the ^{13}C NMR spectrum of cyclooctene (M_1) / norbornene (M_2) copolymers are depicted in Figure 4.40. The peak positions and assignments are recorded in Tables 4.19 and 4.20. In every region of the ^{13}C NMR spectrum of the copolymer synthesized there are peaks additional to those present in the spectra of homopolymers. All the resonances in the homodyads, M_1M_1 and M_2M_2 are the same as those assigned previously in detail for the homopolymers. M_1M_2 and M_2M_1 heterodyads occur as well as M_1M_1 and M_2M_2 homodyads. The *trans* and *cis* olefinic lines of poly(NBE-co-COE) are given in Table 4.19 together with their assignments. The 4 *c/t* M_2M_1 and 5 *c/t* M_1M_2 peaks indicate the formation of cyclooctene/norbornene copolymers.

The mole fraction of the 1-octenylene units in the copolymer, F_1, was calculated to be 0.53. The fractions of *cis* double bonds (σ_c) in M_1M_1 and M_2M_2 dyads were estimated as 0.32 and 0.45, respectively. For M_2M_2M triads, the cis/trans reactivity ratios, r_t = tt / tc and r_c = cc / ct, were calculated as $r_t = 1.468$ and $r_c = 0.580$, giving an r_tr_c value of 0.852. In a similar way, for M_1M_2M triads, these values were found as $r_t = 1.343$, $r_c = 0.627$, and $r_tr_c = 0.842$. The r_tr_c values thus obtained characterize a copolymer with an alternating distribution of *cis*/*trans* double bond pair sequences for both M_2M_2M and M_1M_2M triads.

Table 4.19 Assignment of C^4 and C^5 lines in the ^{13}C NMR spectrum of cyclooctene (M_1) / norbornene (M_2) copolymers produced by the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 / Bu_4Sn$ catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm
4c (M_2M_1)	135.22 135.06
4t (M_2M_1)	134.90 134.76
4c (M_2M_2)	133.99 133.92 133.85 133.77
4t (M_2M_2)	133.14 133.03 132.88
5t (M_1M_1) 5c (M_1M_1)	130.34 129.88
5c (M_1M_2) 5t (M_1M_2)	128.59 128.48

For the poly(NBE-co-COE), signals were seen in both the olefinic region and in the alkyl region (Figure 4.41). ^1H NMR spectrum of co-NBE-COE polymer had olefinic proton signals at 5.16–5.53 ppm, the *cis* and *trans* proton signals attached to C^2 carbon in the cyclopentane ring at 2.80 and 2.45 ppm and the other proton signals at 0.93–2.17 ppm. ^1H and ^{13}C NMR spectroscopic data for copolymers formed by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 / Bu_4Sn$ catalyst system are consistent with data previously reported for NBE/COE copolymers prepared via ROMP (Ivin et al., 1982).

The peak positions and assignments for the non-olefinic region of co-COE-NBE polymers are listed in Table 4.20.

Table 4.20 Assignment of C^1, C^2, C^3, C^6, C^7 and C^8 lines in the ^{13}C NMR spectrum of cyclooctene (M_1) / norbornene (M_2) copolymers produced by the W(O-2,6-$C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm	Designation and assignment	Peak position in ppm
2tc (M_2M_2M) 2tt (M_2M_2M) 2cc (M_2M_2M) 2ct (M_2M_2M)	43.41 43.13 38.66 38.42	1cc (M_2M_2) 1ct (M_2M_2) 1cc (M_1M_2) 1ct (M_1M_2)	33.12 32.94 32.82 32.66
2tc (M_1M_2M) 2tt (M_1M_2M) 2cc (M_1M_2M) 2ct (M_1M_2M)	43.51 43.25 38.27 38.02	1tc (M_2M_2) 1tc (M_1M_2) 1tt (M_2M_2) 1tt (M_1M_2)	32.37 32.21
3cc ($M_2M_2M_2$) 3cc ($M_1M_2M_2$)	42.75 42.45	6t (M_1M) 6t (M_1M_2) 6c (M_1M_2) 6c (M_1M_1)	32.60 32.52 27.49 27.22
3cc ($M_1M_2M_1$) 3ct ($M_1M_2M_2$) 3ct ($M_2M_2M_2$)	42.08		
3ct ($M_1M_2M_1$) 3tc ($M_1M_2M_2$)	41.78	7c (M_1M_2) 7c (M_1M_1) 7t (M_1M)	29.92 29.75 29.63
3tt ($M_1M_2M_1$) 3tt ($M_1M_2M_2$) 3tt ($M_2M_2M_2$)	41.36	8c (M_1M) 8t (M_1M)	29.18 29.04

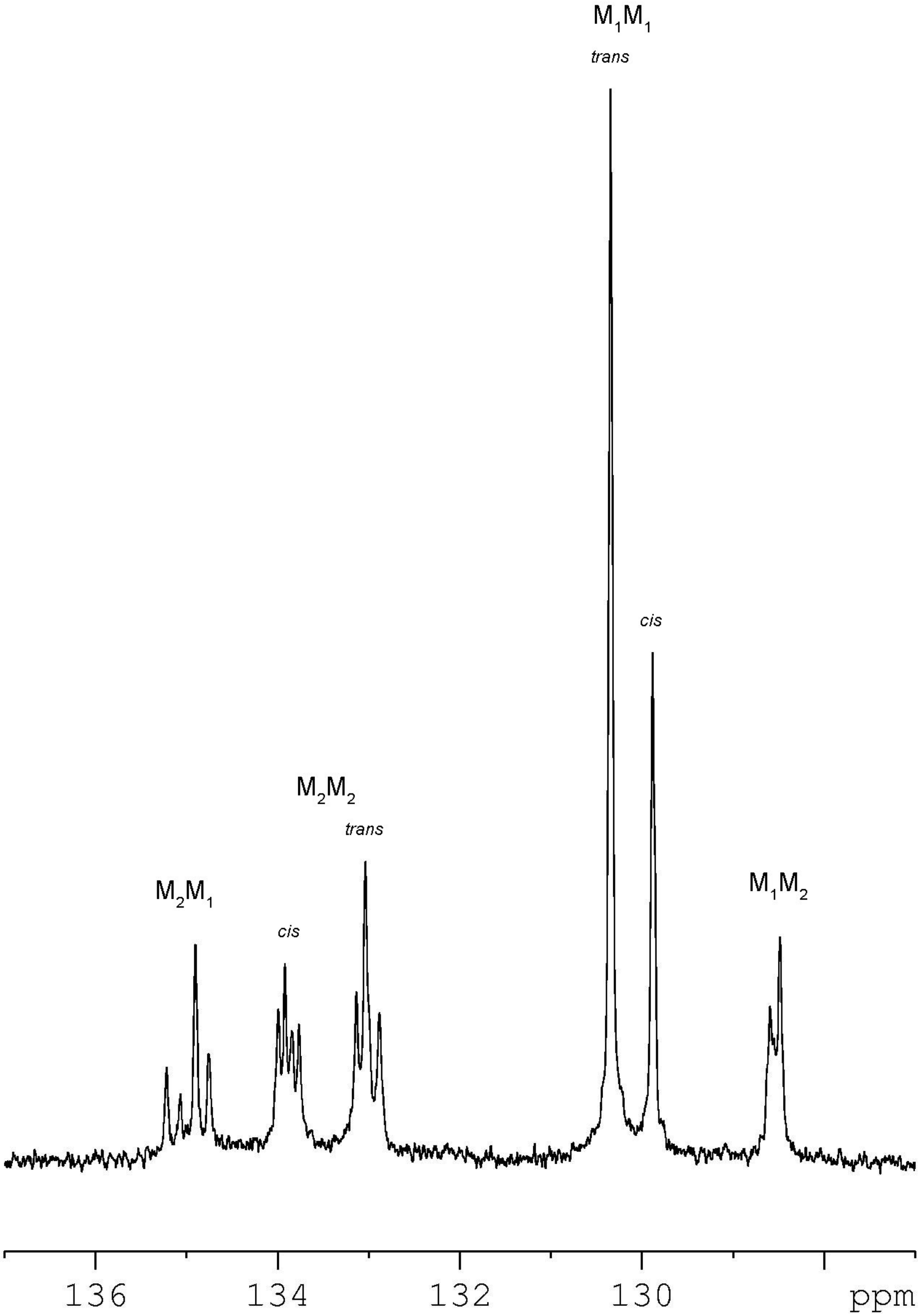


Figure 4.40 Olefinic region of the ^{13}C NMR spectrum (400 MHz, in $CDCl_3$) of copolymer prepared from cyclooctene (M_1) and norbornene (M_2) using $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn as catalyst.

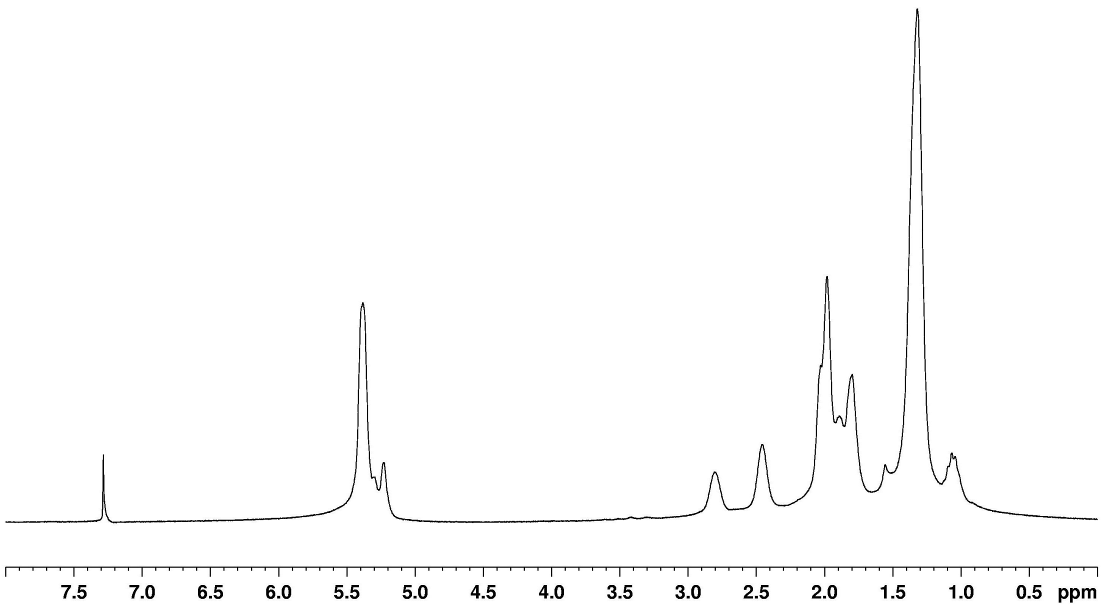
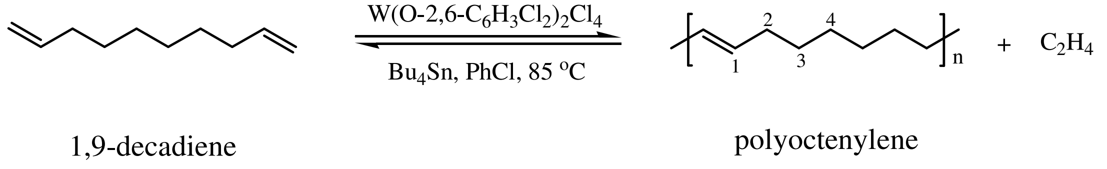


Figure 4.41 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$) of copolymer prepared from cyclooctene (M_1) and norbornene (M_2) using $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn as catalyst.

4.4.4 ADMET polymerization reactions by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ catalyst

Acyclic diene metathesis (ADMET) polymerization reaction of 1,9-decadiene was explored by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system. This catalytic system produced polyoctenylene via the ADMET polycondensation of 1,9-decadiene. Soluble, linear polymers were obtained; the general polymerization scheme is shown below. The carbon atoms in the polymer are numbered from 1 to 4.



^{1}H and ^{13}C NMR spectra demonstrated the typical structure of a polyoctenylene synthesized according to ADMET polymerization (Fig. 4.42, 4.43 and 4.44). The spectral features are consistent with the data reported in the literature. The results obtained for ADMET polymerization of polyoctenylene is summarized in Table 4.21.

Table 4.21 The results obtained in ADMET polymerization of 1,9-decadiene by the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4 / Bu_4Sn$ catalyst system.

σ_c (^{1}H)[a]	σ_c (^{13}C)[a]	$\overline{M}_n$ (NMR)[b]	$\overline{M}_n$ (GPC)[c]	PDI	Yield (%)
0.15	0.14	1850	4200	1.76	74.1

[a] Fraction of double bonds having cis-configuration, σ_c calculated from ^{1}H and ^{13}C NMR.
[b] Calculated via end-group analysis from ^{1}H NMR data, by integrating the signals corresponding to the terminal vinyl groups vs. internal olefin .
[c] Determined by gel permeation chromatography (GPC) using polystyrene standards .

Polymerization of 1,9-decadiene occurred in good yield (74%). Freshly precipitated and dried polymers were soluble in common organic solvents. Molecular weights and distributions of polyoctenylene samples were determined by gel permeation chromatography (GPC) and ^{1}H NMR. Molecular weight determination by GPC (polystyrene standards) shows that low molecular weight ($\overline{M}_n$ = 4200) was obtained for polyoctenylene samples. Its polydispersity index (PDI) is 1.76, indicating that polymer was formed by an equilibrium step polymerization reaction. However, a number-average molecular weight, $\overline{M}_{n,}$ of 1850 g/mol was calculated from ^{1}H NMR end-group analysis of the polymer, verfying the low molecular weight.

^{1}H and ^{13}C NMR data show that the end groups (vinyl groups) are also exist, typical for ADMET chemistry. ^{13}C NMR spectrum shows carbon resonances in both the olefinic region (δ = 110.0–140.0 ppm) and in the alkyl region (δ = 20.0–50.0 ppm). The signal around 139.16 ppm refers to terminal vinyl methylene carbons, the signal around 130 ppm refers to trans and cis internal olefinic carbons, and the signal around 114.13 ppm refers to terminal vinyl methine carbons (Fig. 4.42) (Wagener, 1990). It is possible to distinguish between both the cis and trans internal sp^2 carbons from the ^{13}C NMR, as well as for the allylic carbon adjacent to the internal vinyl position. The internal cis olefinic carbon (C^1) appears at 129.87 ppm, and the trans internal olefinic carbon appears at 130.34 ppm. The carbon atom (C^2) adjacent to the internal olefinic carbon also has two different resonances, i.e., the cis carbon at 27.23 ppm and the trans carbon at 32.62 ppm. A direct correlation between the peak intensities of these allylic carbon resonances and those of the internal vinyl carbons corroborates the assignments of the percentage trans stereochemistry (86%) for the obtained polymer.

The results obtained by ^{13}C NMR agree well with the ^{1}H NMR spectrum. ^{1}H NMR spectrum shows signals in both the olefinic region (δ = 5.0–6.0 ppm) and in the alkyl region (δ = 1.0–3.0 ppm). The signal around 4.97 ppm refers to terminal vinyl methine protons, and the signal around 5.40 ppm refers to internal olefinic protons, and the signal around 5.83 ppm refers to terminal vinyl methylene protons, and signals around 2.00 and 1.25 ppm demonstrate non-olefinic protons (Fig. 4.44). The signals at 5.33 ppm and 5.41 ppm correspond to cis and trans internal olefinic protons respectively. The relative intensities of the olefinic peaks at 5.33 and 5.41 ppm give a cis/trans ratio of 15/85. Moreover, the relative integrated peak areas of the two signals at 2.13 and 1.99 ppm reveal a similar trans-content of the polymer.

It is particularly important to note that no evidence of vinyl addition chemistry is apparent in these NMR spectra since vinyl addition reactions is well known to be the principle competing reactions in ADMET polymerization chemistry.

As noted from these obtained results, the most important feature of this aryloxide tungsten-based catalyst system is its ability to produce linear, soluble polymer in a clean metathesis process under bulk conditions, in comparison to the classical catalyst systems.

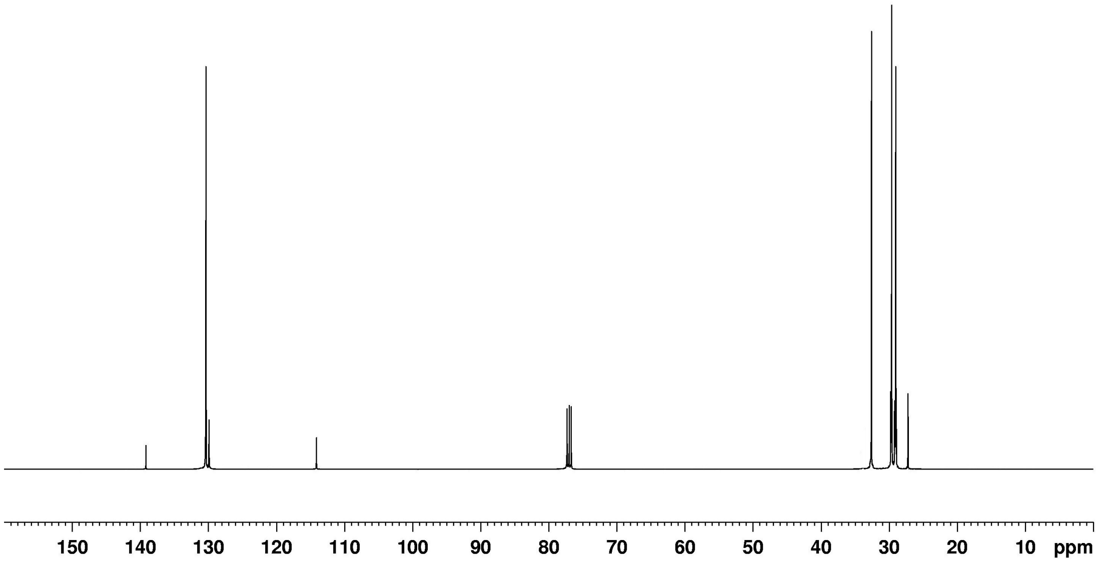


Figure 4.42 ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polyoctenylene obtained with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system *via* ADMET.

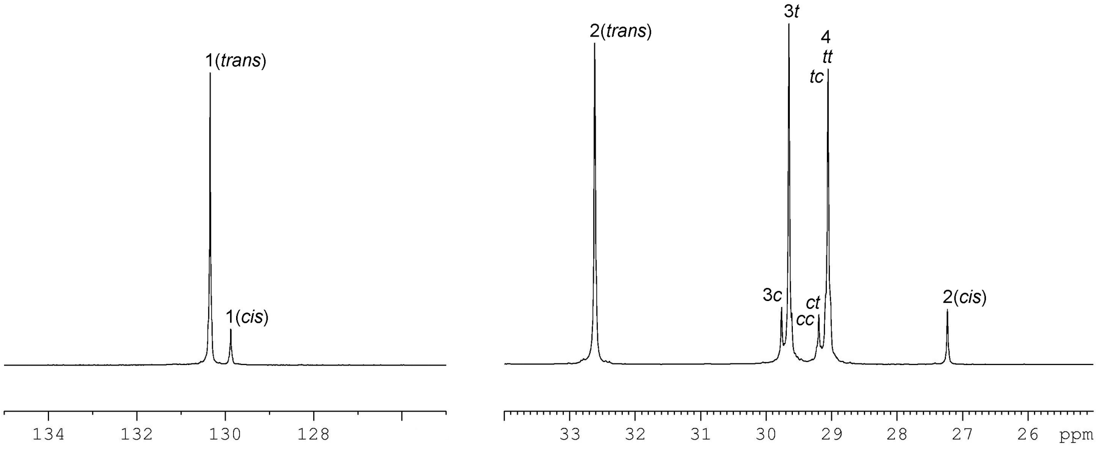


Figure 4.43 Expanded ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polyoctenylene obtained with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system *via* ADMET.

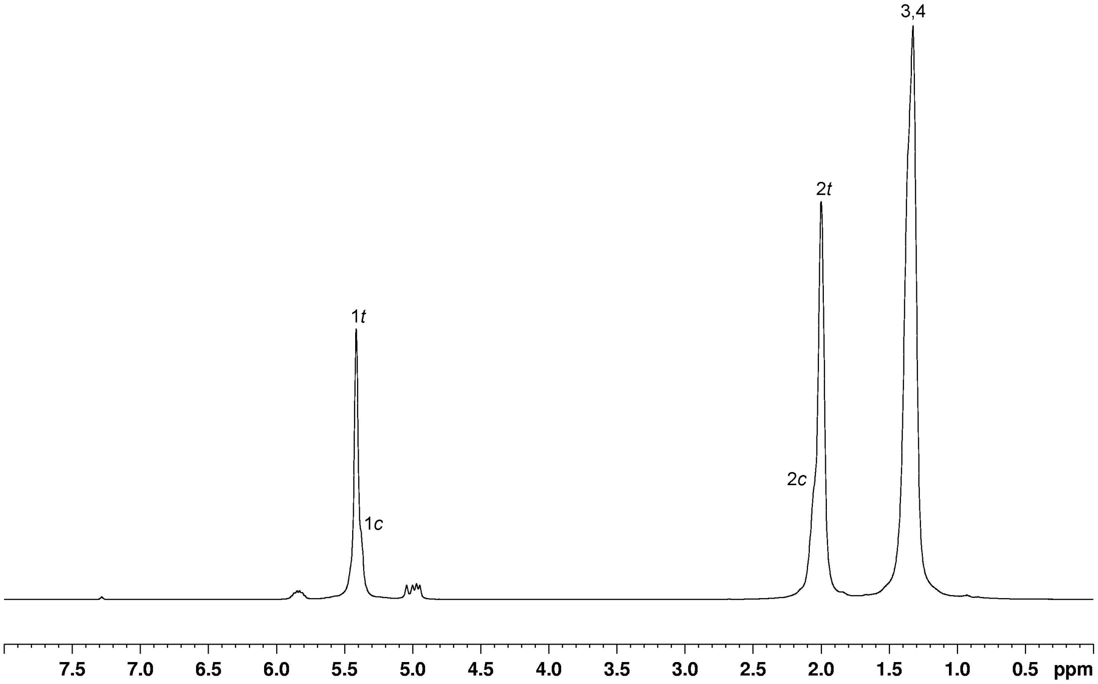


Figure 4.44 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polyoctenylene obtained with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system *via* ADMET.

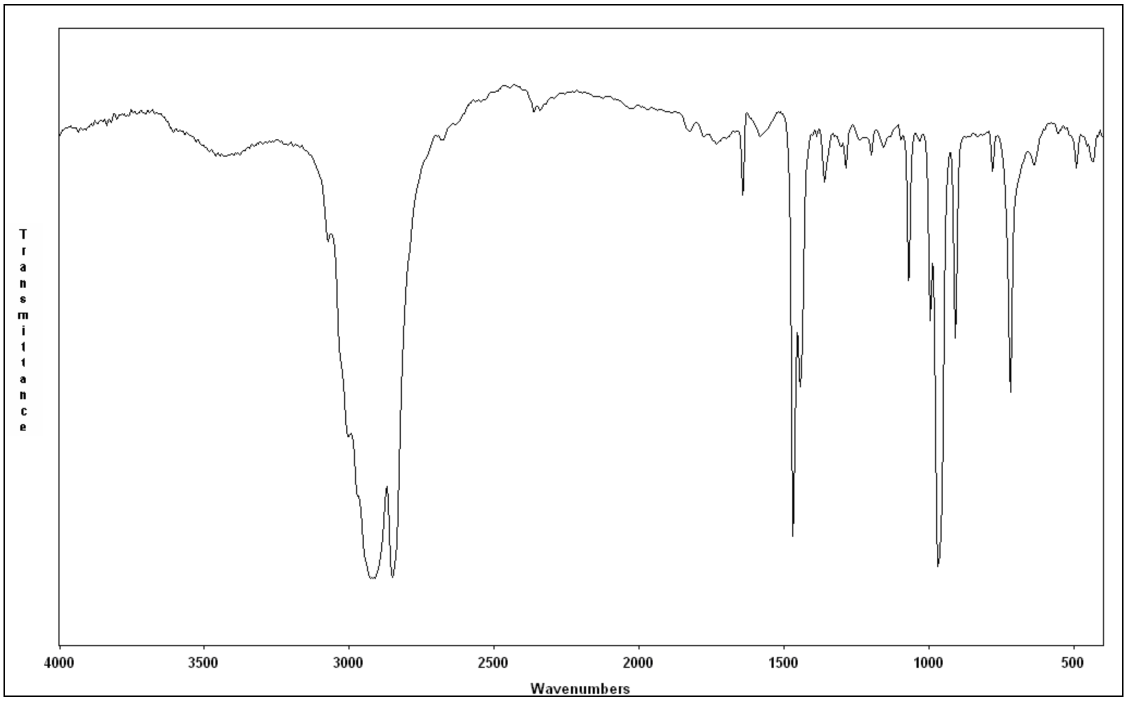


Figure 4.45 FT-IR spectrum of polyoctenylene obtained with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system *via* ADMET.

4.4.5 Ring-closing metathesis (RCM) reactions by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ catalyst

In this study, ring-closing metathesis (RCM) reaction of 1,7-octadiene, an acyclic diene, was studied by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system (Figure 4.46).

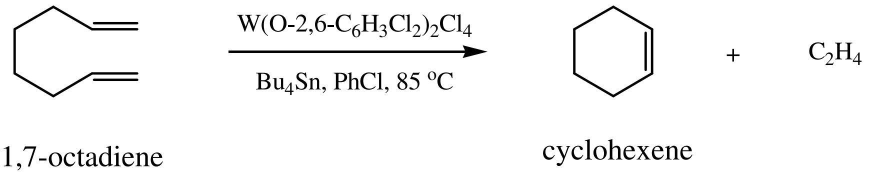


Figure 4.46 Ring-closing metathesis (RCM) reaction of 1,7-octadiene by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system.

Gas chromatographic analysis of the reaction mixture indicated the formation of metahtesis product. Ring-closing metathesis (RCM) reaction of 1,7-octadiene in the presence of this two-component system resulted in the formation of the metathesis product cyclohexene. The products observed are given in the Table 4.22 with respect to their retention times. GC-MS spectra of the products formed in the ring-closing metathesis (RCM) reaction of 1,7-octadiene are given in Figure 4.47 and Figure 4.48. The main product of the reaction is cyclohexene. The other peaks belong to unreacted olefin, solvent and internal standard.

A yield of 43,1 % cyclohexene was obtained with the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system.

Table 4.22 The products in the ring-closing metathesis reaction of 1,7-octadiene.

Retention time (min)	Product	Molecular formula	Molecular weight
4.9	Cyclohexene	C_6H_{10}	82
6.8	1,7-octadiene	C_8H_{14}	110
8.6	Chlorobenzene	C_6H_5Cl	112
23.8	n-Hexadecane	$C_{16}H_{34}$	226

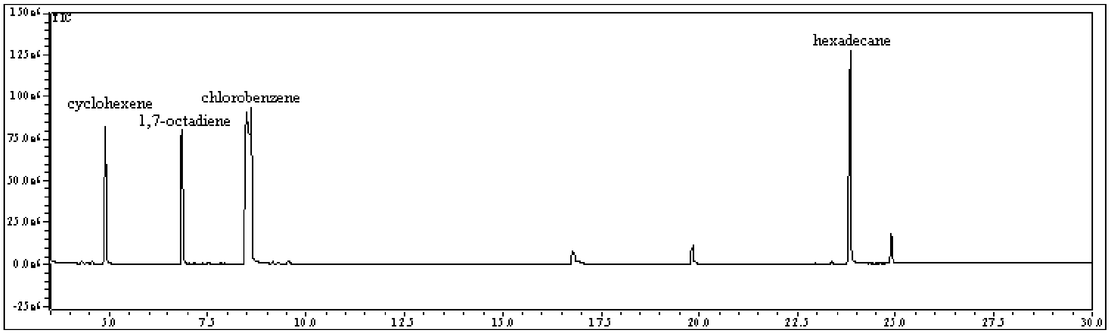
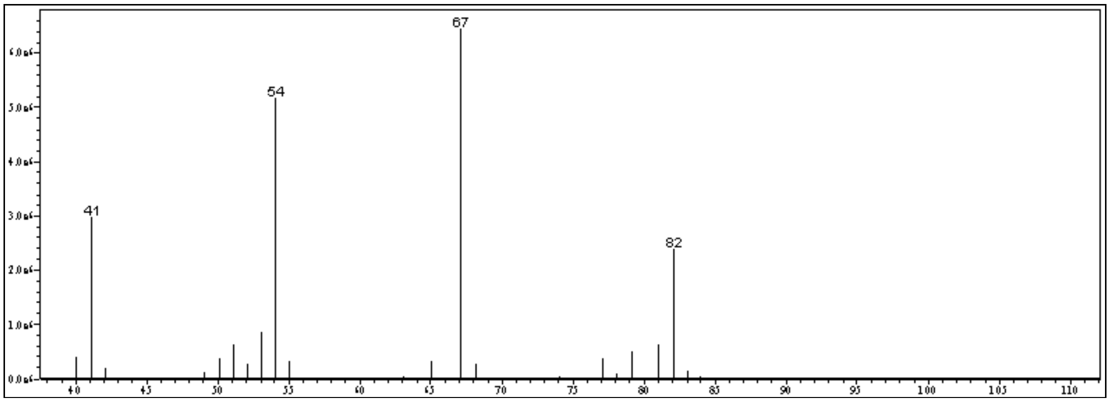


Figure 4.47 Gas chromatogram of the ring-closing metathesis (RCM) products of 1,7-octadiene.

Name: cyclohexene **Ret. Time:** 4.9



Name: 1,7-octadiene **Ret. Time:** 6.8

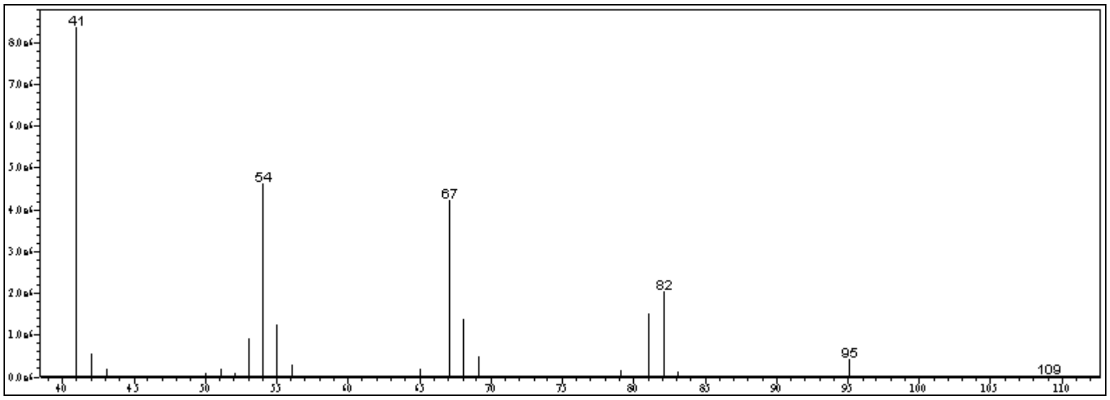


Figure 4.48 Mass spectra of the ring-closing metathesis (RCM) products of 1,7-octadiene.

4.5 Applications of Metathesis Reactions by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ Catalyst

In this study, the oxy derivative of tungsten compound with aryloxo ligand, $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$, was investigated as catalyst for the first time for all types of metathesis reactions.

4.5.1 Olefin metathesis (OM) reactions by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalyst

Olefin metathesis reactions of 1-octene were studied by using the two-component systems containing $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ precatalyst and Bu_4Sn as a cocatalyst (Figure 4.49).

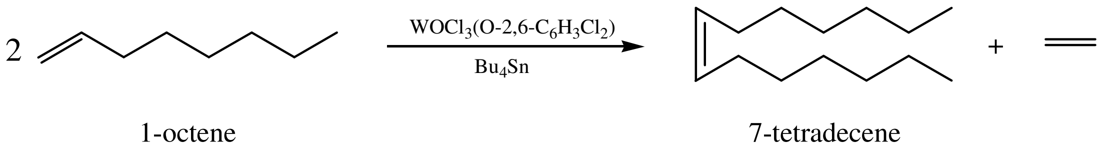


Figure 4.49 Olefin metathesis reaction of 1-octene.

Gas chromatographic analyses of the reaction mixtures indicated the formation of metahtesis products. Olefin metathesis of 1-octene in the presence of this two-component system resulted in the formation of the metathesis product 7-tetradecene. The products observed are given in the Table 4.23 with respect to their retention times. GC-MS spectrum of the products formed in the olefin metathesis of 1-octene are given in Figure 4.50 and Figure 4.51. The main product of the reaction is 7-tetradecene. The other peaks belong to unreacted olefin, solvent and internal standard.

Table 4.23 The products in the olefin metathesis of 1-octene.

Retention time (min)	Product	Molecular formula	Molecular weight
7.0	1-Octene	C_8H_{16}	112
8.6	Chlorobenzene	C_6H_5Cl	112
20.1	7-Tetradecene	$C_{14}H_{28}$	196
23.8	n-Hexadecane	$C_{16}H_{34}$	226

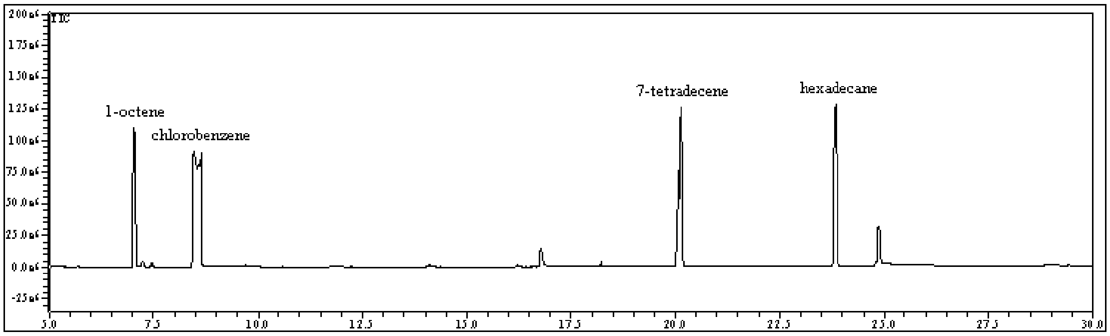


Figure 4.50 Gas chromatogram of the olefin metathesis products of 1-octene.

Name: 7-tetradecene **Ret. Time:** 20.1

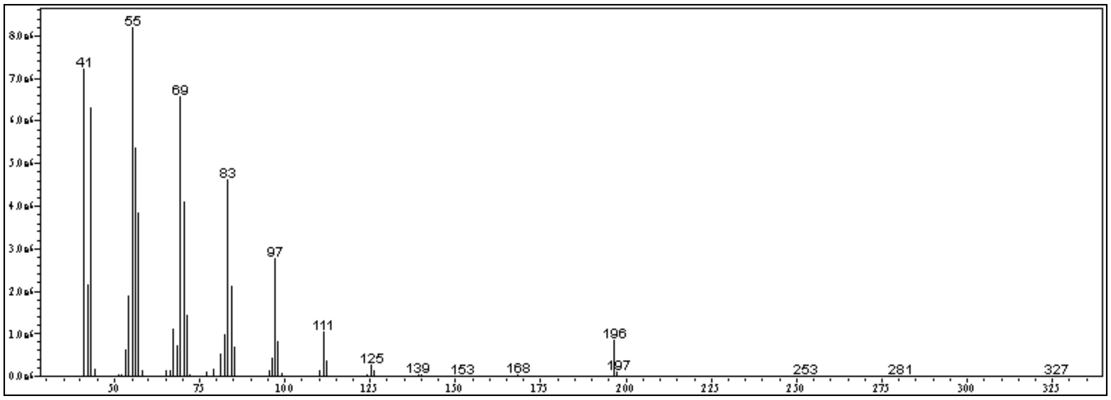


Figure 4.51 Mass spectrum of the olefin metathesis product, 7-tetradecene.

4.5.1.1 Influence of cocatalyst / W molar ratios

In this stage, the effect of cocatalyst / W molar ratio on the catalytic activity of $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ precatalyst towards the metathesis of 1-octene was investigated by varying the cocatalyst / W molar ratio (1 to 6). The results of the investigation with cocatalyst Bu_4Sn at different cocatalyst / W molar ratios are given in Fig. 4.52.

A little increase in metathesis product yield was observed with an increase in the cocatalyst / W molar ratio. A maximum yield of metathesis products is obtained at cocatalyst / W molar ratios of 2 to 4. The yields slightly decrease at higher cocatalyst / W molar ratios. From the results obtained, the optimal value for the Sn / W ratio appears to be 3.

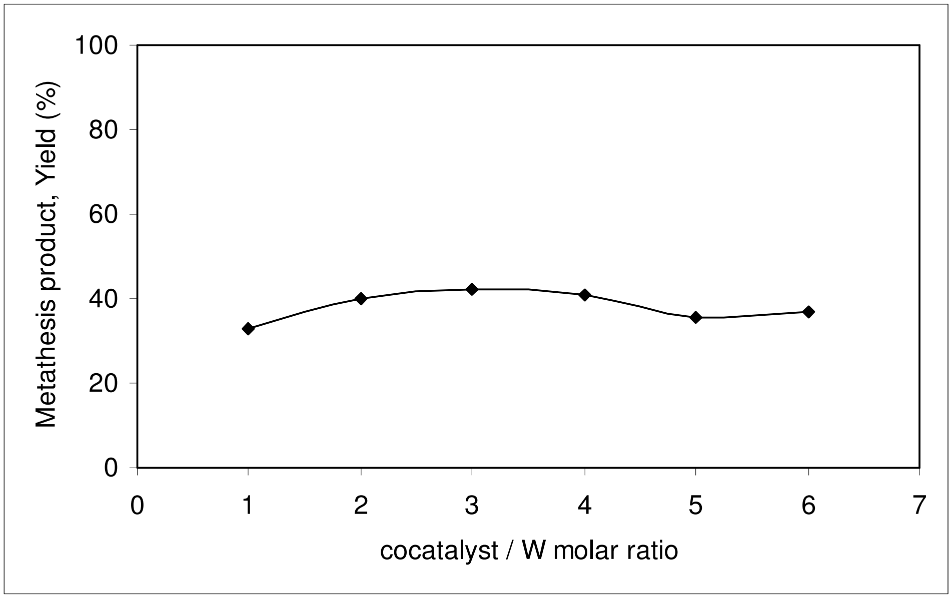


Figure 4.52 Influence of the cocatalyst / W molar ratio on the metathesis activity of the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalytic system (temperature = 85 ºC; time = 2 h).

4.5.1.2 Influence of interaction time

At this step, the effect of the interaction time on metathesis activity of $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ precatalyst was investigated. Interaction time is defined as the period before the 1-octene is added to a mixture of the catalyst and cocatalyst in chlorobenzene. The metathesis product yields at various interaction times ranging from 0 to 30 min is given in Figure 4.53.

In this experiment, cocatalyst / W molar ratio was kept as 3. As it is seen clearly from Figure 4.53. An increase is observed with an increase in interaction time from 0 to 10 min. A constant yield of metahesis product is found at interaction times greater than about 10 min. From these results, it can be seen that the maximum yield of metathesis product is obtained after interaction time of 10 min between catalyst and cocatalyst.

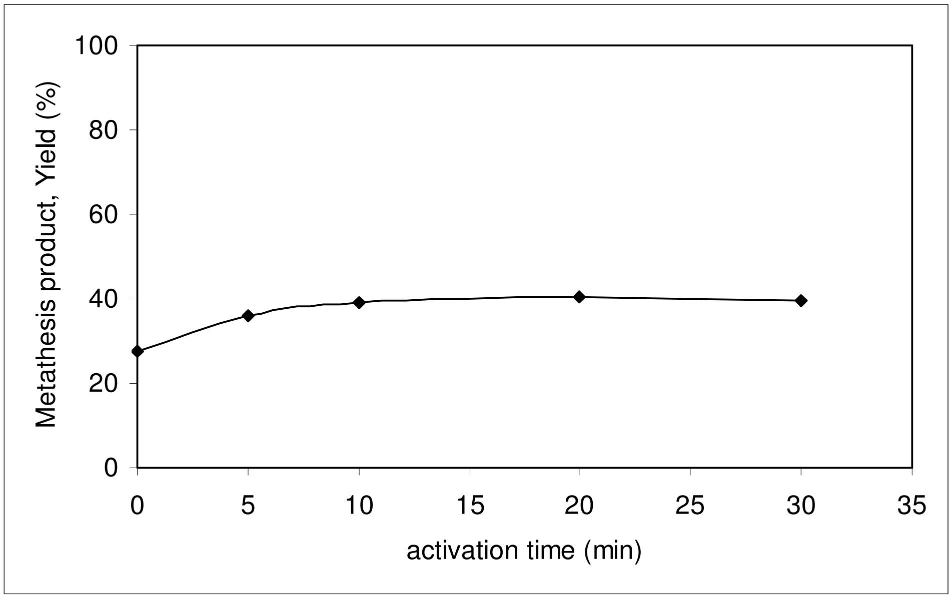


Figure 4.53 Influence of the interaction time on the metathesis activity of the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalytic system (temperature = 85 ºC; cocatalyst / W molar ratio = 3).

4.5.1.3 Influence of reaction time

At this stage, the effect of reaction time on the yield of metathesis products was examined. The cocatalyst / W molar ratio, interaction time and reaction temperature were kept as 3, 10 min and 85 ºC, respectively. The kinetic profile of the metathesis reactions of 1-octene is illustrated in Figure 4.54.

Figure 4.54 demonstrates that the changes in yield of metathesis product, 7-tetradecene during the course of reaction. The metathesis yield increases with time, and then tends to a constant value as a consequence of a significant decrease of the reaction rate. As illustrated in Figure 4.54, the metathesis equilibrium is reached within about 60 min with this catalytic system.

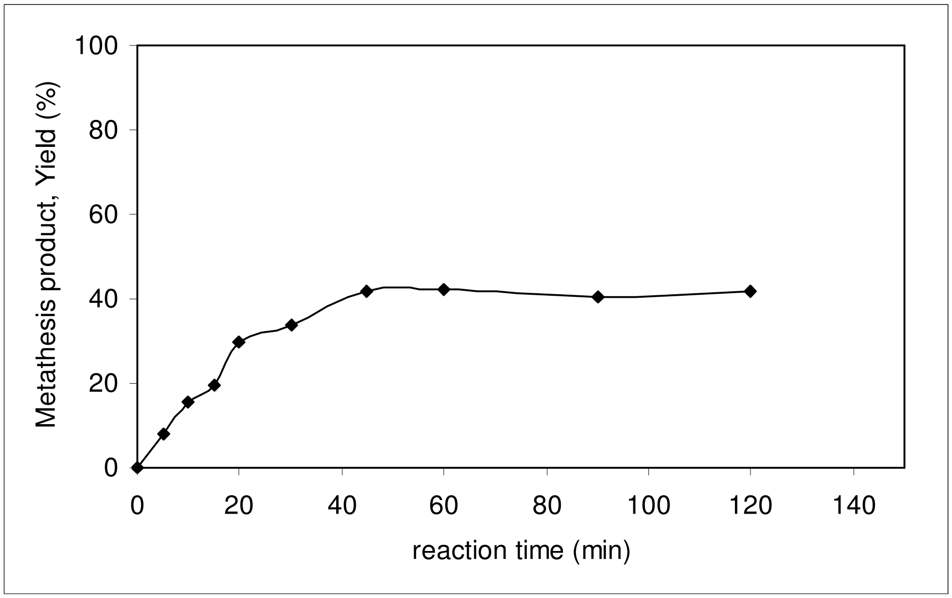
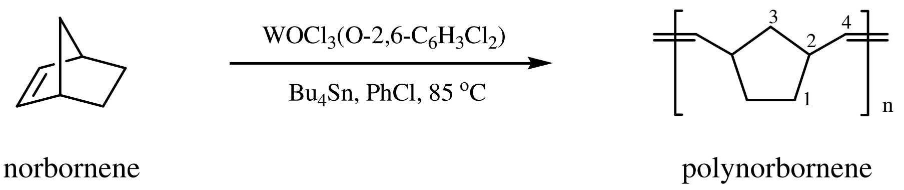


Figure 4.54 Influence of the reaction time on the metathesis activity of the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalytic system (temperature = 85 ºC; cocatalyst / W molar ratio = 3; activation time = 10 min).

4.5.2 ROMP reactions by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalyst

4.5.2.1 ROMP of norbornene by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalyst

The geometric structure of poly-NBE produced by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn was determined from ^1H and ^{13}C NMR spectra. All these values are in good agreement with various literature data related to polynorbornene prepared via ROMP (Fig. 4.55, 4.56 and 4.57). NMR spectra of the polymer exhibited the similar characteristics as observed for polynorbornene obtained by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ indicating that the product is a metathetic polymer.



The carbon atoms in the poly-NBE are numbered from 1 to 4. The two multiplets corresponding to C^4 carbon centered at 133.83 and 133.02 ppm refer to *cis*- and *trans*-vinylic carbon atoms, respectively. A comparison of these two peaks related to C^4 carbon allows estimation of the trans stereoselectivity of the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system. Table 4.24 gives the peak assignments of polymer obtained in the presence of $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system. The reactivity ratios, r_t = tt/tc and r_c = cc/ct, were calculated as r_t = 4.35 and r_c = 0.26, giving the r_tr_c value of 1.120. The fraction of cis-double bonds (σ_c), was estimated as 0.22 (Fig. 4.56). The σ_c and r_tr_c values thus obtained characterize a mainly trans polymer with a slightly blocky distribution of cis and trans structures.

The results obtained by ^{13}C NMR are consistent with the ^1H NMR spectrum shown in Figure 4.57. The fact that the polymer is mainly trans may also be visualized from its ^1H NMR spectrum, when the resonances at 5.22 ppm and 5.37 ppm, assigned respectively to the cis and trans ethylenic protons, were considered. The σ_c (ca 22%) calculated from the ^1H NMR spectrum agrees well with that obtained from the ^{13}C NMR. Additionally, the relative integrated peak areas of the two signals at 2.81 and 2.45 ppm, demonstrating the cis and trans protons attached to C^2 carbon in the cyclopentane ring, indicate a similar trans-content of the polymer.

Table 4.24 ^{13}C NMR peak assignments (ppm from TMS) of polynorbornene produced by the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

Carbon	Position and asssignment			
C^4	133.98 (tcc)	133.92 (tct)	133.83 (ccc)	133.75 (cct)
	133.15 (ttc)	133.02 (ctc ≡ ttt)	132.86 (ctt)	
C^2	43.42 (tc)	43.12 (tt)	38.67 (cc)	38.41 (ct)
C^1	33.10 (cc)	32.94 (ct)	32.37 (tc)	32.22 (tt)
C^3	42.75 (cc)	42.09 (tc ≡ ct)	41.37 (tt)	

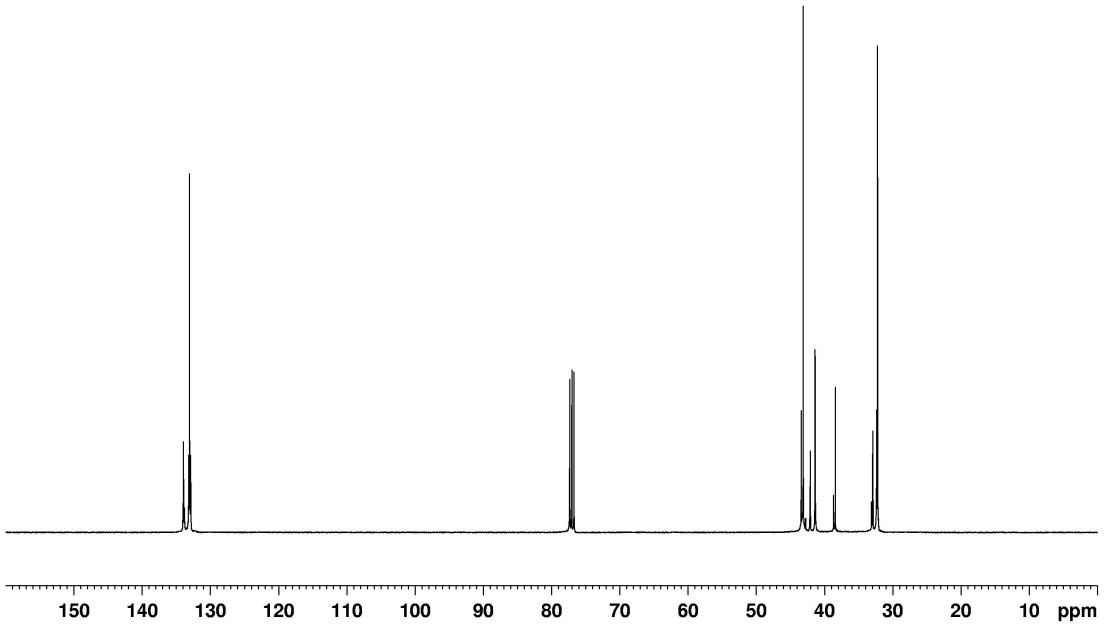


Figure 4.55 ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of poly-NBE obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

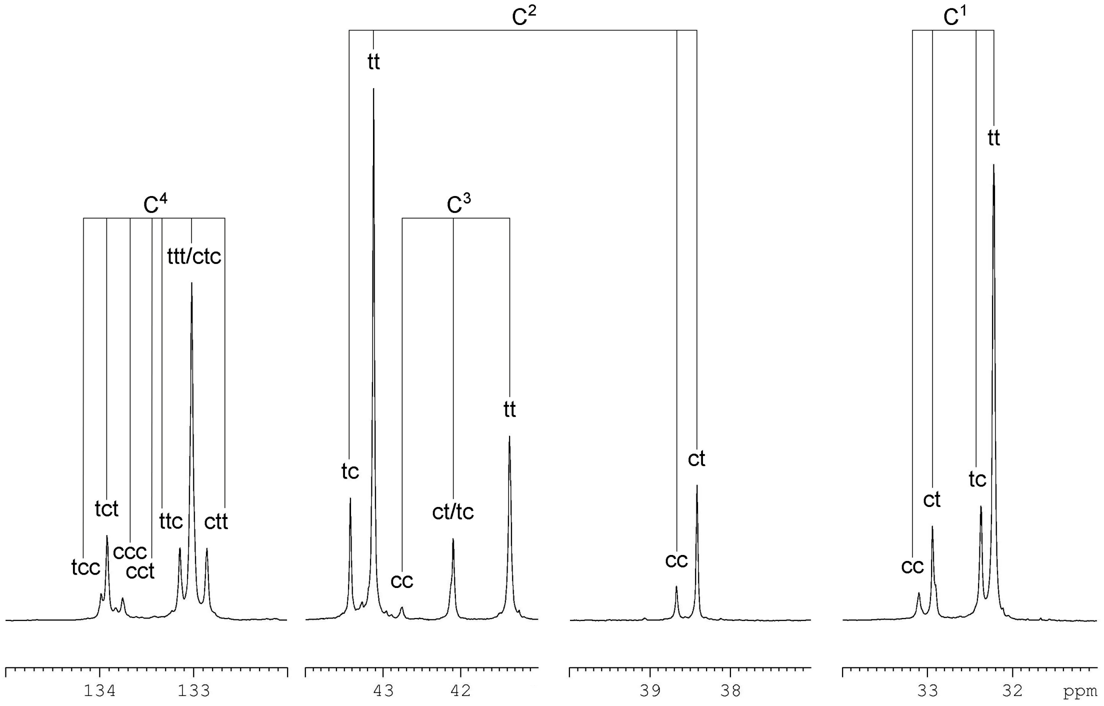


Figure 4.56 Expanded ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of poly-NBE obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

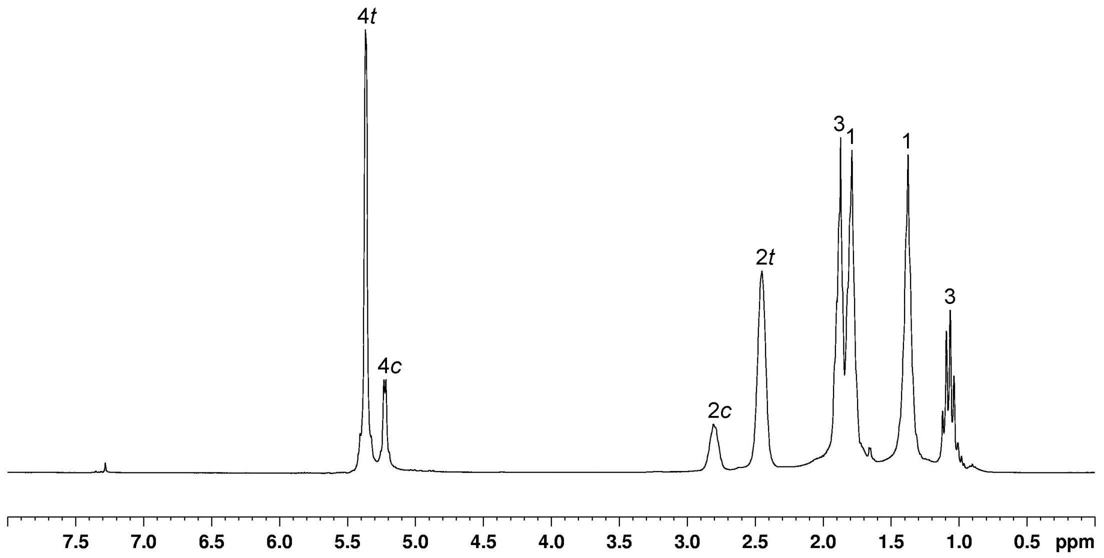
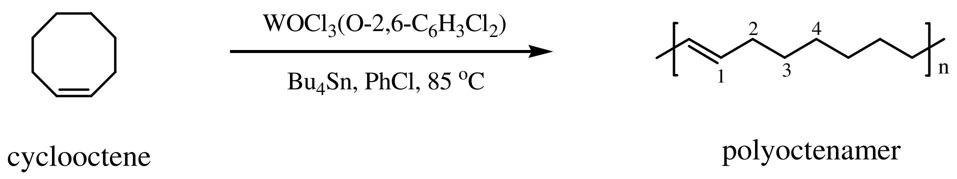


Figure 4.57 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of poly-NBE obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

4.5.2.2 ROMP of cyclooctene by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalyst

With $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn classical catalytic system, the ring-opening polymerization of cyclooctene leads to the high-*trans* polyoctenamer. The carbon atoms in the polyoctenamer are numbered from 1 to 4. The microstructure of the resulting polyoctenamer was deduced from the ^{13}C NMR spectra (Table 4.25, Fig. 4.58 and 4.59).



The *cis* olefinic carbon appears at 129.88 ppm, and the *trans* olefinic carbon appears at 130.34 ppm. The carbon atom adjacent to the olefinic carbon also has two different resonances, i.e., the *cis* carbon at 27.22 ppm and the *trans* carbon at 32.61 ppm. The relative intensities of cis and trans olefinic peaks at the C^1 region and of the cis and trans non-olefinic peaks at the C^2 region give similar trans-contents of the polyoctenamer, i.e. 84%.

The results obtained by ^{13}C NMR agree well with the ^{1}H NMR spectrum. The ^{1}H NMR spectrum of the polyoctenamer has olefinic proton signals at 5.37 ppm and 5.41 ppm corresponding to cis and trans peaks respectively and non-olefinic proton signals between 2.2 ppm and 1.0 ppm (Fig. 4.60). The relative intensities of the olefinic peaks at 5.37 and 5.41 ppm give a cis/trans ratio of 18/82. Moreover, the relative integrated peak areas of the two signals at 2.03 and 1.99 ppm reveal a similar trans-content of the polymer.

Table 4.25 ^{13}C NMR peak assignments (ppm from TMS) of polyoctenamer produced by the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

Carbon	Position and asssignment			
C^1	130.34 (ttt)	129.88 (ccc)		
C^2	32.61 (t)	27.22 (c)		
C^3	29.75 (c)	29.64 (t)		
C^4	29.23 (cc)	29.18 (ct)	29.11 (tc)	29.05 (tt)

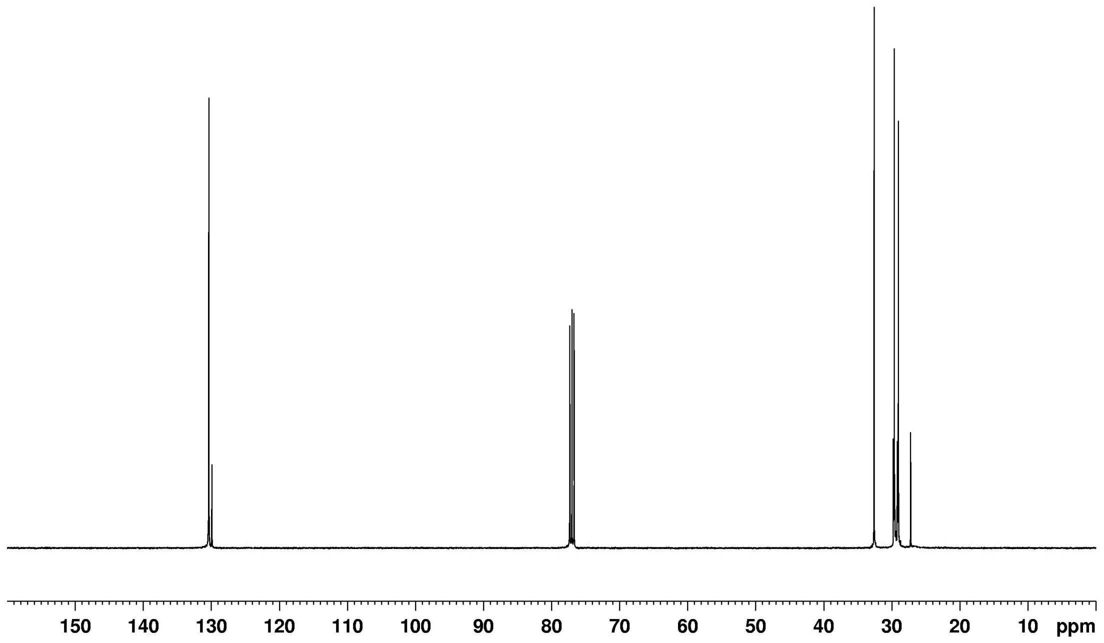


Figure 4.58 ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polyoctenamer obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

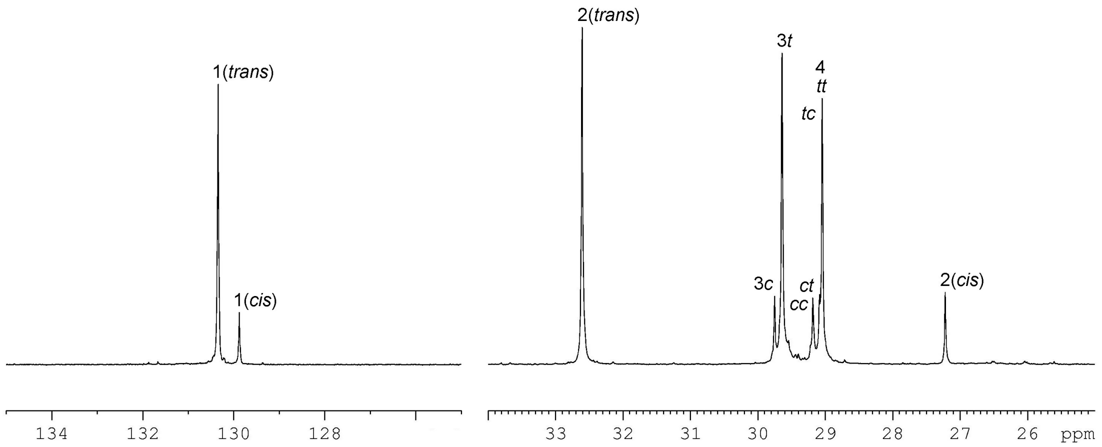


Figure 4.59 Expanded ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polyoctenamer obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

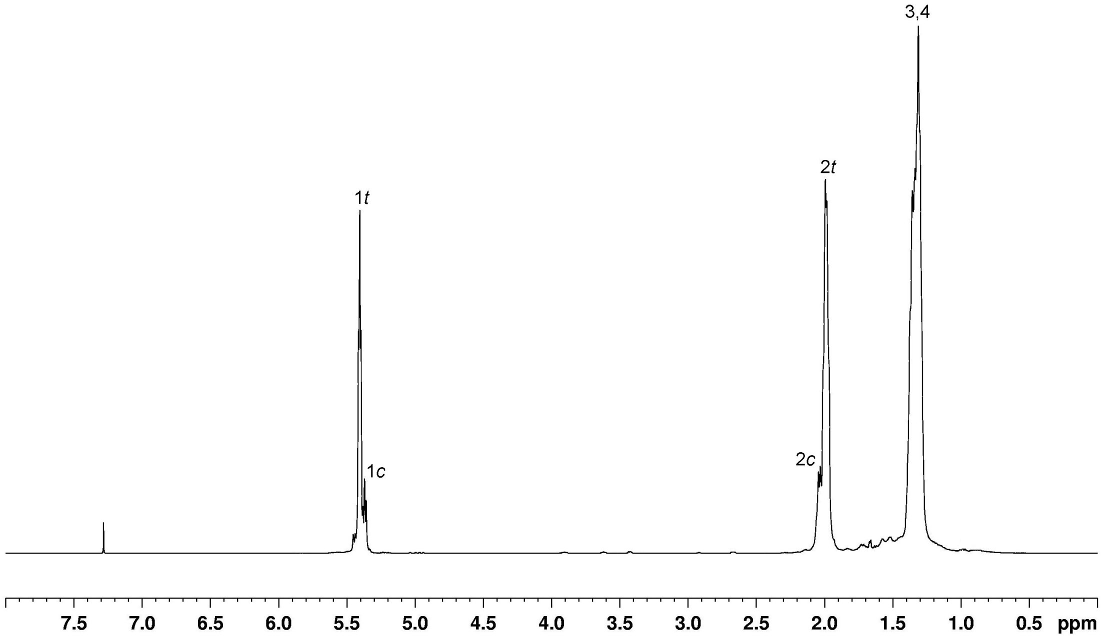


Figure 4.60 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polyoctenamer obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

In the IR spectra of the polymers, the high amount of trans double bonds is confirmed by the stronger absorption of the trans C=CH out-of-plane bending at 968 cm^{-1} compared with the absorption at 725 cm^{-1} for the cis C=CH out-of-plane bending (Figure 4.61).

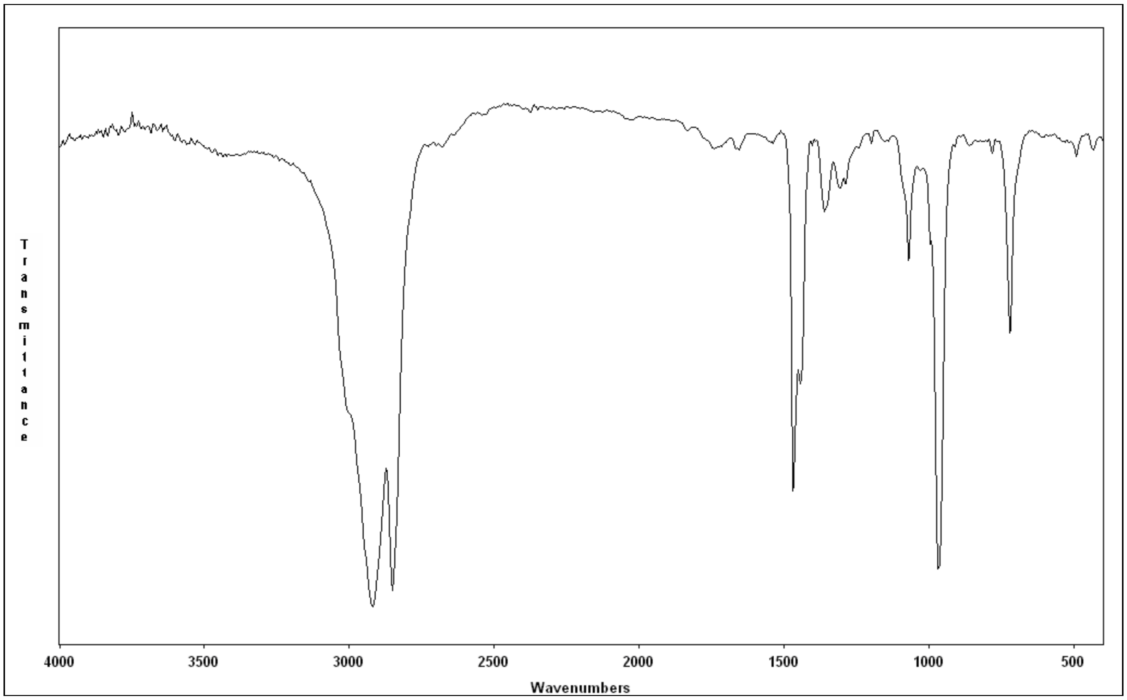
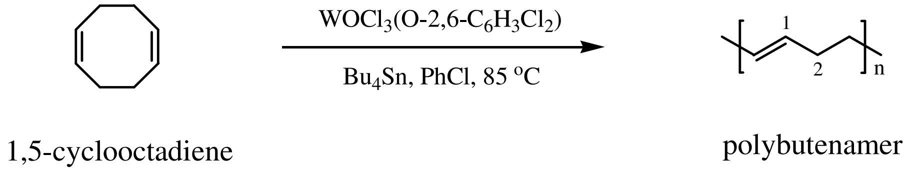


Figure 4.61 FT-IR spectrum of polyoctenamer obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

4.5.2.3 ROMP of 1,5-cyclooctadiene by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalyst

Investigation of the stereochemistry of the ROMP reaction of 1,5-cyclooctadiene was made by ^{13}C and ^{1}H NMR. The microstructure of the resulting polybutenamer was deduced from the ^{13}C NMR spectrum (Fig. 4.62 and 4.63). The carbon atoms in the polybutenamer are numbered as 1 and 2, as indicated in Table 4.26.



The $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$/ Bu_4Sn catalyst system produced high-*trans* polybutenamer. ^{13}C NMR spectrum of polybutadiene has resonances in both the olefinic region and in the alkyl region. A comparison of the *cis* and *trans* olefinic peaks related to C^1 carbon gave *trans* stereoselectivity (80 %) of polybutenamer produced by this catalyst system.

The results obtained by ^1H NMR agrees with that estimated from the ^{13}C NMR spectrum. In the ^1H NMR spectrum of the polybutadiene there are two groups of peaks: one group corresponds to non-olefinic proton signals, and the second group of peaks is related to the olefinic proton signals (Fig. 4.64). The relative intensities of the cis and trans olefinic peaks at 5.41 ppm and 5.45 ppm respectively give a cis/trans ratio of 19/81. Additionally, the relative integrated peak areas of the two signals at 2.10 and 2.07 ppm indicate a similar trans-content of the polymer.

Table 4.26 ^{13}C NMR peak assignments (ppm from TMS) of polybutenamer produced by the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

Carbon	Position and asssignment			
C^1	130.15 (tc)	130.02 (tt)	129.63 (cc)	129.44 (ct)
C^2	32.73 (tt)	32.69 (tc)	27.43 (cc ≡ ct)	

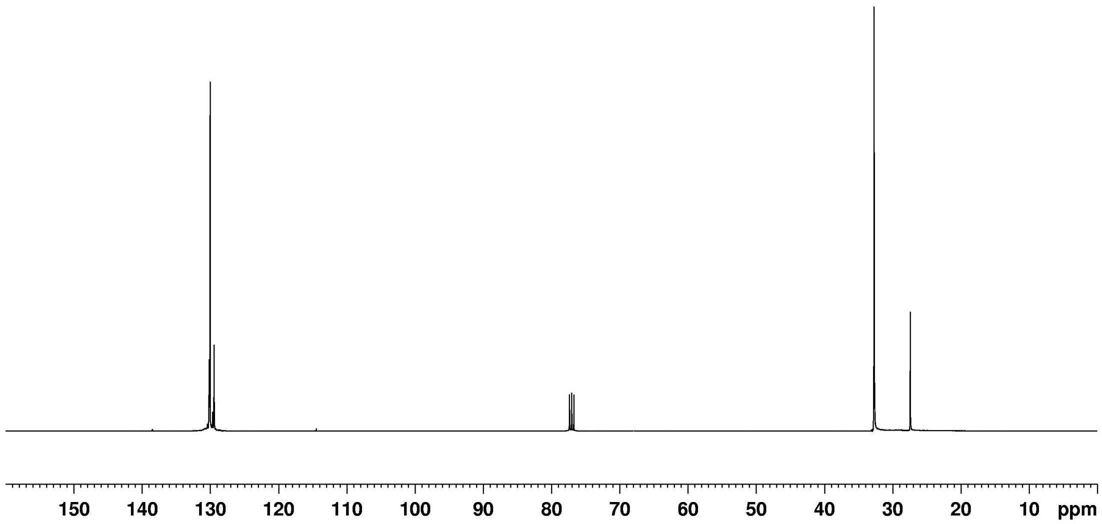


Figure 4.62 ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polybutenamer obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

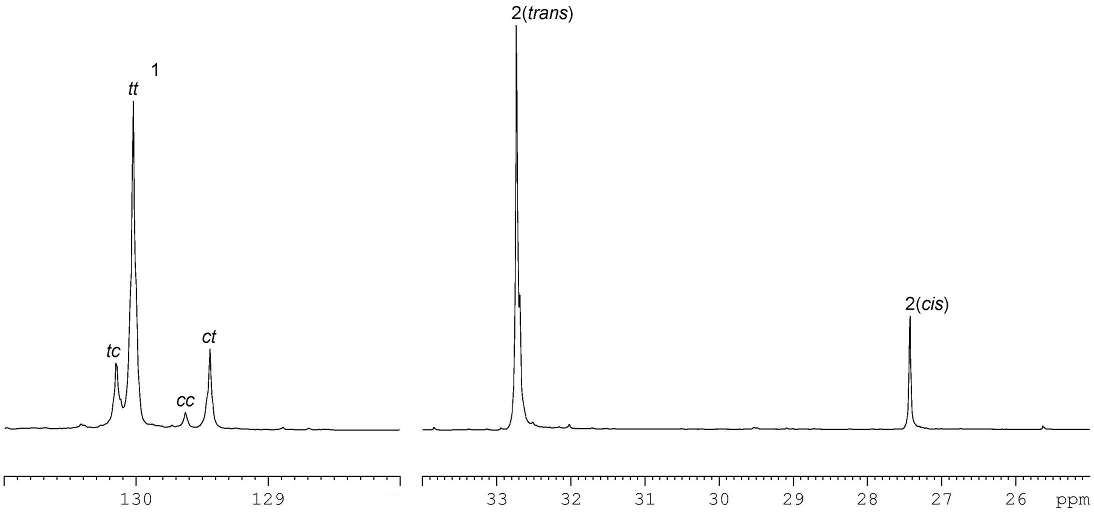


Figure 4.63 Expanded ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polybutenamer obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

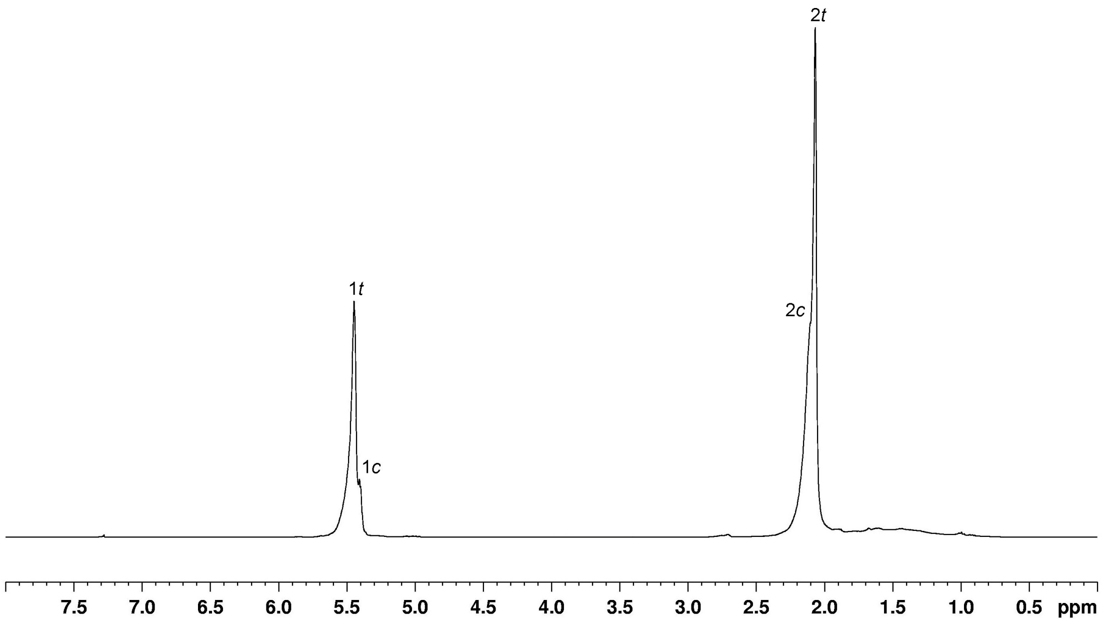


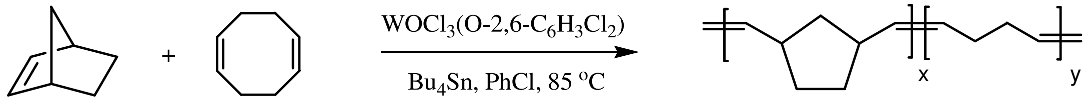
Figure 4.64 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polybutenamer obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

4.5.3 Metathesis reactions between cyclic alkenes by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalyst

In this study, ring-opening copolymerization reactions of 1,5-cyclooctadiene (COD), cyclopentene (CPE) and cyclooctene (COE) respectively with norbornene (NBE) were investigated by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system. All reactions were initiated in the bulk, at 85 ºC and under nitrogen atmosphere. The geometric structures of copolymers produced were characterized by ^1H and ^{13}C NMR, and GPC techniques. The microstructures of copolymers have been analysed in detail.

4.5.3.1 Metathesis reaction of 1,5-cyclooctadiene with norbornene

Metathesis copolymerization reaction of 1,5-cyclooctadiene (COD) with norbornene (NBE) was studied. The $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalytic system produced the ring-opened copolymers of 1,5-cyclooctadiene and norbornene.



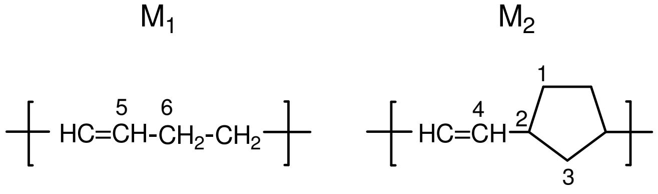
norbornene 1,5-cyclooctadiene poly(NBE-co-COD)

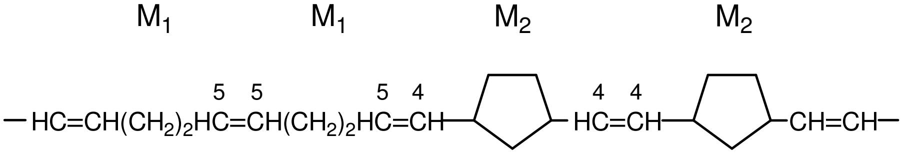
A summary of the polymerization results is shown in Table 4.27. A single GPC peak was observed, illustrating a homogeneous product rather than a blend of homopolymers. The microstructure of the resulting polymer has been analyzed by its ^1H and ^{13}C NMR spectra and is consistent with analogs produced by other catalyst systems. The peak positions and assignments are recorded in Tables 4.28 and 4.29. The spectrum of the olefinic carbons is given in expanded form in Fig.4.65. In the olefinic region of the copolymer of 1,5-cyclooctadiene and norbornene, M_1M_2 and M_2M_1 heterodyads occured as well as M_1M_1 and M_2M_2 homodyads. The presence of 4 *c/t* M_2M_1 and 5 *c/t* M_1M_2 peaks confirms the formation of 1,5-cyclooctadiene/norbornene copolymers.

Table 4.27 Characterization of polymer obtained by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn (COD/NBE/cocatalyst/catalyst = 50:50:3:1; activation time:10 min; at 85 ºC).

Monomer	Properties of polymers	
1,5-cyclooctadiene (COD)	σ_c	0.20
	$\overline{M}_w$	7100
	PDI	1.76
	Yield (%)	39.4
Norbornene (NBE)	σ_c	0.22
	$\overline{M}_w$	21800
	PDI	2.69
	Yield (%)	94.7
1,5-cyclooctadiene:Norbornene (1:1)	σ_c	0.20 (M_1M_1); 0.37 (M_2M_2)
	$\overline{M}_w$	13600
	PDI	1.92
	Yield (%)	71.0

Further analysis of the ^{13}C NMR spectrum revealed that the copolymer formed by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalytic system contains 71 mole % M_1 units, butadiene, and 29 mole% M_2 units, 1,3-cyclopentenylenevinylene.





The fractions of cis double bonds, σ_c, for M_1M_1 and M_2M_2 dyads were calculated as 0.20 and 0.37, respectively. M_2M_2M triads have values of $r_t = 3.462$, $r_c = 0.253$, and $r_tr_c = 0.877$, whereas M_1M_2M triads have values of $r_t = 4.104$, $r_c = 0.276$, and $r_tr_c = 1.133$. These r_tr_c values thus obtained characterize a copolymer with an alternating distribution of *cis*/*trans* double bond pair sequences for M_2M_2M triads, while a slightly blocky distribution for M_1M_2M triads.

Table 4.28 Assignment of C^4 and C^5 lines in the ^{13}C NMR spectrum of 1,5-cyclooctadiene (M_1) / norbornene (M_2) copolymers produced by the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm
4c (M_2M_1)	135.49 135.32
4t (M_2M_1)	135.21 135.08
4c (M_2M_2)	133.99 133.91 133.84 133.77
4t (M_2M_2)	133.12 133.03 132.89
5tc (M_1M_1)	130.15
5tt (M_1M_1)	130.02
5cc (M_1M_1)	129.62
5ct (M_1M_1)	129.43
5c/t (M_1M_2)	127.93 127.84

Table 4.29 Assignment of C^1, C^2, C^3 and C^6 lines in the ^{13}C NMR spectrum of 1,5-cyclooctadiene (M_1) / norbornene (M_2) copolymers produced by the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm	Designation and assignment	Peak position in ppm
1cc (MM_2)	33.10	3cc ($M_2M_2M_2$)	42.74
1ct (MM_2)	32.93	3cc ($M_1M_2M_2$)	42.41
1tc (MM_2)	32.36	3cc ($M_1M_2M_1$)	42.06
1tt (MM_2)	32.19	3ct ($M_1M_2M_2$)	
		3ct ($M_2M_2M_2$)	
2tc (M_2M_2M)	43.41	3ct ($M_1M_2M_1$)	41.73
2tt (M_2M_2M)	43.15	3tc ($M_1M_2M_2$)	41.66
2cc (M_2M_2M)	38.65	3tt ($M_1M_2M_1$)	41.39
2ct (M_2M_2M)	38.41	3tt ($M_1M_2M_2$)	41.32
		3tt ($M_2M_2M_2$)	41.26
2tc (M_1M_2M)	43.49	6t (M_1M_2)	32.83
2tt (M_1M_2M)	43.24	6t (M_1M_1)	32.71
2cc (M_1M_2M)	38.30	6c (M_1M_2)	27.65
2ct (M_1M_2M)	38.05	6c (M_1M_1)	27.41

^1H NMR spectrum of poly(NBE-co-COD) exhibits similar characteristics seen in the previous catalytic systems (Figure 4.66). The spectrum had olefinic proton signals at 5.20–5.51 ppm, the *cis* and *trans* proton signals attached to C^2 carbon in the cyclopentane ring at 2.80 and 2.46 ppm and the other proton signals at 0.99–2.17 ppm.

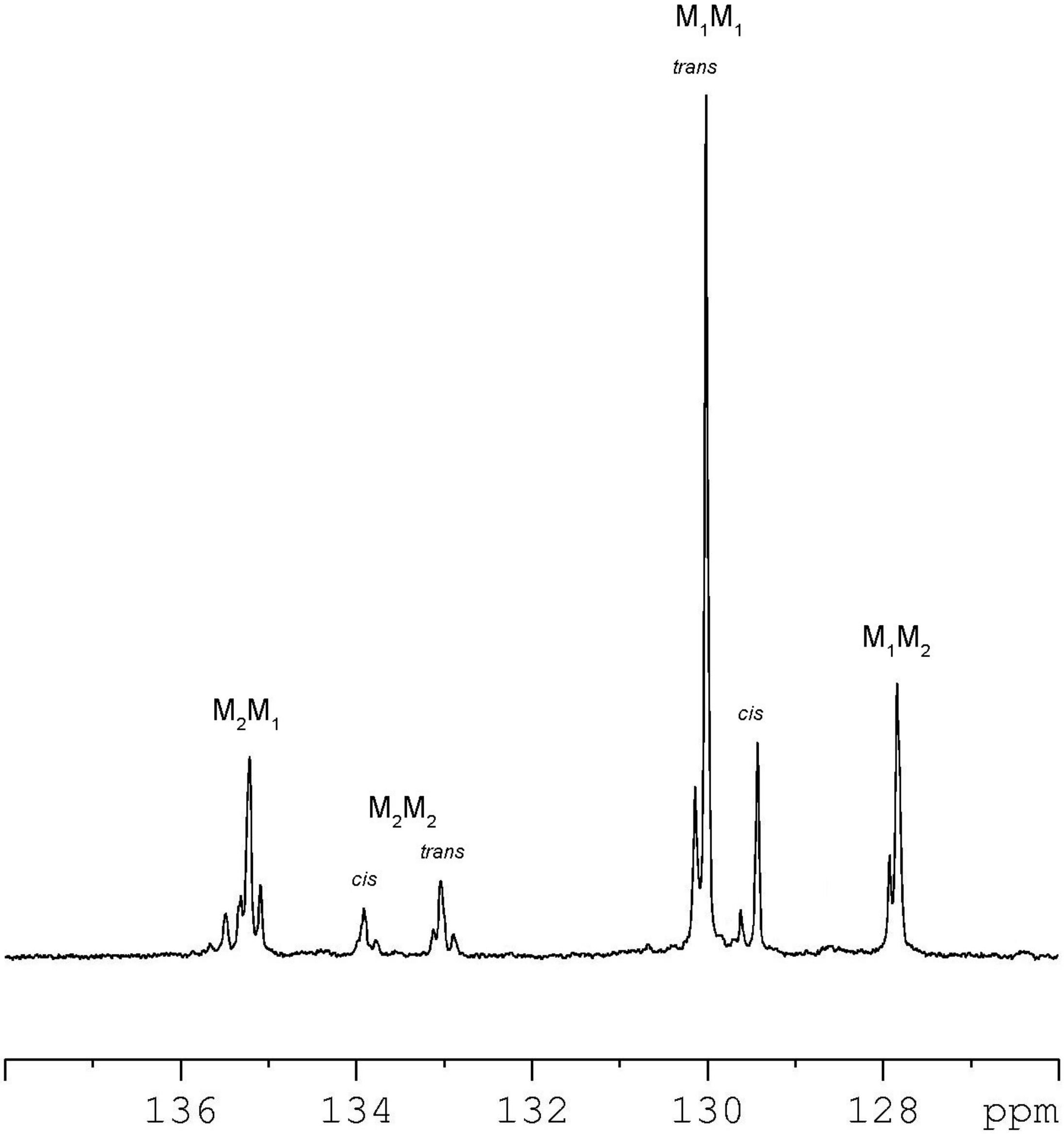


Figure 4.65 Olefinic region of the ^{13}C NMR spectrum (400 MHz, in $CDCl_3$) of copolymer prepared from 1,5-cyclooctadiene (M_1) and norbornene (M_2) using $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn as catalyst.

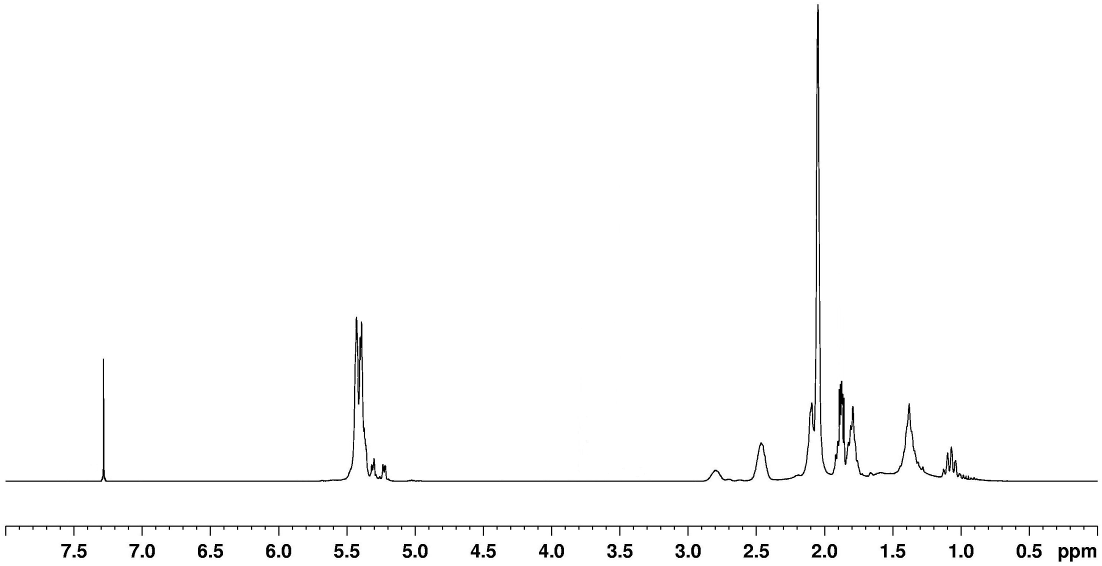


Figure 4.66 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$) of copolymer prepared from 1,5-cyclooctadiene (M_1) and norbornene (M_2) using $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn as catalyst.

4.5.3.2 Metathesis reaction of cyclopentene with norbornene

In this work, metathesis copolymerization of cyclopentene with norbornene was investigated. The metathesis reaction of these two cycloalkenes with $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalytic system yielded the ring-opened copolymers of cyclopentene and norbornene.

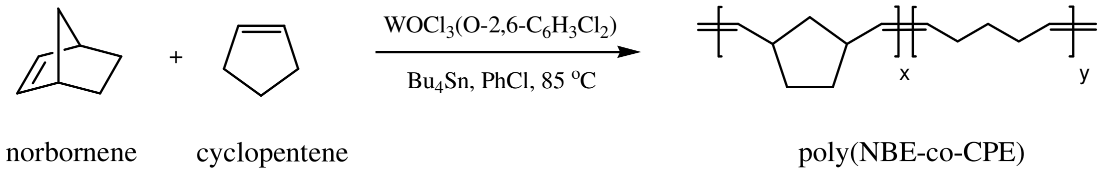


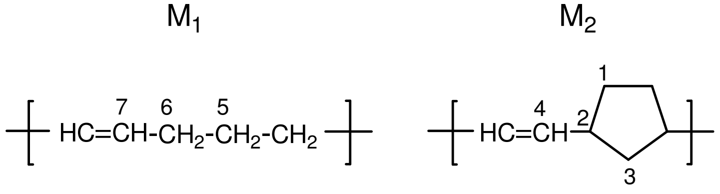
Table 4.30 summarizes the results obtained from the copolymerization of cyclopentene and norbornene. Figure 4.67 shows the olefinic region of the ^{13}C NMR spectrum of the copolymer of CPE (M_1) and NBE (M_2) obtained with $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system. The olefinic region of the copolymer, which has the two multiplets centered at 135.2 ppm and 128.2 ppm assigned the two olefinic carbon atoms in M_2M_1 and M_1M_2 heterodyads, respectively, clearly confirms the

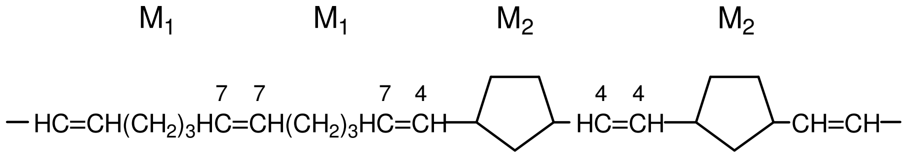
formation of copolymers. The peak positions and assignments are recorded in Tables 4.31 and 4.32.

Table 4.30 Characterization of polymer obtained by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn (CPE/NBE/cocatalyst/catalyst = 50:50:3:1; activation time:10 min; at 85 ºC).

Monomer	Properties of polymer	
Cyclopentene:Norbornene (1:1)	σ_c	0.20 (M_1M_1); 0.29 (M_2M_2)
	$\overline{M}_w$	15300
	PDI	2.10
	Yield (%)	59.7

The copolymers obtained by using this catalyst system contains 29 mole % M_1 units, 1-pentenylene, and 71 mole% M_2 units, 1,3-cyclopentenylenevinylene.





The fractions of cis double bonds, σ_c, for M_1M_1 and M_2M_2 dyads were calculated as 0.20 and 0.29, respectively. M_2M_2M triads have values of r_t = 2.898, r_c = 0.308, and r_tr_c = 0.893, whereas M_1M_2M triads have values of r_t = 2.708, r_c = 0.349, and r_tr_c = 0.946. These r_tr_c values thus obtained characterize a copolymer with an alternating distribution of *cis*/*trans* double bond pair sequences for M_2M_2M triads, while a random distribution for M_1M_2M triads.

Table 4.31 Assignment of C^4 and C^7 lines in the ^{13}C NMR spectrum of cyclopentene (M_1) / norbornene (M_2) copolymers produced by the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm
4c/t (M_2M_1)	135.54 135.42 135.19 135.03
4c (M_2M_2)	133.98 133.92 133.83 133.76
4t (M_2M_2)	133.14 133.02 132.87
7t (M_1M_1) 7c (M_1M_1)	130.33 129.82
7c/t (M_1M_2)	128.29 128.17

^1H NMR spectroscopic data for copolymers produced by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system are good agreement with data previously reported for cyclopentene/norbornene copolymers (Figure 4.68). The spectrum had olefinic proton signals at 5.16–5.48 ppm, the *cis* and *trans* proton signals attached to C^2 carbon in the cyclopentane ring at 2.79 and 2.45 ppm and the other proton signals at 0.91–2.16 ppm.

Table 4.32 Assignment of C^1, C^2, C^3, C^5 and C^6 lines in the ^{13}C NMR spectrum of cyclopentene (M_1) / norbornene (M_2) copolymers produced by the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm
2tc (M_2M_2M)	43.42
2tt (M_2M_2M)	43.13
2cc (M_2M_2M)	38.67
2ct (M_2M_2M)	38.42
2tc (M_1M_2M)	43.52
2tt (M_1M_2M)	43.25
2cc (M_1M_2M)	38.28
2ct (M_1M_2M)	38.03
3 ($M_2M_2M_2$)	42.75
3 ($M_1M_2M_2$), ($M_2M_2M_2$) or ($M_1M_2M_1$)	42.09
3 ($M_1M_2M_2$), ($M_2M_2M_2$) or ($M_1M_2M_1$)	41.34
1cc (M_2M_2)	33.09
1ct (M_2M_2)	32.93
1cc (M_1M_2)	32.83
1ct (M_1M_2)	32.65
1tc (M_2M_2 / M_1M_2)	32.36
1tt (M_2M_2 / M_1M_2)	32.20
6tc (MM_1M_1 / MM_1M_2)	32.05
6tt (MM_1M_1 / MM_1M_2)	31.96
5cc ($M_1M_1M_1$)	29.84
5tc ($M_1M_1M_2$)	
5ct/tc ($M_2M_1M_2$)	
5ct/tc ($M_1M_1M_1$)	29.67
5ct ($M_1M_1M_2$)	
5tt ($M_1M_1M_1$ / $M_1M_1M_2$ / $M_2M_1M_2$)	29.52
6cc (MM_1M_2)	27.16
6ct (MM_1M_2)	26.92
6cc (MM_1M_1)	26.83
6ct (MM_1M_1)	26.70

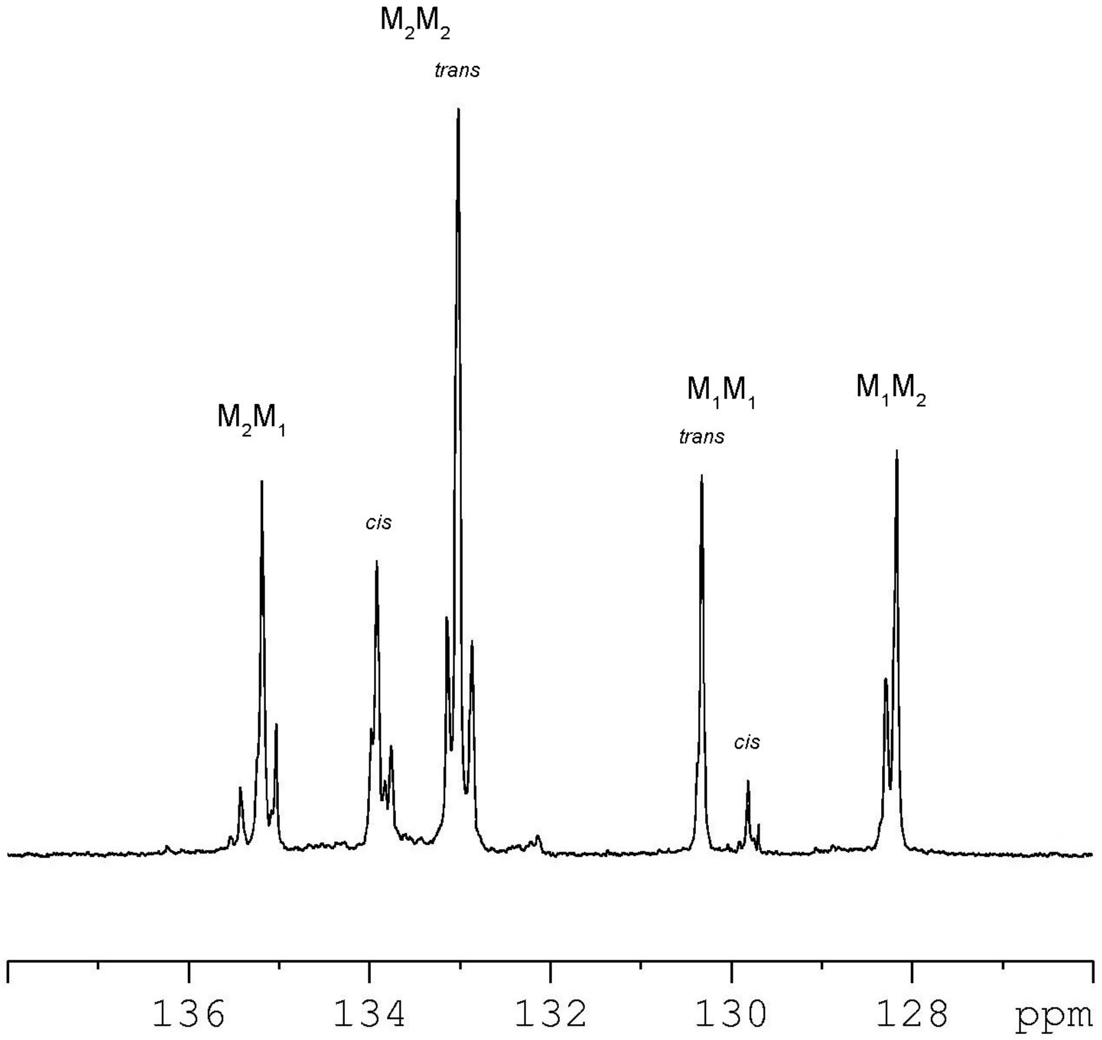


Figure 4.67 Olefinic region of the ^{13}C NMR spectrum (400 MHz, in CDCl$_3$) of copolymer prepared from cyclopentene (M$_1$) and norbornene (M$_2$) using WOCl$_3$(O-2,6-C$_6$H$_3$Cl$_2$) / Bu$_4$Sn as catalyst.

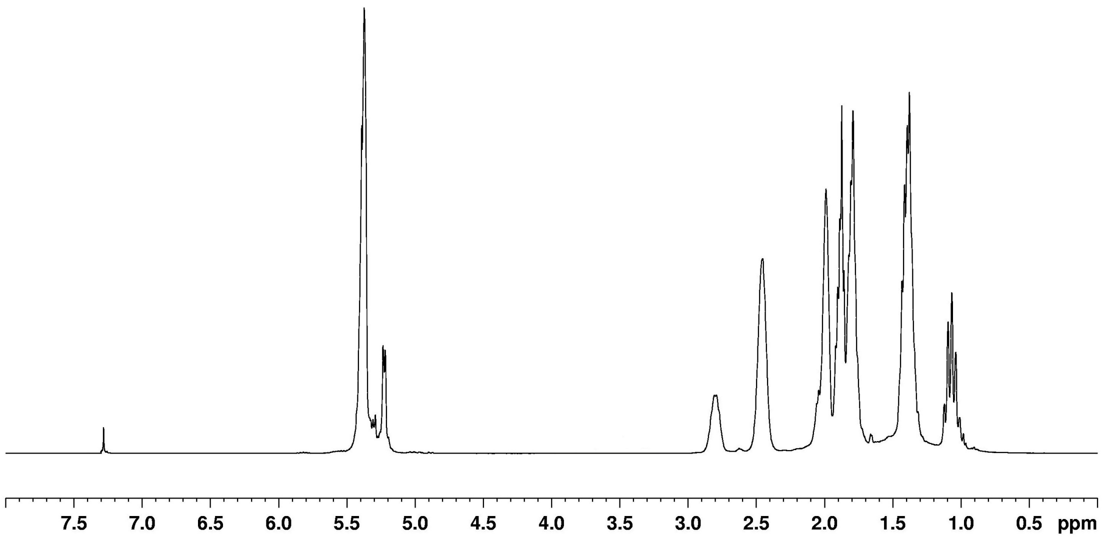


Figure 4.68 ^{1}H NMR spectrum (400 MHz, in $CDCl_3$) of copolymer prepared from cyclopentene (M_1) and norbornene (M_2) using $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn as catalyst.

4.5.3.3 Metathesis reaction of cyclooctene with norbornene

Metathesis studies were made on the system cyclooctene/norbornene using the same catalyst. Metathesis reaction of cyclooctene with norbornene resulted in the formation of co-COE-NBE polymers as depicted below.

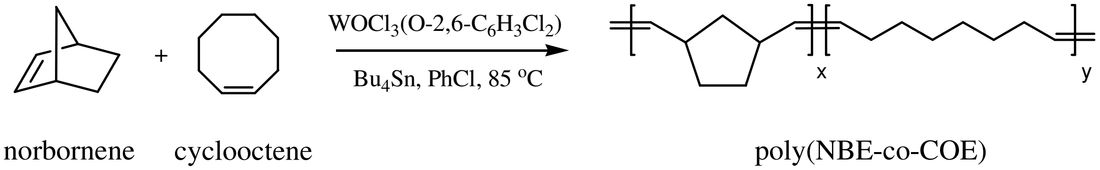
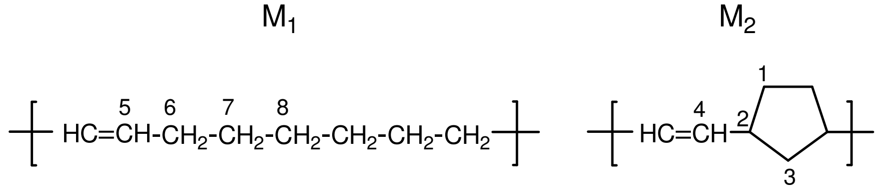


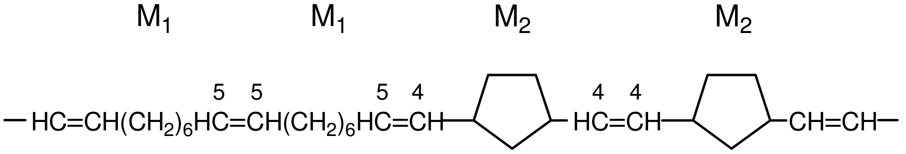
Table 4.33 summarizes the results obtained from the homopolymerization and copolymerization of COE and NBE under the same conditions. The microstructure of the copolymer obtained was determined by ^{1}H and ^{13}C NMR spectroscopy.

Table 4.33 Characterization of polymer obtained by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn (COE/NBE/cocatalyst/catalyst = 50:50:3:1; activation time:10 min; at 85 ºC).

Monomer	Properties of polymers	
Cyclooctene (COE)	σ_c	0.16
	$\overline{M}_w$	12300
	PDI	1.93
	Yield (%)	78.2
Norbornene (NBE)	σ_c	0.22
	$\overline{M}_w$	21800
	PDI	2.69
	Yield (%)	94.7
Cyclooctene:Norbornene (1:1)	σ_c	0.17 (M_1M_1); 0.35 (M_2M_2)
	$\overline{M}_w$	16700
	PDI	2.06
	Yield (%)	84.3

The peak positions for the olefinic region of the ^{13}C NMR spectrum of cyclooctene (M_1) / norbornene (M_2) copolymers are depicted in Figure 4.69. The peak positions and assignments are recorded in Tables 4.34 and 4.35.





All the resonances in the homodyads, M_1M_1 and M_2M_2 are the same as those assigned previously in detail for the homopolymers. M_1M_2 and M_2M_1 heterodyads occur as well as M_1M_1 and M_2M_2 homodyads. The *trans* and *cis* olefinic lines of poly(NBE-co-COE) are given in Table 4.34 together with their assignments. The 4 *c/t* M_2M_1 and 5 *c/t* M_1M_2 peaks indicate the formation of cyclooctene/norbornene copolymers.

Table 4.34 Assignment of C^4 and C^5 lines in the ^{13}C NMR spectrum of cyclooctene (M_1) / norbornene (M_2) copolymers produced by the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm
4c (M_2M_1)	135.21 135.05
4t (M_2M_1)	134.89 134.75
4c (M_2M_2)	133.98 133.91 133.83 133.75
4t (M_2M_2)	133.14 133.03 132.87
5t (M_1M_1) 5c (M_1M_1)	130.33 129.87
5c (M_1M_2) 5t (M_1M_2)	128.58 128.47

The peak positions and assignments for the non-olefinic region of co-COE-NBE polymers are listed in Table 4.35.

Table 4.35 Assignment of C^1, C^2, C^3, C^6, C^7 and C^8 lines in the ^{13}C NMR spectrum of cyclooctene (M_1) / norbornene (M_2) copolymers produced by the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system (Solvent: $CDCl_3$; M denotes M_1 or M_2).

Designation and assignment	Peak position in ppm	Designation and assignment	Peak position in ppm
2tc (M_2M_2M)	43.42	1cc (M_2M_2)	33.09
2tt (M_2M_2M)	43.15	1ct (M_2M_2)	32.93
2cc (M_2M_2M)	38.67	1cc (M_1M_2)	32.81
2ct (M_2M_2M)	38.42	1ct (M_1M_2)	32.66
2tc (M_1M_2M)	43.52	1tc (M_2M_2)	32.36
2tt (M_1M_2M)	43.26	1tc (M_1M_2)	
2cc (M_1M_2M)	38.27	1tt (M_2M_2)	32.20
2ct (M_1M_2M)	38.01	1tt (M_1M_2)	
3cc ($M_2M_2M_2$)	42.75	6t (M_1M)	32.60
3cc ($M_1M_2M_2$)	42.45	6t (M_1M_2)	32.52
		6c (M_1M_2)	27.48
3cc ($M_1M_2M_1$)	42.07	6c (M_1M_1)	27.21
3ct ($M_1M_2M_2$)			
3ct ($M_2M_2M_2$)			
3ct ($M_1M_2M_1$)	41.75	7c (M_1M_2)	29.92
3tc ($M_1M_2M_2$)		7c (M_1M_1)	29.74
		7t (M_1M)	29.62
3tt ($M_1M_2M_1$)	41.35	8c (M_1M)	29.17
3tt ($M_1M_2M_2$)		8t (M_1M)	29.03
3tt ($M_2M_2M_2$)			

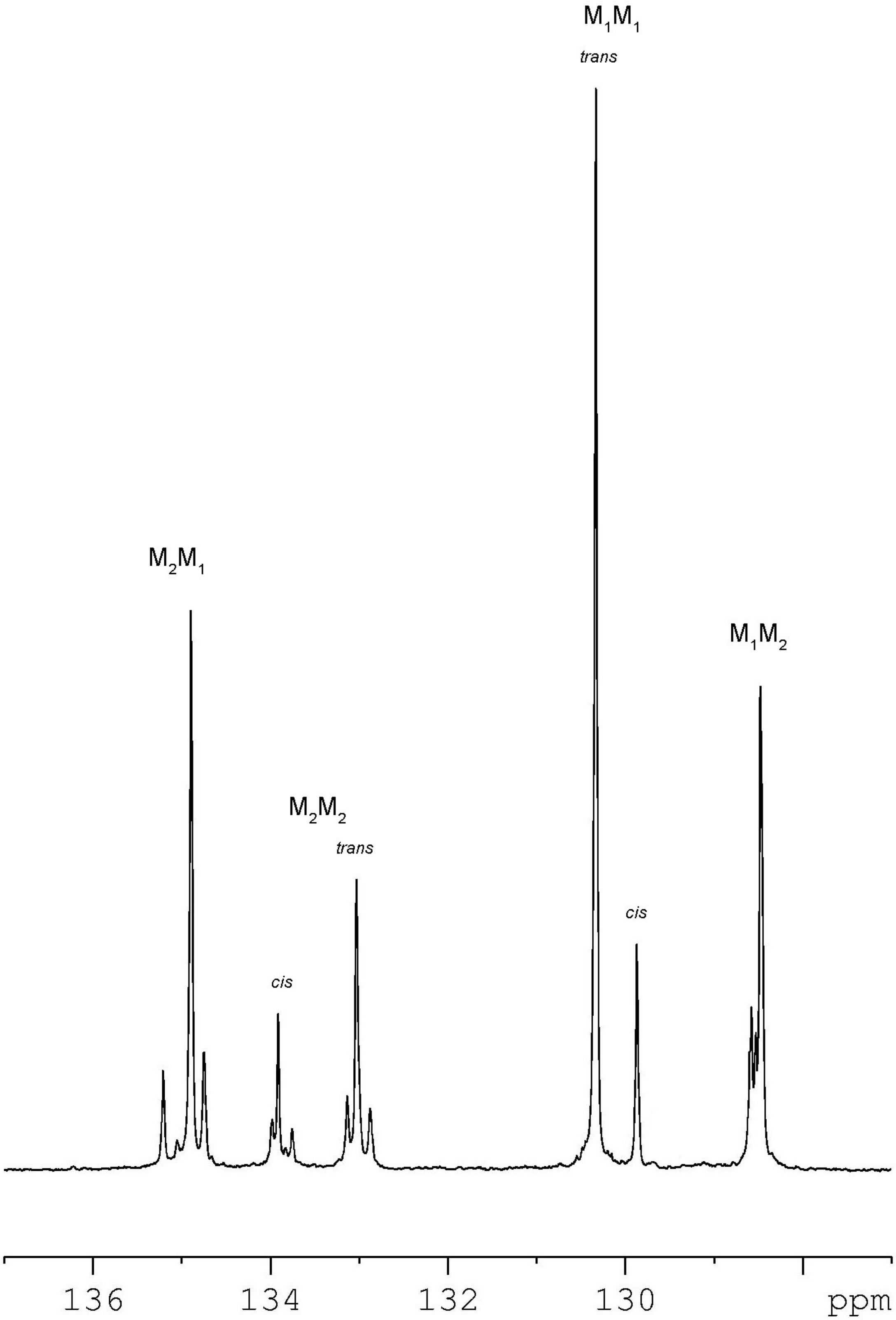


Figure 4.69 Olefinic region of the ^{13}C NMR spectrum (400 MHz, in $CDCl_3$) of copolymer prepared from cyclooctene (M_1) and norbornene (M_2) using $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn as catalyst.

The mole fraction of the 1-octenylene units in the copolymer, F_1, was calculated to be 0.55. The fractions of *cis* double bonds (σ_c) in M_1M_1 and M_2M_2 dyads were estimated as 0.17 and 0.35, respectively. For M_2M_2M triads, the cis/trans reactivity ratios, r_t = tt / tc and r_c = cc / ct, were calculated as $r_t = 2.954$ and $r_c = 0.260$, giving an r_tr_c value of 0.769. In a similar way, for M_1M_2M triads, these values were found as $r_t = 3.191$, $r_c = 0.242$, and $r_tr_c = 0.773$. The r_tr_c values thus obtained characterize a copolymer with an alternating distribution of *cis*/*trans* double bond pair sequences for both M_2M_2M and M_1M_2M triads.

The ^1H NMR spectrum of NBE/COE copolymer is given in Figure 4.70. The spectrum shows signals in both the olefinic region and in the alkyl region. ^1H NMR spectrum of poly(NBE-co-CPE) had olefinic proton signals at 5.18–5.47 ppm, the *cis* and *trans* proton signals attached to C^2 carbon in the cyclopentane ring at 2.80 and 2.46 ppm and the other proton signals at 0.98–2.11 ppm. ^1H and ^{13}C NMR spectroscopic data for copolymers formed by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system are consistent with data previously reported for NBE/COE copolymers prepared via ROMP (Ivin et al., 1982).

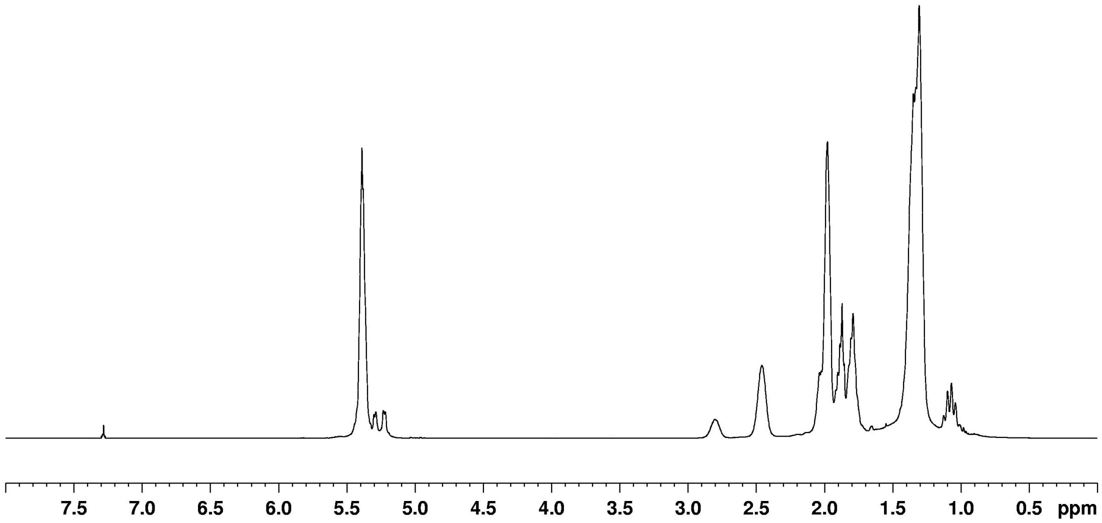
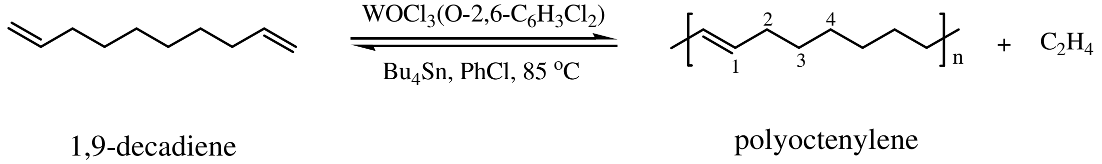


Figure 4.70 ^1H NMR spectrum (400 MHz, in $CDCl_3$) of copolymer prepared from cyclooctene (M_1) and norbornene (M_2) using $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn as catalyst.

4.5.4 ADMET polymerization reactions by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalyst

The $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system catalyzed the acyclic diene metathesis (ADMET) polymerization of 1,9-decadiene to give polyoctenylene. The resulting polymers were soluble and linear; the general polymerization scheme is shown below. The carbon atoms in the polymer are numbered from 1 to 4.



The NMR spectra of the polymeric product are as expected for polyoctenylene. All these values are in good agreement with various literature data related to polyoctenylene prepared via ADMET polycondensation (Fig. 4.71, 4.72 and 4.73). Table 4.36 summarize the ADMET polymerization results of 1,9-decadiene.

Table 4.36 The results obtained in ADMET polymerization of 1,9-decadiene by the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

σ_c (^1H)[a]	σ_c (^{13}C)[a]	$\overline{M}_n$ (NMR)[b]	$\overline{M}_n$ (GPC)[c]	PDI	Yield (%)
0.19	0.17	1300	2400	2.08	68.6

[a] Fraction of double bonds having cis-configuration, σ_c calculated from ^1H and ^{13}C NMR.
[b] Calculated via end-group analysis from ^1H NMR data, by integrating the signals corresponding to the terminal vinyl groups vs. internal olefin .
[c] Determined by gel permeation chromatography (GPC) using polystyrene standards .

Polymerization of 1,9-decadiene occurred in good yield (69%). Both gel permeation chromatography (GPC) and ^1H NMR end-group analysis reveal that the polymer of low molecular weight was formed. The polyuniformity (PDI) of the product is 2.08.

The NMR spectra of the polymer show that resonances are present that are identical with those for the polyoctenylene, in addition to two other sp^2 resonances, which is assigned to the vinyl end groups present in the polymer. ^1H NMR spectra show signals in both the olefinic region and in the alkyl region, where terminal vinyl methine proton (4.97 ppm), internal olefinic proton (5.40 ppm), terminal vinyl methylene proton (5.83 ppm) and non-olefinic proton signals (2.00 and 1.25 ppm) can be clearly visualized (Fig. 4.71). The signals at 5.38 ppm and 5.41 ppm correspond to cis and trans internal olefinic protons respectively. The relative intensities of the olefinic peaks at 5.38 and 5.41 ppm give a cis/trans ratio of 19/81. Moreover, the relative integrated peak areas of the two signals at 2.06 and 2.00 ppm reveal a similar trans-content of the polymer.

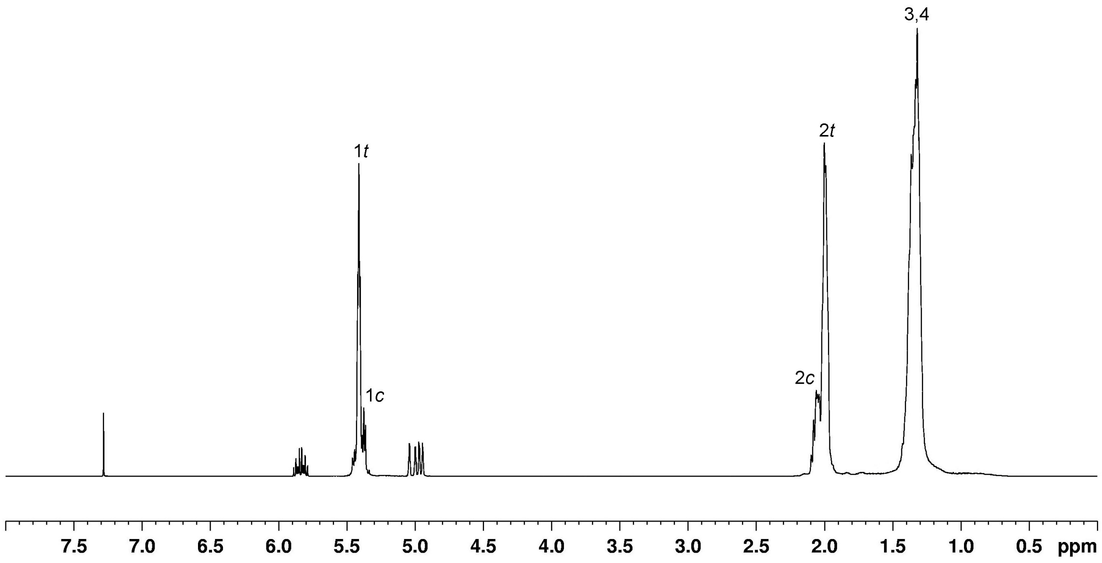


Figure 4.71 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of polyoctenylene obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system *via* ADMET.

The results obtained by ^{1}H NMR agree well with the ^{13}C NMR spectrum. The sp^2 region (129-131 ppm) in the ^{13}C NMR spectrum confirms the retention of the C=C bonds during polymerization. The signal around 139.17 ppm refers to terminal vinyl methylene carbons and the signal around 114.12 ppm refers to terminal vinyl methine carbons (Fig. 4.72). The two signals at 129.88 ppm and 130.34 ppm refer to *cis* and *trans* internal olefinic carbon atoms (C^1) respectively (Fig 4.73). Integration of these two olefin signals shows that the polymer contains highly *trans* linkages between repeat units, an observation consistent with many other ADMET polymers which agrees with the relative stability of the *trans* and *cis* isomers formed in an equilibrium process. The carbon atom (C^2) adjacent to the internal olefinic carbon also has two different resonances, i.e., the cis carbon at 27.23 ppm and the trans carbon at 32.61 ppm. Based on the intensities of these peaks, the polymer is assigned to have a high percentage of trans stereochemistry (83%).

The fact that no signals attributed to vinyl addition reactions competing in ADMET chemistry was observed in the NMR spectra is particularly important point.

Figure 4.72 ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polyoctenylene obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system *via* ADMET.

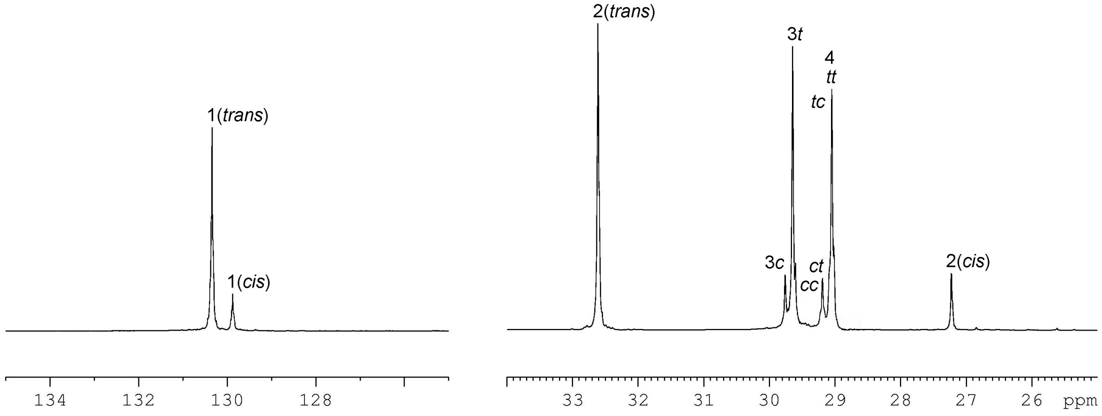


Figure 4.73 Expanded ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of polyoctenylene obtained with the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system *via* ADMET.

4.5.5 Ring-closing metathesis (RCM) reactions by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalyst

In this study, ring-closing metathesis (RCM) reaction of 1,7-octadiene was studied by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system (Figure 4.74).

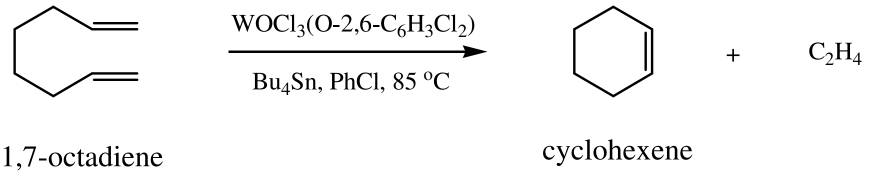


Figure 4.74 Ring-closing metathesis (RCM) reaction of 1,7-octadiene by $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system.

Gas chromatographic analysis of the reaction mixture exhibited the similar characteristics to those obtained by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system. Ring-closing metathesis (RCM) reaction of 1,7-octadiene in the presence of this two-component system resulted in the formation of the metathesis product cyclohexene.

The $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system yielded 48,2 % cyclohexene.

5. CONCLUSION

In the present work, the activation of some transition metal halides such as $MoCl_5$, $ReCl_5$ and the synthesized aryloxide tungsten complexes *via* electrochemical or classical method and their applications on all types of metathesis reactions (olefin metathesis (OM), ring-opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET) polymerization and ring-closing metathesis (RCM) reaction), were first experimented.

The effects of parameters such as the olefin/catalyst ratio, cocatalyst/catalyst ratio, reaction time, electrolysis time, activation time and reaction temperature on metathetical product formation were examined for both the electrochemical and classical catalyst systems.

The metathetic products obtained were characterized by ^1H and ^{13}C NMR, GC-MS, IR and gel permeation chromatography (GPC) techniques.

- The electrolysis experiments showed that only the $MoCl_5$ precursor could be activated *via* electrochemical technique for olefin metathesis reactions. With the other catalyst precursors, $ReCl_5$ and W-based complexes, metathetically active species couldn't obtained for olefin metathesis reactions *via* 'electrogeneration'.

- The products expected from the ROMP reactions by electrochemically generated Mo-based catalyst system ;
  polydicyclopentadiene, polynorbornene and polynorbornadiene, were produced with high conversion of the monomer.

- IR spectral results indicated that the products obtained are metathetic polymers, which form via ring-opening metathesis polymerization. ^1H NMR and ^{13}C NMR spectra showed that the C=C double bonds are retained during polymerization.

- IR spectra of polymers also indicated that polymers have high-trans content.

- Conversion to the polymers increases with the amount of olefin used, and reaches a maximum at a certain olefin/catalyst ratio. Optimum olefin/catalyst ratios for maximum conversions of dicyclopentadiene, norbornene and norbornadiene were found as 300, 160, and 200, respectively. At these optimal conditions, the conversions were 93 %, 87 %, and 96 %, respectively, for dicyclopentadiene, norbornene and norbornadiene.

- ROMP reactions were conducted at short periods of time. Optimum reaction time was 4 min. for dicyclopentadiene and norbornene, 1 min. for norbornadiene.

- With increasing electrolysis time, concentration of the active catalyst formed during the electrolysis and conversion to the polymer increases, and maximum conversion was obtained with the active species produced in 2.5-3 hours of electrolysis time.

- The $MoCl_5$-ē-Al-CH_2Cl_2 system appears to be an efficient catalyst system for the ROMP of bicyclic olefins such as norbornene.

- The electrochemical molybdenum-based system leads to a mainly trans product ($\sigma_c = 0.41$), in contrast to the mainly cis polymer ($\sigma_c = 0.61$) obtained with the tungsten-based analogue in the production of polynorbornene, which exhibits similar stereochemical characteristics to those seen in the other ROMP systems based on $MoCl_5$ and WCl_6. The polynorbornene produced is slightly blocky, with a higher cis composition ($\sigma_c = 0.41$) when compared with the random commercial polymer 'Norsorex' ($\sigma_c = 0.21$).

- GPC performed in THF allowed determination of $\overline{M}_w = 130000$ and polydispersity index PDI = 2.15. The electrochemical molybdenum-based system leads to polymers of higher molecular weight and lower polydispersity in comparison with the electrochemical tungsten-based system.

- It was found that the catalytically active species formed from $MoCl_5$ during electrolysis retain their activity for nearly 32 h when kept under nitrogen atmosphere.

- The expected products from the other metathesis-related reactions were not observed by the $MoCl_5$-ē-Al-CH_2Cl_2 system. Therefore, the electrochemically generated Mo-based catalyst appears to be ineffective for the other metathesis-related reactions. On the other hand, the electrochemically generated molybdenum- and tungsten-based catalysts both seem to be more active than the other catalyst systems in the ROMP of bicyclic olefins such as norbornene due to higher polymerization yields and shorter reaction periods.

- The two-component classical catalyst systems consisting of aryloxide-tungsten complexes, $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ or $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$, and a cocatalyst such as Bu_4Sn were succesfully applied on all types of metathesis reactions.

- Optimum conditions for the metathesis reactions were found as: cocatalyst / W molar ratio = 3, interaction time = 10 min and reaction temperature = 85 ºC for both aryloxide catalyst systems.

- The product expected from olefin metathesis reaction of 1-octene, 7-tetradecene, by both aryloxide catalyst systems was produced with good conversion of the monomer. The yields were 83.2 % and 42.4 %, respectively, for $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ and $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalysts, and also the conversions to the product reached a maximum at a reaction time of nearly 1 h.

- When the reaction is conducted in air atmosphere by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ catalyst, very little deactivation of both the catalytic systems (with Sn- and Pb-cocatalysts) was found in metathesis reactions of 1-octene. Therefore, the results indicated that $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ catalyst is highly active even in air atmosphere (Yields of 74.5 % and 59.8 %, respectively, for Sn- and Pb-cocatalysts).

- For ROMP and ADMET polymerization reactions by both aryloxide catalysts, ^1H NMR, ^{13}C NMR and FTIR spectra showed that the C=C double bonds are retained during polymerization.

- The products expected from ROMP reactions by both aryloxide catalysts were generally obtained in high yields. The $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system produced polynorbornene (96.8 %, 1 min), polyoctenamer (83.8 %, 2 h) and polybutenamer (35.6 %, 2 h). Also, the $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn system yielded polynorbornene (94.7 %, 1 min), polyoctenamer (78.2 %, 2 h) and polybutenamer (39.4 %, 1.5 h).

- The $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system produced slightly blocky polynorbornene with almost the same cis composition ($\sigma_c = 0.22$) when compared with the random commercial polymer 'Norsorex' ($\sigma_c = 0.21$). On the other hand, the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system led to a mainly trans polynorbornene ($\sigma_c = 0.43$) with a slightly blocky distribution of cis and trans structures.

- With $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn classical catalytic system, a small increase in cis-content ($\sigma_c = 0.48$) of polynorbornene was observed while polymerization yield (65.8 %) decreases when the catalytic reaction is carried out in air atmosphere. Furthermore, the cis content of polynorbornenes (σ_c) prepared using the various cocatalysts varied from about 0.28 to 0.49.

- Both the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ and $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalysts gave high content of trans polyoctenamer ($\sigma_c = 0.16$ and $\sigma_c = 0.16$, respectively) and polybutenamer ($\sigma_c = 0.31$ and $\sigma_c = 0.20$, respectively).

- Metathesis reactions of 1,5-cyclooctadiene, cyclopentene and cyclooctene with norbornene resulted in the formation of poly(COD-co-NBE), poly(CPE-co-NBE), and poly(COE-co-NBE), respectively, with both aryloxide catalysts.

- ^1H NMR and ^{13}C NMR spectroscopic data for copolymers obtained by both $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ and $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalysts are consistent with data previously reported for copolymers of 1,5-cyclooctadiene, cyclopentene and cyclooctene respectively with norbornene prepared via ROMP.

- Molecular weight and polydispersity indexes of homo- and copolymers obtained by both aryloxide catalysts via ROMP are between 4900–27400 and 1.76–2.84, respectively.

- In the olefinic regions of co-COD-NBE, co-CPE-NBE and co-COE-NBE polymers, M_1M_2 and M_2M_1 heterodyads occur as well as M_1M_1 and M_2M_2 homodyads. All the resonances in the homodyads, M_1M_1 and M_2M_2 are the same as those assigned previously in detail for the homopolymers.

- For $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ / Bu_4Sn catalyst system, the fractions of cis double bonds for M_1M_1 and M_2M_2 dyads in the copolymer of 1,5-cyclooctadiene and norbornene are $\sigma_c = 0.32$ and $\sigma_c = 0.56$, respectively. The fractions of cis double bonds for M_1M_1 and M_2M_2 dyads in the copolymer of cyclopentene and norbornene are $\sigma_c = 0.14$ and $\sigma_c = 0.30$, respectively. The fractions of cis double bonds for M_1M_1 and M_2M_2 dyads in the copolymer of cyclooctene and norbornene are $\sigma_c = 0.32$ and $\sigma_c = 0.45$, respectively. The mole fractions of M_1 units in co-COD-NBE, co-CPE-NBE and co-COE-NBE polymers, F_1, were calculated to be 0.69, 0.24 and 0.53, respectively.

- For $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ / Bu_4Sn catalyst system, the fractions of cis double bonds for M_1M_1 and M_2M_2 dyads in the copolymer of 1,5-cyclooctadiene and norbornene are $\sigma_c = 0.20$ and $\sigma_c = 0.37$, respectively. The fractions of cis double bonds for M_1M_1 and M_2M_2 dyads in the copolymer of cyclopentene and norbornene are $\sigma_c = 0.20$ and $\sigma_c = 0.29$, respectively. The fractions of cis double bonds for M_1M_1 and M_2M_2 dyads in the copolymer of cyclooctene and norbornene are $\sigma_c = 0.17$ and $\sigma_c = 0.35$, respectively. The mole fractions of M_1 units in co-COD-NBE, co-CPE-NBE and co-COE-NBE polymers, F_1, were calculated to be 0.71, 0.29 and 0.55, respectively.

- The product expected from the ADMET polymerization of 1,9-decadiene, polyoctenylene, by both aryloxide catalyst systems, was produced with high conversion of the monomer. The yields were 74.1 % (24 h) and 68.6 % (18 h), respectively, for $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ and $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalysts.

- Both gel permeation chromatography (GPC) and ^1H NMR end-group analysis revealed that polyoctenylenes of low molecular weight were formed for both aryloxide catalysts. The polyuniformity (PDI) of the products is 1.76 and 2.08, respectively, for $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ and $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalysts.

- Both the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ and $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalysts produced high trans polyoctenylene ($\sigma_c = 0.14$ and $\sigma_c = 0.17$, respectively) via ADMET.

- It is particularly important to note that no evidence of vinyl addition chemistry is apparent in the NMR spectra since vinyl addition reactions is well known to be the principle competing reactions in ADMET polymerization chemistry. Therefore, the most important feature of this aryloxide tungsten-based catalyst systems is its ability to produce linear, soluble polymer in a clean metathesis process under bulk conditions, in comparison to the classical catalyst systems.

- Ring-closing metathesis (RCM) reaction of 1,7-octadiene in the presence of these two-component aryloxide-based systems resulted in the formation of the metathesis product cyclohexene. A yield of 43.1 % and 48.2 %, respectively, was obtained by $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ and $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ catalysts.

- The obtained experimental results revealed that $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ and $WOCl_3(O\text{-}2,6\text{-}C_6H_3Cl_2)$ complexes are both very active catalysts towards all types of metathesis reactions.

- Especially, the $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ catalyst appears to be a very useful and effective catalyst since it is highly active even in air atmosphere.

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