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Optimization of Catalyst Loadings in Various Olefin Metathesis Reactions

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Dedicated to my parents Mr. and Mrs. Prof. Muhammad Abbas

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Abstract

Within this work, the successful optimization of reaction conditions for the cross metathesis of methyl vinyl ketone (MVK) and ethyl acrylate with different olefins yielding α,ß-unsaturated ketones or esters respectively, is presented.

Olefin metathesis has emerged as a powerful synthetic tool in many areas of chemistry, including organic synthesis or polymer chemistry. The employment of transition metal catalysts in the conversion of olefins facilitates the efficient preparation of molecules that are hardly accessible by other means. Thus olefin metathesis is of great value for pharmaceutical and other industrial products. Ruthenium based metathesis catalysts play an important role for this type of reaction due to their high functional group tolerance and ease of reaction in air or in moist. Regarding economic and environmental aspects, a minimal catalyst loading is of tremendous interest. Herein, a series of ruthenium based catalysts has been evaluated in the cross metathesis of different olefins with ethyl acrylate and methyl vinyl ketone. Individual optimization regarding catalyst loading, dilution, choice of solvent and other reaction parameters resulted in a distinctive amelioration compared to literature examples, also regarding the “green aspects” of chemical synthesis. For complete conversion of terminal olefins to β-substituted compounds, catalyst loadings as low as 100 ppm for cross metathesis with ethyl acrylate and 500 ppm in case of methyl vinyl ketone turned out to be sufficient with the right catalyst ((SPY-5-31)-dichloro-(κ^2(C,O)-(2-isopropylester-5-methoxybenzylidene)-(1,3-bis(2,6-diisopropyl-phenyl)-4,5-dihydroimidazol-2-ylidene)ruthenium) and ((SPY-5-34)-dichloro-(κ^2(C,O)-(2-isopropylester-5-methoxybenzylidene)-(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)ruthenium respectively). Additionally, the studies were expanded to olefins from renewable resources like methyl oleate, pinenes and commercially available cyclic olefins. A part of this work is also dedicated to ring closing metathesis (RCM) to produce lactone and cyclopentene derivatives. Finally, cross metathesis was employed for the preparation of antimicrobially active polymers. Therefore, dicyclopentadiene (DCPD) was cured by means of ring opening metathesis polymerization (ROMP), while specifically designed oleate functionalized silver nanoparticles were concurrently incorporated into the material.

Kurzfassung (Abstract German)

In dieser Arbeit wird die effektive Optimierung von Reaktionsbedingungen für die Crossmetathese (CM) von Methylvinylketon (MVK) sowie Ethylacrylat mit verschiedenen Olefinen behandelt, wodurch α,ß-ungesättigte Ketone bzw. Ester dargestellt werden können. Die Olefinmetathese manifestiert sich als vielseitig einsetzbare Synthesemethode in vielen Bereichen der Chemie, z. B. organische Synthese oder auch Polymerchemie. Die Verwendung von Übergangsmetallkomplexen als Katalysatoren für die Umsetzung von Olefinen ermöglicht die effiziente Darstellung von Molekülen die ansonsten nur schwer zugänglich sind. Aus diesem Grund ist die Olefinmetathese auch für pharmazeutische und andere industrielle Produkte von großer Bedeutung. Rutheniumkatalysatoren spielen in diesem Zusammenhang eine wichtige Rolle, da sie sich durch eine hohe Toleranz gegenüber verschiedener funktioneller Gruppen auszeichnen und so auch Reaktionen unter Sauerstoff- oder Feuchtigkeitseinfluss ermöglichen. Hinsichtlich ökonomischer sowie umweltrelevanter Aspekte ist ein minimales Katalysatorloading erwünscht. In dieser Arbeit wurde eine Reihe verschiedener Rutheniumkomplexe in der CM verschiedener Olefine mit Ethylacrylat und MVK evaluiert. Durch die jeweils individuelle Optimierung bezüglich Katalysatormenge, Verdünnung, Lösungsmittelwahl und anderer Reaktionsparameter konnte eine deutliche Verbesserung gegenüber in der Literatur veröffentlichten Beispielen erreicht werden, auch in Bezug auf „grüne Aspekte“ in der chemischen Synthese. Für vollständigen Umsatz von endständigen Olefinen zu β-substituierten Verbindungen reichten bei Ethylacrylat bereits 100 ppm des entsprechenden Katalysators ((SPY-5-31)-dichloro-(κ^2(C,O)-(2-isopropylester-5-methoxybenzylidene)-(1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene)ruthenium, bei MVK 500 ppm ((SPY-5-34)-Dichlor-(κ^2(C,O)-(2-isopropylester-5-methoxybenzyliden)-(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-yliden)ruthenium).). Die Studie wurde auch auf Olefine aus erneuerbaren Ressourcen wie z.B. Ölsäureester oder Pinene ausgeweitet. Ein Teil der Arbeit beschäftigt sich mit Ringschlussmetathese (RCM) für die Herstellung von Laktonen und Cyclopentenderivaten. Schließlich wurde CM für die Herstellung biozider Polymere verwendet. Dazu wurde Dicyclopentadien mittels ringöffnender Metathesepolymerisation (ROMP) polymerisiert, gleichzeitig wurden eigens designte Silbernanopartikel in das Material eingebaut.

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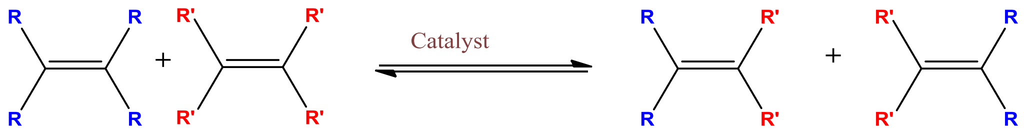
Chapter 1

Introduction and Motivation

Olefin metathesis is a versatile carbon-carbon bond forming tool for the synthesis of various organic- and macro-molecules used in materials, medicines and industrial products.[1] The contribution of Grubbs and Schrock is important in this regards which led them to win Nobel Prize for Chemistry in 2005 along with Chauvin who had proposed the mechanism for olefin metathesis reactions in 1971.[2] The reaction proceeds via metallacyclobutene formation by [2+2] cycloaddition of metal carbene to an olefin, followed by cycloreversion.[3] The reaction proceeds to yield productive metathesis reaction if the substituted olefins are different than the reactants and non-productive if the complete cycle reproduces the starting materials.



Scheme 1.1: Olefin metathesis reaction of two different olefins

Ruthenium based metathesis complexes like **1** or **2** are important precursors (or pre-catalysts) in this regard which give high yields of the metathesis products and which are applicable for a wide range of substrates. Besides the flexibility to cope with a variety of functional groups, their tolerant nature towards air and water makes them practically applicable precursors for many metathesis reactions.[4] Using these catalysts, many new high yield syntheses have been made easily accessible in modern organic chemistry. However, conversion of sterically demanding substrates via olefin metathesis still remains a challenge.[5] Besides stereo selectivity, for the economic and practical application of metathesis reactions the most demanding issue was optimization of reaction conditions for various olefin metathesis reactions. For example in ring closing metathesis (RCM) reactions targetting unfavourable ring sizes, comparatively high loadings of initiators are required.[6] Similarly, for high yields in

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[1] Handbook of Metathesis, Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol. 1-3.

[2] (a) Grubbs, R. H., *Angew. Chem. Int. Ed*. **2006**, *45*, 3760-3765; (b) Schrock, R. R., *Angew. Chem. Int. Ed*. **2006**, *45*, 3748-3759.

[3] Chauvin, Y., *Angew. Chem. Int. Ed*. **2006**, *45*, 3740-3747.

[4] (a) Samojlowicz, C.; Bieniek, M.; Grela, K.; *Chem. Rev*. **2009**, *109*, 3708-3742; (b) Jafarpour, L.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5416-5419; (c) Fürstner, A.; Grabowski, J.; Lehmann, C. W. *J. Org. Chem.*, **1999**, *64*, 8275-8280.

[5] Tinland, B. *J. Am. Chem. Soc.* **1983,** *105*, 2924-2925.

[6] Pentzer, E. B.; Gadzwika, T.; Nguyen, S. *Org. Lett.* **2008,** *10*, 5613-5615.

stereo selective cross-metathesis, optimization regarding the amount of initiator, and other reaction parameters (e.g. using a “greener” or no solvent) display a remaining issue that has been thoroughly treated within this work. These endeavours are important in olefin metathesis reactions to reduce the cost of reactions promoted by expensive initiators, but also in the interest of environmentally more benign chemistry.

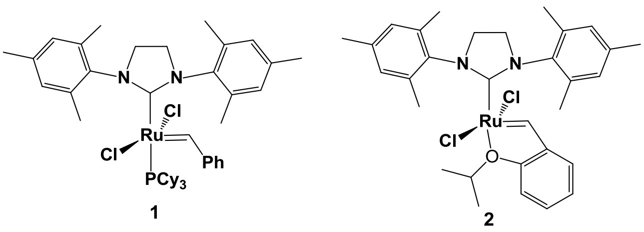

Figure 1.1: Grubbs (left) and Hoveyda (right) 2nd generation catalysts

In the past, cross metathesis reactions of olefins with acrylates have been performed with comparatively high amounts of catalysts (5 mol % and more), harsh reaction conditions like high temperature for long reaction times and by using unconventional heating systems like microwave radiations.[7] Besides these parameters, the effect of changing solvent and using specially designed initiators for this type of cross metathesis are also well thought-out.[8] Among a large variety of available initiators, two most commonly used initiators are Grubbs 2nd generation initiators **1** and Hoveyda type 2nd generation initiator **2**. Recently, in finding the most appropriate reaction conditions for cross metathesis of olefins with methyl acrylate some solvent free reactions were reported by Meier at al. This reaction in five to ten excess folds of methyl acrylate using 0.1mol% of Hoveyda type initiators **2** resulted in 99% and 69% conversion of alpha-, beta unsaturated ester cross metathesis products with olefins 10-undecanoate and methyl oleate respectively.[9] Olefins from renewable resources like methyl oleate contribute to valuable reactions for the synthesis of monomers which later can be used in many other reactions including polymer synthesis. The reported conditions most of all the very low catalyst loadings are outstanding compared to previously used reaction conditions in which 5-10 mol% loadings of the initiator in relatively longer reaction time were needed.[10] However, the reaction could be further optimized with using higher temperatures and especially in presence of initiators which are not only stable at higher temperatures but

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[7] Fustero, S.; Sanchez-Rosello, M.; Sanz-Cervera, J. F.; Fernandez, B.; Bartolome A.; Asensio, A. *Org. Lett.*, **2006**, *8*, 4633–4636.

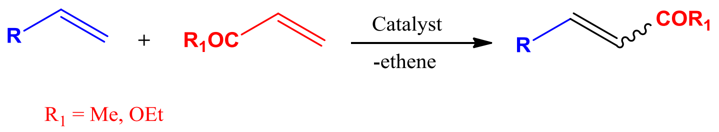
[8] Bilel, H.; Fischmeister, C.; Bruneau, C. *Green Chem.* **2011,** 13, 1448-1452.

[9] Rybak, A.; Meier, M.A.R. *Green Chem.* **2007**, *9*, 1356–1361.

[10] Bieniek, M.; Michrowska, A.; Usanov, D. L.; Grela, K. *Chem. Eur. J.*, **2008**, *14*, 806-818.

perform the cross metathesis with higher turn-over-number (TON). However, increased probability of getting some unwanted products due to free radical or by other mechanism when performing this reaction at distinctly higher temperatures, have to be considered. However, a better understanding about the details of cross metathesis reaction and initiator reactivity within the system can be gained.

Also, the cross metathesis of olefins with methyl vinyl ketone to yield α-, β-unsaturated ketones is the reaction of significant importance in modern organic chemistry (*cf.* Scheme below).[11] The resulting substrate is a highly reactive precursor and is helpful for the synthesis of many other valuable substrates, for examples with cyclopentadiene to yield norbornene derivatives via Dials-Alder reaction and formation of furan and pyridine substituted products which later can be applied in polymer and medicinal applications.[12]



Scheme 1.2: Cross-metathesis of olefins with ethyl acrylate and methyl vinyl ketone

Previously, for the synthesis of these molecules among many other reaction techniques, aldol condensation and Wittig reaction were frequently used.[13] But olefin metathesis with vinyl ketone is the most feasible reaction for the direct conversion to α-, β-substituted ketones from olefins. Two major advantages of using methyl vinyl ketone (MVK) are *(i)* its flexibility to form a large variety of products and ease of removal after cross metathesis *(ii)* comparatively low cost and easy commercial availability compared to other vinyl ketones. To improve the yield of the cross metathesis products, different approaches have been followed, like the employment of co-catalysts together with metathesis cataylsts, protection of the ketone's carbonyl group, statistically changing the ratio of olefins and MVK and, after all targeted design of new initiators which could help in increasing the yield.[14] Grubbs et al. reported that cross metathesis of methyl vinyl ketone with olefins require relatively large amount of solvents compared to acrylates.[15] Recently, Maudit et al. reported more sterically hindered N-heterocyclic carbene legated ruthenium based initiators as promising precursors for this type

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[11] Purnama, D.; Randl, S.; Blechert, S. *Tetrahedron Lett.* **2005**, *46*, 577-580.

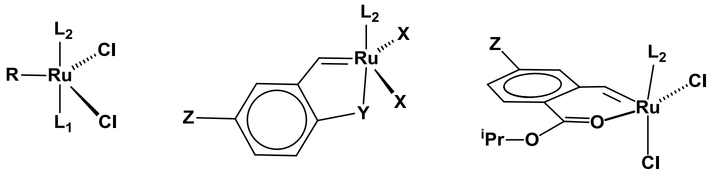
[12] (a) Kim, S-G.; Park, T-H.; Kim, B.J. *Tetrahedron Lett.* **2006**, *47*, 6369-6372; (b) Bellassoued, M.; Aatar, J.; Bouzid, M.; Damak, M. *Taylor & Francis* **2010**, *185:9*, 1886-1895.

[13] *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, March, J. Willey interscience, **1992**, vol. 4.

[14] (a) Ettari, R.; Micale, N. *J. Organomet. Chem.* **2007**, *692*, 3574–3576. (b) Michrowska, A.; Bujok, R.; Harutyunyan, S.; Sashuk, V.; Dolgonos, G.; Grela, K. *J. Am. Chem. Soc*. **2004**, *126*, 9318–9325.

[15] Chatterjee, A. K.; Choi, T.-L.; Grubbs, R. H. *J. Am.Chem. Soc.* **2001**, *125*, 10417-10418.

of cross metathesis reactions.[16] However, highly optimized reaction conditions for the cross metathesis of MVK with olefins to obtain high yields is still demanded.



X = -Cl, -Br, -I
L_1 = $-PCy_3$, Py
L_2 = SIMes, SIPr
R = benzylidene, Indenylidene
Y = $-O^iPr$, $-COO^iPr$, $-OCH(CH_3)COCH_3$
Z = -H, -OMe

Figure 1.2: Catalysts screened for cross metathesis of olefins with acrylates or vinyl ketones

Another principal reaction in olefin metathesis that has been investigated within this work is polymerization of diacrylates with diolefins to give co-polymers with alternating chain with perfectly arranged sequence. This reaction is called alternating metathesis polycondensation (ALMET)[17] and has been mainly performed with Grubbs second generation initiator **1**. Polymers for variable lengths with perfectly alternating monomer sequence have been obtained. The scope of this reaction may be expanded by also using other initiators which later may help in optimizing the reaction conditions. The same reaction could be expanded to try many other olefins and diacrylates especially with challenging substrates like 1,1-substituted olefins and disubstituted methacrylates.

Ring closing metathesis (RCM) of olefins with α-, ß-unsaturated ester functional group can yield lactones which is a favourable reaction for many advanced applications in organic synthesis. Substituted olefins that will yield di, tri- or even tetra substituted cyclic olefins are comparatively hard substrates for this type of metathesis reaction and usually require high loadings of the catalyst. Similarly, ring closing metathesis to yield lactones of unfavourable ring size is a difficult task. An effort to make these reactions accessible is also accomplished and presented in this work.

In the advanced age of technology, nanomaterials are gaining much attention. In particular, silver nanoparticles cleaved from big clusters of silver metal to small scale molecules are used for the advanced applications for luminescence and antimicrobial activities.[18] Many methods

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[16] Borre, E.; Dinh, T. H.; Caijo F.; Mauduit M. *Synthesis* **2011**, *13*, 2125-2130;

[17] Demel, S. Slugovc, C. Stelzer, F. Fodor-Csorba, K. Galli, G. *Macromol. Rapid. Commun.* **2003**, *24*, 636-641.

[18] Lewis, L.N. *Chem Rev.* **1993**, *93*, 2693–2730.

for the synthesis of silver nanoparticles using silver salts and oleylamine have already been reported in literature, but the green process for the synthesis of nanoparticles in shorter reaction times and maximum yield was still a demanding issue.[19] Materials formed by combining olefin metathesis products with silver nanoparticles can be advantageous for multiple industrial applications. Ring opening metathesis polymerization (ROMP) was used for the polymerization of DCPD which is a cheap raw material and yields materials with numerous applications.[20] These light weight hard materials can be used for the resins in cosmetics, pool panels, golf tips and wings of aeroplane or windmills etc. These materials, when equipped with silver based nanoparticles, could show antimicrobial effects and for the safe and clean water supply. The antimicrobial equipment via copolymerization of silver nano particles has been investigated within this work.

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[19] Nadawy, A. M.; Tolaymat, T. M.; Suidan M. *Science of the Total Environment* **2010,** *408*, 999-1006.

[20] *Olefin Metathesis and Metathesis Polymerization*; Ivin, K.J.; Mol, J. C.; Academic Press: San Diego, 1997.

Major motivations to start this work were...

(i) To evaluate a number of initiators for various olefin metathesis reactions, especially for cross metathesis along with conventionally used 2nd generation ruthenium based initiators **1** and **2**. A series of commercially available and inexpensive initiators as well as some newly synthesized complexes from our laboratory considering different parameters will be presented. The ruthenium based initiators vary their characteristics (activity, solubility, stability...) due to modification of various ligands at ruthenium centre or at their side chains. The new catalysts turned out to be helpful in many metathesis reactions including cross-metathesis of ethyl acrylate and MVK with olefins.

(ii) High catalyst loadings that have been necessary for various reactions gave rise to the second motivation of optimizing the reaction condition for various olefin metathesis reactions especially of electron withdrawing olefins like alpha-, beta-unsaturated ketones and esters. Reported works describing the solvent free reaction in excess of methyl acrylate for cross metathesis of olefins with acrylates and CuI assisted cross metathesis with methyl vinyl ketone were used as exemplary references. In the same way, optimal solvent and reaction conditions could improve ALTMET polymerizations and also RCM reactions to produce lactones. These factors were further evaluated for the optimization of reactions in order to use the lowest possible amount of catalyst loading and complete the reactions in a minimum time duration.

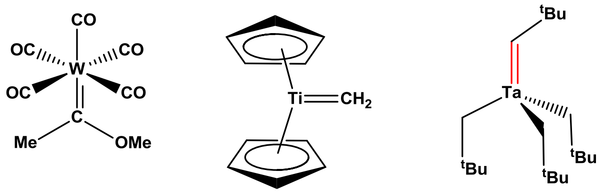
(iii) Besides optimization of the reaction conditions, the third and most promising motivation was to produce new materials for advanced applications, especially starting from commonly available cheap raw materials.

Chapter 2

Theoretical Background

2.1 Olefin metathesis

A great revolution in the field of olefin polymerization started with the invention of catalysts by Karl Ziegler and Giulio Natta, which led them to win the Noble Prize in chemistry in 1963.[21] These pioneering and later also modified transition metal catalysts have been used for producing saturated polymers with controlled stereochemistry e.g. poly(propylene) for applied fields industrial chemistry. Detected as a side reaction at first, olefin metathesis that yields unsaturated products was a by-product of these fundamental findings of the Ziegler-Natta polymerization. Later, metal-carbene-complexes for olefin polymerization and other olefin reactions were developed by Fischer, Tebbe and Schrock.[22] (*cf.* **Figure 2.1**) By now, olefin metathesis is one of the significant carbon-carbon bonds forming tools, which can help in the synthesis of a large variety of substrates.[23]



Fischer's Carbene **Tebbe's Carbene** **Schrock's Carbene**

3 **4** **5**

Figure 2.1: Metal carbene complexes of early times

The progress in this field is notable since some early reactions were reported in 1956 with tungsten based initiators.[24] When performing the polymerization of norbornene with titanium based metal complexes, the scientists at DuPont formed a polymer with high degree of unsaturation. During this reaction, not only the strained norbornene ring was opened but new polymers with high olefin contents were also observed.[25] In another experiment, when performing the addition polymerization with molybdenum on alumina catalyst for

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[21] *Encyclopaedia of Polymer Science and Technology: Wood to Ziegler-Natta Catalysts* Marks, H. F. *John Wiley & Sons Inc.* **1972.**

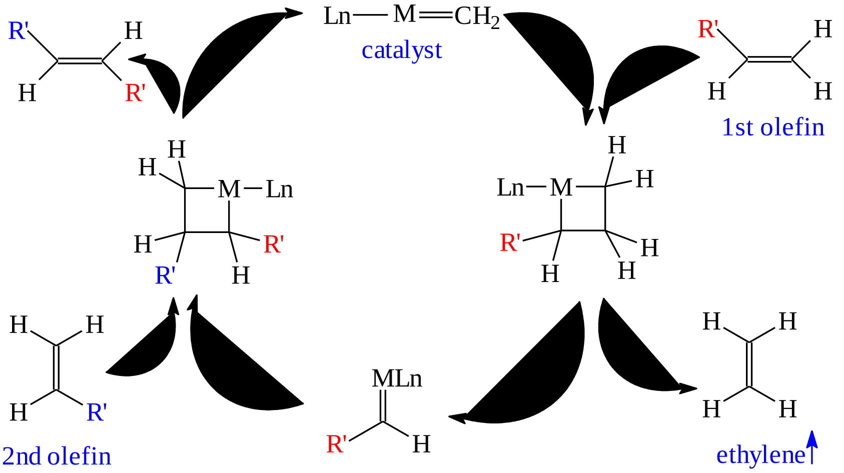
[22] *Handbook of Transition Metal Polymerization Catalysts* R. Hoff, R. T. Mathers, *eds. John Wiley & Sons Inc.* **2010**.

[23] Natta, G. *Angew. Chem.* **1956,** *68*, 393-403.

[24] Ziegler, H. *Angew. Chem.* **1955**, 67, 541-543.

[25] Truett W. L.; Johnson D.R.; Robinson I.M.; *J. Am. Chem. Soc.* **1960,** 2337-2341.

copolymerization of ethylene and propylene, 1-butene was produced as a side product. Besides these reactions, the formation of highly unsaturated polymers was observed when performing the polymerization of cyclooctene. These finding led to the conclusion that in a side reaction some exchange of the substituents of the olefins also occurred which resulted in the synthesis of substituted olefin products along with desired major addition products.[26] This reaction was one of its own type and its details were not much known until for the first time the term "*olefin metathesis*" was introduced. According to that, "*one carbon of the double bond with everything attached to it exchanges its position with one carbon of double bond of the other olefin with everything attached to it*".[27] In order to understand the reaction in detail, an experiment was designed by a team at Goodyear with 2-butene and deuterated 2-butene[28] and at the same time another team in the Netherlands designed the experiment with propylene and C-14 labelled propylene to understand the detailed mechanism of metathesis reactions.[29]



Scheme 2.1: Reaction mechanism for olefin metathesis reactions

At the start, a metallacyclobutane complex was assumed to be involved in the mechanism, but other postulates of reaction intermediates like existing of tetramethylene complex (i.e. four methylene units binding to the central metal atom) were also assumed to be plausible to initiate the metathesis reaction. In early 1972 Grubbs proposed "*the reaction proceeded with the distribution of the groups around double bonds was due to metallacyclopentene*

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[26] Banks, R. L.; Bailey, G. C.; *Ind. Eng. Chem. Prod. Res.* **1964,** *3,* 170.

[27] Calderon N.; Chen H. Y.; Soott K. Y.; *Tetrahedron Lett.* **1967**, *34*, 3327-3329

[28] Calderon, N., Ofstead E.A., Ward J.P., Judy W. A., Scott K. W., *J. Am. Chem. Soc.* **1968,** *90,* 4133-4140.

[29] Mol, J. C. Maoulijn J. A. Boelhouwer C.; *Chem. Commun.* **1968**, 633-633.

intermediate". Later it was also suggested that this intermediate after rearranging could lead to the cyclobutane complexed to the metal carbene.[30]

Yves Chauvin working with his graduate student Jean Loius Herrison at the French petroleum institute proposed the detailed mechanism of olefin metathesis in 1971. According to that first olefin through a reversible step forms a metallacyclobutene complex, which later upon cycloreversion yields a newly substituted metal complex. This new metal complex when repeating the same procedure with second olefin yields the substituted metathesis product.[31] This exchange between metal carbene and olefin has been appeared to be fundamental step in olefin metathesis reactions. (**Scheme 2.1**)

Even after great advancement in understanding olefin metathesis reactions, the mechanism proposed by Chauvin is still supposed to be the best description of the mechanism of olefin metathesis reactions. Firstly, proposed titanium and tungsten based initiators were modified and in exploring the complexes of different metals of low or higher oxidation states a series of initiators were synthesized. Corresponding complexes of tantalum, titanium, tungsten, molybdenum and ruthenium were introduced. Complexes with the metal at high oxidation states were named as metal alkylidenes whereas those with low oxidation state metal the complexes were called as carbene complexes.[32] Among many other scientists, the contributions by Grubbs, Schrock, Katz and Chauvin are appreciable and fundamental for the further development of the olefin metathesis reaction since its first discovery.

A key step to recent findings in applications of olefin metathesis chemistry were the highly efficient, single-site catalysts that are tolerant to many organic functional groups and can be used without complicated experimental setups. As the early catalysts were not tolerated by most functional groups so the initial focus was on hydrocarbon olefins only. For example, the Shell higher olefin process (SHOP) was an important pre-process at that time for the synthesis of fatty aldehydes or alcohols used as detergents.[33] But this process and the compounds prepared through this technique lack in functional group flexibility. New catalysts have been developed and the functional group tolerance problem was overcome with new, well defined ruthenium and osmium based catalysts. The reason for giving ruthenium preference over other metals in the same group (i.e. Fe, Co and Rh) is their formation of cyclopropane-associates in stoichiometric reactions[34], while ruthenium and osmium form metal carbon double bond intermediates. Some olefin metathesis initiators were also designed using iridium

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[30] Grubbs, R.H.; *J. Am. Chem. Soc.* **1971,** *93***,** 7087-7091.

[31] Chauvin, Y., Hérisson, J-L. *Makromol. Chem.* **1971,** *141,* 161-162.

[32] Grubbs, R.H. *J. Am. Chem. Soc.* **1992,** *114*, 3974-3977.

[33] Mol, J.C.; *J. Mol. Catal. A: Chemical*, **2004**, *213*, 39-45.

[34] Boyle, M. P.; Ren, T. Prog. *Inorg. Chem.* **2001**, *49*, 113–168.

metal but these along with metal complexes of osmium are ill-defined and comparatively little active than their analogue ruthenium catalysts.

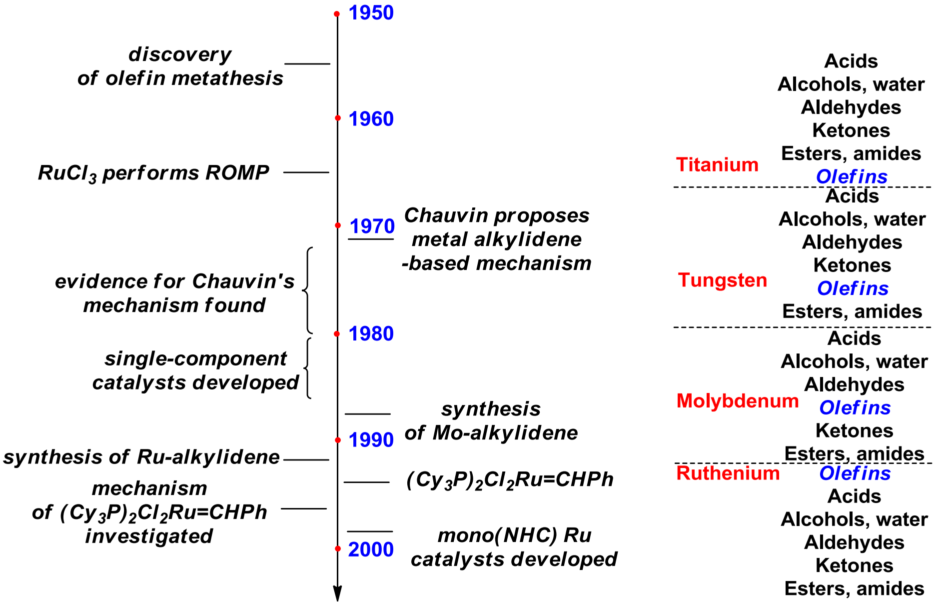

Figure 2.2: (left) General history of olefin metathesis (right) functional group tolerance of metal complexes

All that progress using well-defined initiators in olefin metathesis system has resulted in accessibility of many complex molecular structures. Small chain cross metathesis reactions and the synthesis of ring of larger size are the key steps in synthesis of agrochemicals and pharmaceutical products such as macro cyclic peptides, insect pheromones, cyclic sulphonamides and new macrolides.[35] Among other highlighted products epothilones, amphidinolides, spirofungin A, and archazolid are also important products synthesized using olefin metathesis as a major tool.

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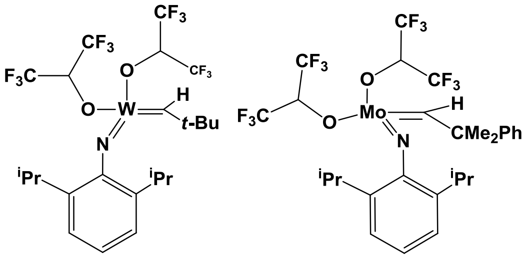
[35] “*Alkene metathesis in organic synthesis*” Fuerstner, A.; *Springer* **1998.**

2.2 Metal Complexes

Transition metal complexes represent the heart of olefin metathesis, as they are the catalysts (or pre-catalysts) and keep the reaction going. The first metal found to be active in metathesis is titanium, but the scope of these initiators was limited due to very low reactivity towards olefins and also poor functional group tolerance. The metal initiator's activity was much improved by well defined tungsten and molybdenum catalysts like **6** and **7** respectively, as depicted in **Figure 2.3**. Still a lot of new initiators are being reported every year for selective and high yield procedures towards required stereo isomers based on these metals.[36] However, these initiators still lack in functional group tolerance, and also, they tend to be sensitive towards air and moisture.



6 **7**

Figure 2.3: Schrock's catalysts used for olefin metathesis reactions

These two important issues are largely compensated by initiators based on the transition metal ruthenium. Especially due to their high functional group tolerance and high resistance to air and moisture, a butenylidene legated ruthenium complex (**9**) and a ruthenium bi-phosphine complex featuring a benzylidene carbene ligand brought a breakthrough in olefin metathesis. The latter complex later became known as the "Grubbs 1st generation catalyst" (**8**).[37]
(*cf.* **Figure 2.4**)

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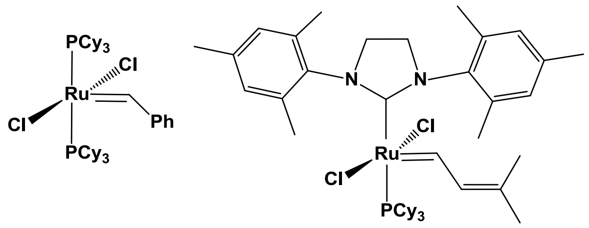
[36] Schrock, R. R.; *J. Mol. Catal.* **1980,** *8,* 73-75.

[37] Grubbs, R.H. *J. Am. Chem. Soc.* **1992,** *114*, 3974-3977.



8 **9**

Figure 2.4: Grubbs 1st generation and butyniledene catalysts

The development of the ruthenium based Grubbs catalysts **-** isobutenyl carbene catalyst **9**, bi-tricyclohexyl phosphine based 1st generation initiator **8** and later 2nd generation complex **1** (*cf.* **Figure 1.1**) that bears an N-heterocyclic carbene instead of the second phosphine ligand, made olefin metathesis feasible for a large variety of substrates and eventually resulted in a veritable boost of research interest in that reaction. The following table established by Grubbs et al. displays reactivity trends of different transition metal carbene complex towards various substrates.[38] It becomes clear why ruthenium based catalysts are somewhat superior to other transition metal complexes, especiall regarding their sensitivity. As shown, they will rather react with olefins (meaning they perform metathesis) and are not easily disturbed by functional groups that might occur at the substrates.

Table 2.1: Reactivity trends of metal carbene complexes towards various substrates[38]

Ti	W	Mo	Ru	reactivity
Acids	acids	acids	**olefins**	↑
alcohols, water	alcohols, water	alcohols, water	acids	
Aldehydes	aldehydes	aldehydes	alcohols, water	
Ketones	ketones	**olefins**	aldehydes	
esters, amides	**olefins**	ketones	ketones	
Olefins	esters, amides	esters, amides	esters, amides	

A phosphine free, 2nd generation catalyst was coincidentally produced in the reaction of phenyl ether substituted cyclooctene with 2-isopropoxy styrene to give cross metathesis products. However, the reaction instead stopped midway in presence of the substrates. Detailed analysis revealed the formation a new form of stabilized (due to the chelating ether) ruthenium complex.[39] This air and moisture stable complex obtained from Grubbs 1st generation complex **8** was isolated in high yields and later upon evaluation it was found that this compound also is an active catalyst for olefin metathesis. Eventually, also its 2nd

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[38] Schwab, P.; Grubbs, R. H.; Ziller, *J. W. J. Am. Soc.*, **1996**, *118*, 100-110.

[39] Kingsbury, J.S. Hoveyda, A.H. *J. Am. Chem. Soc.* **1999,** *121*, 791-799.

generation analogous complex **2** (*cf*. **Figure 1.1**), nowadays often referred to as the “Hoveyda catalyst”, was synthesized.[40]

Soon after the invention of Grubbs and Hoveyda type catalysts a large number of other catalysts have been synthesized within the last twenty years, which all have particular characteristics depending on the ligands attached. Some are latent in nature for various reasons and their half life is varying from minutes to years.[41] But not only the rate of reaction is tunable by various modifications, also special catalysts for reactions in water or in ionic liquids or even on solid supports for being recycled several times have been designed.[42]

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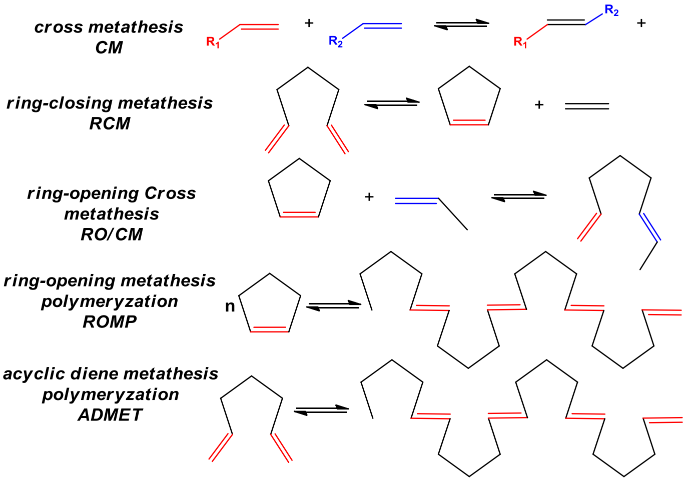
[40] Garber, S. B.; Kingsbury, J. S.;Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, 122, 8168–8179

[41] Vougiouklakis, G.C. Grubbs, R.H. *Chem. Rev.* **2010**, *110*, 1746-1787.

[42] Hong, H. S. Grubbs, R. H. *J. Am. Chem. Soc.* **2006,** *128*, 3508-3509.

2.3 Types of olefin metathesis reactions

Among the various metathesis reactions, the three most frequently used techniques are cross-metathesis (CM), ring closing metathesis (RCM) and ring opening metathesis polymerization (ROMP). Besides, ring expansion metathesis (REM), ring opening metathesis (ROM), acyclic diene metathesis (ADMET), ring opening / cross metathesis (RO/CM), alternating diene metathesis polycondensation (ALTMET), ring opening insertion metathesis polycondensation (ROIMP), and ene-yne metathesis are frequently used metathesis reactions for the synthesis of a large number of diverse products. An overview is provided in the following **Scheme 2.2**. How to best proceed the metathesis reaction, significantly depends upon the nature of reacting molecules, reaction conditions and on type of catalysts used. For example, in the olefin metathesis of terminal bi-olefinic substrates, the dilution factor and type of olefin determines the reaction to proceed in yielding either the ring closing metathesis (RCM) product or the ADMET polymer. If the product to be formed is of unfavourable ring size than ADMET is preferred but if a five or six membered olefin is being formed, then the reaction proceeds through RCM mechanism; provided the dilution is high enough.[43] Similarly in cross metathesis of olefins, Schrock type molybdenum catalysts are useful for the synthesis of *cis*-arranged stereo selective isomers and performing the same reaction in presence of ruthenium based Grubbs type initiators high ratios of *trans*- isomeric products are obtained.[44] En-yne metathesis is also of the importance in olefin metathesis, besides this reaction is totally atom economical, meaning no side products occur during this process.



Scheme 2.2: Selected examples of olefin metathesis reactions[45]

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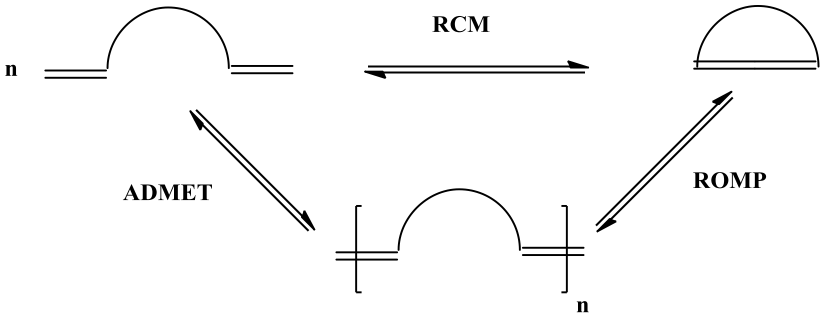
[43] Kadyrof, R.; Wolf, D.; Ostgard, D. J. *Top. Catal.* **2010**, *53*, 1066-1072.

[44] Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. M. *J. Am. Chem. Soc.*, **2009**, *131*, 16630-16631.

[45] Astruc, D.; *New J. Chem.*, **2005**, *29*, 42-56.

2.4 Ring Closing Metathesis (RCM)

Ring closing metathesis is an adorable technique used for the synthesis of various molecules, thas has particularly become useful for the synthesis of larger unusual ring systems that oftenly occur in pharmaceutical products or other advanced material chemistry.[46] Some early ring closing metathesis reactions were reported by Villemen and Tsuji.[47] Grubbs explored the RCM reaction with deuterated octadiene substrates and formed cyclohexene products which later helped in proving the formation of metallacyclobutene intermediate during metathesis.[48] Since these early discoveries, the RCM reaction technique has been employed in forming many industrial and pharmaceutical products. Rings of various sizes and with various functional groups are accessible which is important for many advanced applications including natural product synthesis.[49] Five and six membered rings are easily produced via the RCM route but the synthesis of medium or large size ring molecules is also feasible, although a little tricky. The key competing reactions when performing RCM of these types of substrates are oligomerization also called acyclic diene metathesis (ADMET), macro ring formation and ring expansion metathesis. Higher dilutions, catalyst loadings in portions and optimized temperatures are the helpful tools in synthesis of both carbocycles and heterocyclic via RCM.[50]



Scheme 2.3: RCM, ROMP and ADMET polymerization of biolefins

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[46] Fuerstner, A. *Alkene Metathesis in Organic Synthesis*; Springer-Verlag: New York, **1998**.

[47] Villemin, D. *Tetrahedron Lett.* **1980**, *21*, 1715.

[48] Grubbs, R. H.; Burk, P. L.; Carr, D. D. *J. Am. Chem. Soc.* **1975**, *97*, 3265-3266.

[49] Yu, M.; Wang, C.; Kyle, A. F.; Schrock, R.R.; Hoveyda, A. H. *Nature* **2011**, *479*, 88-93.

[50] Fuerstner, A. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 3013–3043.

2.4.1 Factors effecting RCM

The conversion of medium or large molecules in either cyclization or oligomerization reactions was first studied by Ziegler, Ruggli and Ruzicka.[51] Two important factors which come into play are *the kinetic factor* and *the thermodynamic factor*. These factors will be explained on the basis of change in equilibrium at different stages which change the metathesis product distribution and overall yield.

2.4.1.1 Kinetic factor

RCM reactions follow first order kinetics whereas oligomerization proceeds according to second order reactions. Hence, Ziegler proposed that by using “infinitely dilute solutions” the RCM of substrates can be achieved.[52] The structure of the ring to be formed is an important factor for cyclization. First, RCM was thought to be limited to medium size ring molecules (8- to 11-membered), because ring strain and many other factors are determining the reaction progress. Clearly, detailed kinetic studies of the reaction were required. The rate of cyclization depends on the structure of initial state and intramolecularly formed transitions states (e.g. chelation via heteroatoms within the ring to be closed) resembling the final cyclic product. If this transition state is not stable then oligomerization is the favourable pathway. It has to be kept in mind that the tendency to form strained rings is naturally rather small for any system and has to be facilitated by optimized reaction conditions. In this regard the activation energy of this intermediate is also important in consideration with ring strain energy which depends upon the yielded ring size.[53]

Three major ring strains involved are:

1. Pitzer strain due to eclipsing of non bonded atoms,
2. Baeyer strain due to deformation of ring bond angles, and
3. Trans annular strain of ring bonded angles when they are close enough to each other.

1 and 3 are important consideration for medium size ring formation but so far these strains have only been calculated for cycloalkanes.[54]

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[51] L. Ruzicka, M. Stoll, and H. Schinz, *Helu. Chim. Acta*, **1926,** *9,* 249.

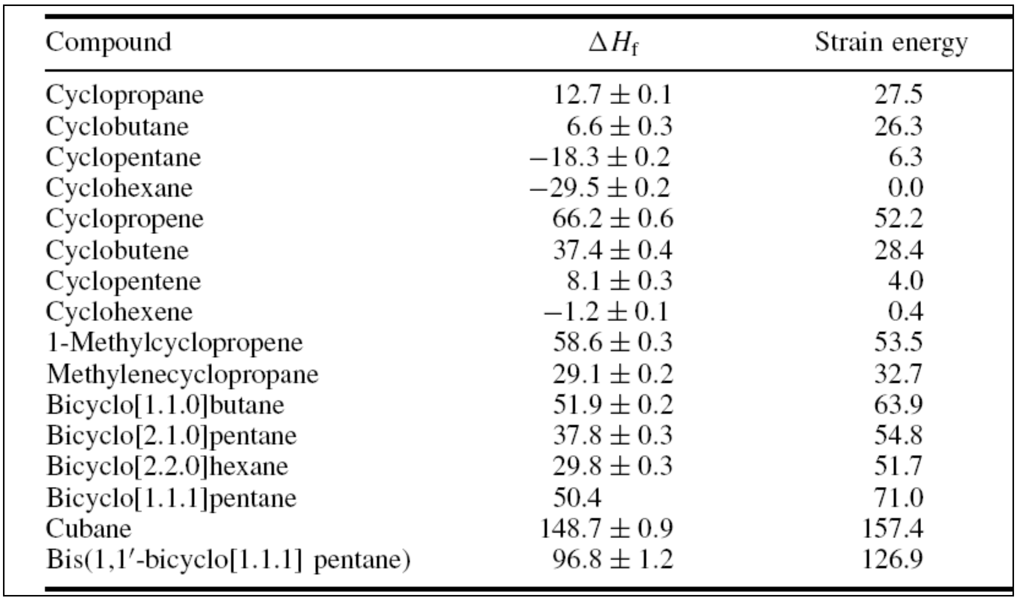
[52] M. I. Page, Chem. SOC ***R.e u.,*** **1973,** *2,* 295

[53] Fuerstner, A.; Seidel, G.; Kindler, N. *Tetrahedron* **1999**, *55*, 8215-8230.

[54] (a) Dunitz, J. D.; Shomaker, V.; *J. Chem. Phys.*, **1952**, *20*, 1703 (b) Wiberg, K. B.; *Angew. Chem.,Int. Ed. Engl.*, **1986,** *25*, 312.

The kinetic effect of cyclization of organic molecules can be explained by the effective molarity (EM) and the ratio $\mathbf{k}_{\text{intra}} / \mathbf{k}_{\text{inter}}$. This ratio manipulates the effective concentration of the first order cyclization reaction to the second order oligomerization reaction. An overview is given in the following table (***cf.*** **Table 2.1**).[55] But the real aspect of EM is that it clearly demonstrates that the probaility for the formation of a cyclized product from bi-olefinic substrates over polymerization thereof is very high whenever the concentration of substrate is considerably lower than EM value.[56]

Table 2.2: Heats of formation enthalpies (H_f) and strain energies of different cycloalkanes at 25°C in gas phase (kcal / mol)



Compound	ΔH_f	Strain energy
Cyclopropane	12.7 ± 0.1	27.5
Cyclobutane	6.6 ± 0.3	26.3
Cyclopentane	-18.3 ± 0.2	6.3
Cyclohexane	-29.5 ± 0.2	0.0
Cyclopropene	66.2 ± 0.6	52.2
Cyclobutene	37.4 ± 0.4	28.4
Cyclopentene	8.1 ± 0.3	4.0
Cyclohexene	-1.2 ± 0.1	0.4
1-Methylcyclopropene	58.6 ± 0.3	53.5
Methylenecyclopropane	29.1 ± 0.2	32.7
Bicyclo[1.1.0]butane	51.9 ± 0.2	63.9
Bicyclo[2.1.0]pentane	37.8 ± 0.3	54.8
Bicyclo[2.2.0]hexane	29.8 ± 0.3	51.7
Bicyclo[1.1.1]pentane	50.4	71.0
Cubane	148.7 ± 0.9	157.4
Bis(1,1′-bicyclo[1.1.1] pentane)	96.8 ± 1.2	126.9

2.4.1.2 Thermodynamic effect

Thermodynamic effect can generally be explained by the Gibbs-Helmholtz equation.[57]

$$\Delta G = \Delta H - T\Delta S$$

The enthalpy changes with the ring size and positive enthalpy reaches a maximum with medium ring sized molecules due to imperfect staggering and transannular strain between the atoms. Cyclization of these rings depends upon nature of hybridization of atoms. The extent

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[55] *"The Chemistry of Cyclobutanes"*Rappoport, Z. *John Willey & Sons Ltd.* pat 1, **2005.**

[56] Liebman, J. F.; Greenberg, A. *Chem. Rev.,* **1976**, *76*, 311

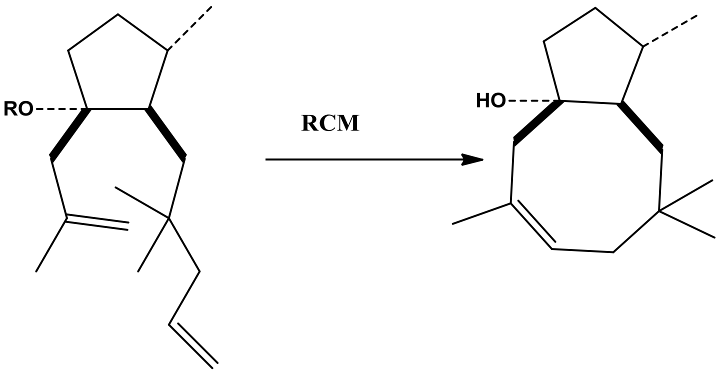
[57] L. Mandolini, *J. Am. Chem. SOC.* **1978,** ***100*****,** 550-552.

of cyclization mainly depends upon the factor of temperature T and entropy change delta S. As we increase the temperature, the entropic factor increases and degree of cyclization is also increased. Hence the dilution factor and high temperature increases the rate of cyclization.

Other factors which may count for cyclization are:

2.4.1.3 Gem-dimethyl substitution effect Thorpe-Ingold effect[58]

For the cyclization of medium size rings, replacement of hydrogen atoms in the neighbourhood of terminating chains by methyl groups increases the chance of cyclization. The increase in angle due to methyl groups decreases the angle between combining hydrogen of the terminal atoms and hence chances of cyclization increases due to less annular strain.



Scheme 2.4: RCM for the synthesis of gem dimethyl natural product[59]

2.4.1.3 Oxygen atom effect[60]

Similarly, if one of the methylene is replaced by an oxygen atom in the neighbourhood of the terminating chain atoms, the annular stain is decreased and bond opposing forces results in ease of cyclization.

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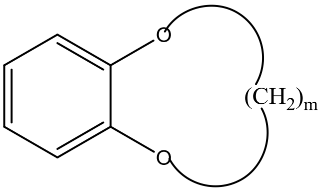
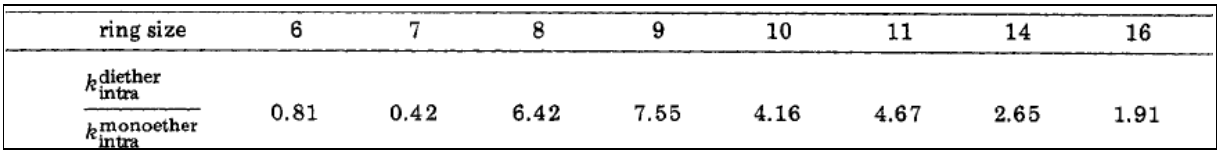
[58] B. Capon and S. P. McManus, *"Neighboring Group Participation",* Vol. 1, Plenum Press, New York**, 1976.**

[59] Langeman, K; Fuestner, A. *J. Org. Chem.* **1996**, *25*, 8746-8749.

[60] L. Mandolini and B. Masci, *J.* Am. Chem. Soc., **1977**, *99*, 7709-7711.





ring size	6	7	8	9	10	11	14	16
$\frac{k_{intra}^{diether}}{k_{intra}^{monoether}}$	0.81	0.42	6.42	7.55	4.16	4.67	2.65	1.91

Figuer 2.5: The rate of conversion of diether and monoether of rings of different sizes[61]

2.4.1.4 Role of equilibrium[62]

Previous studies and analysis of RCM reaction clearly show that these reactions are totally reversible. In reality, the equilibrium (and reversibility) is determined upon the presence or optional removal of the formed side products (usually ethylene), inhibition of backbiting (dilution, etc.), catalyst deactivation prior to equilibrium and other factors.

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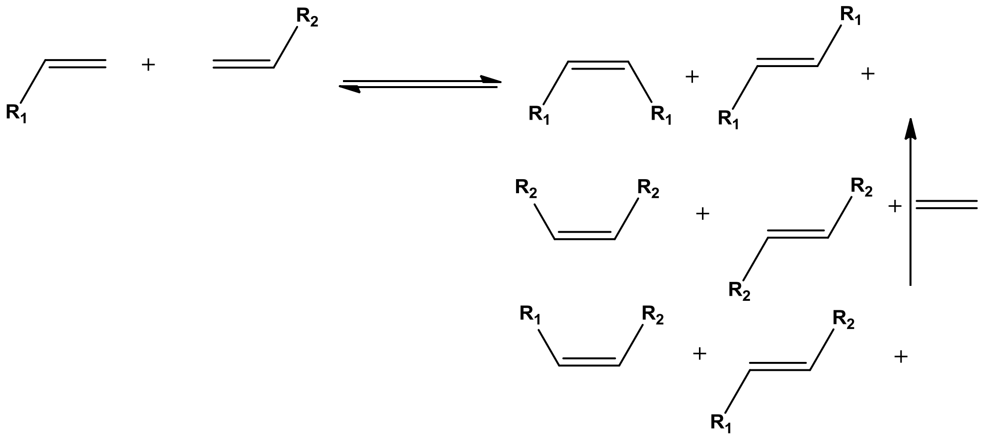
[61] Dale, J. *Tetrahedron*, **1974**, *30*, 1684.

[62] Takagi, H.; Sisido, M.; Imamishi, Y.; Higashimura, T. *Bull. Chem. SOC. JPN.*, **1977**, 50, 1807.

2.5 Cross-metathesis

In contrast to RCM, cross metathesis is different in the aspect that the intermolecular reaction between two separate olefins is performed yielding a new, substituted olefinic product. The cross metathesis reaction is preferred over other metal catalyzed couplings due to ease of reaction and high catalyst stability. With the development of well defined ruthenium based catalysts **1**, **2**, **8** and **9** and molybdenum based catalysts **6** and **7** cross metathesis has enabled the synthesis of valuable products. According to some recent findings in comparison of Grubbs (**1**) and Hoveyda (**2**) type catalysts, the use of **2** in cross-metathesis is to be preferred over **1**.



Scheme 2.5: Possible stereoisomer in cross-metathesis of two different olefins

2.5.1 Stereochemistry of cross metathesis products

Besides a lot of advantages, there are some limitations of cross metathesis reactions over other metal catalyzed reactions. For example in Pd (0) catalyzed Suzuki coupling reactions aryl halides give diastereoselective reactions with boronic acid or esters to yield desired coupled products.[63] The metathesis products generally lack in diastereoselectivity coupling of the educts. For example, if two different olefins react, the cross metathesis product can consist of six stereoisomers, three *cis* and three *trans* products.(*cf.* **Scheme2.4**) Four of the isomers are obtained via self metathesis reaction of either of the olefins, and two products via cross metathesis reaction, resulting in total six products. Besides, ethylene is also produced after each metathesis cycle, but can easily be removed from the reaction mixture.[64] Out of the six

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[63] Suzuki, A. Journal of Organometallic Chemistry **1999**, 576, 147–168.

[64] Bussmann, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 58-63.

products, generally only one product is desired with particularly *cis* or *trans* configuration of the olefins. Even when the statistical mixtures in 1:1 of olefins are used only 50% of the desired product can be produced. The conversion of olefins totally depends upon the nature and therefore the reactivity of the substrates along with other factors (concerning mostly the catalyst) which occurred for the distribution of the cross metathesis products. For example, in cross metathesis of acylates with olefins Schrock type catalysts yielded the *E* in more than 90% but using ruthenium based catalysts like Grubbs 2nd generation (**1**) this ratio has been increased. Similarly in the cross metathesis of olefins with methyl vinyl ketone, *E*-stereo isomer is selectively formed using Grubbs type catalysts.

2.5.2 Classification of olefins with respect to reactivity for cross metathesis

Olefins can be classified according their different reactivity in olefin metathesis reactions due to functional groups. The olefins are divided into four groups with respect to their reactivity towards olefin metathesis. The group-I olefins are easy precursors to form oligomers by self metathesis, but these oligomers can be re-consumed during the reaction. Group-II olefins form oligomers and these oligomers show little tendency towards consumption. Group-III is very inert to homodimerization but can yield cross metathesis reaction with group I and II partners but last group (group-IV) olefins are completely inert for metathesis. They do not contribute in metathesis but also are not disturbing other metathesis reactions when performed in presence of them. Outside these categories there are the olefins which are not only inhibiting metathesis reaction but it is hard to perform any metathesis reaction in presence of them because they are also found to inhibit or kill the catalyst (e.g. amines).[65]

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[65] Astruc, D.; *News J. Chem.*, **2005**, *29*, 42-56.

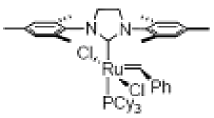
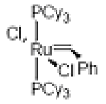
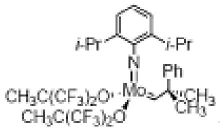
Olefin type			
Type I (fast homodimerization)	terminal olefins, 1° allylic alcohols, esters, allyl boronate esters, allyl halides, styrenes (no large ortho substit.), allyl phosphonates, allyl silanes, phosphine oxides, sulfides, protected amines	terminal olefins, allyl silanes, 1° allylic alcohols, ethers, esters, allyl boronate esters, allyl halides	terminal olefins, allyl silanes
Type II (slow homodimerization)	styrenes (large ortho substit.), acrylate, acrylamides, acrylic acids, acrolein, vinyl ketones, unprotected 3° allylic alcohols, vinyl epoxides, 2° allylic alcohols, perfluorinated alkane olefins	styrene, 2° allylic alcohols, vinyl dioxolanes, vinyl boronates	styrene, allyl stannanes
Type III (no homodimerization)	1,1-disubstituted olefins, non-bulky trisub. olefins, vinyl phosphonates, phenyl vinyl sulfone, 4° allylic carbons (all alkyl substituents), 3° allylic alcohols (protected)	vinyl siloxanes	tertiary allyl amines, acrylonitrile
Type IV (spectators to CM)	vinyl nitro olefins, trisubstituted allylic alcohols (protected)	1,1-disubstituted olefins, disub. α,β-unsaturated carbonyls, 4° allylic carbon containing olefins, perfluorinated alkane olefins, 3° allylamines (protected)	1,1-disubstituted olefins

Figure 2.6: Classification of olefins for selective cross-metathesis[66]

When performing the cross metathesis, olefins of different groups should be chosen for a satisfactory result. For example, performing cross metathesis of one olefin from group I, like a terminal olefin, and an olefin from group II, like methyl acrylate, more than 95% yield of the cross metathesis product can be obtained by using suitable catalysts and optimized reaction conditions.[67] The limitation of this reaction is the occurrence of undesired stereoisomers along with unreacted substrates and chances of self metathesis products are also high. In spite of other trickiness of the system a lot of cross metathesis products have been obtained via cross-metathesis reaction using combination of these two groups.[68] Although the reaction of olefins with ruthenium based catalysts have generated a large variety of products due to flexibility in

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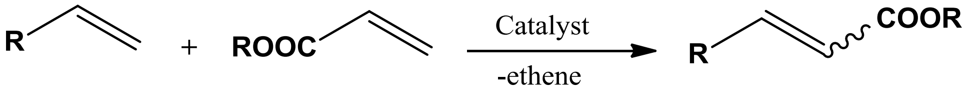
[66] Chaterjee, A. K.; Choi, T-L.; Sanders, D. P. ; Grubbs, R. H. *J. Am. Chem. Soc.*, **2003**, *125*, 11360-11370.

[67] Ryback, A. Meier, M. A. R. *Green Chem.* **2008**, *10*, 1099-1104.

[68] Ho, T. T. T.; Jacobs, T.; Meier, M. A. R. *Chem. Sus. Chem.* **2009**, *2*, 749–754.

the system but still cross metathesis reactions of electron poor olefins is one of the important and demanding reaction in modern chemistry. In contrast, electron donating olefins do not normally contribute in the metathesis reaction due to their Lewis basic nature, which is assumed to be responsible for killing the catalyst by donating the electron to transition metal of the catalyst.[69]

2.5.3 Cross metathesis of olefins with acrylates



Scheme 2.6: Cross metathesis of olefins with acrylates

Besides stereo selectivity, other major issues which count in cross-metathesis are optimized reaction conditions to give the high yield cross metathesis products especially with low catalyst loadings. Optimization in this context is necessary due to the high price of transition metal based catalysts on the one hand, but also to minimize residual metal content in the final products. The wrong choice of solvent or wrong dilution is often found to be responsible for the consumption of extra catalyst and separation of the products after synthesis is also difficult in cross metathesis with acrylates.[70] Besides other endeavours, the use of microwave irradiation, Lewis acids as co-catalysts and protecting of carbonyl functional group of the acrylate has been used for the successful cross metathesis of acrylates with other olefins.[71] Summarizing, the most favourable processes were reported by Forman et al, using p-cresols as solvents comparatively low catalyst loadings.[72] Cross metathesis reaction was also possible with various olefins including unstrained cyclic olefins that are usually not consumed in other olefin metathesis reactions. Grubbs proposed that the ester carbene is the key intermediate involved in the cross metathesis of acrylates with alkenes using ruthenium based catalysts.[15] While in earlier case he had reported that these isolated ester carbene catalysts are highly active catalysts for metathesis and the only issue for their practical use in metathesis as catalysts is their stability. The half life of these catalysts was found to be very short.

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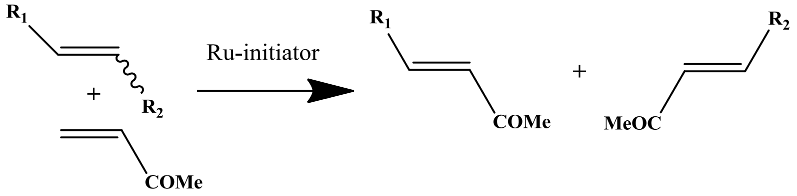
[69] Mickroska, A.; Grela, K. *Pure Appl Chem.* **2008**, *80*, 31-43.

[70] Bussmann, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 58-63.

[71] Clavier, H.; Grela, K.; Kirschning, A.; Mauduit, M.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 6786–6801.

[72] Forman, G. S.; Toose, R. P.; *J. of Organomet. Chem.* **2005**, *690*, 5863–5866.

2.5.4 Cross metathesis of olefins with methyl vinyl ketone (MVK)



Scheme 2.7: The cross metathesis reaction of various olefins with MVK

Methyl vinyl ketone (MVK) is one of these types of olefin which not only introduces the new functionality to olefins but can also be helpful for the synthesis of variety of many other substrates.[73] Besides the synthesis of new catalysts[74] other measures to enhance the reactivity of MVK to improve the yield and selectivity for cross metathesis product are necessary. These include reactions under microwave irradiation[75], using Lewis acid as co-catalyst[76] and protection of carbonyl functional group.[77] As these reactions are of industrial interest (so there are potential large scale applications), also environmental issues become important when it comes to optimization.

Grubbs et al. reported the successful cross metathesis of vinyl ketones with olefins, yet the reactions required higher dilutions of solvent compared to analogue reactions with acrylates.[15,78] Recently, the significance of copper salts (CuCl, CuI) has been described as a valuable additive for the synthesis of high yield cross-metathesis products with commercially available catalyst **2**.[79] Furthermore, halogen free solvents like ether or water make this type of reactions more environmentally benign and also more convenient and reliable for various practical applications.[80]

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[73] (a) Donohoe, T. J.; Basutto, J. A.; Rathi, A. *Org. Lett.* **2010**, *13*, 1036-1039.

[74] Grela, K.; Harutyunyan, S.; Michrowska, A.; *Angew. Chem. Int. Ed.* **2002**, *41*, 4038-4040.

[75] Murray, W.C.; Bargiggia, F.C.; *J. Org. Chem.* **2005**, *70*, 9636-9639

[76] Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000,** *122*, 3783-3784.

[77] (a) Chatterjee, A. K.; Toste, F. D.; Choi, T.-L.; Grubbs, R. H. Adv. Synth. Catal. **2002**, *344*, 634-637; (b) Chatterjee, A. K.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 3171-3174.

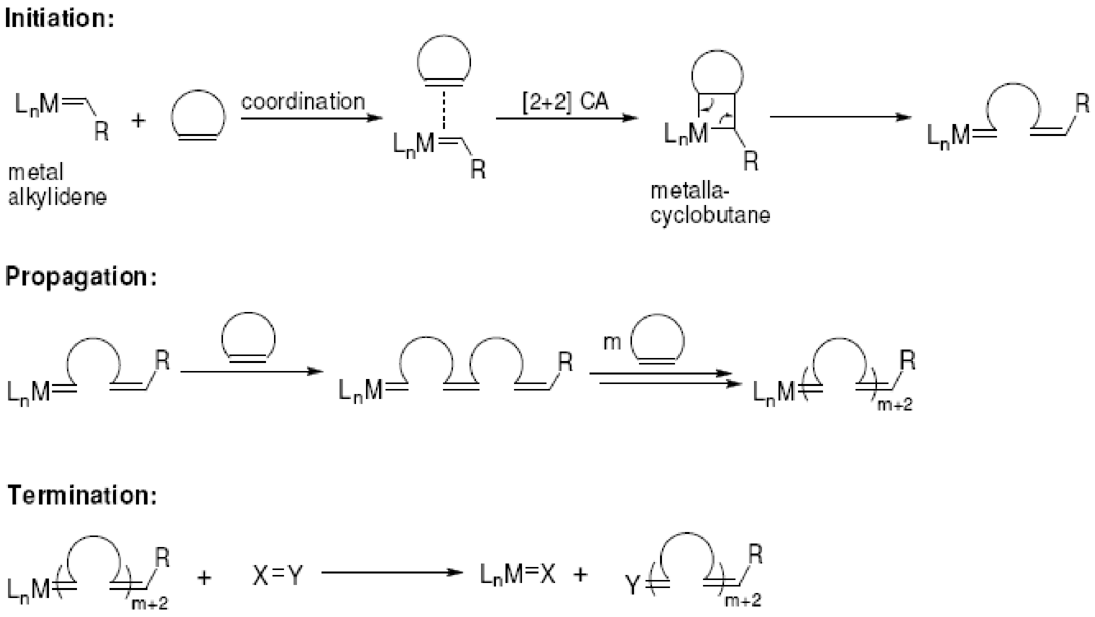
[78] Abbas, M.; Slugovc, C.; *Tetrahedron Lett.* **2011,** 52, 2560-2562.

[79] Voigtritter, K.; Ghorai, S.; Lipshutz, H. *J. Org. Chem.* **2011,** *76*, 4697–4702.

[80] Leong, W. W. Y.; Taft, B.R.; Ghorai, S.; Lipshutz, H. *J. Org. Chem.* **2011,** *76*, 5061–5073.

2.6 Living ring opening metathesis polymerization (ROMP)

Szwarc introduced the term living polymerization for the first time in 1956 while working on anionic polymerization.[81] Accordingly, out of three major steps in polymerization (a) initiation, b) propagation and c) termination), living polymers are formed without passing through the termination step. Polymers formed in this way possess symmetry during their chain formation and they also do not undergo chain transfer steps. The rate of initiation in living polymerization reaction is faster than rate of propagation, resulting in chains of uniform length and arrangement. These polymers are characterized by defined molecular weights and low polydispersities.



Scheme 2.8: Reaction mechanism of ROMP

In 1928 Ziegler studied the principles of living polymers when performing the polymerization of styrene and butadiene and alkyl butadiene first time.[82] This ratio of products to the organometallic catalyst (2-phenylisopropyl potassium) was directly proportional to the ratio of reactants to the organometallic compound. This was clearly indicating the reactivity of intermediates formed during each step was similar to the intermediate formed by alkyl potassium initiator at the very start of the reaction. He concluded that the synthesis of large molecules was only possible by reacting large amount of olefins with small amount of catalysts. Another group established the mechanism for polymerization and oligomerization

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[81] (a) Szwarc, M. *Nature* **1956**, *178*, 1168-1173; (b) Szwarc, M.; Levy, M.; Milkovich, M. *J. Am. Chem. Soc.* **1956**, *78*, 2656.

[82] Ziegler, K.; Baehr, K. *Chem. Ber.* **1928**, *61*, 253.

investigated by Ziegler.[83] The polymerization reaction continued even after adding more amount of monomer styrene after the complete consumption of already present monomer in reaction mixture. Addition of different monomers like isoprene resulted in block copolymers of poly(styrene) and poly(isoprene). These polymers have very narrow molecular weight distribution and the molecular weight could be controlled by monomer to initiator ratio and by changing the type of monomer. To obtain the polymer of perfect chain length and living nature after polymerization, air and moisture free environment for reaction and completely dried solvents and reacting substrates are required. This reaction requirements consequently limits the number of suitable monomers.

In recent years the progress in this field has been remarkable for the development of polymers via radical, cationic, group transfer and specially olefin metathesis polymerization.[84] Especially the progress is remarkable for a large variety of monomers which can be applied for various polymerization reactions. Absence of chain transfer and chain terminating group make these polymerization a special case for block copolymers, comb and star shaped polymers. Macromolecules designed in this way can find uncountable applications in industrial and medicinal chemistry.[85]

According to IUPAC definition[86] "*The living polymerization is the technique in which chain transfer and chain terminating agents are absent*"

2.6.1 Major features of an ideal living polymerization[87]

1. Complete and rapid initiation: the ratio of monomer to initiator must be very high and upon reaction of monomer with initiator should create active species for the reaction prolongation. Rate of initiation should be equal or greater than rate of propagation.
2. Irreversible propagation: propagation step of the reaction should be completely irreversible to form the polymer of living nature
3. Absence of chain termination /chain transfer agents: The active intermediates formed during the polymer process inhibit the chain termination. These intermediates do not react with solvent or result in the side chain production of the molecule and continue

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[83] Ziegler, K.;Dersch, F.; Wollthan, H. Justus Liebigs *Ann. Chem*. **1934**, *511*, 13.

[84] Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921-2990.

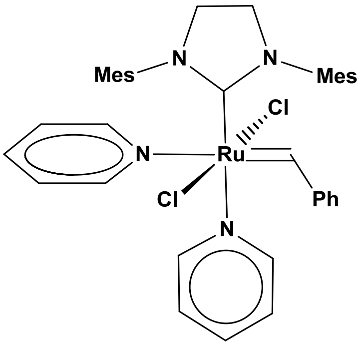
[85] Cowie, J. M. G. Polymers: Chemistry & Physics of Modern Materials, 2nd. ed., Chapman and Hall, New York, USA, **1991**.

[86] Jenkins, A. D.; Kratchovil, P.; Stepto, R. F. T.; Suter, U. W. *IUPAC Commission on Macromolecular Nomenclature, Pure Appl. Chem.* **1996**, *68*, 2287-2311.

[87] Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561.

the polymerization process until a polymer with definite chain and active terminal group is obtained. Upon adding the second monomer copolymers of type AB or ABA type can be generated.

4. Control of molecular weight and molecular weight distributions: final molecular weights can be controlled via the stoichiometry used. Molecular weight distribution is generally expressed by the polydispersity index (PDI). Which is simply the ratio of weight average M_w and number average M_n. PDI of living system is typically 1.0- 1.1



10

Figure 2.7: Grubbs 3rd generation initiator

2.6.2 ROMP of different substrates

Among many ruthenium based olefin metathesis initiators Grubbs 3rd generation initiator **10** (**Figure 2.6**) is the best suitable initiator for fast, controlled and living polymerization. The weakly coordinated pyridines lead to an extremely fast (and complete) initiation in presence of metathesis monomers. Pyridine bearing Grubbs 3rd is preferable over tricyclohexyl phosphine containing Grubbs 1st and 2nd generation initiators **1** and **8** respectively, when it comes to living ROMP.[88] ROMP is very common among cyclic hydrocarbons exhibiting high ring strains. Cyclobutene, cyclopentene, cyclooctene, norbornene and dicyclopentadiene are important examples of this type of olefins. (*cf.* **Figure 2.7**) Cyclohexene is the exception in this regard due to stable ring strains but cyclooctene and norbornene are ideal monomers for ROMP due to ring strains of more than 15 kcal/mol. In a series of other cyclic olefins available for ROMP, dicyclopentadiene (DCPD) is special, as it has two unsaturated ring systems. Thus, ROMP will lead to cross-linked thermosets instead of linear polymers with

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[88] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2004**, *20*, 5314-5317.

defined chain length. Therefore, DCPD is not used for the synthesis of defined special polymers, but rather in material chemistry. However, being a cheap by-product from petro industry, it is an economically interesting raw material for the production of a huge palette of plastic-products. For homogenous catalysis, latent initiators are required that will allow for mixing of the initiator and DCPD without concomitant polymerization before processing according to the required needs.[89]

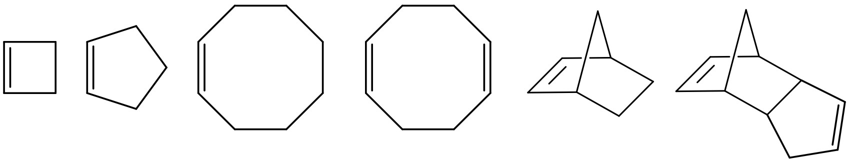

Figure 2.8: Few cyclic olefins favourable for ROMP

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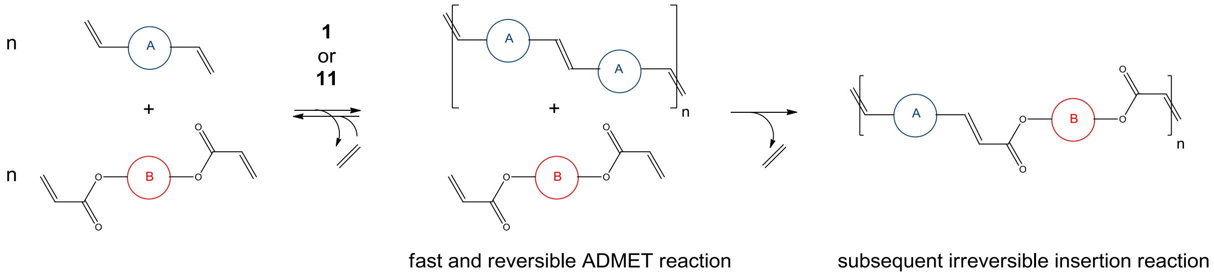
[89] Monsaert, S.; Drozdak, R.; Nishioka, N. *J Polym Sci Part A: Polym Chem.* **2010**, *48*, 302-310.

2.7 Alternating Diene Metathesis Polycondensation (ALTMET)

In polymer chemistry, ring opening metathesis polymerisation (ROMP) and acyclic diene metathesis (ADMET) are polymerisation (or polycondensation) methodologies which are used when precision in macromolecular architecture and/or high functional group tolerance is required.[90] Novel implementations of olefin metathesis in polymer synthesis include ring opening insertion metathesis polymerisation (ROIMP)[91] and alternating diene metathesis polycondensation (ALTMET). ROIMP and ALTMET allow for the preparation of strictly alternating copolymers by means of olefin metathesis. A drawback of these methodologies with more conventional polycondensation protocols is the use of relatively high amounts of expensive ruthenium based catalysts. Also, control of the target molecular weight is not satisfactorily feasible.



Scheme 2.9: Proposed reaction mechanism for ALTMET[17]

Presumably the reaction mechanism proceeds with the ADMET polymerization of relatively flexible diene substrates. This reaction is relatively fast and reversible. In the next step, the incorporation of diacrylate in this ADMET polymer forms the alternating copolymers with absolute chain growth. The rate of reaction depends upon the second step which is considerably slower than the first ADMET step.

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[90] A. Leitgeb, J. Wappel, C. Slugovc, *Polymer* **2010**, *51*, 2927.

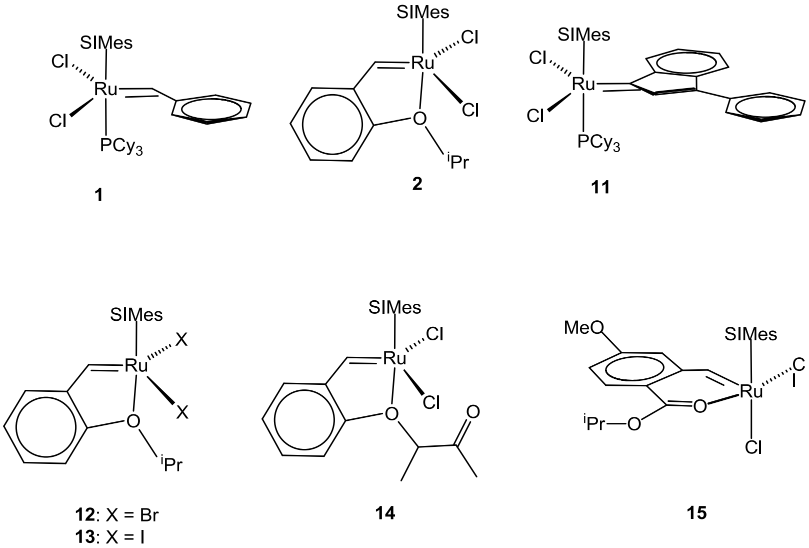
[91] T.-L. Choi, I.M. Rutenberg, R.H. Grubbs, *Angew. Chem. Int. Ed*. **2002**, *21*, 3839.

Chapter 3

Cross Metathesis of Olefins with Acrylates

3.1 As low as reasonably achievable (ALARA) catalyst loadings in cross metathesis of terminal olefins with ethyl acrylate

Starting our investigations on the cross metathesis reaction of olefins with ethyl acrylate, the first and foremost motivation was to find the reaction conditions at which the lowest possible amount of catalyst could be loaded to get complete conversion towards the cross metathesis products. Furthermore, the stereoselectivity of the reaction was examined. The purpose of estimating lowest possible catalyst loadings for cross metathesis was not only due to its economic implications but also for the environmental counts of metathesis reactions. A series of catalysts screened for this purpose is given in **figure 3.1.**



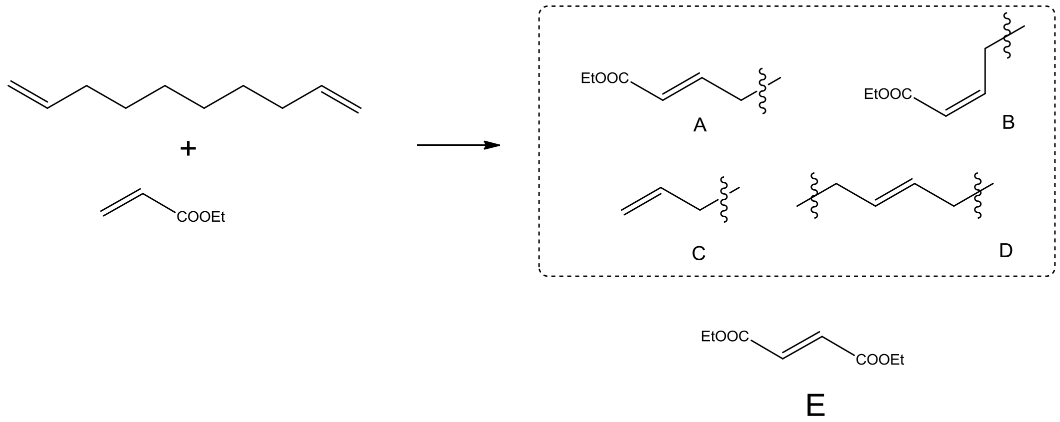
1 **2** **11**

12: X = Br
13: X = I

14 **15**

Figure 3.1: Catalysts used for cross metathesis of 1, 9-decadiene with ethyl acrylate

Commercially available 1,9-decadiene and ethyl acrylate were selected for this purpose. Chemicals were used with no further purification and their cross metathesis reaction in presence of a series of catalysts was performed. Highly optimized reaction conditions recently discovered by Meier et al. in which five to ten folds excess of ethyl acrylate without presence of any solvent were used at the starting point.[9] For some initial tries temperature was kept constant at 50°C and activity of eight different catalysts were examined. In all cases stereochemically *trans*-configured cross metathesis product **A** was formed in excess and minor amount of *cis*-arranged product **B** was also observed along with other products. When no complete cross metathesis reaction was observed the oligomeric product or ADMET polymer product of 1,9-decadiene **D** containing internal olefins was also observed along with un-reacted terminal olefinic double bonds **C**. While performing the reaction in excess of ethyl acrylate the self metathesis products of ethyl acrylate, **E** were also observed especially when excess catalyst was used.



Scheme 3.1: Cross-metathesis of 1,9-decadiene with ethyl acrylate[92]

The examination started with catalyst loadings of 0.1mol% with respect to terminal olefin decadiene that corresponds to 0.05mol% with respect to one double bond. This loading was well below the catalyst loadings previously reported for such reactions.[93] Grubbs second generation catalyst **1** yielded 76% conversion to the α-, β-unsaturated moiety **A** and **B**. whereas 14% of the terminal olefins remain unreacted along with 10% of internal double bond products **D** in first 30 minutes. Running the reaction to total 4 hours did not yield much change in total products concluding the activity of catalyst was finished before this time. The commercially available and inexpensive indenylidene derivative **11**(analogue to Grubbs 2nd generation catalyst) gave 75% of the products **A** and **B**. Running the reaction for distinctly longer durations gave 85% and 88% respectively in 4 and 16 hours duration, stating clearly the more stable nature of catalyst **11**. The ratios of unreacted olefinic product **C** and **D** were 14% and 10% respectively. Trace amount of self metathesis product of ethyl acrylate diethyl fumarate E were also observed along with these products.

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[92] Conversion of 1,9-decadiene to **A**, **B**, **C** and **D** are given in %; percentage of **E** is calculated by the formula 100[**E**] / [**A**+**B**+**C**+**D**+**E]**

[93] Connon, S. J.; Blechert, S. Angew. Chem. Int. Ed. 2003, 42, 1900-1923.

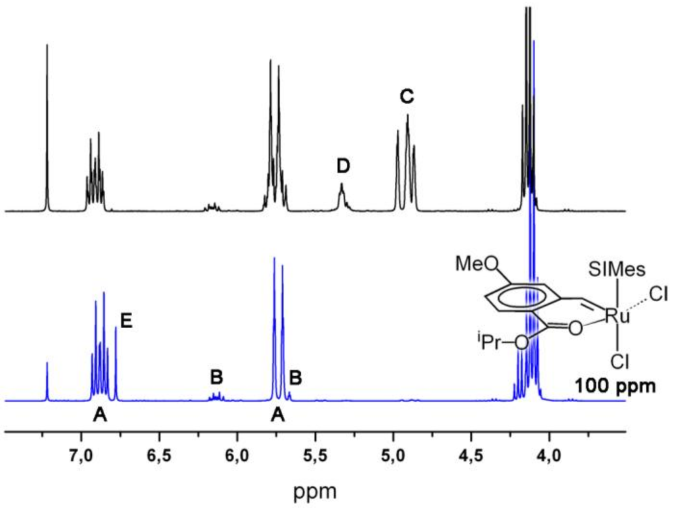

Figure 3.2: ^{1}H-NMR spectra of two typical experiments; above: incomplete conversion towards A and B; below: complete conversion[94]

Hoveyda type 2nd generation catalyst **2** gave more than 99% of the conversions to products **A** and **B**. Comparatively higher amounts of self metathesis product of ethyl acrylate **E** were also observed in this reaction showing the enhanced reactivity of **2**. The activity of dibromo and diiodo substituted Hoveyda type catalysts **12** and **13** were also tested in these cases yielding 84% and 45% of cross-metathesis products. Interestingly to note, the activity of diiodo catalyst **13** is slow but stability for longer reaction time was comparatively higher than **12** yielding 84% of the products **A** and **B** in 16 hours reaction time.[95] Another commercially available double chelated catalyst **14** was tested and its activity was comparable to complex **2**. Total 92% of the products **A** and **B** were observed in first 30 minutes but the ratios of the products did not increase by increasing time. The most interesting results were observed using *cis*-arranged dichloro ester chelated catalyst **15**.[96]

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[94] ^{1}H-NMR was taken in $CDCl_3$ at 25°C.

[95] Wappel, J.; Urbina-Blanco, C. A.; Abbas, M.; Albering, J. H.; Saf, R.; Nolan S. P.; Slugovc, C. *Beilstein J. Org. Chem.* **2010**, *6*, 1091-1098.

[96] Zirngast, M.; Pump, E.; Leitgeb, A.; Albering, J. H.; Slugovc, C. *Chem. Commun.* **2011**, *47*, 2261-2263.

Table 3.1: Ccross-metathesis of 1,9-decadiene and ethyl acrylate at 0.1 mol% loadings of catalysts at 50°C.

Entry	Catalyst	Time [h]	A : B : C : D / E [%]
1	1	0.5	72 : 4 : 14 : 10 / < 1 [a]
2	1	4	72 : 4 : 14 :10 / < 1
3	11	0.5	69 : 6 : 12 : 13 / < 1
4	11	4	80 : 5 : 6 : 9 / < 1
5	11	16	83 : 5 : 4 : 8 / < 1
6	2	0.5	93 : 7 : < 1 : < 1 / 4
7	12	0.5	78 : 6 : 14 : 2 / 1
8	12	4	78 : 7 : 14 : 1 / 1
9	13	0.5	42 : 3 : 27 : 27 / < 1
10	13	16	78 : 6 : 15 : 1 / < 1
11	14	0.5	86 : 6 : 6 : 2 / <1
12	14	4	86 : 7 : 6: 1 / <1
13	15	0.5	50 : 5 : 35 : 10 / <1
14	15	16	87 : 8 : 2 : 3 / 0

At the beginning, only little cross metathesis products **A** and **B** were obtained in 30 minutes using **15** but the results for cross metathesis reactions were interestingly increased in 16 hours duration. The catalyst’s nature was explored and it showed slow initiation and high thermal stability of catalyst **15**. In the next step among all catalysts the two best found catalysts **2** and **15** were selected and loadings of the catalyst was further reduced. At 0.05mol% (i.e. 250ppm with respect to double bond) loading of the catalysts full conversions were obtained with Hoveyda type second generation imitator **2** but ester chelated catalyst **15** yielded only 85% of the cross metathesis products in over night reaction. This reactivity was further proven at 0.03mol% of catalyst loadings where **2** gave still almost full conversions while **15** gave only 55% of the α-, β-substituted products in 16 hours. At 0.01mol% of **2** a conversion of 54% was observed via NMR. In sum, 0.05mol% of **2** is the lowest possible amount of catalyst for the conversion of 1,9-decadiene to diethyl didodecadienoate (**A** & **B**).

Table 3.2: Cross-metathesis to determine the lowest possible catalyst loadings at 50°C

Entry	Catalyst	Loading [mol%]	Time [h]	A : B : C : D / E [%]
1	2	0.05	0.5	81 : 5 : 3 : 11 / <1
2	2	0.05	16	92 : 7 : < 1 : < 1 / 2
3	15	0.05	16	77 : 8 : 10 : 5 / < 1
4	15	0.03	16	92 : 6 : 1 : 1 / 2
5	15	0.03	16	50 : 5 : 40 : 6 / 0
6	15	0.01	16	50 : 4 : 42 : 4 / < 1

In the second step for further decreasing the amount of catalyst to accomplish the complete cross metathesis, the temperature was increased to 80°C. Previously found best catalyst **2** was tested for the cross metathesis at this temperature and upon all loadings from 0.05mol% to 0.02 mol% of the catalyst more than 98% of **A** and **B** were converted from 1,9-decadiene in just thirty minutes. So from the above experiments it could be concluded that 100ppm of the catalyst is sufficient for the full conversion of all terminal double bonds to α-, β-unsaturated moiety.

Table 3.3: Cross-metathesis with different catalysts at 80°C.

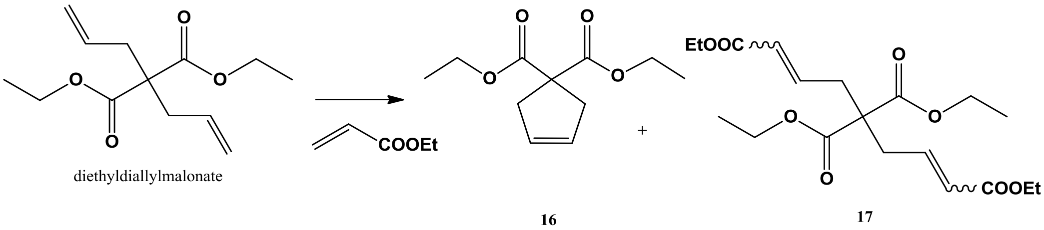
Entry	Catalyst	Loading [mol%]	Time [h]	A : B : C : D / E [%]
1	2	0.05	0.5	92 : 7 : < 1 : < 1 / 3
2	2	0.03	0.5	92 : 7 : < 1 : < 1 / 2.5
3	2	0.02	0.5	91 : 7 : < 1 : < 1 / 2
4	1	0.02	0.5	46 : 4 : 41 : 9 / <1
5	11	0.02	0.5	42 : 5 : 39 : 14/<1
6	12	0.02	0.5	75 : 7 : 8: 10 / <1
7	14	0.02	0.5	76 : 6 : 13 : 5 / <1
8	15	0.02	0.5	87 : 6 : 3 : 4 / <1
9	15	0.02	16	93 : 7 : < 1 : < 1 / 6
10	2	0.016	0.5	85 : 7 : 5 : 3 / <1
11	2	0.016	16	87 : 8 : 2 : 3 / <1
12	15	0.016	32	91 : 8 : < 1 : 1 / 3

At this elevated temperature the activity of other catalysts listed in **figure 3.1** was also tested. The Grubbs 2nd generation catalyst **1** and its analogue catalyst **11** were not particularly suited especially compared to Hoveyda type catalyst **2**. No more than 50% of the products were converted using terminal olefins at 0.02mol% of the catalyst loadings. The conversions were not increased even prolonging the reaction for longer run. Similarly, no high conversions were obtained using 100ppm of **12** and **14.** Although the activity of these catalysts was better than **1** and **11** but activity was still less than with **2**. The conversions were as high as 82% using 0.02mol% of **12** and **14** in first 30 min but no further activity was observed after this time. Catalyst **15** was performing better among all these catalysts giving 93% of conversions to **A** & **B** at this much loadings in first 30 min and full conversions were observed after 16hours. Again the higher amounts of self metathesis product **E** in this case showed the thermal stability of catalyst. So, further decrease in loadings of this catalyst was possible in this case. The activity of **2** and **15** was tested at 80ppm with respect to double bonds and it was observed that full conversions were only observed with **15** in 2 days reaction time. It means **15** was the best found catalyst at 80°C whose 80ppm loadings with respect to double bond were sufficient for the full conversion of 1,9-decadiene to **A** and **B**. In all case where full conversions of products were observed, both **A** and **B** were isolated and yields were determined. The yields were as high as 92-95% in all cases.

Table 3.4: The cross-metathesis of 1,9-decadiene and ethyl acrylate (5 eq.) at 100°C

Entry	Catalyst	Loading [mol%]	Time [h]	A : B : C : D / E [%]
1	2	0.01	0.5	88 : 8 : 3 : < 1 / 5[97]
2	2	0.01	4	partly polymerized[98]
3	15	0.01	0.5	82 : 7 : 8 : 3 / <1
4	15	0.01	4	90 : 8 : < 1 : 2 / 2
5	15	0.01	16	partly polymerized

By increasing the temperature to 100°C catalyst loading could be further reduced. Using 0.01mol% of **15** more than 98% conversions of **A** and **B** were obtained from 1,9-decadiene in 4 hour reaction time. However at this elevated temperature some unwanted polymers of ethyl acrylate were also observed along with the desired product. In some cases this polymerization started even before completion of cross metathesis. These precipitate somehow show the incorporation of **A** and **B** along with ethyl acrylate which were completely cross-linked in nature. The hypothesis was also proven by getting comparatively less amount (87%) of **A** and **B** in reaction mixture as compared to full conversion at 80°C. The detailed analysis of these polymers is presented in **section 3.5**.



Scheme 3.2: Olefin metathesis of diethyldially malonate in presence of ethyl acrylate.

The work elucidated by Meier and Forman excess of ethyl acrylate and in absence of solvent the lowest loading of catalyst can be achieved. In order to measure how the change in ratios of ethyl acrylate and olefin changes the conversion of cross metathesis products. Firstly, some

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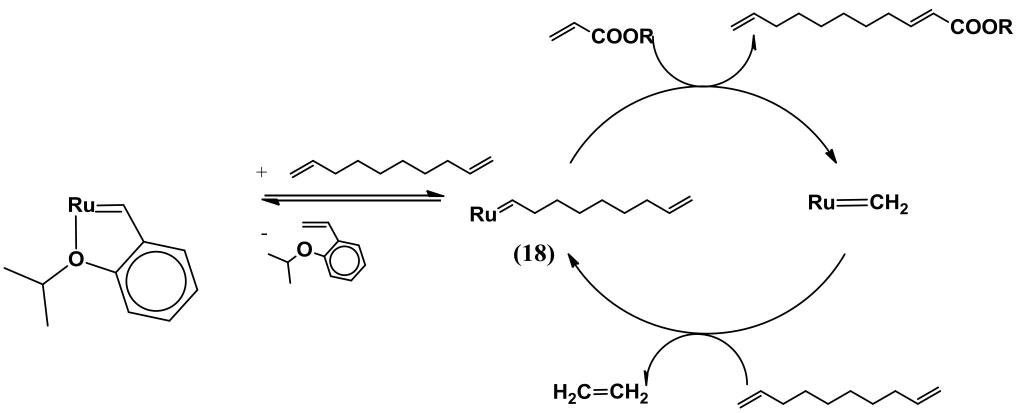
[97] small amounts (< 2 %) of a polymeric byproduct characterized by broad, peaks at 4.1 and 2.2 ppm in the corresponding ^{1}H-NMR spectra are present.

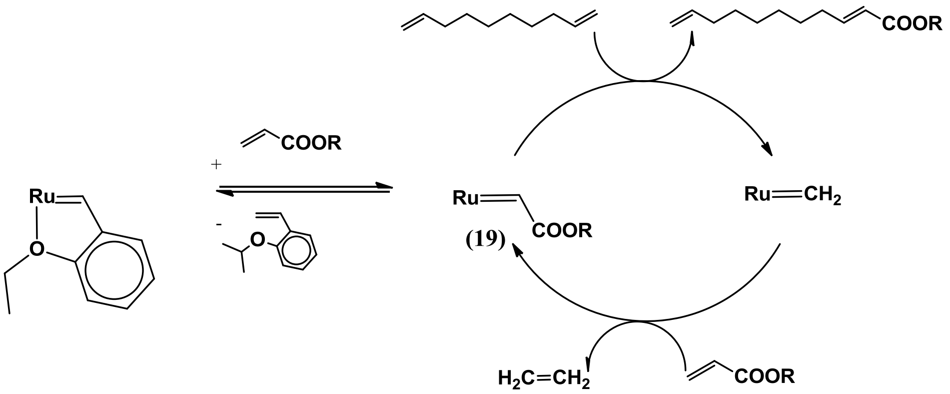
[98] the polymeric byproduct is formed in higher amounts (> 5%), precipitate can be observed.

reactions were performed in three excess of ethyl acrylate in spite of conventionally used five folds excess of ethyl acrylate. The conversions were 83% **A** and 4% **B** with 100ppm of catalyst loadings. In contrast full conversions were achieved when using five excess folds of ethyl acrylate (*cf.* table 4.3 entry 3). Similarly, when performing the reaction in ethylacetate as a solvent in presence of 0.05mol% of **2** only 54% of decadiene were converted at 50°C in 4 hours reaction time. The change in reactivity due to presence of solvent can be best elucidated by performing cross metathesis of diethyldiallylmalonate (DEDAM) in presence of ethyl acrylate. DEDAM is the most favorable substrate for giving ring closing metathesis products in which substituted cyclopentene ring products are formed very easily in presence of Grubbs or Hoveyda type catalysts **1** or **2**. However in presence of 5eq. of ethyl acrylate in presence of 0.1mol% of **2** at 100°C in 30min all of the DEDAM was consumed and along with 62% of the ring closed metathesis product **16,** 38% of doubly crossed metathesized products **17** were observed. In contrast when performing the same reaction in presence of 10eq. of toluene keeping all the conditions mentioned above same, the ratio of ring closing metathesis product to doubly cross metathesized product was increased to more than 4:1.



Scheme 3.3: Proposed reaction mechanism for cross metathesis via olefins reacting first

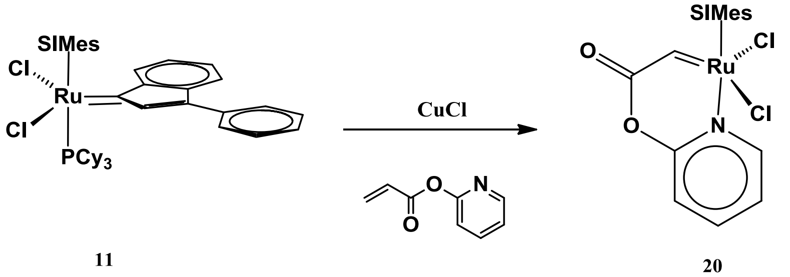
In cross metathesis with terminal olefins with acrylates small molecule of ethylene is evolved along with major product ß-substituted acrylates. There are two proposals for such reactions to proceed either *(i)* the mechanism can follow through the reaction intermediate with attachment of decadiene first to make carbene intermediate **18** Which later reacts with acrylate to give monosubstitueted product and in the second cycle again with an acrylate to give disubstituted cross metathesis product **A** or **B**. *(ii)* The formation of ester-carbene intermediate **19** when pre catalyst reacts with ethyl acrylate and later upon reacting with decadiene this reactive precursor can yield substituted cross metathesis products.



Scheme 3.4: Proposed reaction mechanism for cross metathesis via acrylates

These ester carbenes were first reported in literature by Grubbs et al. where he tried to synthesize these types of catalysts and found that these highly reactive precursors for metathesis are unstable in nature and have very short half life.[99] Solvent free reaction in higher amounts of acrylate can also be attributed to the reaction to proceed via ester carbene intermediate **19**. The excess of acrylate present can also be the source of stabilization of reaction intermediate and hence giving productive metathesis with large turn over.

In order to understand the detailed mechanism and analyze that ester carbene intermediate **19** is being formed and it is being stabilized with excess of acrylate. Some tries were also made to synthesize new ester carbene type catalyst **20** with pyridine ligand. Unfortunately, this acrylate-pyridine type catalyst could not be isolated.



Scheme 3.5: Synthesis of six membered ester-carbene pyridine chelated catalyst

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[99] Ulman, M.; belderrain, T. R.; Grubbs, R. H. *Tetrahedron lett.* **2000**, *41*, 4689-4693.

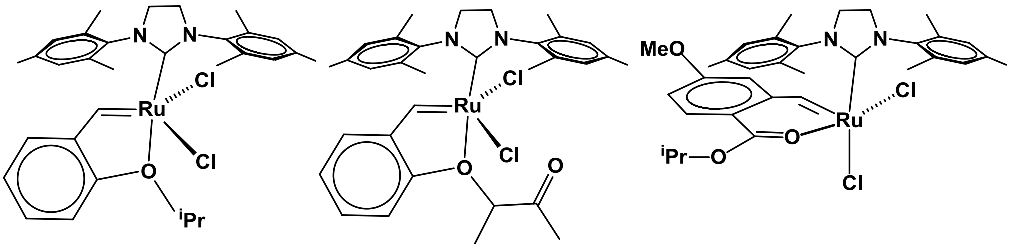
In conclusion, we have demonstrated that catalyst loadings as low as 100 ppm per double bonds are sufficient for virtual complete conversion in the cross metathesis of terminal olefins with ethyl acrylate provided that no solvent and a reaction temperature of 80°C is used. 2nd generation Hoveyda type catalyst **2** and the recently disclosed 2nd generation ruthenium catalyst bearing a *cis* dichloro stereochemistry and a chelating ester-based benzylidene ligand **15** are the best choices for reactions carried out at 80°C. Catalyst loading of **15** could be even reduced to 80 ppm per olefinic double bond but at the price of a long reaction time. 2nd generation Hoveyda type catalyst **2** is the preferred catalyst for performing the reaction at 50°C. In this case 250 ppm catalyst per olefinic double bond is needed. Increasing the temperature to 100°C causes concomitant polymerization of the reaction mixture and formation of an insoluble residue decreasing the product yield.

3.2 Optimizing the cross metathesis of olefins from renewable resources with ethyl acrylate

After finding the lowest possible catalyst loadings in cross metathesis of terminal olefins with ethyl acrylate. The scope of these studies was further expanded to olefins from renewable resources like oleates and pinenes. The enhanced activity of previously found best catalysts (**2**, **14** and **15**) was tested for the cross metathesis of methyl oleate, oleylamine α-pinene, β-pinene, limonine and myrcene with ethyl acrylate and results are presented now.

3.2.1 Cross metathesis of methyl oleate and oleylamine with ethyl acrylate

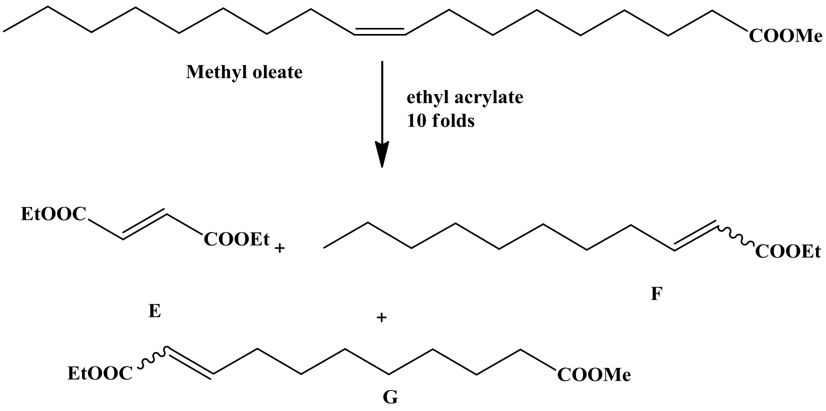
Prior to perform cross metathesis with oleylamine optimization of reaction conditions for respectively flexible substrate of this type, methyl oleate with ethyl acrylate is examined. The chemicals methyl oleate (60~70%, Fluka) and ethyl acrylate (99%, Aldrich, stabilized with 0.002% hydrochinone monoethylether) and catalysts **2** and **14** were purchased from available commercial resources. Catalyst **1** was synthesized in our laboratory according to procedure already reported.



2 **14** **15**

Figure 3.3: Selected catalysts for cross metathesis of methyl oleate and oleylamine

Combined with the optimized reaction conditions by Meier et al. with our recent findings for cross metathesis of olefins with ethyl acrylate solvent free reaction conditions in ten folds excess of ethyl acrylate were used. The temperature was set to 80°C in all reactions and 1mol% of free radical inhibitor *tert*-butylated hydroxytoluene (BHT) was used to avoid unwanted polymerization of acrylates at higher temperatures. The results with three different catalysts are given in table 3.5. Complete cross metathesis yielded only **E**, **F** and **G** as the major products.



Scheme 3.6: Cross metathesis of methyl oleate with ethyl acrylate (with observed major products only

For our first tries in finding the optimal catalyst loadings for the complete conversion of methyl oleate into products **F** and **G,** the reaction was performed with 0.1mol% of conventional Hoveyda type catalyst **2** and in four hours only 55% of the internal olefins were converted to β-substituted esters. Self metathesis product of ethyl acrylate **E** was 6% in this case. Running this reaction for distinctly longer durations could not increase the amount of products significantly but trace amounts of polymers were formed for these durations. In the next step the catalyst loading was increased to 0.3mol%. The internal olefins yielded 90% of the cross metathesis products **F** and **G** and again 6% of the self metathesis product **E** in first thirty minutes. In the next step **14** was tested at different loadings. The reaction at 0.1mol% of **14** in first four hours only 20% of the methyl oleate was consumed. However a significant amount of i.e. 4% of **E** was obtained in this case. Increasing the catalyst loadings to 0.3mol% in first four hours the products **F** and **G** were found 43% in total, while running the same reaction for overnight reaction time again resulted in the unwanted polymers.

Finally *cis*-chelated catalyst **15** was screened for this cross metathesis of methyl oleate at various loadings and for different reaction times. Similarly starting the reaction with 0.1mol% of **15** and running the reaction for overnight only 66% of methyl oleate were converted to products **F** and **G**. The conversion of this catalyst was tested for distinctly longer times due to latent nature of the catalyst. In the next step when catalyst concentration were increased to 0.3mol%, conversion of methyl oleate was poor in start yielding only in 27% of consumption of methyl oleate in first thirty minutes. However stirring the reaction for overnight resulted while keeping all other parameters same resulted in full conversions (>97%). Besides full conversions, 21% of the self metathesis product **E** showed the enhanced catalytic activity of

15 as compared to 2 and 14. Surprisingly, no polymers were observed in presence of **15** even when running the reaction for longer times. (Table 3.6, entry 10)

Table 3.5: cross metathesis of methyl oleate in 10 folds of ethyl acrylate[100]

Entry	Catalyst	Loading [mol%]	Time [h]	Conversions[101] [%]
1	2	0.1	4	55
2	2	0.1	16	polymer[102]
3	14	0.1	4	22
4	14	0.1	16	polymer
5	15	0.1	16	58
6	2	0.3	0.5	90
7	2	0.3	4	92
8	14	0.3	4	88
9	15	0.3	4	35
10	15	0.3	16	>97

In next step the scope of this studies was expanded for the cross metathesis of oleylamine with ethyl acrylate. Commercially available oleylamine (70%, Fluka) when tested for this reaction without any protecting group or additives did not yield any cross metathesis products even at higher catalyst loadings up to 1mol% of **2** (Table2, entry 1). Upon adding one equivalent of 1N HCl and one equivalent of glacial acetic acid separately in two different reactions could not even start the reaction. Similarly, no conversion were observed by adding 20mol% of the Lewis acid titanium isopropoxide $Ti(i\text{-}OPr)_4$ which previously has been reported as a good additive to enhance the olefin metathesis reactions. In retrieving the cross metathesis product of oleylamine in excess of ethyl acrylate no cross metathesis products were obtained but Michael addition product **20** was observed due to addition of ethyl acrylate into oleylamine.

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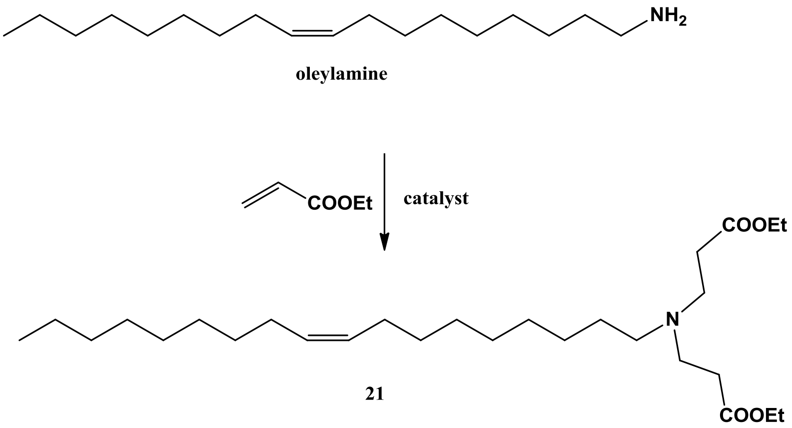
[100] Reaction conditions: no solvent used, 80 °C.

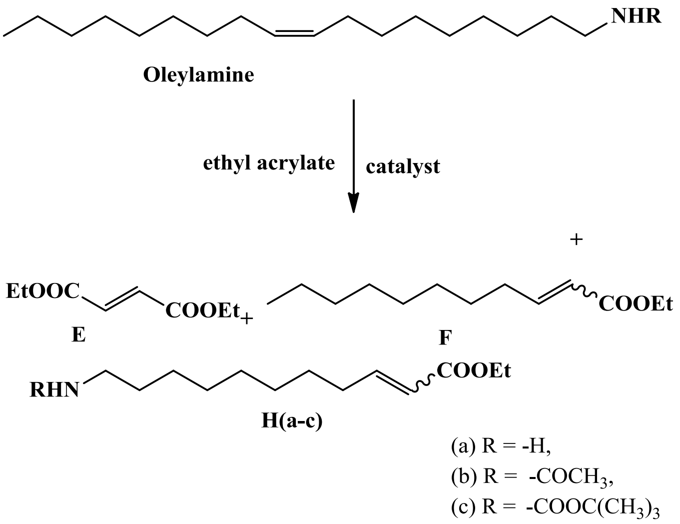
[101] Conversion of methyl oleate towards **F** and **G** was determined by integration of ^{1}H-NMR spectra

[102] Significant polymerisation (> 5 %) of ethylacrylate occurred.



Scheme 3.7: Michael addition reaction of oleylamine during cross metathesis

By assuming the protection of amine by some functional group may help in successful cross metathesis of oleylamine with ethyl acrylate, it was protected with t-Boc and acetyl groups in two different reactions. Surprisingly, high yield cross metathesis products were obtained with acetyl protected oleylamine and t-Boc protected amine with 43 and 55% conversions of internal olefins respectively. The introduction of protecting group by acetyl chloride and di-*tert*-butyl dicarbonate used for protecting groups in solvents required higher reaction time and separation of fatty acid derived products was also difficult. The distillation of these highly dense organic compounds was also not easy to perform. Therefore, a reaction procedure with highly optimized reaction conditions for protection of oleylamine was required, which could provide fully protected amines in high yields. For this purpose, the solvent free environment friendly reaction condition in presence of acetic anhydride was applied. Acetyl protected oleylamine was thus obtained in five minutes reaction time.



Scheme 3.8: Cross metathesis of oleylamine and its derivatives with ethyl acrylate

The electron donating nature of oleylamine could be involved in inhibiting the cross metathesis reaction by considering the catalyst with amino functional group in it. In order to study the effect of presence of base in cross metathesis reaction, some tries of cross metathesis of 1,9-decadiene with ethyl acrylate in presence of different amine containing bases were made. 1,9-Decadiene was selected as a test system due to highly reactive cross metathesis products at very low catalyst loadings has already been obtained using this system. Oleylamine **1** (0.2 eq.) when added as primary amine additive in this system for cross metathesis at 100ppm of catalyst loadings of **2** gave no cross metathesis products. However, very little conversions were observed using diethylamine and triethylamine as additives in this cross metathesis.

Table 3.6: cross metathesis of Acetyl protected oleylamine with 10 folds ethyl acrylate at 80°C

Entry[103]	Catalyst	Loading [mol%]	Time [h]	Conversions[104] [%]
1	2	0.1	16	12
2	2	0.5	16	36
3	2	1	16	58
4	14	0.5	16	33
5	14	1	16	48
6	2	1	16	33[105]
7	2	1	4	88
8	15	1	4	96
9	2	1	4	>97[106]
10	14	1	4	>97

The cross metathesis reaction was not disturbed in presence of acetic acid the by-product produced during the protecting group introduction reaction. Similarly, removing the excess acetic anhydride and acetic acid could not affect the cross metathesis yield. Besides the major products **F** and **H**, a significant amount of unreacted acetylated oleylamine was also present in the reaction mixture when reaction was performed in absence of solvent. Acetylated

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[103] Entries 1-5 were tried withought any solvent, dichloromethane was used in entry6 as a solvent and toluene was used in all entries 6-10 as a solvent.

[104] Conversion of **F** and **H** were determined by integration of ^{1}H-NMR spectra

[105] reflux temperature of DCM(i.e. 40°C) was applied.

[106] Protection of oleylamine and cross-metathesis were performed in one pot.

oleylamine due to poor solubility was not easy to separate from other products. Higher temperatures, heavy catalyst loadings and longer reaction time were also not helpful using neat reaction conditions for complete conversion of all internal olefins completely to β-substituted products. Rather formation of polymer from ethyl acrylate was observed in all that cases where harsh reaction conditions were used. A significant amount of diethylfumarate **E** was also observed using these reaction conditions. Now use of some solvent was found necessary step for cross metathesis of protected oleylamine and ethyl acrylate. Hence dichloromethane and toluene were chosen for this purpose. When first reaction performed in refluxing dichloromethane with 1 mol% of **14** only 33% of the products were obtained in an overnight reaction. However full conversion of acetyl products oleylamine were observed using 1molar solution of toluene as a solvent at its reflux temperature in just four hours. When tried cross metathesis products with 0.5mol% of the **14** only 55% of the products **F** and **H** were obtained in first four hours increasing the reaction time for distinctly longer duration could not significantly increase the amount of products. However using 1mol% of the catalyst the conversions were increase to 88%. Comparatively low yield of cross metathesis products in solvents is due to better solubility of catalysts in toluene as compared to ethyl acrylate.

In the last step, the introduction of protection group and cross metathesis reaction was performed in stepwise in one pot. Firstly oleylamine was treated with 1.2equivalents of acetic anhydride at room temperature in neat reaction conditions and after five minutes the cross metathesis reaction with ethyl acrylate in toluene as a solvent were performed in the same flask with 1mol% of catalyst **2.** Full conversions of all internal double bonds present in acetylated oleylamine were observed in four hours only.

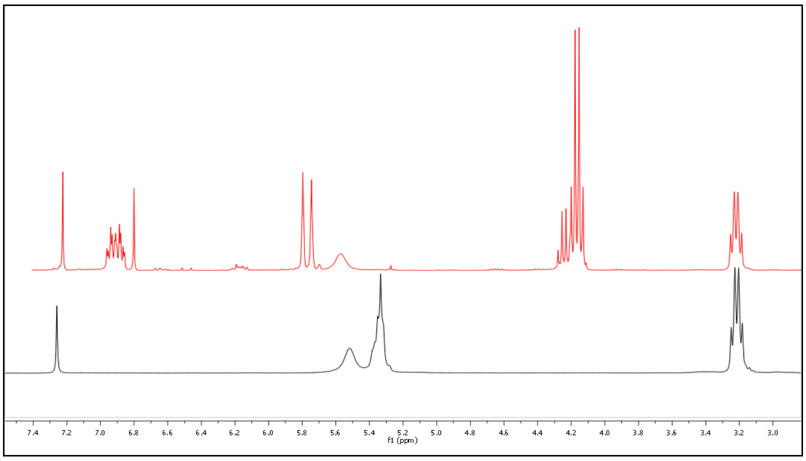


Figure 3.4: ^{1}H-NMR spectra of acetyl protected oleylamine (below) and cross metathesis products F and H (above)[94]

In conclusion, optimized cross-metathesis reaction conditions for methyl oleate and acetylated oleylamine with ethyl acrylate were disclosed. While cross-metathesis of methyl oleate is best performed in the presence of 10 equiv. of ethyl acetate without using an additional solvent, best results for N-acetyl oleylamine were obtained in a solution of toluene.

Methyl oleate is completely converted with 0.3 mol% catalyst **15** in 16 h. Key for this success is the latent nature of the used (pre-) catalyst. Thus, the actually active species is slowly released during the progress of the reaction. This principle is an approach to keep the concentration of the actual active species low, i.e. simulated high dilution conditions regarding the catalyst can be conveniently achieved. The cross-metathesis of oleylamine is harder to accomplish. Firstly it was demonstrated, that the amino group has to be protected to achieve cross-metathesis of the double bond. For the protection a convenient procedure using acetic anhydride as the reagent was developed. The protected oleylamine underwent the desired cross-metathesis reaction, but because of the low solubility of acetylated oleylamine in ethyl acrylate conversions at conditions similar for methyl oleate were poor. This obstacle could be resolved by using toluene as a solvent. Nevertheless, under the best conditions elaborated here, a high catalyst loading of 1 mol% has to be used in order to achieve complete conversion of the substrate.

3.2.2 Cross metathesis of terpenes with ethyl acrylates.

Terpenes are another class of renewable olefin containing molecules which are abundantly found in nature. The application of such cheap raw materials in cross metathesis is of multiple advantages due to accomplishment of large number of valuable products to be used in many applications including pharmaceutical research. After finding our advanced approach towards cross metathesis towards terminal olefins and olefin from renewable resources like methyl oleate and oleylamine the scope of the studies was expanded to cross metathesis of ethyl acrylate with commonly available terpenes.

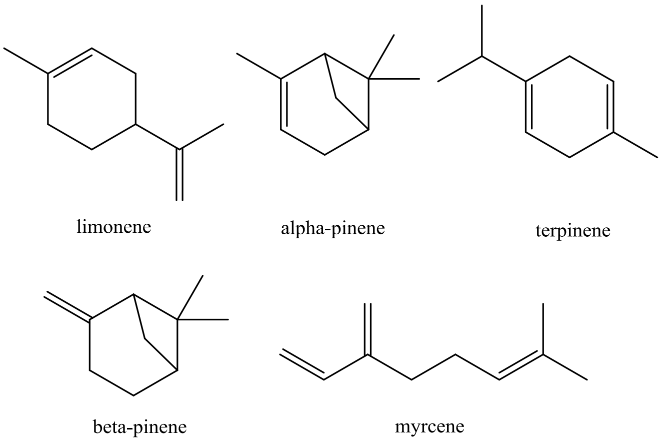
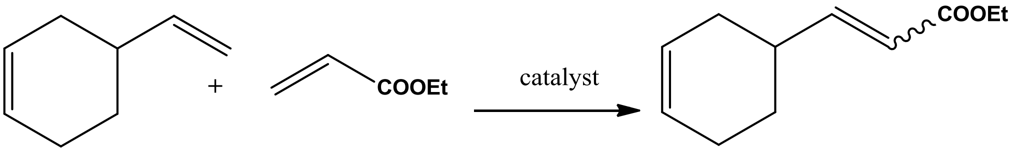


Figure 3.5: Pinenes used for cross metathesis with ethyl acrylate.

In all our tries for cross metathesis of pinenes present in **figure 3.3** with ten folds excess of ethyl acrylate with 1mol% of **14,** no significant cross metathesis products were observed. Rather self metathesis product of ethyl acrylate, **E** was formed in 4-6%. Among all pinenes inert for olefin metathesis myrcene even containing terminal olefins did not yield any cross metathesis products.

To test the reactivity of olefins with terminal olefins and inert olefins with respect to cross metathesis some reactions were also performed with vinyl hexene and ethyl acrylate and under very mild conditions in contrast to used for cross metathesis of pinenes i.e. 0.1mol% of **14** full consumption of terminal olefins were observed in and overnight reaction while only 12% of internal olefinic double bond were converted.



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Scheme 3.9: Cross metathesis of vinylcyclohexene with ethyl acrylate

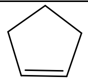
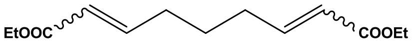
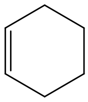
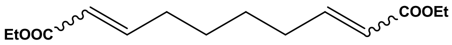
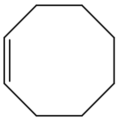
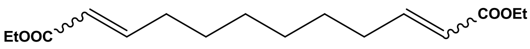
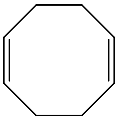
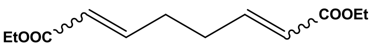
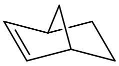
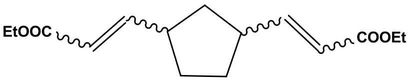
In sum, the terpenes presented in **figure 3.3** are inert towards cross metathesis with ethyl acrylate using solvent free reaction conditions. These substrates are hard to functionalize through this process even in higher loadings of the initiator.

3.3 Ring opening cross metathesis (RO/CM) of cyclic olefins with ethyl acrylate

Tandem ring opening cross metathesis reaction is valuable reaction in modern organic chemistry as it just not gives the new functionality to olefins but it is also an economical process and valuable functional materials can be synthesized according to this procedure. Especially RO/CM for unstrained cyclic olefins like cyclopentene and cyclohexene is important for these cheap solvents commonly available in the market.

In our tries for RO/CM with unstrained challenging substrates for olefin metathesis like cyclopentene, cyclohexene full cross metathesis products were observed by using 1 mol% of the catalyst **14** and at the reflux point of respective olefin in ten excess folds of ethyl acrylate. For cross metathesis of cyclooctene, a comparatively easy substrate for olefin metathesis successful cross metathesis products with little traces of poly(cyclooctene) polymers was obtained.

Table 3.7: RO/CM of cyclic olefins with ethyl acrylate[107]

Entry	**Cycloalkene**	**Product**	**Conversion**[108] **[%]**
1		 **23**	**88**
2		 **24**	**75**
3		 **25**	**88**
4		 **26**	**43**
5		 **27**	**95**

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[107] Solvent free cross metathesis reaction was performed in presence of 0.1 to 1 mol% of **14** at 60°C**.**

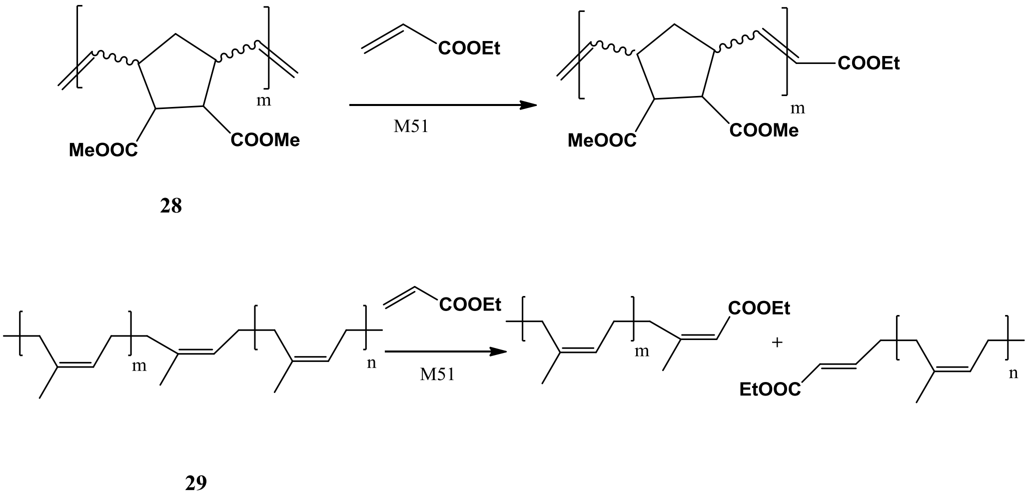
[108] Conversions were determined by ^{1}H-NMR

While preceding these studies for polyolefin containing cyclic olefins like 1, 3-cyclooctadiene in respectively 20 folds excess of ethyl acrylate only 43% of the doubly substituted cross metathesis products were observed. Finally, the ring-system of norbornene was opened in this cross metathesis analysis where more than 90% of cyclopentane substituted products were obtained.

In sum, cross metathesis of cyclic olefins in presence of ethyl acrylate without any solvent can yield disubstituted unsaturated esters **23-27** in high yields (cf. table 3.7) with catalyst loading as high as 1mol%, which is even less than the catalyst loadings for this type of reactions.

3.4 Functionalization of ROMP derived polymers and natural rubber via cross metathesis with ethyl acrylate

ROMP of norbornene derivates in presence of acrylate has already been reported by our group in which ethyl acrylate were used as terminating group for the ROMP derived polymers.[109] The molecular weights and distribution ratios were well controlled in presence of ethyl acrylate. However the presence of acrylate has obviously dramatic effect on polymerization. But after developing the advanced system for cross metathesis of acrylates with various olefins, applying this system to ROMP the degradation of polymers bearing unsaturated polymers backbones is of interest.



Scheme 3.10: Funtionalization of living polymers with ethyl acrylate

The degradation of olefin derived polymers, most importantly ROMP *endo-,exo*-dimethyl bicyclo [2.2.1] hept-5-ene-2,3-dicaboxylate ester **28** with molecular weight of approximately 60,000 g/mol was performed, dissolving it in excess of ethyl acrylate (20eq.) and reaction was performed in presence of 1mol% **14** for 12h at 60°C. Upon this treatment the molecular weight was reduced to 12,000 g/mol. The decrease in molecular weight clearly states some cross metathesis reaction of ethyl acrylate with olefinic double bonds in the polymer occurred. This new functionalized double bond was also detected via NMR. In a second try, this technique was applied to polymers derived from nature like natural rubber. Highly cross linked natural rubber **29** (latex) with molecular weight more than 1,000,000 g/mol was used. Initially, this polymer was not soluble in ethyl acrylate but when stirred for 24 hours it dissolved completely producing a homogeneous mixture. After making the reaction mixture

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[109] Lexer, C.; Saf, R. Slugovc, C. *J. Polym. Sci. Part A: Polym. Chem*. **2009**, *47*, 299-305.

completely homogenised adding the catalyst and performing the cross metathesis reaction in presence of 1mol% of **14** in an overnight reaction at 60°C resulting in reducing the molecular weight of the polymer to 5,000 g/mol only. The reverse process of converting the natural polymer olefin to substrate of respectively low molecular weight with using comparatively low amount of catalyst is important for the degradation of natural polymers. Another advantage of this process is to functionalize the polymer with new alpha beta unsaturated ester functional group which is not only gives new functionality to molecules but a large number of other functional group can also be obtained from it. The functionalized polymer after cross metathesis of **29** was also characterized by NMR and the formation of new product was clearly observed in it.

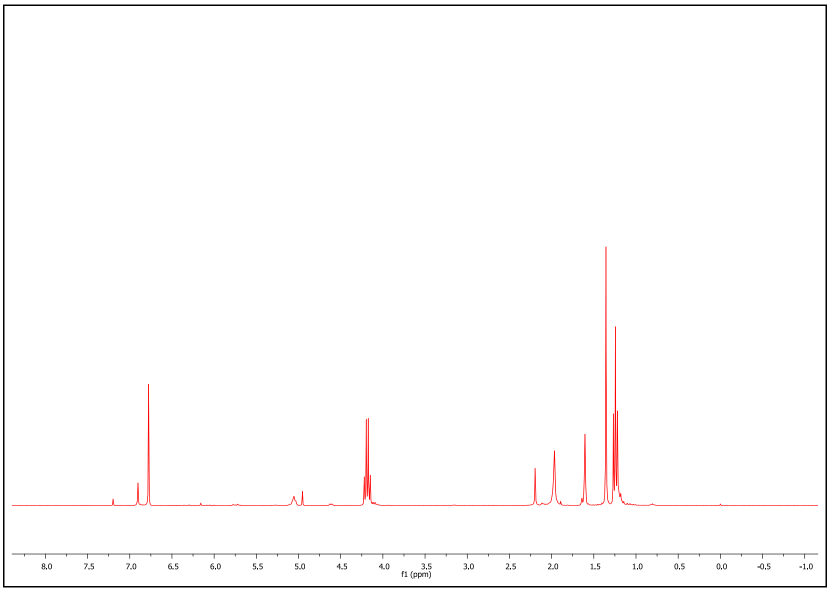

Figure 3.6: ^{1}H-NMR of degraded natural rubber with trace amount of E[94]

In sum, the cross metathesis of olefins with acrylates is also expanded towards olefinic containing polymers like poly(norbornen) ester **28** and natural rubber **29** and it was observed that degradation of such polymers can be established using **14** as an initiator and molecular weights of resulting polymers are much below than the reacting substrates.

3.5 Tandem olefin-acrylate copolymerization during cross metathesis

Our previous studies during cross metathesis of 1,9-decadiene in excess of ethyl acrylate at higher temperatures resulted in the insoluble precipitates of cross linked copolymers.[110] We started our investigations with mono-functional olefin 1-octene for the first few tries with ethyl acrylate to obtain the copolymer via tandem copolymerization technique. Ruthenium based commercial precursor **14** was used for this purpose.

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Scheme 3.11: Copolymers of 1-octene with ethyl acrylate and its predictive structure

In first step we started our investigations from already established reaction conditions i.e. five equiv. ethyl acrylate with respect to 1-octene and a reaction temperature of 100°C. A viscous polymer was obtained in 30 minutes. Upon examining the reaction mixture only un-reacted monomers along with polymer were identified and no cross or self-metathesis products were observed. The detailed analysis through NMR and elemental analysis clearly indicated a stoichiometry of 4 eq. of ethyl acrylate and 1eq. of 1-octene. In accordance to decrease the ratio of ethyl acrylate in the copolymer, its ratio with respect to olefin was also reduced in next few tries but no significant changes in the polymer structure were observed. However, longer reaction time was required for the optimum polymer formation with decreased amount of ethyl acrylate. Reducing the acrylate ratio also reduced the polymer chain length and overall polymer yield.

Analysing the reaction mixture and NMR of crude product ensured the presence of un-reacted reactants in small amounts but no cross metathesis product was present and the ratio of ethyl acrylate was also reduced as it was used in start with respect to olefin. The polymeric appearance in the reaction mixture and the NMR studies ensured the formation of polymer the monomers were washed with nonpolar aprotic solvent like cyclohexane and analysed again showed the alkenoate acrylate copolymer in quantitative amounts. When the ratio of acrylate to olefin was reduced in next step to optimize the reaction condition and lowering the ratio of acrylate with respect to olefin was still giving the polymer but with longer reaction times. The

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[110] Some early findings are already presented in section 3.1 table 3.4

chain length and molecular weights of the polymers strongly depend upon the ratio of acrylate to olefin.

Table 3.8: Cross linked Copolymerization of 1-octene with ethyl acrylate[111]

Entry	Ethyla crylate : 1-octene	X : Y[112]	M_n[113]	PDI
1	**5 : 1**	**5 : 1**	**61000**	**2.8**
2	**3 : 1**	**3 : 1**	**44000**	**2.6**
3	**1.5 : 1**	**3 : 1**	**15000**	**2.9**
4	**1 : 1**	**3 : 1**	**15000**	**2.9**
5	**1 : 0**	**-**	**-**	**-**
6[114]	**5 : 1**	**5 : 1**	**17000**	**2.1**

Identifying compounds present in the reaction mixture gave the result that alkenoate was present. Accordingly, it was assumed that alkenoate formed during the cross metathesis reaction it does not form the copolymer via insertion mechanism. The involvement of alkenoate in metathesis was also checked by inserting the commercially available *trans*-methyloctenoate and its different ratios when added with respect to olefin and acrylate but no major incorporation of external octenoate were observed. Same type of polymers was observed when methyloleate was used in place of 1-octene but polymers of same nature were only observed in those cases where catalyst during cross metathesis process creates some terminal olefins. Besides NMR studies, the involvement of olefin in polymer was also tested using diolefins like 1, 9-decadiene where highly cross linked insoluble polymers were obtained. By changing the terminal olefins of different chain lengths ranging from 6-12 it was observed that there was no sharp change in polymer nature until 10 carbons but for 11 and 12 carbon chain length molecular weight of the polymer was dropped to 18000 from 45000. This abrupt change in polymer density may be due to higher boiling points of the olefins from ethyl acrylate making the incorporation of the olefins comparatively less than the olefins of shorter chain lengths.

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[111] All reactions were performed in neat reaction conditions in presence of 0.01mol% of **14** at 100°C.

[112] ratio of acrylate and olefin in polymer was determined by using NMR statistical methods like elemental analysis

[113] GPC mesurements were used to evaluate the molecular weights and distribution of the polymers

[114] 2eq. E-methyl octenoate were used

Table 3.9: Cross linking copolymerization of different terminal olefins with ethyl acrylate[115]

Entry	Olefin	Olefin : acrylate	M_n[20] [g / mol]	PDI
1	1-heptene	1 : 3	43000	3.1
2	1-octene	1 : 3	44000	2.6
3	1-decene	1 : 3	45000	2.8
4	1-undecene	1 : 3	18000	5.2
5	1-dodecene	1 : 3	15000	4.8

Similarly when polymers of different acrylates available in laboratory were tested whit 1-octene at 100°C and only methyl acrylate and ethyl acrylate yielded copolymers of similar chain length and nature while no sharp polymers could be obtained using *tert*-butyl acrylate, n-hexyl acrylate and lauryl acrylate. Again the refluxing temperature of later three acrylates was more than the olefins resulting in no or very little polymer using these substrates. These polymers were also compared to polymers synthesized through some other route for example by free radical polymers obtained by using azobisisobutyronitrile (AIBN) but these polymers was absolutely different in nature than what we prepared using olefin metathesis initiator **14**. The polymers obtained in this way were highly cross linked and were not soluble in any of the media, whereas we produced jelly like sticky polymers soluble in many polar and apolar solvents available in laboratory.

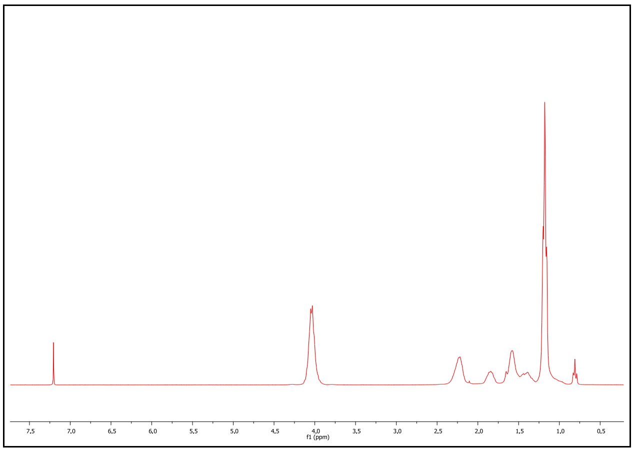

Figure 3.7: ^{1}H-NMR spectra of ethyl acrylate 1-octene copolymer[94]

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[115] All reaction was performed in neat reaction conditions at 100°C.

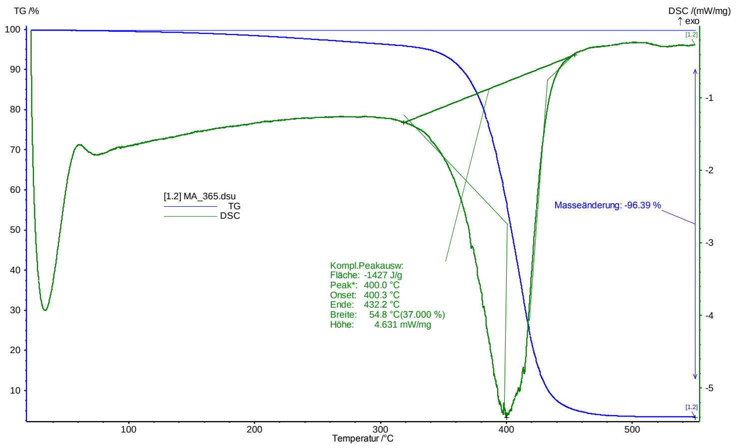

Figure 3.8: TG and DSC analysis of copolymer

In sum, high temperature reactions for cross metathesis of olefins with acrylates may lead to synthesis of unwanted polymers. These polymers are assumed to be produced via free radical mechanism as the reaction can be inhibited or can be slowed down using free radical inhibitor BHT. The ratio of acrylate to olefin in all polymers is 3:1 or more even when acrylate is not in excess. This sticky non linear polymer may lead to study the detailed analysis of many other polymerization reactions of acrylates.

3.7 Novel Polymerization by Alternating Diene Metathesis (ALTMET) using Catalyst 11

In past these type of reactions are only reported with terminal olefins and diacrylates but scope of this studies could be expanded to many other olefins, diacrylates and dimethacrylates available in laboratory and with newly synthesized monomers to yield alternating polymers. These polymers with variant characteristics depending upon the different nature of olefins and reaction conditions used may lead to examine the process in details. In this regard various other substrates examined for this type of reaction are given in **Figure 3.3**.

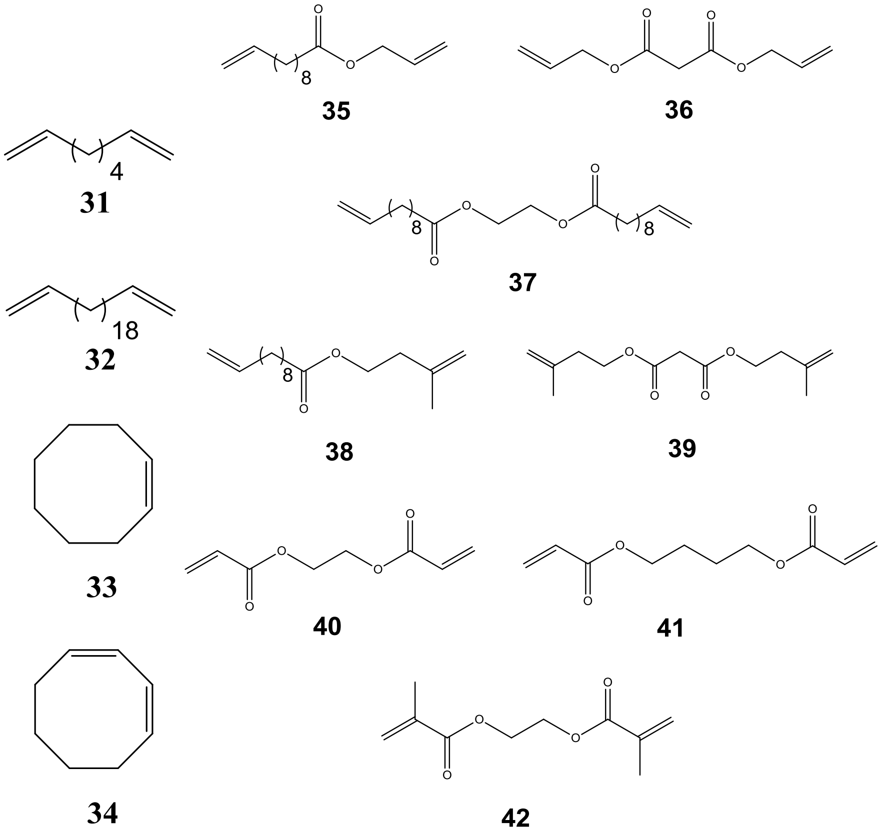

Figure 3.9: Selected olefins, diacrylates and dimethacrylates used for ALTMET

Polymer synthesis of olefins **31-39** were performed with selected acrylates and methacrylate **40-42** present with 1mol% of catalyst **11** and the results are given in **table 3.10.** Our first few tries with olefins **31** and **32** with ethanediol diacrylate **40** yielded more than 80% of the polymers in all tries. Similarly cyclic olefins cyclooctene **33** and cyclooctadiene **34** with **40** also yielded ROIMP polymers in high yields. Besides these hydrocarbons some other olefins containing ester functional group and substituted olefins **38** and **39** were also examined. Olefins **35-37** with diacrylate **40** yielded polymers with alternating chain more than 73% in all cases but olefins **38** and **39** were inert for this reaction with **40** where no or very little polymers were obtained. Similarly, dimethacrylate substrate **42** did not yield any polymer when reacted with all olefins **31**-**34**.

Table 3.10: ALTMET polymer of different olefins with diacrylates or dimethacrylates[116]

Entry	**Monomer 1**	**Monomer 2**	**Monomers : 11**	**Yield**[117] **[%]**
1	**31**	**40**	**50 : 50 : 1**	**86**
2	**32**	**40**	**50 : 50 : 1**	**87**
3	**33**	**40**	**50 : 50 : 1**	**83**
4	**34**	**40**	**50 : 50 : 1**	**74**
5	**35**	**40**	**50 : 50 : 1**	**75**
6	**36**	**40**	**50 : 50 : 1**	**73**
7	**37**	**40**	**50 : 50 : 1**	**82**
8	**38**	**40**	**50 : 50 : 1**	**-**
9	**39**	**40**	**50 : 50 : 1**	**-**
10	**31**	**41**	**50 : 50 : 1**	**84**
11	**32**	**41**	**50 : 50 : 1**	**85**
12	**33**	**41**	**50 : 50 : 1**	**71**
13	**34**	**41**	**50 : 50 : 1**	**71**
14	**35**	**41**	**50 : 50 : 1**	**71**
15	**36**	**41**	**50 : 50 : 1**	**75**
16	**37**	**41**	**50 : 50 : 1**	**76**
17	**31**	**42**	**50 : 50 : 1**	**-**

In the second series of experiments only successful olefins **31**-**37** were used and their polymerization reaction was performed with butanediol diacrylate and all gave polymers in respectively higher yields. In last try commercially available butanediol dimethacrylate **42** was tested with **31** but no cross polymers were obtained rather olefin being an easy substrate for metathesis only yielded ADMET polymer of decadiene.

In sum, we found that Umicore`s Neolyst catalyst **11** is well suited for ALTMET and disubstituted olefins and methacrylates are not applicable as monomers in ALTMET.

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[116] Monomers were dissolved in 1M CH_2Cl_2 and was refluxed at 45°C in presence of 1mol% of **11.**

[117] Yield of polymers was determined after sepraraitng the ppts in CH_3OH

3.6 Optimizing catalyst loadings in Alternating Diene Metathesis Polycondensation (ALTMET)

After testing different diolefins and diacrylates of dimethacrylates, the scope of the reaction was also expanded for the optimizing the reaction conditions of ALTMET reaction. A series of catalysts were tested for this purpose and also ALTMET of bifunctional single molecule was tested in these studies.

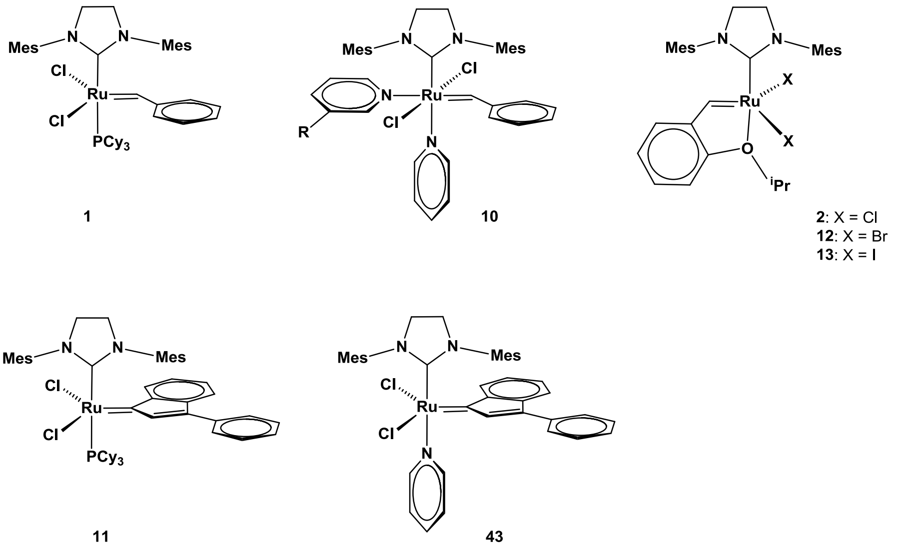
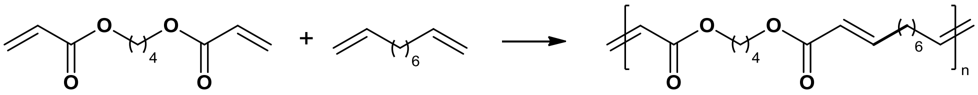


Figure 3.10: Catalysts under investigation for ALTMET

We started our investigations with the cross metathesis of 1,9-decadiene **31** and 1,4-butanediol diacrylate **41** as the test system. The reaction was carried out under inert atmosphere (Ar) in CH_2Cl_2 at 45°C for 4 h at a concentration of 0.5 M in respect to each monomer. The catalyst and the catalyst concentration were varied according to Table 3.11. Longer reaction times did not change the outcome of the reactions. Conversion was determined by drying the sample and integration of according signals in the proton NMR spectrum. Gel permeation chromatography (GPC) using THF as the solvents and referencing against poly(styrene) was used to determine the number molecular weight (M_n) and the poly dispersity index (PDI) of the samples.

Table3.11: Preparation of alternating copolymers from a diolefin and a diacrylate[118]



Entry	31 : 41 : catalyst	Catalyst	Conversion[119] [%]	M_n/PDI[120] [g/mol]
1	50 : 50 : 1	1	100	22600 / 1.8
2	100 : 100 : 1	1	90	2640 / 2.0
3	50 : 50 : 1	11	90	3800 / 1.9
4	50 : 50 : 1	10	40	nd[121]
5	100 : 100 : 1	2	100	29900 / 1.9
6	250 : 250 : 1	2	80	2870 / 2.0
7	500 : 500 : 1	2	70	2300 / 2.3
8	100 : 100 : 1	12	96	7890 / 2.1
9	100 : 100 : 1	13	53	nd

Firstly, standard catalyst **1** was tested. Results reveal a necessary catalyst loading of 1 mol% in respect to the total amount of monomers for preparing appealing polymers. The corresponding polymer is characterized by a M_n of 22600 g/mol (*cf.* Table 3.11, entry 1). Lowering the catalyst amount results in lower yield and distinct reduction of the M_n value of the polymer (*cf.* Table 1, entry 2). The next catalyst under investigation was **11** a close relative of **1**. **11** is bearing an indenylidene ligand instead of the benzylidene ligand present in **1**. **11** is commercially available and is known to be more stable than **1**.[10] Disappointingly, **11** is a less potent catalyst for ALTMET as can be seen from the corresponding experiment listed in Table 3.11 (entry 3). Using 1 mol% of **11** gave only 90% conversion and an oligomer with a M_n of 3800 g/mol. Similarly, pyridine bearing **43** is not the catalyst of choice. Only 40% conversions were obtained. This result is remarkably in the light of the high potential of **43** as catalyst for controlled living ROMP of norbornenes.[122] The next compound tested was the Hoveyda 2nd generation catalyst (**1**). Complex **1** gave the best results since only 0.5 mol% in respect to the total amount of monomers is sufficient to achieve complete conversion towards the alternating copolymer (*cf.* Table 3.11, entry 5). A satisfying molecular weight (M_n = 29900 g/mol) was obtained. Lowering the catalyst concentration to 0.2 mol% or even 0.1 % resulted in lower conversions and oligomers (*cf.* Table 1, entries 6 and 7). Finally, the halide

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[118] All reactions were performed in 1M (in regard to both monomers) CH_2Cl_2 solution at 45°C for 4 h.

[119] Conversion was calculated using NMR data.

[120] M_n and PDI were determined from gel permeation chromatography (GPC) in THF relative to poly(styrene) standards.

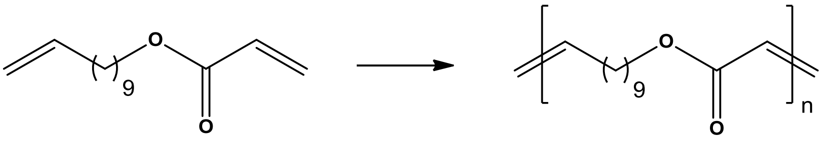
[121] Not determined.

[122] Burtscher, D.; Lexer, C.; Mereiter, K.; Winde, R.; Slugovc, C.; *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 4630.

exchanged analouges of **2**, the dibromo- (**12**) and the diiodo derivative (**13**) were tested. In comparison to **1** both catalysts are less active.

Our studies were complemented with a second test system comprising undec-10-en-1-yl acrylate as a bifunctional monomer. Only the catalysts **1** and **2** were compared to each other. Results are presented in **Table 3.12**.

Table 3.12: Preparation of alternating copolymers from a bifunctional monomer[123]



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Entry	44 : catalyst	Catalyst	Conversion[124] [%]	M_n / PDI[125] [g/mol]
1	50 : 1	1	100	12700 / 3.0
2	100 : 1	1	95	2400 / 2.1
3	200 : 1	1	64	1000 / 1.3
4	500 : 1	1	33	1100 / 2.4
5	100 : 1	2	100	19910 / 3.0
6	200 : 1	2	100	18700 / 2.8
8	500 : 1	2	100	5600 / 1.7

2 mol% of catalyst **1** are necessary to obtain complete conversion. Lowering the catalyst loading (1 mol%, 0.5 mol% and 0.2 mol%) caused a pronounced drop in conversion (*cf*. Table 2, entries 2-4) and the formation of oligomers with M_n values below 2500 g/mol. In contrast, the catalyst loading in case of **1** could be reduced to only 0.5 mol% without making a compromise in molecular weight (*cf*. Table 2, entry 6). Even 0.2 mol% catalyst loading affected complete conversion of this substrate, although the molecular weight was only 5600 g/mol.

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[123] All reactions were performed in 1M of CH_2Cl_2 solution at 45°C for 4 h.

[124] Conversion was calculated using NMR data.

[125] M_n and PDI were determined from gel permeation chromatography (GPC) in THF relative to poly(styrene) standards.

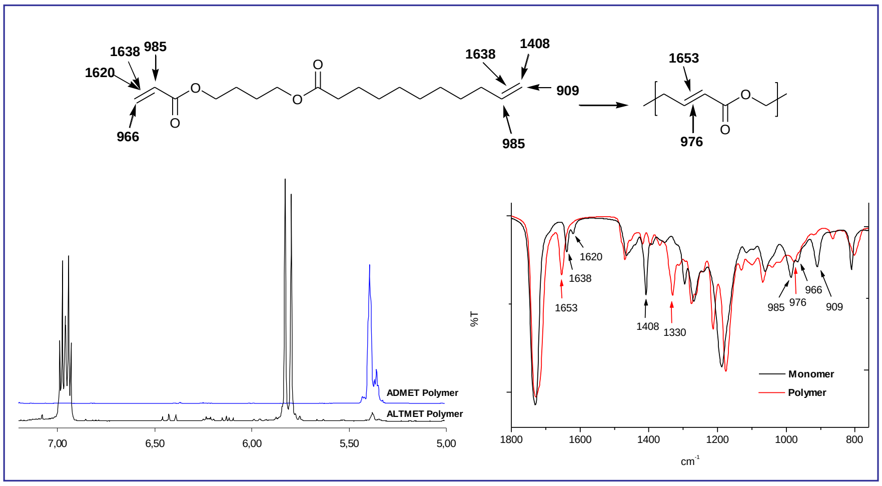

Figure 3.11: ^{1}H-NMR and IR spectra of typical polymer obtained via ALTMET[126]

The present study reveals Hoveyda 2nd generation catalyst **2** as the preferred catalyst for ALTMET. In comparison to the hitherto used **1**, catalyst loadings could be reduced by the factor of 2 for the preparation of alternating copolymers from a diolefin and a diacrylate and by the factor of 4 in case of polymerising a difunctional monomer.

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[126] The characterization of the ALTMET polymer is already presented by Sandra Demel in her PhD work.

Chapter 4

Cross Metathesis of Olefins with Methyl vinyl ketone (MVK)

4.1: Unprecedented low catalyst loadings in cross metathesis of terminal olefins with methyl vinyl ketone

A variety of ruthenium based catalysts are examined for the cross metathesis of 1-hexene with methyl vinyl ketone (*cf.* **Figure 4.1**). We started our investigations with cross metathesis of 1-hexene (~98%, Fluka) and MVK (99%, Aldrich, stabilized with 1000ppm BHT). The chemicals were used as received that means with no further purification was done. Based on Lipschutz work ether was used as a solvent and 3mol% of CuI was added as a co-catalyst in all reactions.[53] Temperature was kept constant at reflux temperature of ether (35°C). Successful cross metathesis released the *trans* isomer **47** as the only product in all cases and no *cis*-configured product **48** was observed in all tries. The self metathesis products **49** and **50** are mentioned only if they were observed.

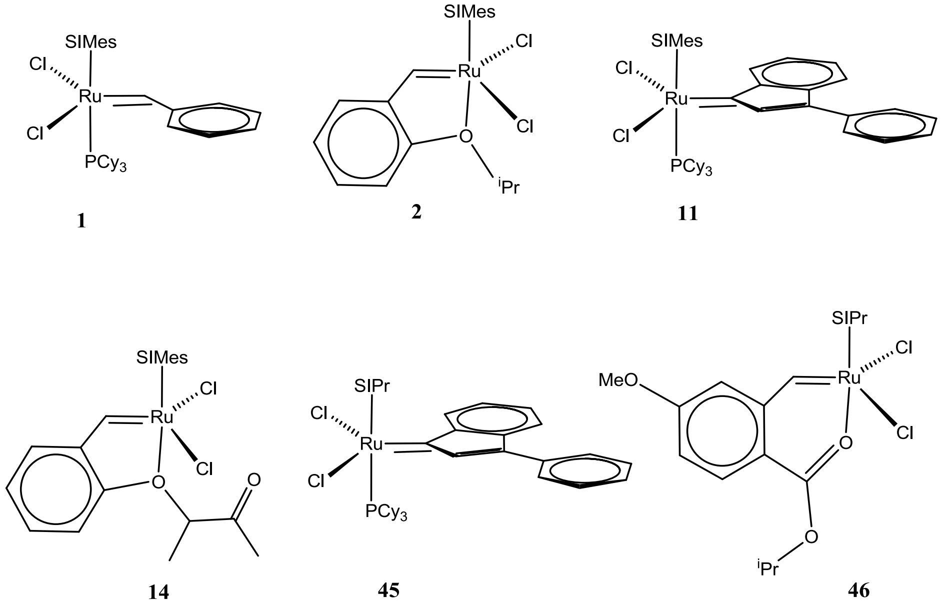
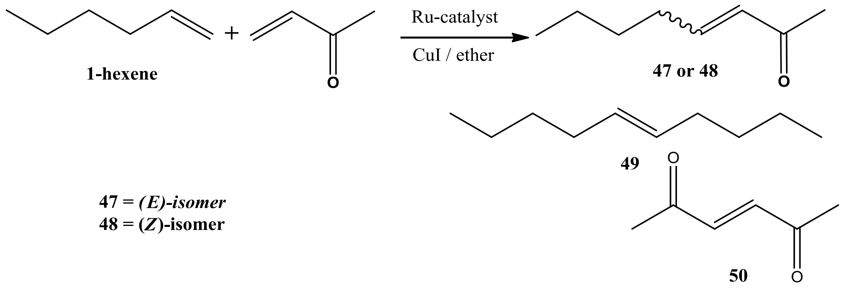


Figure 4.1: Catalysts for cross-metathesis of MVK with olefins

Grubbs et al. reported the successful cross metathesis of vinyl ketones with olefins to be only possible at high dilutions which is in sharp contrast to the case of acrylates, where no or little solvent was required.[12] So, in the first few tries we tried to optimized the dilution factor to avoid the use of excess solvent in our cross metathesis reactions using 1mol% of commercially available catalyst **14.** The reaction was performed in Et_2O at reflux and in most cases for 12hours. Without any additive or in presence of 3mol% of CuCl no full consumption of 1-hexene was observed at this loading of catalyst. However, best results were observed with CuI for this reaction (table 4.1, entries 1-3). Theses results were in accordance to the results already reported in literature.[57] The amount of solvent for the successful cross metathesis reaction was modified using different dilutions. Keeping all the other parameters constant, it was observed that successful cross metathesis product **47** after full consumption of 1-hexene was observed with optimal concentration of 0.2M or lower (table 4.1, entries 3-5)

Table 4.1: Cross-metathesis of 1-hexene with MVK to optimize the reaction conditions[127]



Entry	**Dilution**[128] **[mol/dm^3]**	**Additive (3 mol%)**	**Conversion**[129] **[%]**
1	**0.05**	**-**	**33**
2	**0.05**	**CuCl**	**80**
3	**0.05**	**CuI**	**100**
4	**0.1**	**CuI**	**100**
5	**0.2**	**CuI**	**100**
6	**0.5**	**CuI**	**66**

In the next step, we expanded our investigation to optimize the reaction conditions to test different catalysts. Keeping 0.2M concentration as a benchmark for olefin 1-hexene was screened with six different catalysts (c.f. Figure 4.1) for cross metathesis with MVK. In all our tries no less than 1mol% of catalysts **2** and **14** were required to give the complete conversion of terminal olefin 1-hexene**.** A reaction tried with conventional 2nd generation Grubbs catalyst **1** using 0.5mol% loading of this catalyst could not completely convert the olefin into α-, β-substituted moiety. **1**, at this loading, yielded 74% of the major product **47** and 4% of the dimer **49**. The remaining reaction mixture contained un-reacted olefin 1-hexene (table 4.2, entry 7). The product ratios were not increased even running the reaction for longer

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[127] 1mol% of **14** was used in all reactions in ether as a solvent at reflux conditions for 16 hrs.

[128] concentration of reaction mixture was maintained by using 1mol of 1-hexene.

[129] Conversions were determined by analysing the NMR of crude reaction mixture.

times. However when using the commercially available catalyst **11,** in which indenylidene is used in place of benzenylidene**,** the olefin 1-hexene was fully consumed in eight hours keeping all the other parameters same. The enhanced activity with **11** was also tested at 0.25mol% and the conversions were as high as 96%, The conversions of product using 0.1mol% of **11** were 88% which were higher than **1** at 0.25 mol% in 16 hrs reaction time.

Figure 4.2: ^{1}H-NMR spectra of typical cross metathesis experiment to yield product 47[94]

Recent findings for the cross metathesis of electron withdrawing olefins revealed the rate of conversion can be increased by using SIPr substituted N-heterocyclic carbenes instead of SIMes ligands in ruthenium catalysts.[16] So, in the next step we used SIPr substituted N-heterocyclic carbene based ester chelated catalyst **46** synthesized in our laboratory.[130] The NMR analysis shows full conversions to **47** using all loadings from 0.1 to 0.5mol% of this catalyst. The reaction at 0.05mol% with **46** without CuI produced 48% of the product **47** only. Enhanced effect of SIPr ligand was also verified by the formation of self metathesis product **50** in different ratios besides the complete conversion of olefin 1-hexene into **47**. 17, 10 and 3% of the product **50** were observed using 0.5, 0.25 and 0.1 mol% of the catalyst **46**. Intriguing by the findings from the SIPr substituted catalyst **46**, in the next step indenylidene based SIPr substituted catalyst **45** was tested while loading the 0.25mol% of the catalyst keeping all the reaction conditions same, the total conversion dropped to 80% in longer reaction time of 16 hours. The performance of catalyst Ester chelated SIPr substituted catalyst **46** was also examined by adding extra 1 equivalent of 1-hexene after 16 hours to already running reaction at 0.5 mol%. It was observed that 50% more of the newly added olefin was consumed in next 24 hours.

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[130] Leitgeb, A. PhD Thesis **2012**, Graz University of Technology

Table 4.2: Catalyst studies for Cross metathesis of 1-hexene with MVK[131]

Entry	Catalyst	Loadings[132] [mol / dm^3]	Conversion[133] [%]
1	**14**	**0.5**	**45**
2	**2**	**0.5**	**48**
3	**11**	**0.5**	**100**
4	**11**	**0.25**	**96**
5	**11**	**0.1**	**88**
6	**11**	**0.05**	**74**
7	**1**	**0.25**	**73**
8	**45**	**0.5**	**80**
9	**46**	**0.5**	**100**
10	**46**	**0.25**	**100**
11	**46**	**0.1**	**100**
12	**46**	**0.05**	**98**
13	**46**	**0.02**	**76**

In the next step catalyst activity of **46** were compared with second best found catalyst **11** by measuring the rate of conversion at different intervals. When performing the cross metathesis reaction at 0.25mol% both the catalysts consumed 86% and 80% of 1-hexene respectively in first two hours but the total conversions were almost similar after four hours and 1-hexene was completely consumed at the same catalyst loading after 8 hours. In the next step, the cross metathesis at low loadings i.e. 0.05mol% of both catalysts were performed. **11** is distinctly less active than **46.** 42% of the product **47** was obtained in first two hours and in the next two hours the conversion increased to 57% and reaction stopped after eight hours giving 74% of conversion to **47** only. No significant increase in conversion was observed after this time. While at the same catalyst loadings of **46** conversions to yield the product **47** were 75%, 94% and 96% in two, four and eight hours reaction time. Remaining 4% of the monomer was oligomerized to product **49** and no self metathesis product of MVK (**50**) was observed. For evaluating the catalyst loadings below 0.05mol%, a reaction was also tried at 0.02 mol% of the catalyst **46,** but only 74% of the cross metathesis product was obtained in 16hrs. The ratio of **47** to 1-hexene could not be increased significantly after this time.

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[131] Previously used optimized reaction conditions (i.e. in 0.2M ether reflux and with 3mol% of CuI for 16 hrs.) were used.

[132] The catalyst loadings are with respect to 1-hexene.

[133] The conversion was estimated through NMR of raw products in reaction mixture

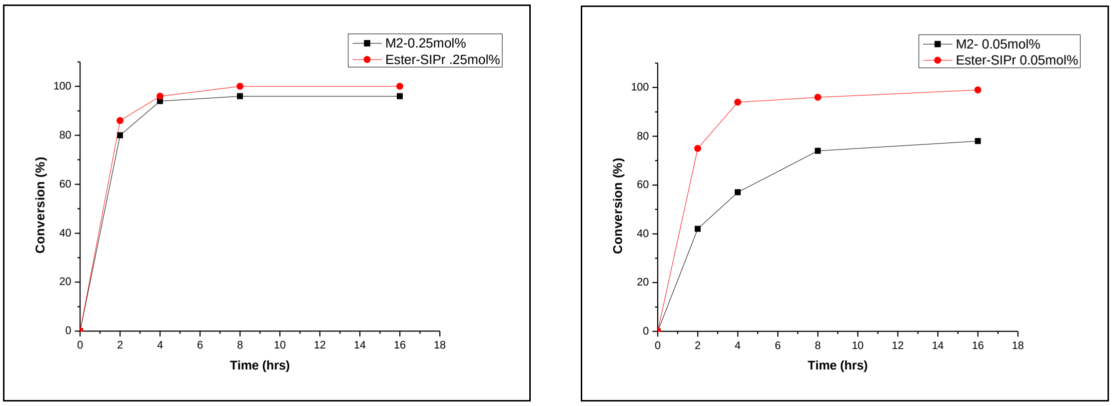

Figure 4.3: The rate of conversion for obtaining 47 with catalysts 11 and 46 at 0.25 mol% (left) and 0.05 mol % (right)[134]

In summary, we have concluded that the catalyst loading as low as 500ppm with respect to double bond is sufficient to give full conversion of terminal olefins into alpha-, beta-unsaturated ketones. The green process using ether as a solvent and volatile cross partner MVK makes it a feasible and environmentally benign reaction for various practical applications. Our studies upon different ligands on ruthenium based 2nd generation catalysts revealed the Ester-SIPr substituted N-heterocyclic carbene catalyst **46** the best for this type of cross metathesis reactions. Commercially available inexpensive catalyst **11** is the second best catalyst for this type of reactions whose 0.25 mol% amount is sufficient for complete conversion of terminal olefin double bonds.

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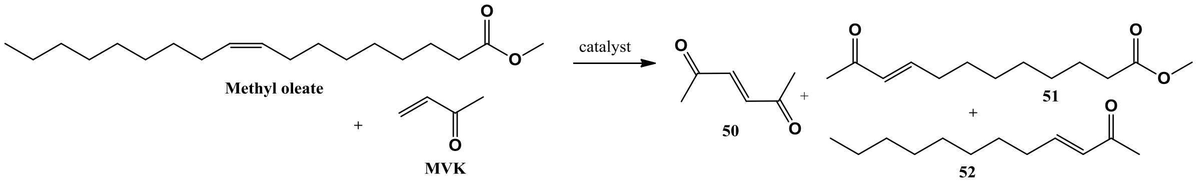
[134] Kinetic studies of the reaction were studied by NMR analysis of the reaction mixture.

4.2 Optimizing cross metathesis reaction of methyloleate with MVK

Olefins from renewable resources have also gained much attention due to synthesis of valuable raw precursors and monomers for various materials including polymers. The scope of this studies is expanded to investigate the highly optimized reaction conditions for cross metathesis of olefins from renewable resources like methyloleate with MVK and is reported here.

The chemicals were used as received that means with no further purification was done. Based on Lipschutz[49] work ether was used as a solvent and 3mol% of CuI was added as a co-catalyst in all reactions. Temperature was kept constant at reflux temperature of ether (35°C). In the first few tries the dilution factor was optimized and it was found that optimal concentration of olefin methyl oleate in ether is 0.1mol/dm^3. Successful cross metathesis released the products **51** and **52** along with traces of **50** in all cases where excess of catalyst is used. In a second series the cross metathesis was performed with three different catalysts and is given in **table 4.3**



Scheme 4.1: Cross metathesis of methyloleate with MVK

While examining the cross metathesis products **51** and **52** from methyloleate we started our tries by using catalyst **14**. Using 1mol% of the catalyst, only 43% of both of the products were obtained. However adding 1mol% more catalyst and running the reaction for another 24 hours converted 74% of the total monomer into cross metathesis products. Some reactions were also tried in dichloromethane as a solvent and CuCl as co-catalyst with **14** but higher yields were only obtained using the reaction conditions previously used for cross metathesis of 1-hexene with MVK (*cf.* t**able 4.2)**.

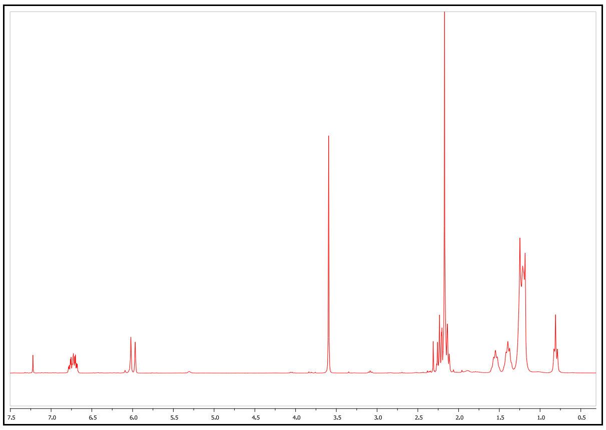


Figure 4.4: ^{1}H-NMR spectra of 51 and 52 after cross metathesis of methyl oleate with MVK[94]

Our studies were then expanded to the best found catalysts **11** and **46**. **11** at 1mol% loadings was giving high conversions of 84% in 16 hours while decreasing the catalyst loading to 0.5mol% decreased the conversion to 45%. Increase in reaction time to forty hours could not even increase the cross metathesis products **51** and **52** in this case. However, **46** was again the best in this type of cross metathesis reactions where overall conversion of **51** and **52** from methyloleate was 95% using 0.5mol% of the catalyst. Further decreasing the amount of catalyst to 0.2mol% decreased the ratio of product to 25% in 16 hrs while traces of cleaved products of terminal olefins were also observed in this case. The reactivity of Hoveyda type second generation catalyst **2** was also less compared to **11** and **46**, giving only 80% conversion using 2 mol% of the catalyst (**table 4.3**, entry 3)

Table 4.3: The cross metathesis of methyloleate with MVK in presence of different catalysts[135]

Entry	Catalyst	Loadings [mol / dm^3]	[51 + 52] [%]
1	14	1	43
2	14	2	78
3	2	2	80
4	11	1	88
5	11	0.5	45
6	11	0.5	48
7	46	1	95
8	46	0.5	94
9	46	0.2	25
10	46	0.2	28

The optimized reaction conditions for cross metathesis of 1-hexene with methyl vinyl ketone is also applied for olefins from renewable resources and after finding the optimal amount of solvent, the catalyst loadings of **46** has also been optimized to as low as 0.5mol% with respect to methyl oleate for complete conversion of all internal double bonds to α-, β- unsaturated ketones.

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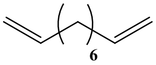
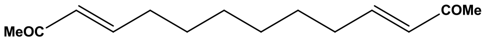
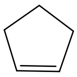
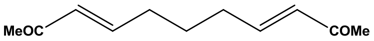
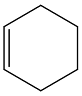
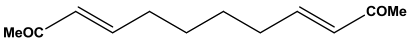
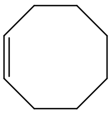
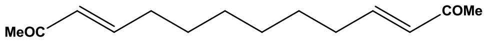
[135] Same reaction conditions were used as described for cross metathesis of 1-hexene with MVK.

4.3: Synthesis of doubly substituted α-, β-unsaturated ketone via cross metathesis of diolefins and cyclic olefins with MVK.

After finding highly optimized reaction conditions for the cross metathesis of terminal olefin 1-hexene and internal olefin from renewable resources like methyloleate this analysis was also applied to the cross metathesis of other olefins including diolefin 1, 9-decadiene and (5, 6 and 8-membered) cyclic olefins to yield the products **53-56**. In presence of 0.25mol% of catalyst **46** and in 6eq. of MVK, successful cross metathesis products were observed in all cases except cyclohexene, where even less than 5% of the product **55** was observed. All other olefins yielded more than 80% products in total. In case of cyclooctene some minor amount of polymers were also obtained along with major product **56**. All other products were isolated in high yields.

Table 4.4: synthesis of bi-substituted α-, β-unsaturated ketones via cross metathesis[136]

Entry	**Alkene**	**Product**	**Yield [%]**
1		 53	**98**
2		 54	**75**
3		 55	<5
4		 53	**80**

In sum, the optimized reaction conditions for cross metathesis was also expanded to commercially available cyclic olefins and di-olefins and it was found that complete cross metathesis products **53-55** could be obtained by using 0.25mol% of previously found best initiator **46**.

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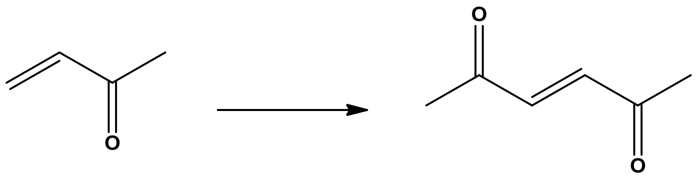
[136] The reaction was performed in 6eq. of MVK and 0.25mol% of the catalyst 46 in 0.1M ether reflux for 16hrs.

4.4 Self metathesis of methyl vinyl ketone

The formation of self metathesis product of MVK in different cross metathesis reactions with olefins gave motivation to perform the self metathesis of MVK. In past this reaction has been performed with comparatively high catalyst loadings due to inert nature of methyl vinyl ketone towards self metathesis.[43] Grubbs et al. proposed higher dilutions is effective for high yield self metathesis products of vinyl ketones[48] other endeavours counted in this regard also include use of microwave radiation in place of conventional heating systems.[45] In order to optimize the reaction conditions for the synthesis of **50,** 1mol% of catalyst 14 were used for our several tries in various dilutions (0.05-1M) and also few tries in presence of microwave radiation using the same concentration as in conventional heating reactions but no full conversion to **50** of MVK were observed at this much catalyst loadings. Performing the same reaction in presence of 3mol% yielded 66% of 50 at concentration of 0.1mol/dm^3. In the next step, self metathesis reactions of MVK with different catalysts at 1mol% catalyst loadings to yield **50** were performed. 24 and 33% of **50** were obtained with **14** and **11** respectively whereas again comparatively high yields of 66% were obtained using **46** as catalyst.[137]



50

Scheme 4.2: self metathesis of MVK

The enhanced activity of catalyst **46,** determined from cross metathesis of terminal olefin with methyl vinyl ketone is also applied for cross metathesis cyclic olefins and for self metathesis of MVK to yield **50** and the lowest possible amount of catalyst was determined.

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[137] higher dilutions of 0.01M with respect to MVK were required.

Chapter 5

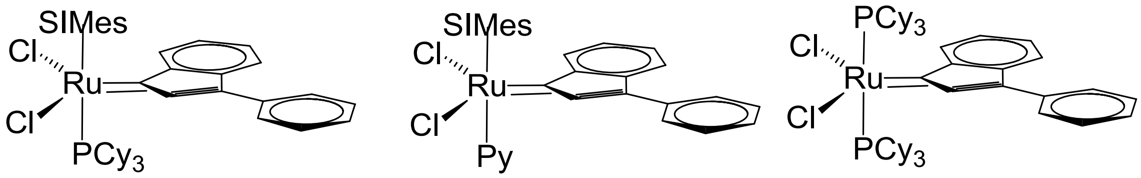
Ring Closing Metathesis

5.1: Ring closing metathesis to yield substituted cyclopentene products

The scope of these studies was further expanded to ring closing metathesis products. As discussed in section 2.4 rings closing metathesis is comparatively tricky especially for the synthesis of molecules with unfavourable ring size and substrates which are basic in nature. The RCM of these substrates is hard to accomplish because the presence of base causes the inhibition of reaction due to killing the catalyst by making chelated complexes with ruthenium based complexes.

5.1.1 Ring closing metathesis to yield pyridine substituted cyclopentene products

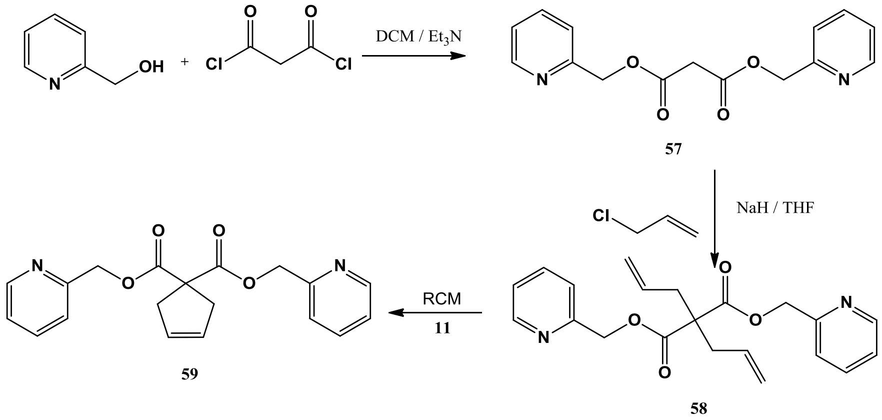
To study the effect of these compounds pyridine substituted dially derivatives were synthesized and their RCM to yield cyclopentene derivatives were studies. Grubbs indenylidene based 1st generation catalyst **56**, 2nd generation catalyst **11** and 3rd generation catalyst **43** were selected for this purpose. (*cf.* **Figure 5.1**)



11 **43** **56**

Figure 5.1: Catalysts screened for RCM

Pyridine substituted diallyl precursor **58** was synthesized stepwise, firstly by using commercially available substrates 2-methylol pyridine and malonylchloride in presence of base to yield disubstituted pyridine **57**. Besides unreacted molecules monosubstituted derivatives were also observed in this case but conversion to **57** were as high as 45%. In the next step two allyl groups were attached to the substrate **57** for the synthesis of RCM precursor **58**. The yield of isolated product **58** was 77% in this case.



Scheme 5.1: RCM of pyridine substituted diallyl substrate 58

In the next step after the synthesis of pyridine substituted substrate **58**, its ring closing metathesis was studied. When testing the ring closing metathesis of **58** in presence of 1mol% of the catalyst **56** only 10% of the product **59** was observed when running it at room temperature (23°C) for 24 hours. But when the same reaction was performed in presence of 1mol% of **11** in the same solvent at room temperature 50% of the product **59** was observed in first 24 hours and full conversions were observed in 3days reaction time. Performing the same reaction at higher temperatures of 70°C in toluene with the same catalyst loadings of **11** all the olefins in **58** were converted to ring closing metathesis product **59** in just one hour. However, with Grubbs indenylidene 3rd generation catalyst **43** only 45% of the products were obtained in 24 hours at room temperature. But no further activity of the catalyst to give more conversions to **59** was observed after this time.

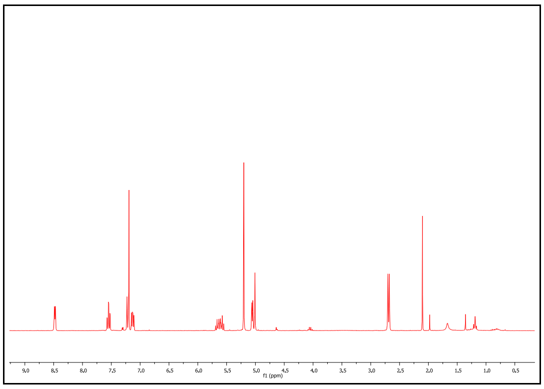
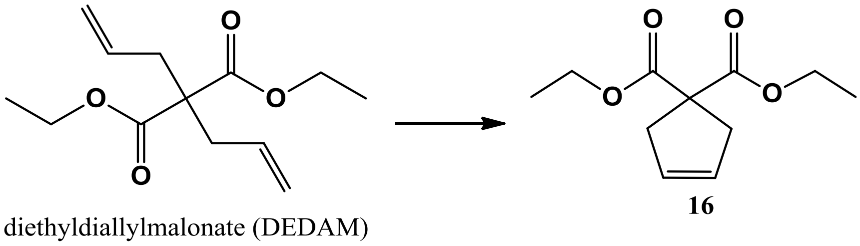


Figure 5.2: ^{1}H-NMR of pyridine substituted dially product (58)[94]

In the next step ring closing metathesis of diethyldiallylmalonate (DEDAM), an easy precursor for RCM was studied in presence of different catalysts given in figure 5.1. The effect of presence of pyridine in such RCM reactions was also observed. Firstly when the

RCM of DEDAM was performed in presence of 1mol% of **11** full conversions were observed at room temperature in dichloromethane as a solvent in 24 hours. These results were different than the results already reported by Grela et al.[10] The same conversions to synthesize RCM product **59** were observed in just one hour using **11** as a catalyst at higher temperatures of 70°C in one hour only.



Scheme 5.2: RCM of DEDAM

This reaction when observed in presence of 3 eq. of pyridine in various reaction conditions and in presence of different catalysts no high conversions of products were observed. (Table 5.1, entries 9-10) Only minor amounts of product **16** were observed in all cases for the RCM of DEDAM.

Table 5.1: RCM of DEDAM and pyridine substituted cyclopentene (59)

Entry	Catalyst	Reaction Conditions[138]	Product	Conversion[139] [%]
1	56	X	59	10
2	11	X	59	50
3	11	Y	59	>98
4	11	Z	59	>98
5	43	X	59	45
6	43	Y	59	48
7	11	X	16	95
8	11	Z	16	>98
9	11	X + 3eq. py	16	7
10	11	Z + 3 eq. py	16	11

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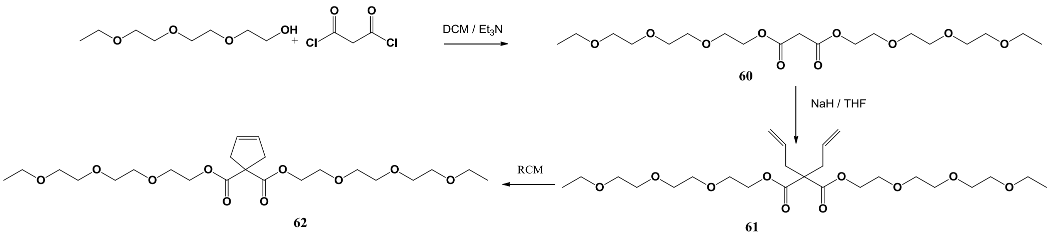
[138] X = in 1M dichloromethane at room temperature for 24 hours, Y= X + 48 hours and Z = in toluene at 70°C for 1hours.

[139] Conversion of crude product was determined by NMR and only high yield RCM products were isolated.

In sum, when pyridine substituted substrate **58** was tested in RCM of with indenylidene based 1st, 2nd and 3rd generation catalyst (**43, 11** and **56**), **11** is best suitable catalyst for RCM of such substrate. The rate of formation of ring closing product **59** can be increased by using the reaction conditions at higher temperature in toluene. (entry 4, **table 5.1**). Similarly **11** is also the best initiator for RCM of diethy diallymalonate (DEDAM) to yield **16** and RCM reaction of DEDAM is inhibited in presence of pyridine.

5.1.2 Ring closing metathesis of diallyl (poly) ethoxyethyl malonate

In according to select various alcohols and preparing their allyl substituted malonyl derivatives polyethoxyethyl alcohol was chosen as a side chain in malonate. and its coupling with ethyl malonate was performed to get polyethoxyethyl malonate derivative **60**, later upon substituting two allyl groups the substrate **61** for ring closing metathesis was synthesized and its RCM to yield **62** was performed in presence of 1mol% of **11**. In all reactions with 1mol% of **11** in DCM reflux or in toluene the product **62** was obtained in high yields and was isolated.



Scheme 5.3: Synthesis of Diallyl polyethoxyethyl malonate 61 and its RCM to yield 62

In the first step the yield of malonate diester substrate **60** was 77% which after introduction of two ally group lowered to 69% but the RCM product of **61** yielded 88% conversion of olefins of dially to cyclopentene substituted products **62**. Poly(ethoxy) substrates are advantageous in various practical application especially when studying the metathesis reaction of such substrates in water.

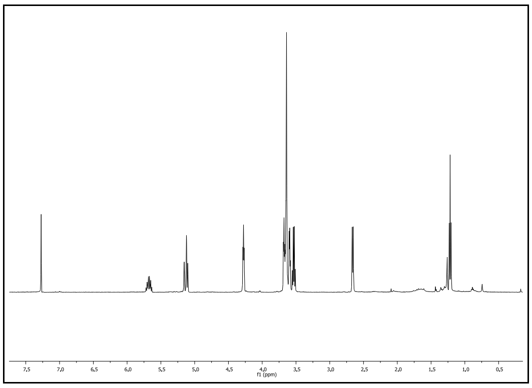
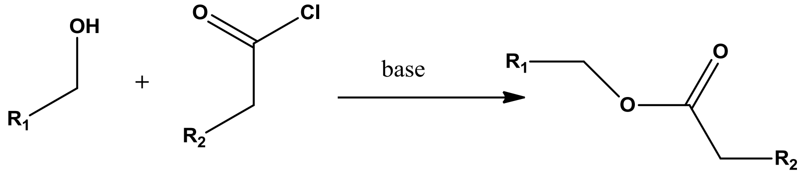


Figure 5.3: ^{1}H-NMR of polyethoxy dially product (61)[94]

5.3: RCM of ester containing olefins

Lactones and ester containing functionalized cyclic olefins are important substrates in modern organic and synthetic chemistry. In this regard various ester containing molecules are synthesized and their RCM to lactones of various ring size are established. Under highly optimized conditions only six membered rings from **63** was synthesized while in other tries for the synthesis of other molecules with different ring sizes only 14 member ring from **66** was formed.



R_1 & R_2 = olefins

Scheme 5.4: Synthesis of ester containing olefins

For the introduction of an alpha-,beta-unsaturated ester group to one end of olefins various alcohols containing terminal olefins were selected and their reaction with acrolyl chloride in presence of triethylamine as a base in dichloromethane high yields of substrates were synthesized. Similarly some diacrylates were also synthesized for this purpose. (**Scheme 5.4**) A list of these substrates is given in **figure 5.4**.

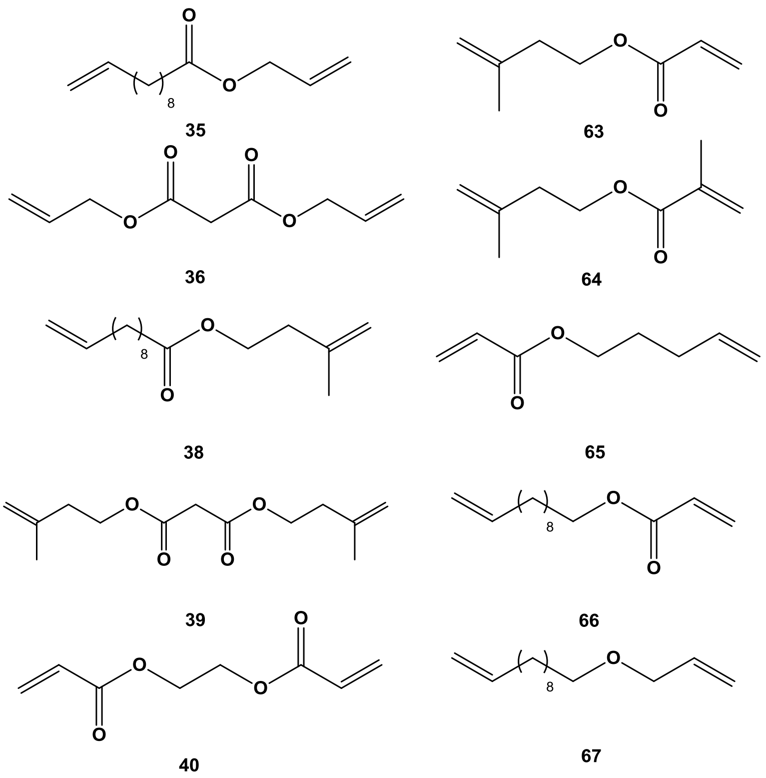
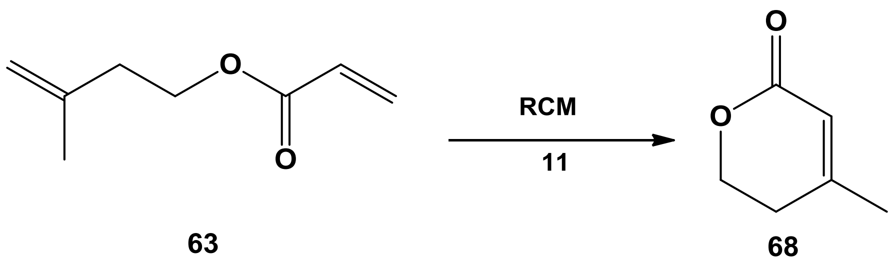


Figure 5.4: Substrates studied for RCM

After the synthesis of such substrates which have terminal olefins or beta substituted olefins at one end and acrylate at the other end the reaction for cross metathesis was performed with indenylidene type catalyst **11**. In all our tries 0.1 mol / dm^3 dichloromethane and 1mol% of the catalyst **11** was used as the standard reaction. For the ring closing metathesis only the product of six member ring with substituted olefin at one end and acrylate at other end product **63** was observed. The reaction was performed in deuterated chloroform to study the completion of reaction via proton NMR. Full conversions were observed in all cases and no post treatment was used due to volatile nature of the resulting substrate.



Scheme 5.5: RCM for the synthesis of lactone

After the successful cyclization to six membered rings some tries for the ring closing metathesis reaction to give different ring sized molecules were tested. Besides acrylate containing long chain olefin **66,** other long chain olefin like ether containing olefin **67** was also tested. The detailed analysis of ring closing metathesis product of acrylate substituted product **66** were as high as 33% at very high dilutions of 0.01M or lower.

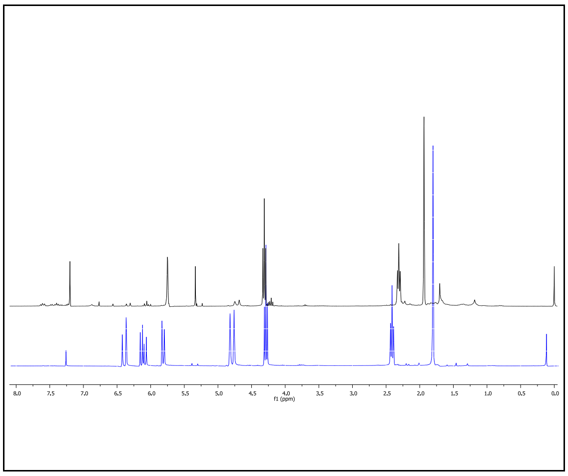
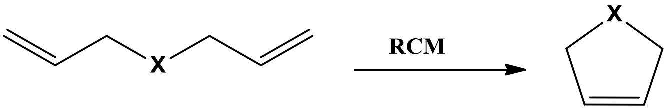


Figure 5.5: ^{1}H-NMR spectra of 63 and its RCM product; above: complete conversion towards RCM product (68); below: reacting precursor 63[94]

However, the isolated product was only examined by NMR analysis while MALDI or other analysis for the isolated products could not be established. RCM of other molecules **36**, **38** and **65** could not be accomplished. Rather, oligomers or polyolefin derived products were obtained in all cases. While all other substituted olefins and acrylates (**39**, **40** and **64**) did not yield any metathesis products. All the reactions for ring metathesis reaction were not applicable to ring size of seven or above but the successful metathesis reactions were observed only for the olefin **63, 66** and **67**.

5.4: RCM for the synthesis of heterocyclic five membered rings

The scope of RCM was also expanded to diallyl substituted molecules containing a nitrogen or sulphur atom, yielding 5-membered rings. RCM of diallyl amine and diallyl sulphide was performed in presence of 1mol% of catalyst **11**. All tries to get 5-memberd cyclic ring were hampered by low yield and also handling of product was also difficult due to lower boiling points then the reacting substrates. Diallyl amine, when protected with acetyl functional group, gave a real entry into metathesis. The protection of diallylamine and its RCM was performed in one pot and high yields of acetyl pyrole products were observed in this case. This one step protecting group introduction and metathesis reaction has already been discussed in details in section **3.2.2.** The catalyst loading was also optimized in this type of reactions where RCM of acetyl protected diallyl amine after purification and isolation was cyclized by using 0.1 mol% of **14**.



X = S, NH, NCOMe

Scheme 5.6: RCM for the synthesis of heterocyclic rings

RCM of diallyl amine is hard to establish without introduction of a protecting group. Hassner et al. prepared six membered ring pyridine type substrate using Grubbs 2nd generation initiator (**1**) but high loadings of 5mol% catalyst loadings were used to make these type of substrates.[140] In contrast, acetyl protected pyrrolidine type precursor **68** was prepared by using 0.1mol% of **14** only.

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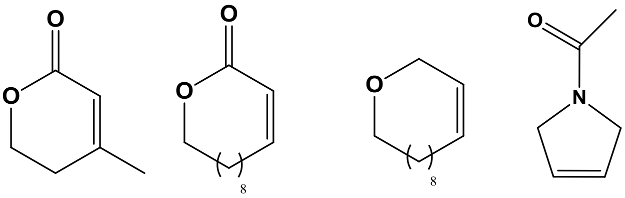
[140] Hassner, A.; Balasubramaian, T.; *Tetrahedron Lett.* **2000**, *41*, 8157-8162.



68 **69** **70** **71**

Figure 5.6: Successfully synthesized RCM product

In sum, successful RCM of different substrates especially of more demanding substrates which are generally hard to cyclise via olefin metathesis was demonstrated. Also, lactones of 6 and 14 atom sizes were synthesized. Besides it, pyridine effect on RCM of DEDAM and pyridine substituted and polyethoxyethyl substituted derivatives of cyclopentene were also synthesized which have never been reported in literature. The last part was dedicated to synthesis of heterocyclic 5 membered compounds via RCM and optimized reaction condition for these molecules was also determined.

Chapter 6

Designed silver nanoparticles for antimicrobially equipped pDCPD

In recent years, silver nanoparticles have gained remarkable importance for their use in optical sensors, printed electronics, photonics, antimicrobial coatings and many other advanced applications.[19] In particular, antimicrobial silver nanoparticles and their derivatives make them versatile substrates for use in the field of health and environment.[141] The alternation in reaction media, reducing agents, heating systems and solvent used for the synthesis of oleylamine based silver nanoparticles can yield variety of nanoparticles with different size and shape and hence their activity against bacteria can be varied. In some cases direct reflux method of silver and oleylamine has also been used but the reaction at high temperature in presence of solvent makes it less feasible for the practical application but optimizing of the reaction conditions for these type of synthesis was still demanding.

6.1 Synthesis and characterization of silver nanoparticles

In past, various methods have been used for the synthesis and characterization of oleylamine capped silver nanoparticles.[142] Main reactions include the reactions in solvents while refluxing at higher temperature and using different reducing agents.[143]

In the first attempt we tried to find a green synthesis route for the nanoparticles of oleylamine with silver. Commercially available chemicals were used and the reaction of oleylamine with silver nitrate was performed in different solvents but the real issue was solubility of the reaction mixture containing an inorganic salt (silver nitrate) and other lipophilic substrate like oleylamine. So the reactions were performed in 50% aqueous ethanol this mixture was selected not only due to miscibility of the solvents but also due to greener aspects of synthesis in chemistry. The only limitation of this reaction mixture was the control of temperature because synthesis of this type of nanoparticles usually requires higher temperatures but with ethanol water containing solvent mixture the reaction temperature of as high as 78°C could be established. So using these parameters the reaction in presence of different reducing agents was performed.

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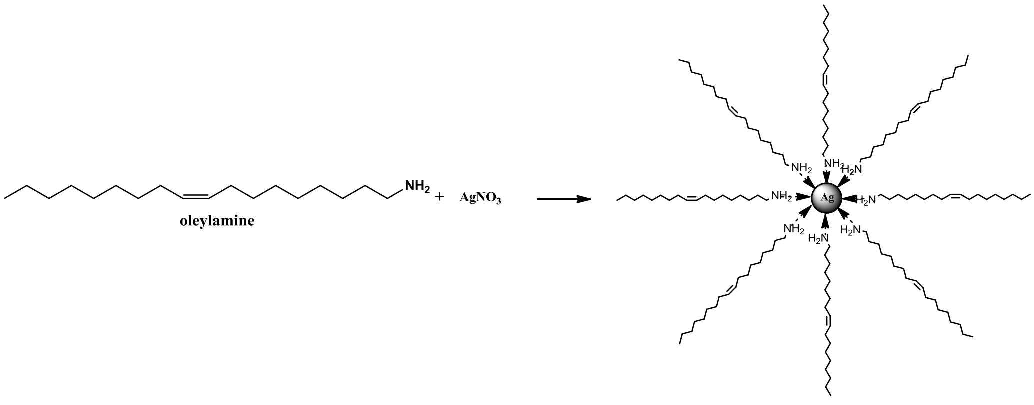
[141] I. Sondi, B. Salopek-Sondi, *Journal of Colloid and Interface Science*, **2004**, *275*, 177-182.

[142] Qian, D-J.; Zhang, J-Y. ; Li, T-C. Chen, M. *Langmuir*, **2007**, *23*, 5296-5304.

[143] Sun, S.; Chan, R. Yin, H. Wang, C.; *Chem. Mater.* **2009**, *21*, 433-435.



72

Scheme 6.1: Synthesis of oleylamine based silver nanoparticles

The solubility of oleylamine and its insertion in silver metal to produce properly defined nanoparticles with appropriate size and shape could not be established with mild reducing agents like citric acid and tartaric acid. In the next step, when glucose was used as reducing sugar, still the nanoparticles could not be synthesized in high yields. The need of increasing temperature was found mandatory for yielding nanoparticles which could reduce the oleylamine and produce nanoparticles. In next step the temperature was increased to 150°C when performing the reaction without presence of any solvent and only in tenfold excess of oleylamine with respect to silver salt. The black precipitates were obtained in the reaction time of five minutes even without using any reducing agent. This reaction was further optimized to optimize ratio of oleylamine to silver nitrate but in all our tries ten times olelyamine with respect to silver nitrate was the most optimized ratio.

Table 6.1: The reaction conditions used for the synthesis of nanoparticles(72)

Entry	Silver salt + Doping agent	Reducing agent	Solvent	Temperature [°C]
1	$AgNO_3$ + Oleylamine	Citric acid	EtOH +H_2O	80
2	$AgNO_3$ + Oleylamine	Tartaric acid	EtOH +H_2O	80
3	$AgNO_3$ + Oleylamine	Glucose	EtOH +H_2O	80
4	$AgNO_3$ + Oleylamine	Oleylamine	EtOH +H_2O	80
5	$AgNO_3$ + Oleylamine	Oleylamine	-	150

The nanoparticles synthesized by direct combination of oleylamine and silver nitrate in refluxing 10:1 ratio were later characterized by UV-Vis absorbance and dynamic light scattering (DLS) technique. The ultra fine nanoparticles precipitated in ethanol showed very good solubility in chloroform which helped to measure its absorbance spectra at 415 nm and size distribution of the most particles at 30-40nm according to data already reported in literature.[144]

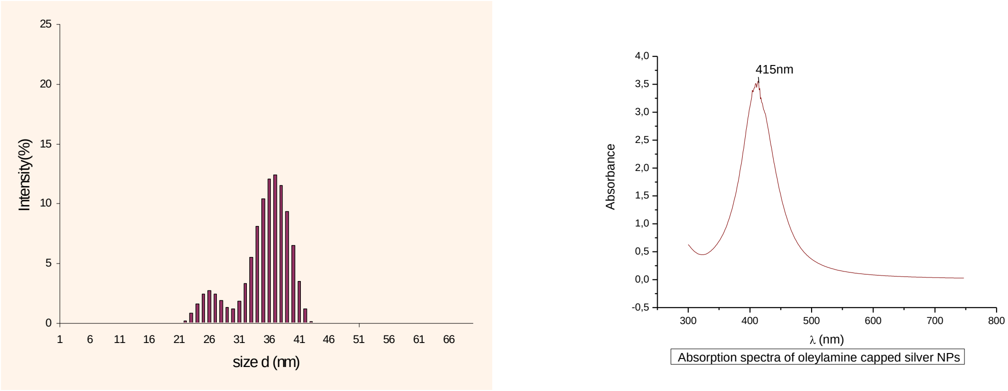


Figure 6.1. (Left) size distribution of nanoparticles (right) Absorption spectrum of the nanoparticles

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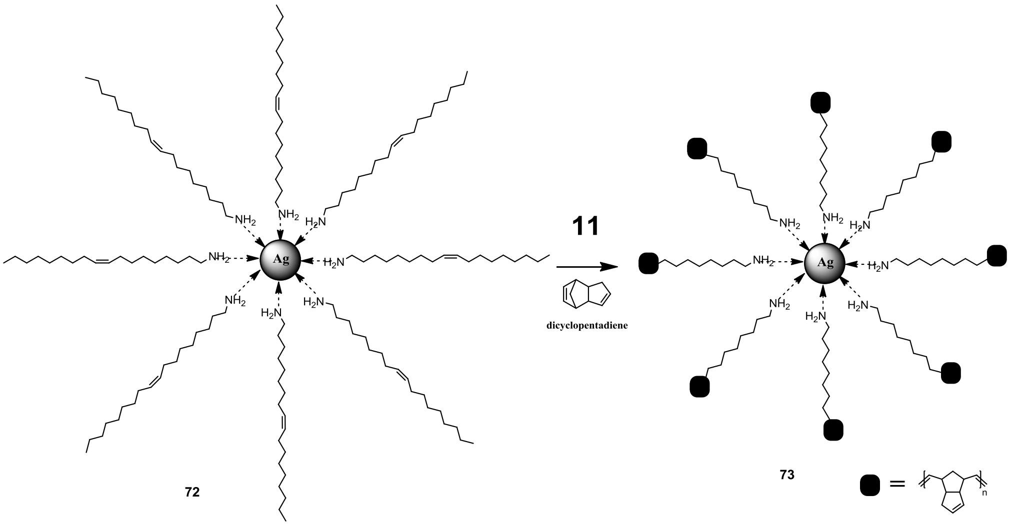
[144] Fernandez E.,J., Laguna A., Monge M., Torres C.; *Nanotechnology*, *19*, **2008**, 158602

6.2 synthesis of silver nanoparticle based polydicyclopentadiene material

In the next step, the oleylamine capped silver nanoparticles were used in different ratios with dicyclopentadiene (DCPD) to yield ROMP of different size and characteristics. pDCPD plates with a silver nanoparticle content of 0.5-1 w% were prepared by ROMP using commercially available **11** as initiator and a catalyst loading of 20 ppm with respect to the monomer.[145] The mould was configured of two separate glass plates with a distance holder of 0.9 mm and hence formed pDCPD plate in this mould was cut into 4x4 cm square for further analysis.



Scheme 6.2: Silver nanoparticles based pDCPD material synthesis (73)

The incorporation of silver nanopartilces in these pDCPD based plates was not only observed by physical change in colour but some more advanced methods like single electro microscopic (SEM) methods were also used for these materials. When magnifying the image at very narrow size of the plates it was observed that silver nanoparticles were equally distributed in the materials and presence of these particles were observed in the material after regular intervals.

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[145] Leitgeb, A.; Slugovc, C.; Grela, K. *J Polym Sci Part A: Polym Chem*. **2011,** *49*, 3448-3454.

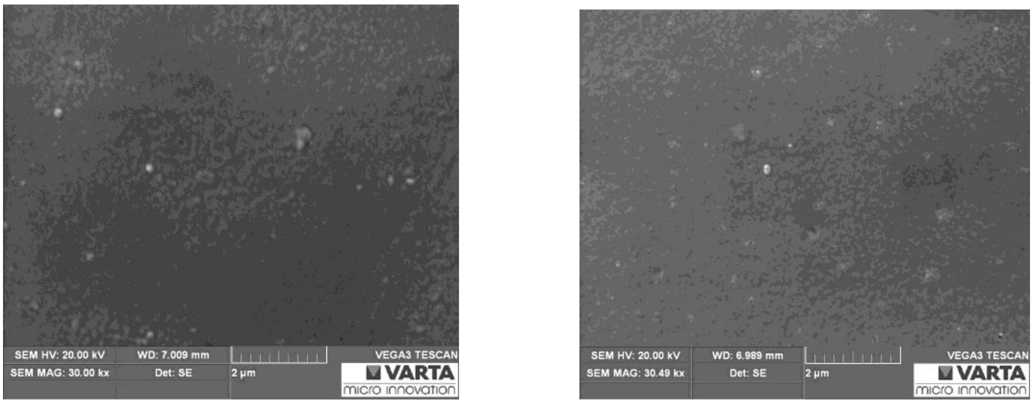

Figure 6.2: SEM images of pDCPD plates

6.3 Antimicrobial activity of silver nanoparticle equipped pDCPD plates

Some biological activity including activity against gram positive and gram negative bacteria was studied using these materials and according to some initial results it was observed that in all cases where even very little amount of silver nanoparticles were used, these polymers were active against gram positive and gram negative bacteria. Japanese industrial standards were used to study the anti bacterial activity of these polymers.[146]

In sum, the new environment friendly solvent free method for the synthesis of silver nanopaticles and their ROMP with DCPD to yield pDCPD plates is reported. The activity against of this polymer against gram negative and positive bacteria is in progress.

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[146] Noormofidi, N.; Slugovc, C.; Kern, W. *J Polym Sci Part A: Polym Chem*. **2010,** *48*, 4504-4514.

Chapter 7

Experimental Work

Materials and methods

All chemicals as substrates or initiators were used which were either prepared in laboratory or purchased from commercial sources. Catalysts **11**, **14, 43, 45** and **56** were obtained from UMICORE AG and catalysts **12**, **13**, **15** and **46** were synthesized as the procedure already reported in literature. Solvents and auxiliaries were used as received. All reactions were carried out under nitrogen in pre-dried glassware using Schlenk technique. Other materials were obtained from commercial sources (Aldrich, Fluka or Alfa Aesar) and were used without further purification.

Instrumental Analysis

NMR (^{1}H, ^{13}C) spectra were recorded on a Bruker Avanze 300MHz and INOVA 500 MHz spectrometer, respectively in $CDCl_3$. Chemical shifts are given in ppm relative to a $SiMe_4$ standard. The solvent peak of $CDCl_3$ was used for referencing the NMR spectra to 7.26 (^{1}H) and 77.16 ppm (^{13}C), respectively.

GPC measurements for obtaining both number average molecular weight (M_n) and polydispersity index (PDI) were performed in THF using following settings: Merck Hitachi L6000 pump, separation columns of Polymer Standards Service, 8x300 mm STV 5µm grad size (10^6 Å, 10^4 Å and 10^3 Å), refractive index detector from Wyatt Technology, model Optolab DSP Interferometric Refractometer. Calibration was done with polystyrene standards purchased from Polymer Standard Services.

UV-visible absorption spectra were performed on a Varian Cary 50 Conc UV-Visible Spectrophotometer using a cell made of quarz glass (Hellma, d: 10 mm, spectral range: 200-2500 nm).

FT-IR spectra were recorded with a Perkin Elmer Spectrum One and a DTGS-detector. Samples were measured on NaCl-plates (diameter 20 mm, width 2 mm) as thin films.

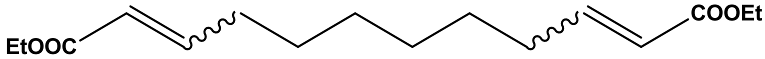
Intensities at different wave numbers (cm^{-1}) were characterized as w (weak), m (medium) and s (strong).

Particle sizes were determined with a Malven Instruments ZetaSizer NanoZS provided with a 633 nm laser. If not otherwise mentioned, the polymers were measured against a polystyrene latex standard at 20 °C, sample concentration was 5 mg mL^{-1} and the equilibration time was 24 hours.

For UV-irradiation a polychromatic medium pressure mercury lamp from Heraeus, bearing an intensity of 45 mW/cm^2, was used. The highest intensitys are obtained at 365, 404 and 437 nm.

Chapter 3 - Experimental

Examplary preparation of diethyl dodeca-2,10-dienedioate (mixture of E and Z isomer)[78]



(for the reaction described in **Table X1**, entry 7, see also **Table X2**, entry 9) A Schlenk tube equipped with a stirring bar was charged with ethyl acrylate (5.00 g, 0.0499 mol) and 1,9-decadiene (1.38 g, 0.00998 mol) under inert atmosphere of nitrogen. The reaction mixture was heated to 80°C (oil bath temperature) and the catalyst **15** (1.30 mg, 0.00198 mmol) was added. The Schlenk tube was closed with a glass cap which was not opened until the indicated time. Afterwards, the reaction mixture was concentrated under reduced pressure in order to remove excess of ethyl acrylate and a sample for NMR measurement was taken. In case of full conversion the product was isolated by passing the reaction mixture over a short silica gel column using cyclohexane/ethyl acetate = 5 : 1 for elution. Drying of the appropriate fractions gave the mixture of the title compounds as colorless oil. Yields are given in table X1.

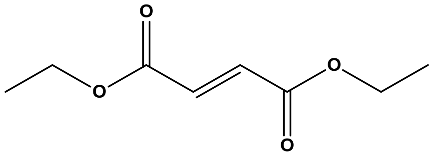
^{1}**H-NMR** (300 MHz, $CDCl_3$): δ = 6.95–6.89 (m, 2H, –C*H*=CH–COO), 5.80–5.74 (d, 2H, –CH=C*H*–COO), 4.18-4.11 (q, 4H, –COOC$\mathit{H_2}$CH$_3$), 2.19–2.12 (m, 4H, C$\mathit{H_2}$–CH=CH–COOCH$_2$CH$_3$), 1,36 (t, 6H, -C$\mathit{H_3}$), 1.29–1.22 (m, 8H, -C$\mathit{H_2}$-),

^{13}**C NMR** (75 MHz, $CDCl_3$): δ = 166.4 (s, –COO), 149.27 (s, –CH=CH–COO), 121.31 (s, –CH=CH–COO), 60.45 (s,–CH=CH–COOCH$_3$), 32.0, 30.88, 28.86 (s, CH$_2$), 14.19 (s, CH$_3$)

Table X1: Yields of cross metahesis product A and B.

Entry	Catalyst	Temperature [°C]	Loading [mol%]	Time [h]	A : B : C : D / E [%]	Yield of A & B [%]
1	**2**	50	0.1	0.5	93 : 7 : < 1 : < 1 / 4	92
2	**2**	50	0.05	16	92 : 7 : < 1 : < 1 / 2	93
3	**2**	50	0.03	16	92 : 6 : 1 : 1 / 2	93
4	**2**	80	0.05	0.5	92 : 7 : < 1 : < 1 / 3	94
5	**2**	80	0.03	0.5	92 : 7 : < 1 : 1 / 2.5	95
6	**2**	80	0.02	0.5	91 : 7 : < 1 : < 1 / 2	95
7	**15**	80	0.02	16	93 : 7 : < 1 : < 1 / 6	94
8	**15**	80	0.016	32	91 : 8 : < 1 : 1 / 3	93
9	**15**	100	0.01	4	90 : 8 : < 1 : 2 / 2	87

Diethyl fumarate (E)[78]



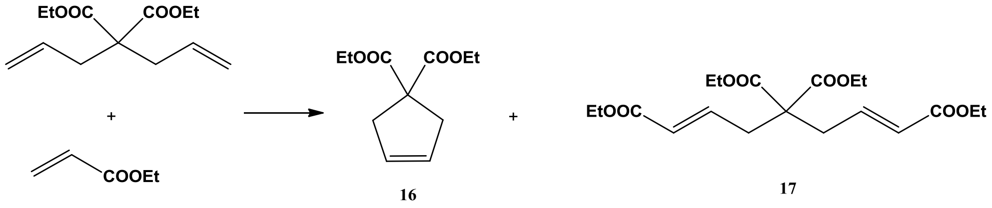
E

^{1}H-NMR of E. (300 MHz, $CDCl_3$): δ = 6.84 (s, 2H, –C*H*=CH–COO), 4.29-4.22 (q, 4H, –$COOCH_2CH_3$), 1.34-1.30 (t, 6H, -CH_3)

^{13}C-NMR of E (75 MHz, CDCl3): δ = 164.96 (s, –COO), 133.72 (s, –CH=CH–COO), 61.31 (s, -CH_2), 14.17 (s, CH_3)

In order to understand the solvent effect in cross metathesis of ethyl acrylate with olefins, DEDAM was selected. The reason for selecting this substrate was its fast trend towards RCM and effect of presence of ethyl acrylate or toluene as solvent was analysed and how the ratios of cross metathesis and RCM products **16** and **17** vary are given in table X_2.

Cross Metathesis of DEDAM with ethyl acrylate



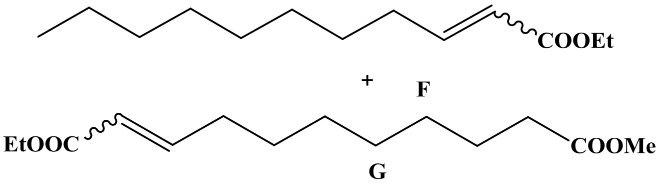
(for the reaction described in **table X2**, entry 3) A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (0.50 g, 0.005 mol), and DEDAM (208 mg, 0.001 mol) in 10mL of toluene under inert atmosphere of nitrogen. The reaction mixture was heated to 80°C and catalyst 2 (0.35mg 0.0005 mmol) was added. After the given time of 4 hours the reaction mixture was analysed using ^{1}H-NMR spectroscopy without further workup.

^{1}H-NMR of mixture 16 and 17: (300 MHz, CDCl$_3$): δ = 6.95–6.89 (m, 2H, –C*H*=CH–COO), 5.80–5.74 (d, 2H, –CH=C*H*–COO), 5.57 (s, 2H, CH$_2$CH=CH CH$_2$) 4.18-4.11 (q, 4H, –COOC*H*$_2$CH$_3$), 2.99 (s, CH$_3$) 2.76-2.73 (m, 2H, CH=CHCH$_2$C) 2.19–2.12 (m, 4H, C*H*$_2$–CH=CH–COOCH$_2$CH$_3$), 1.36 (t, 6H, -C*H*$_3$), 1.29–1.22 (m, 8H, -C*H*$_2$-)

Table X2: Cross metathesis of DEDAM in presence of ethyl acrylate (Scheme 3.2)

Entry	Catalyst	Loading	Ethyl acrylate : Toluene	Time	16 : 17
		[mol%]	[eq.]	[h]	[%]
1	**2**	0.05	5 : 0	0.5	62 : 38
2	**2**	0.05	10 : 0	0.5	59 : 41
3	**2**	0.05	5 : 10	0.5	80 : 20

Exemplary preparation of E-ethyl undec-2-enoate (F) and *E*-1-ethyl 11-methyl undec-2-enedioate (G) by cross metathesis of methyl oleate with ethyl acrylate[147]

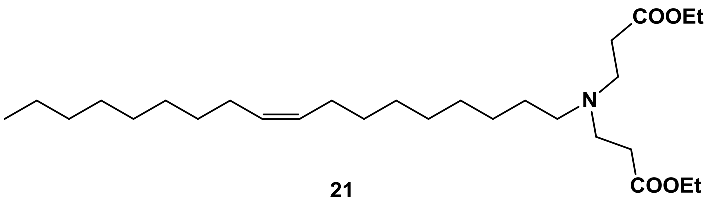


A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (5.00 g, 0.05 mol), BHT (11.2 mg, 0.05 mmol) and methyl oleate (1.50 g, 0.005 mol) under inert atmosphere of nitrogen. The reaction mixture was heated to 80°C (oil bath temperature) and the catalyst (amount according to **Table 3.5**) was added. After the given time (*cf.* **Table 3.5**), excess of ethyl acrylate was removed under reduced pressure and the residue was dried in vacuo. Conversions were checked by integration of the corresponding ^{1}H NMR spectra in $CDCl_3$.

^{1}H-NMR signals for the mixture of **F** and **G** (300 MHz, $CDCl_3$): δ = 7.01-6.88 (m, 1.5H, CO-CH=C*H*-CH_2-*trans*), 6.25-6.13 (m, 0.2H, CO-CH=C*H*-CH_2-*cis*), 5.84-5.70 (2x dd, 1.7H, CO-C*H*=CH-CH_2), 4.17 (q, 3.4H, $COOCH_2CH_3$), 3.65 (s, 3H, $COOCH_3$), 2.28 (t, 2H, CH_2COOMe), 2.17 (vq, 3.4H, CH=CH-CH_2), aliphatic signals not listed, 0.87 (t, 3H, CH_3).

In start, when performing the cross metathesis of oleylamine no sharp cross metathesis products **F** and **H** were observed however some reaction in excess of ethyl acrylate resulted in addition product **21**. So the appropriate synthesis of **21** was established and it was found that this reaction could even be performed without presence of any catalyst.

Z-Diethyl 3,3'-(octadec-9-en-1-ylazanediyl)dipropanoate (21)



21

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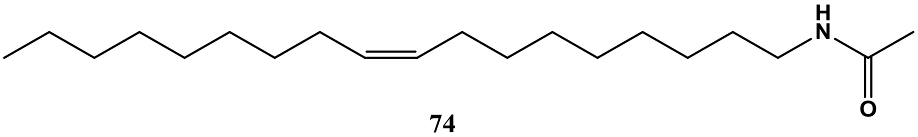
[147] Abbas, M.; Slugovc, C.; *Monatsheft. Chem.* **2012**, In press.

A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (5.00 g, 0.05 mol), BHT (11.2 mg, 0.05 mmol) and oleylamine (1.58 g, 0.005 mol) under inert atmosphere of nitrogen. The reaction mixture was heated to 80°C. After the running time of 24 hours, volatiles was removed under reduced pressure and the residue was dried in vacuo. Yield (88%)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.28 (bm, 2H, -C*H*=C*H*-), 4.09-4.02 (bm, 4.5H, -O-CH_2-CH3), 2.70 (q, 6H, CH_2-N), 1.93 (m, 2H, =CH-CH_2-CH_2-N) 1.21-1.16 (m, 29H, CH_2), 0.81 (t, 3.54H, CH_3).

Cross metathesis reaction of oelylamine when performed in presence of different initiators did not yield any cross metathesis product even when some acids or co-catalysts were used. So protection of oleylamine with different groups was established in the next step and acetyl and t-Boc protecting groups were introduced into oleyl amine to give acetyl protected oleylamine **74** and t-Boc protected oleylamine **75**.

Z-N-(Octadec-9-en-1-yl)acetamide (74)[147]



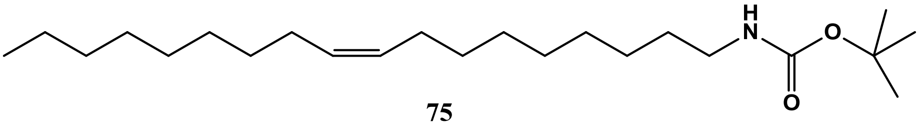
74

A flame dried Schlenk tube equipped with a magnetic stirrer bar was charged with oleylamine (267 mg, 0.995 mmol) and acetic anhydride (125 mg, 1.224 mmol) under inert atmosphere of nitrogen. The reaction mixture was stirred at room temperature for 10 min. Afterwards the reaction mixture was poured into 5 cm^3 of cold water and was extracted three times with dichloromethane. The organic phases were dried over Na_2SO_4 and volatiles were removed under vacuum. Drying under vacuum released pure **74** as a pale yellow wax. Yield: 302 mg (98 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.52 (bs, 1H, NH), 5.33 (bm, 1.96H, -C*H*=C*H*-), 3.21 (q, 2.25H, CH_2-N), 2.08-1.88 (m, 7.35H, =CH-CH_2, NHCOCH_3), 1.48 (m, 2.39H, CH_2), 1.39-1.15 (m, 24.52H, CH_2), 0.87 (t, 3.65H, CH_3).

^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ = 169.9 (1C, NH*C*=O), 129.9, 129.8 (-*C*H=*C*H-) , 39.7, 31.9, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.3, 29.2,29.2, 27.2, 26.9, 23.4, 22.7, 14.1 (*C*H_3).

E-tert-Butyl octadec-9-enylcarbamate (75)



75

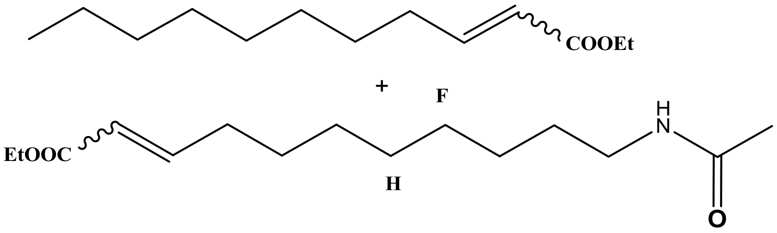
3.0 g Oleylamine (11.22 mmol) were dissolved in 100 mL $CHCl_3$, 1.8 mL triethylamine (Et_3N) were added and the mixture was cooled with an ice bath. Boc_2O (2.69g, 12.34mmol) was dissolved in 50 mL $CHCl_3$ and was added with a dropping funnel. The reaction mixture was stirred at room temperature over night. The next day the solvent was evaporated off and the residue was redissolved in ethylacetate. The mixture was washed 3 times with half-saturated brine and was than dried over Na_2SO_4. The solvent was removed under reduced pressure to give the product as a pale yellow oil. Yield (78%)

^{1}H-NMR of 75. (300 MHz, $CDCl_3$): δ = 5.34 (t, 2H, -C*H*=C*H*-); 3.10 (q, 2H, CH_2-N); 2.04-1.92 (m, 4H, =CH-CH_2, NHCOCH_3); 1.55 (m, 22H, CH_2) 1.44 (s, 9H, Boc-CH_3's); 0.88 (t, 3H, CH_3)

^{13}C-NMR: (δ, 20°C, $CDCl_3$, 75 MHz): 155.9 (1C, NHC(=O)); 129.9, 129.8 (2C); 78.9 (1C, OC(CH_3)); 40.6, 31.9, 30.9, 30.1, 29.7, 29.5, 29.4, 29.3, 29.2, 28.4 (3C, Boc), 27.4, 26.8, 22.7 and 14.1 (CH_3)

After protection of oleylamine with acetyl group the substrates **74.** Its cross metathesis was performed with ethyl acrylate. Previously used best reaction conditions and some reaction in presence of solvent like toluene were also performed to yield the complete cross metathesis products **F** and **H.** Results for the conversion of **74** with ethyl acrylate are given in table 3.6.

Typical procedure for cross metathesis of 74 with ethyl acrylate to yield ethyl undec-2-enoate (F) and ethyl 11-acetamidoundec-2-enoate (H)[147]



A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (5.00 g, 0.05 mol), BHT (11.2 mg, 0.05 mmol) and oleylamine (1.58 g, 0.005 mol) under inert atmosphere of nitrogen. According to Table 3.6 in some cases 5 cm^3 solvent were added. The reaction mixture was heated to temperature given in Table 3.6 and the catalyst (amount according to Table 3.6) was added. After the given time (*cf*. Table 3.6), volatiles was removed under reduced pressure and the residue was dried in vacuo. Conversions were checked by integration of the corresponding ^1H NMR spectra in $CDCl_3$.

^{1}H-NMR signals for the mixture of **F** and **H** (300 MHz, $CDCl_3$): δ = 7.01-6.88 (m, 1.5H, CO-CH=C*H*-CH_2-*trans*), 6.25-6.13 (m, 0.2H, CO-CH=C*H*-CH_2-*cis*), 5.84-5.70 (2x dd, 1.7H, CO-C*H*=CH-CH_2), 5.68-5.49 (bs, 0.9H, N*H*COMe) 4.17 (q, 3.4H, $COOCH_2CH_3$), 3.21 (q, 2H, CH_2NHCOMe), 2.17 (vq, 3H, CH=CH-CH_2), 1.95 (s, 3H, $NHCOCH_3$), aliphatic signals not listed, 0.87 (t, 3H, CH_3).

The optimized reaction conditions for cross metathesis of terminal olefins like and 1,9-decadiene and of olefins from renewable resources like methyl oleate and oleyl amine with ethyl acrylate to yield α-,β-unsaturated esters gave motivation to expand this studies towards other commercially available olefins. Cyclic olefins are important substrates to be applied in this regard because unstrained olefins like cyclopentene and cyclohexene are hard substrate for ring opening cross metathesis. Conversely cyclic olefins like cyclooctene and norbornene which are comparatively easy substrate for ROMP give polymers in such type of reactions so optimized reaction condition studies is also applied for the cross metathesis of different cyclic olefins with ethyl acrylate.

Typical Procedure for the cross-metathesis of cyclic olefins with ethyl acrylate to yield compounds 22-27[148]

A Schlenk tube equipped with a magnetic stirrer bar was charged with 1eq. of cyclic olefin and 5-10eq. of ethyl acrylate under inert atmosphere of nitrogen. The reaction mixture was heated to 45-60°C (oil bath temperature) and the catalyst **14** (0.1-1mol%) was added. After the given time of 16 hours conversion was checked by NMR and excess of ethyl acrylate and cyclic olefins were removed under reduced pressure and the residue was dried in vacuo.

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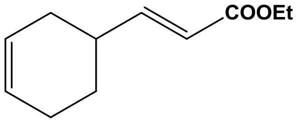
[148] Randl, S.; Connon, S. J.; Blechert, S. *Chem. Comm.* **2001**, 1796-1797.

Ethyl 3-(cyclohex-3-en-1-yl)acrylate (22)



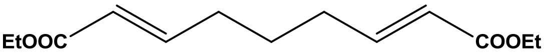
22

A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (5.00 g, 0.05 mol), and vinylcyclohexene (1.10 g, 0.01 mol) under inert atmosphere of nitrogen. The reaction mixture was heated to 60°C (oil bath temperature) and the catalyst **14** (7.24 mg, 0.011 mmol) was added. After the given time of 16 hours conversion was checked by NMR and excess of ethyl acrylate and vinylcyclohexene were removed under reduced pressure and the residue was dried in vacuo. Yield (82%)

^{1}H-NMR of 22. (300 MHz, $CDCl_3$): δ = 6.88–6.83 (m, 1H, –CH=C*H*–COO), 5.83–5.77 (d, 1H, –C*H*=CH–COO), 5.59 (s, 1H, CH_2-C*H*=C*H*-CH_2), 4.20-4.13 (q, 2H, –COOC$H_2$$CH_3$), 2.33 (m, 1H, CH_2-C*H*(CH=)CH_2), 2.09–2.02 (m, 2H, =CH–CH_2-CH), 1.91 (m, 2H, =CH–CH_2-CH), 1.77–1.52 (m, 2H, -CH_2-CH_2-CH-), 1,36 (t, 3H, -CH_3),

^{13}C-NMR of 22 (75 MHz, $CDCl_3$): δ = 168.4 (*C*OO), 152.9 (*C*H=CH–COO), 129.2 (*C*H=*C*H–COO), 121.3 (CH=*C*H–COO), 61.9 (COO*C*$H_2$$CH_3$), 37.8 (-*C*H(CH)-) 29.7, 26.4, 22.5 (CH_2), 14.09 (CH_3).

2*E*,7*E*-Diethyl nona-2,7-dienedioate(23)



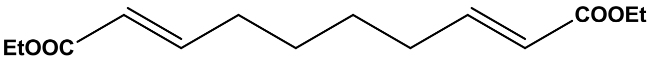
23

A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (5.00 g, 0.05 mol), and cyclopentene (0.34 g, 0.005 mol) under inert atmosphere of nitrogen. The reaction mixture was heated to 45°C (oil bath temperature) and the catalyst **14** (15.72 mg, 0.025 mmol) was added. After the given time of 16 hours conversion was checked by NMR and excess of ethyl acrylate and cyclopentene were removed under reduced pressure and the residue was dried in vacuo. Yield (88%)

^{1}H-NMR of 23. (300 MHz, $CDCl_3$): δ = 6.92–6.87 (m, 2H, –CH=C*H*–COO), 5.88–5.81 (d, 2H, –C*H*=CH–COO), 4.20-4.15 (q, 4H, $–COOCH_2CH_3$), 2.18–2.12 (m, 4H, $=CH–CH_2$-CH), 1.61-1.53 (m, 2H, $=CH_2–CH_2-CH_2$), 1,41 (t, 6H, $-CH_3$),

^{13}C-NMR of 23 (75 MHz, $CDCl_3$): δ = 166.4 (*C*OO), 149.3 (*C*H=CH–COO), 121.8 (CH=*C*H–COO), 60.2 ($COOCH_2CH_3$), 32.8, 29.8 (CH_2), 16.22 (CH_3).

2*E*,8*E*-Diethyl deca-2,8-dienedioate (24)



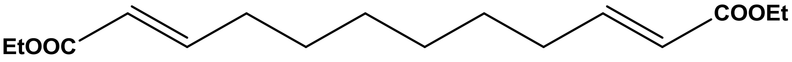
24

A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (5.00 g, 0.05 mol), and cyclohexene (0.40 g, 0.005 mol) under inert atmosphere of nitrogen. The reaction mixture was heated to 60°C (oil bath temperature) and the catalyst **14** (15.68 mg, 0.024 mmol) was added. After the given time of 16 hours conversion was checked by NMR and excess of ethyl acrylate and cyclohexene were removed under reduced pressure and the residue was dried in vacuo. Yield (75%)

^{1}H-NMR of 24. (300 MHz, $CDCl_3$): δ = 6.92–6.88 (m, 2H, –CH=C*H*–COO), 5.91–5.84 (d, 2H, –C*H*=CH–COO), 4.32-4.21 (q, 4H, $–COOCH_2CH_3$), 2.22–2.18 (m, 4H, $=CH–CH_2$-CH), 1.59-1.52 (m, 4H, $=CH_2–CH_2-CH_2$), 1,41 (t, 6H, $-CH_3$),

^{13}C-NMR of 24 (75 MHz, $CDCl_3$): δ = 168.2 (*C*OO), 152.3 (*C*H=CH–COO), 120.2 (CH=*C*H–COO), 61.9 ($COOCH_2CH_3$), 30.8, 28.9 (CH_2), 14.32 (CH_3).

2*E*,10*E*-Diethyl dodeca-2,10-dienedioate (25)[149]



25

A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (5.00 g, 0.05 mol), and cyclooctene (0.55 g, 0.005 mol) under inert atmosphere of nitrogen. The reaction mixture was heated to 60°C (oil bath temperature) and the catalyst **14** (3.72 mg, 0.005 mmol) was added. After the given time of 16 hours conversion was checked by NMR

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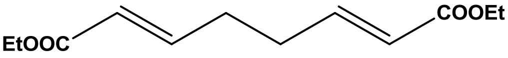
[149] Roey, S. J.; Legeay, J-C.; Aggarwal, P.; Stockman, R. A. *Chem. Commun.*, **2009**, 4399–4401.

and excess of ethyl acrylate and cyclooctene were removed under reduced pressure and the residue was dried in vacuo. Yield (88%)

^{1}H-NMR of 25. (300 MHz, $CDCl_3$): δ = 6.90–6.84 (m, 2H, –CH=C*H*–COO), 5.83–5.79 (d, 2H, –C*H*=CH–COO), 4.22-4.18 (q, 4H, $–COOC\mathit{H}_2CH_3$), 2.18–2.13 (m, 4H, $=CH–C\mathit{H}_2$-CH), 1,33 (t, 6H, $-CH_3$), 1.29-1.22 (m, 6H, $=CH_2–C\mathit{H}_2-CH_2$)

^{13}C-NMR of 25 (75 MHz, $CDCl_3$): δ = 165.9 (*C*OO), 151.2 (*C*H=CH–COO), 122.1 (CH=*C*H–COO), 61.29 ($COO\mathit{C}H_2CH_3$), 33.1, 20.9, 20.8, 20.7, 20.6, (CH_2), 13.68 (CH_3).

2*E*,6*E*-Diethyl octa-2,6-dienedioate (26)



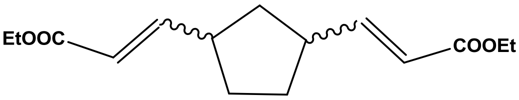
26

A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (5.00 g, 0.05 mol), and cyclooctadiene (0.53 g, 0.005 mol) under inert atmosphere of nitrogen. The reaction mixture was heated to 60°C (oil bath temperature) and the catalyst **14** (3.66 mg, 0.005 mmol) was added. After the given time of 16 hours conversion was checked by NMR and excess of ethyl acrylate and cyclooctadiene were removed under reduced pressure and the residue was dried in vacuo. Yield (43%)

^{1}H-NMR of 26. (300 MHz, $CDCl_3$): δ = 6.88–6.86 (m, 2H, –CH=C*H*–COO), 5.83–5.79 (d, 2H, –C*H*=CH–COO), 4.20-4.16 (q, 4H, $–COOCH_2CH_3$), 2.00–1.96 (m, 4H, $=CH–CH_2$-CH), 1,36 (t, 6H, $-CH_3$).

^{13}C-NMR of 26 (300 MHz, $CDCl_3$): δ = 166.5 (*C*OO), 148.3 (*C*H=CH–COO), 121.8 (CH=*C*H–COO), 60.29 ($COOCH_2CH_3$), 32.1 (CH_2), 14.6 (CH_3).

Diethyl 3,3'-(cyclopentane-1,3-diyl)diacrylate (27):



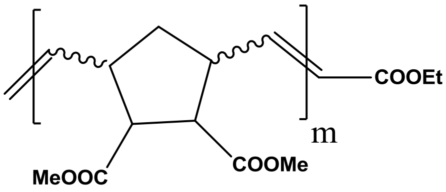
27

A Schlenk tube equipped with a magnetic stirrer bar was charged with (5.00 g, 0.05 mol), and norbornene (0.49 g, 0.005 mol) under inert atmosphere of nitrogen. The reaction mixture was heated to 60°C (oil bath temperature) and the catalyst **14** (3.77 mg, 0.005 mmol) was added. After the given time of 16 hours conversion was checked by NMR and excess of ethyl acrylate and norbornene were removed under reduced pressure and the residue was dried in vacuo. Yield (95%)

^{1}H-NMR of 27. (300 MHz, $CDCl_3$): δ = 6.88–6.86 (m, 2H, –CH=C*H*–COO), 5.83–5.78 (d, 2H, –C*H*=CH–COO), 4.20-4.16 (q, 4H, $–COOCH_2CH_3$), 2.19–2.13 (m, 2H, $=CH–CH_2-CH_2$), 1.64-1.59 (m, 3H, $=CH_2–CH_2-CH_2$) 1.33-1.29 (m, 6H, $=CH_2–CH_2-CH_2$), 1.33 (t, $-CH_3$).

^{13}C-NMR of 27 (75 MHz, $CDCl_3$): δ = 166.5 (*C*OO), 151.5 (*C*H=CH–COO), 123.4 (CH=*C*H–COO), 60.8 (COO*C*H_2CH_3), 45.31, 32.8 (CH_2), 41.28 (*C*H(CH_2)) 14.3 (s, CH_3).

Degradation of polymer 28 with ethyl acrylate[109]



A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (10.00 g, 0.10 mol), and *endo-,exo*-dimethyl bicyclo [2.2.1] hept-5-ene-2,3-dicaboxylate ester **28** (2.0 g) under inert atmosphere of nitrogen. The reaction mixture was stirred for 24 hours at room temperature for solubilizing 28 into ethyl acrylate after that the homogenous reaction mixture was heated to 80°C (oil bath temperature) and the catalyst **14** (7.35mg, 0.01mmol) was added. After stirring the reaction for 16hours at this temperature, reaction mixture was cooled down to room temperature and excess of ethyl acrylate was removed under reduced pressure and the residue was dried in vacuo. Number molecular weight 12,000 g/mol; PDI 1.7

^{1}H-NMR . (300 MHz, $CDCl_3$): δ = 6.88–6.86 (m, 2H, –CH=C*H*–COO), 5.83–5.78 (d, 2H, –C*H*=CH–COO), 4.20-4.16 (q, 4H, –COOC*H_2*CH_3), 2.19–2.13 (m, 2H, =CH–C*H_2*-CH_2), 1.64-1.59 (m, 3H, =CH_2–C*H_2*-CH_2) 1.33-1.29 (m, 6H, =CH_2–C*H_2*-CH_2), 1.33 (t, -C*H_3*).

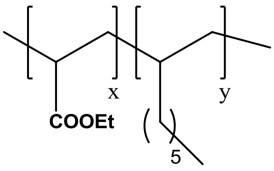
Degradation of natural rubber 29 with ethyl acrylate

A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (10.00 g, 0.10 mol), and natural rubber (2.0 g, 0.005 mmol) under inert atmosphere of nitrogen. The reaction mixture was stirred for 24 hours at room temperature for solubilizing the natural rubber into ethyl acrylate after that the homogenous reaction mixture was heated to 80°C (oil bath temperature) and the catalyst **14** (7.35mg, 0.01mmol) was added. After stirring the reaction for 16hours at this temperature, reaction mixture was cooled down to room temperature and excess of ethyl acrylate was removed under reduced pressure and the residue was dried in vacuo. Molecular weight 5,000 PDI 2.1.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.97 (s, OOCCH=CHCOO) 6.88 (s, MeC=C*H*–COO), 5.12 (s, –C*H*=CH–), 4.28-4.15 (q, –COOC*H*$_2$CH$_3$), 2.26, 1.96, 1.67, 1.47, (s, CMe–C*H*$_2$-C), 1.21-1.09 (t, -C*H*$_3$)

When performing the cross metathesis reaction at higher temperatures some unwanted polymers were formed these polymers appeared in precipitates which were evaluated later in details. Following is the procedure give for formation of these polymers via cross metathesis route of 1-octene with ethyl acrylate and characteristics of this polymer is also given.

Copolymerization of ethyl acrylate and 1-octene to yield 30



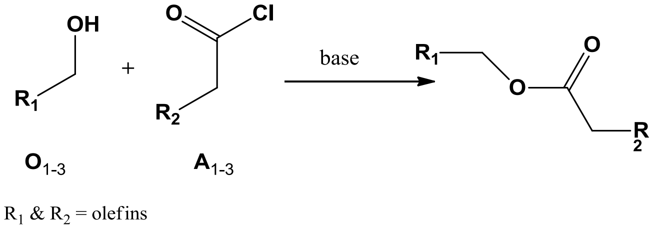
30

A Schlenk tube equipped with a magnetic stirrer bar was charged with ethyl acrylate (5.00 g, 0.0499 mol) and 1-octene (1.22 g, 0.00998 mol) under inert atmosphere of nitrogen. The reaction mixture was heated to 100°C (oil bath temperature) and the catalyst **14** (1.30 mg, 0.00198 mmol) was added. The Schlenk tube was closed with a glass cap which was not opened until the gel type polymer appeared. Afterwards, the reaction mixture was concentrated under reduced pressure in order to remove excess of ethyl acrylate and washed threee times with cyclohexane. The polymer was dried again to remove all the volatiles and octene to acrylate ratios were determined by NMR. Yield (72%)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.03 (s, C*H*$_2$OOC) 6.88 2.02, 1.84, 1.58, (s, –C*H*$_2$-), 1.20-1.16 (t, -C*H*$_3$), 0.81 (t, -CH$_3$)

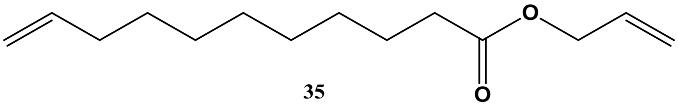
For the synthesis of ALTMET polymers various olefins either prepared in laboratory or available from commercial resources were used. The substrates **31-34** and **41-43** were purchased from commercial resource while compounds **35-40** were synthesized in laboratory according to standard procedure given below.

General reaction procedure for the synthesis of 35-40 & 44:



The condensation with various alcohols (**O**$_{1\text{-}3}$) was made with chloro substituted terminal olefin substrates (**A**$_{1\text{-}3}$) while triethylamine **NEt$_3$** was used as base. (**A**$_{1\text{-}3}$) dissolved in 20mL dry CH_2Cl_2 was added drop wise over a time of 15 min at 0°C to the reaction mixture of alcohol (**O**$_{1\text{-}3}$) and base **NEt$_3$** in 50mL of dry CH_2Cl_2 in 250ml three-necked flask. The whole procedure was done under inert atmosphere of argon. The reaction mixture was allowed to warm to room temperature and was stirred for 5hrs. Afterwards volatiles were removed and product from residue was purified by solvent extraction and/or using column chromatography to give pure compounds 35-40.

Allyl undec-10-enoate(35)[150]



35

Allyl alcohol **O**$_1$ (1.16 g, 20 mmol, 1 eq.) and 10-undecenoyl chloride **A**$_1$ (4.00 g, 19.73 mmol, 0.99 eq.) with triethylamine **NEt$_3$** (2.59 g, 25.34 mmol, 2.53 eq.) yield dry residue (7.33 g) TLC indicated the presence of only 2 spots. Residue was dissolved in ethyl acetate EE and extracted H_2O/EE organic layer was three times washed with water and dried with Na_2SO_4. The final product allyl undec-10-enoate (35) was dried in vacuum. Yield: 3.92 g of a slightly yellow oil (94.7 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.92−5.67 (m, 2H, $CH_2{=}C\mathit{H}CH_2$), 5.28−5.15 (m, 2H, $C\mathit{H}_2{=}CHCH_2O$), 4.96-4.84 (t, 2H, $C\mathit{H}_2{=}CHCH_2$) 4.52-4.49 (d, 2 H, $COOC\mathit{H}_2CH_2$), 2.29-2.24 (t, 2H, $C\mathit{H}_2COOCH_2$), 1.98-1.96 (q, 2H, $={CHC\mathit{H}_2CH_2}$), 1.59-1.54 (m, 2H, $COCH_2C\mathit{H}_2CH_2$), 1.27 (s, 10 H, $C\mathit{H}_2$).

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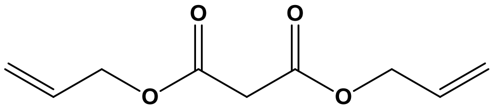
[150] Lee, C.W.; Grubbs, R. H. *J. Org. Chem.* **2001,** *66,* 7155-7158

Diallyl malonate (36)[151]

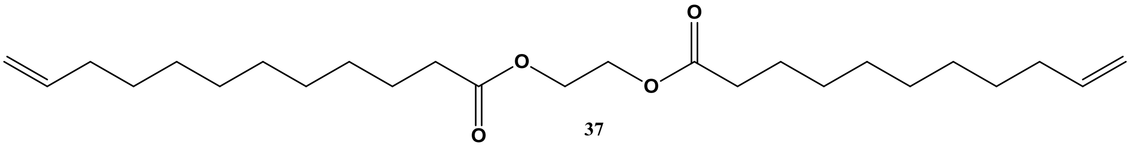


36

Allyl alcohol **O**$_1$ (1.16 g 20 mmol 2.01 eq.) and malonyl chloride **A**$_2$ (1.40 g 9.93 mmol 1.00 eq.) with triethylamine **NEt**$_3$ (4.00 g, 39.13 mmol, 3.94 eq.) yield dry residue (5.29 g). TLC indicated the presence of 3 spots. Residue was dissolved in ethyl acetate EE and extracted H_2O/EE organic layer was three times washed with water and dried with Na_2SO_4. The final product diallyl malonate **36** was purified by column chromatography 10% EE was used in Cy. Rf=0.64 dried in vacuum. Yield: 1.42 g of a brown oil (77.2%).

^{1}**H-NMR** (300 MHz, $CDCl_3$): δ = 5.99−5.97 (m, 2 H, CH_2=C*H*CH_2), 5.42−5.19 (m, 4 H, C*H*$_2$=$CHCH_2O$), 4.59-4.40 (d, 4H, CHC*H*$_2$O) 3.39(s, 2 H, COC*H*$_2$COO).

2-(Undec-10-enoyloxy)ethyl dodec-11-enoate Substrate (37)[152]



37

Ethane diol **O**$_2$ (0.62 g, 10 mmol, 1 eq.) and 10-undecenoyl chloride **A**$_1$(4.00 g, 19.73 mmol, 1.97 eq.) with triethylamine **NEt**$_3$ (3.00 g, 29.35 mmol, 2.93 eq.) yield dry residue (6.85 g). TLC indicated the presence of only 3 major spots. Residue was dissolved in ethyl acetate EE and extracted H_2O/EE organic layer was three times washed with water and dried with Na_2SO_4. The final product 2-(undec-10-enoyloxy)ethyl dodec-11-enoate (**37**) was purified by column chromatography 5% EE was used in Cy. Mono and di substituted products were isolated with Rf_1=0.33 and Rf_1=0.56 dried in vacuum. Yield: 2.16g of a light yellow oil (49.27%).

^{1}**H-NMR** (300 MHz, $CDCl_3$): δ = 5.91−5.77 (m, 2H, CH_2=C*H*CH_2), 5.06−4.93 (t, 4H, C*H*$_2$=$CHCH_2O$), 4.30 (s, 4H, OC*H*$_2$C*H*$_2$O) 4.52-4.49 (d, 2H, COOC*H*$_2$$CH_2$), 2.38-2.33 (t, 4 H, C*H*$_2$$COOCH_2$), 2.08-2.06 (q, 4H, =CHC*H*$_2$$CH_2$), 1.68-1.63 (m, 4H, $COCH_2$C*H*$_2$$CH_2$), 1.27 (s, 20 H, C*H*$_2$).

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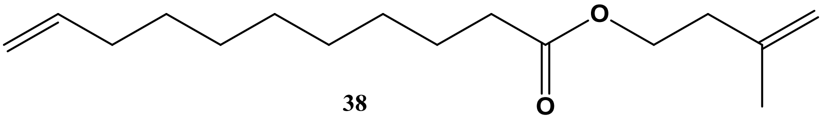
[151] Imao, D.; Itoi, A.; Yamazaki, A.; Ohta, T.; Ito, Y. *J. Org. Chem.* **2007**, *72*, 1652-1658

[152] Lyon, C. K.; Garret, V.H. *AOCS Meeting, Los Angeles* **1972**.

3-Methylbut-3-en-1-yl undec-10-enoate Substrate (38)[153]

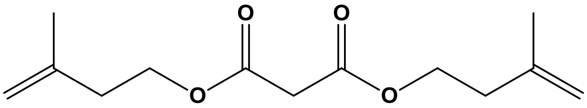


38

3-Methylbut-3-en-1-ol **O**$_3$ (1.66 g, 19.30 mmol, 1 eq.) and 10-undecenoyl chloride **A**$_1$(4.00 g, 19.73 mmol, 1.02 eq.) with triethylamine **NEt$_3$** (2.50 g, 24.46 mmol, 1.26 eq.) yield dry residue (7.09 g). TLC indicated the presence of only 2 spots. Residue was dissolved in ethyl acetate EE and extracted H_2O/EE organic layer was three times washed with water and dried with Na_2SO_4. The final product 3-methylbut-3-en-1-yl undec-10-enoate (**38**) was purified by column chromatography 33% EE was used in Cy. The product was isolated (Rf=0.65) and dried in vacuum. Yield: 4.32g of a light yellow oil (87.80%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.78−5.69 (m, 2H, CH_2=C*H*CH_2), 4.95−4.87 (m, 2H, C*H*$_2$=CHCH_2O), 4.84-4.66 (d, 2H, C*H*$_2$=CHMe) 4.15-4.09 (m, 2H, COOC*H*$_2$$CH_2$), 2.26-2.19 (m, 4H, C*H*$_2$C=C), 1.98-1.93 (q, 2H, C*H*$_2$COOCH_2),), 1.69 (s, 3H, CH_2=CC*H*$_3$) 1.56-1.51 (m, 2H, COCH_2C*H*$_2$$CH_2$), 1.29 (s, 10 H, C*H*$_2$).

Bis(3-methylbut-3-en-1-yl) malonate Substrate (39)



39

3-Methylbut-3-en-1-ol **O**$_3$ (1.60 g, 18.60 mmol, 1.94 eq.) and malonyl chloride **A**$_2$ (1.35 g, 9.57 mmol, 1.00 eq.) with triethylamine **NEt$_3$** (5.00 g, 48.92 mmol, 5.11 eq.) yield dry residue (6.82 g). TLC indicated the presence of 3 major spots. Residue was dissolved in ethyl acetate EE and extracted H_2O/EE organic layer was three times washed with water and dried with Na_2SO_4. The final product bis(3-methylbut-3-en-1-yl) malonate (39) was purified by column chromatography 5% EE was used in Cy. 2.01 g of a light yellow oil (68.13%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.74−4.67 (d, 4H, C*H*$_2$=CMe), 4.21-4.17 (m, 2H, CH_2C*H*$_2$O), 2,31-2.27 (m, 4H, CH_2C*H*$_2$CMe), 2.26-2.19 (m, 4H, C*H*$_2$C=C), 1.69 (s, 6H, CH_2=CC*H*$_3$).

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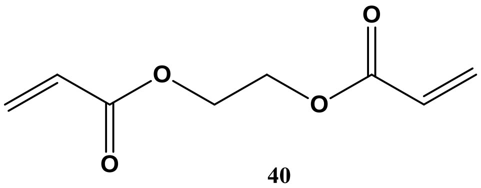
[153] Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. Eur. J.* **2001**, 7, 15, 3236-3253.

Ethane-1,2-diyl diacrylate Substrate (40):

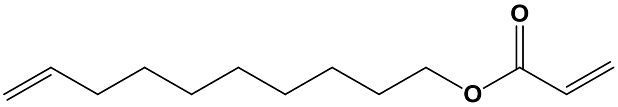


40

Ethane diol **O_2** (1.58 g 10 mmol 1 eq.) and acrolyl chloride **A_3** (2.25 g 19.73 mmol 1.97 eq.) with triethylamine **NEt_3** (5.00 g, 48.92 mmol, 5.11 eq.) yield dry residue (6.85 g). TLC indicated the presence of only 3 major spots. Residue was dissolved in ethyl acetate EE and extracted H_2O/EE organic layer was three times washed with water and dried with Na_2SO_4. The final product **40** was purified by column chromatography 5% EE was used in cyclohexane Cy. Mono and di substituted products were isolated with Rf_1=0.33 and Rf_1=0.56 dried in vacuum. Yield: 2.16g of a light yellow oil (49.27%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.91−5.77 (m, 2H, $CH_2=C\mathit{H}CH_2$), 5.06−4.93 (t, 4H, $C\mathit{H_2}=CHCH_2O$), 4.30 (s, 4H, $OC\mathit{H_2}C\mathit{H_2}O$) 4.52-4.49 (d, 2H, $COOC\mathit{H_2}CH_2$), 2.38-2.33 (t, 4H, $C\mathit{H_2}COOCH_2$), 2.08-2.06 (q, 4 H, $=CHC\mathit{H_2}CH_2$), 1.68-1.63 (m, 4H, $COCH_2C\mathit{H_2}CH_2$), 1.27 (s, 20H, $C\mathit{H_2}$).

Dec-9-en-1-yl acrylate (44)[154]



44

Undecenyl alcohol **O_6** (3.16 g 20.02 mmol 1 eq.) and acrolyl chloride **A_3** (1.81 g 20.00 mmol 1 eq.) with triethylamine **NEt_3** (2.40 g, 22.00 mmol, 1.10 eq.) yield dry residue (3.95 g). TLC indicated the presence of only 2 spots. Residue was dissolved in ethyl acetate EE and extracted H_2O/EE organic layer was three times washed with water and dried with Na_2SO_4. The final product allyl undec-10-enoate (**44**) was dried in vacuum. Yield: 3.62 g of a slightly yellow oil (85.17 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.27-6.25 (d, 1H, $–C\mathit{H_2}=CH–COO$), 6.05-6.03 (t, 1H, $–CH_2=C\mathit{H}–COO$), 5.83–5.77 (m, 1H, $CH_2–C\mathit{H}=CH_2$), 5.59 (d, 1H, $–C\mathit{H_2}=CH–COO$), 5.09-

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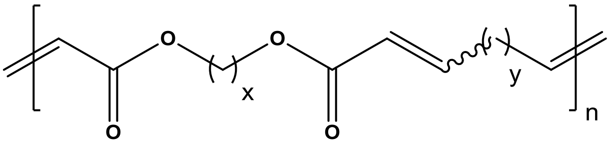
[154] Abbas, M.; Wappel, J.; Slugovc, C. *Macromolecular Symposia,* **2012**, *311*, 122-125.

5.02 (m, 1H, CH_2–C*H*=CH_2), 4.16 (s, 2H, –$COOCH_2$), 2.19–2.17 (m, 2H, CH_2–CH=CH–$COOCH_2$), 1,62 (m, 2H, CH_2), 1,29 (m, 10H, CH_2).

General Procedure for ALTMET polymerization of (31-39) with (40-42)

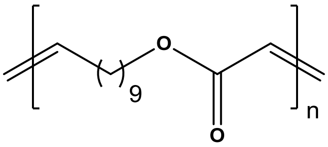


In an oven dried Schlenk tube (10mmol, 1eq) of diolefin or cyclic olefin (**31-39**) and (10mmol 1 eq.) diacrylate or dimethacrylate (**40-42**) were added with 1ml of Dichloromethane and later 1mol% of catalyst **11** was added into the reaction vessel. The reaction mixture was heated at 45° for 4hrs under Argon and sample was taken for NMR. The product was dried under vacuum and results showed different products as a thick polymer.

*Specimen NMR of polymer from monomers **31** and **41** with 1mol% catalyst loading of **11***

^{1}H-NMR (300 MHz, $CDCl_3$): δ =6.97–6.92 (m, 1H, –CH=C*H*–COO), 5.82–5.77 (d, 2H, –C*H*=CH–COO), 4.16-4.12 (t, 4H, –COOCH_2), 2.19–2.17 (m, 4H, CH_2–CH=CH–$COOCH_2$), 1.74 (m, 4H, CH_2), 1,52-1.31 (m, 8H, CH_2).
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.73 (s, –*C*OO), 149.55 (s, –CH=*C*H–$COOCH_3$), 121.15 (s, –*C*H=CH–$COOCH_3$), 63.75 (s, *C*H_2–CH=CH–COO), 32.18, 28.95, 27.91, 25.43 (s, CH_2). Mn=29910, PDI=1.882.

General Procedure for ALTMET polymerization of 44:



In an oven dried Schlenk tube (10mmol, 1eq) of **44** was added with 1ml of Dichloromethane and later different loadings of catalyst **1** or **2** (*cf.* **table 3.8**) was added into the reaction vessel. The reaction mixture was heated at 45° for 4hrs under Argon and sample was taken for NMR.

The product was dried under vacuum and results showed different products as a thick polymer.

NMR of the polymer obtained from monomer **44** with 1mol% **2**.

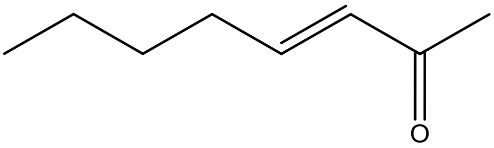
^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.92–6.88 (m, 1H, –CH=CH–COO), 5.83–5.77 (d, 1H, –CH=CH–COO), 4.16 (s, 2H, –$COOCH_2$), 2.19–2.17 (m, 2H, CH_2–CH=CH–$COOCH_2$), 1,62 (m, 2H, CH_2), 1,29 (m, 10H, CH_2),

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 165.88 ($COOCH_3$), 140.22 (CH=CH–COO), 120.51 (CH=CH–COO), 63.55 (CH=CH–COO), 29.8 (CH_2), M_n = 19910; PDI = 3.0

Chapter 4- Experimental

Firstly to optimize reaction conditions with terminal olefins with methyl vinyl ketone, 1-hexene was chosen and its cross metathesis in different solvent concentration of ether was evaluated than with optimized concentration of 0.2M activity of different catalyst was studied. Product **47** produced via cross metathesis under one typical reaction is given below: (entry 10, table 4.2)

(E)-Oct-3-en-2-one



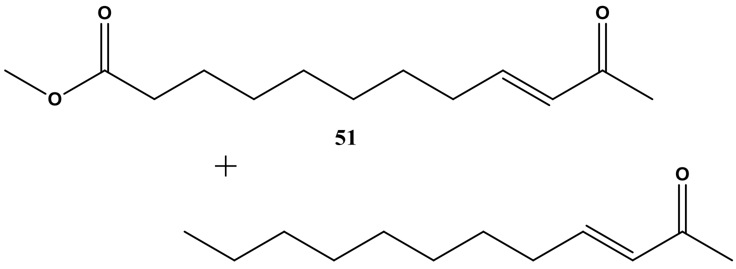
47

A Schlenk tube equipped with a magnetic stirrer bar was charged with methyl vinyl ketone (2.10 g, 0.0299 mol), CuI (57 mg 0.29 mmol) and 1-hexene (0.84 g, 0.00998 mol) were added in 5mL of dried diethyl ether under inert atmosphere of nitrogen. The reaction mixture was heated to 35°C (oil bath temperature) and the catalyst **46** (4.40 mg, 0.00512 mmol) was added. The Schlenk tube was closed with a glass cap which was not opened until the indicated time. The consumption of olefin 1-hexene was monitored by TLC and by NMR of the reaction mixture. Afterwards, the reaction mixture was concentrated under reduced pressure in order to remove excess of methyl vinyl ketone and 1-hexene and a sample for NMR measurement was taken. In case of full conversion yield was determined by adding the ethyl vinyl ether into the reaction mixture and passing the reaction mixture over a short silica gel column using cyclohexane as a solvent. Drying of the appropriate fractions gave the product **47** as colorless oil with bitter almond smell. More than 90% yield of the cross metathesis products **47** were obtained in all cases where full conversion was observed by NMR.

^{1}H-NMR (300 MHz, $CDCl_3$): d =6.73–6.66 (m, 1H, $–CH=CH–COCH_3$), 6.02–5.97 (d, 1H, $–CH=CH–COCH_3$), 2.12-2.06 (t, 3H, $–COCH_3$), 2.12–2.06 (m, 2H, $CH_2–CH=CH$), 1.39-1.04 (m, 4H, CH_2), 0.82-0.64 (7, 3H, CH_3).

In the next step, methyl oleate was chosen to study the cross metathesis of methyl vinylketone with internal olefins. Optimized reaction conditions were maintained according to same procedure as followed in 1-hexene case (cf. **table 4.1** and **4.2**)

E-Methyl 11-oxododec-9-enoate (51) and *E*-dodec-3-en-2-one (52)



51

+

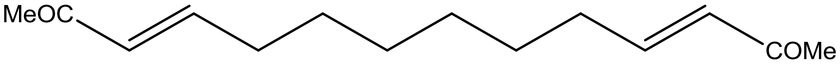
52

A Schlenk tube equipped with a magnetic stirrer bar was charged with methyl vinyl ketone (2.10 g, 0.0299 mol), CuI (2.85 mg 0.0145 mmol) and methyl oleate (1.50 g, 0.00506 mol) were added in 10mL of dried diethyl ether under inert atmosphere of nitrogen. The reaction mixture was heated to 35°C (oil bath temperature) and the catalyst **46** (2.20 mg, 0.00231 mmol) was added. The Schlenk tube was closed with a glass cap which was not opened until the indicated time. The consumption of methyl oleate was monitored by TLC and by NMR of the reaction mixture. Afterwards, the reaction mixture was concentrated under reduced pressure in order to remove excess of methyl vinyl ketone and a sample for NMR measurement was taken. Drying of the appropriate fractions gave the product mixture **51** and **52** as colorless oil. For conversions with different catalysts (*cf.* T**able 4.3**)

^{1}H-NMR of 51 and 52 (300 MHz, $CDCl_3$): d =6.76–6.68 (m, 2H, $–CH=CH–COCH_3$), 6.02–5.97 (d, 2H, $–CH=CH–COCH_3$), 3.59 (s, 3H, CH_3), 2.20-2.06 (t, 8H, $–CH_2$), 2.11 (m, 3H, $CH_3–CH_2$), 1.40-1.37 (m, 2.5H CH_2) 1.25-1.21 (m, 2H, CH_2), 1.21-1.18 (m, 17H, CH_2), 0.83-0.79 (m, 3H, $-CH_3$).

The scope of these studies was further expanded to easily available commercial olefins like 1,9-decadiene and cyclic olefins. Norbornene as previously used in cross metathesis with acrylate and living polymers like natural rubber **29** and poly(norbornene)ester **28** were excluded from these studies due to poor solubility in ether.

3*E*,11*E*-Tetradeca-3,11-diene-2,13-dione (53):

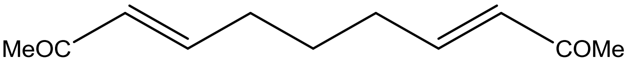


53

A Schlenk tube equipped with a magnetic stirrer bar was charged with methyl vinyl ketone (2.10 g, 0.0299 mol), CuI (5.7 mg, 0.029 mmol) and 1,9-decadiene (0.70 g, 0.00501 mol) were added in 5mL of dried diethyl ether under inert atmosphere of nitrogen. The reaction mixture was heated to 35°C (oil bath temperature) and the catalyst **46** (2.20 mg, 0.00231 mmol) was added. The Schlenk tube was closed with a glass cap which was not opened until the indicated time. The consumption of olefin was monitored by TLC and by NMR of the reaction mixture. Afterwards, the reaction mixture was concentrated under reduced pressure in order to remove excess of methyl vinyl ketone and 1,9-decadiene and a sample for NMR measurement was taken. Yield (98%)

^{1}H-NMR (300 MHz, $CDCl_3$): d =6.73–6.52 (m, 2H, $–CH=CH–COCH_3$), 6.02–5.97 (d, 2H, $–CH=CH–COCH_3$), 2.2-2.0 (t, 6H, $–COCH_3$), 2.12–2.06 (m, 4H, $CH_2–CH=CH$), 1.39-1.04 (m, 8H, CH_2).

3*E*,8*E*-Undeca-3,8-diene-2,10-dione



54

A Schlenk tube equipped with a magnetic stirrer bar was charged with methyl vinyl ketone (2.10 g, 0.0299 mol), CuI (5.7mg 0.029 mmol) and cyclopentene (0.35 g, 0.00499 mol) were added in 5mL of dried diethyl ether under inert atmosphere of nitrogen. The reaction mixture was heated to 35°C (oil bath temperature) and the catalyst **46** (2.20 mg, 0.00231 mmol) was added. The Schlenk tube was closed with a glass cap which was not opened until the indicated time. The consumption of olefin was monitored by TLC and by NMR of the reaction mixture. Afterwards, the reaction mixture was concentrated under reduced pressure in order to remove excess of methyl vinyl ketone and 1-hexene and a sample for NMR measurement was taken. Yield: 82%

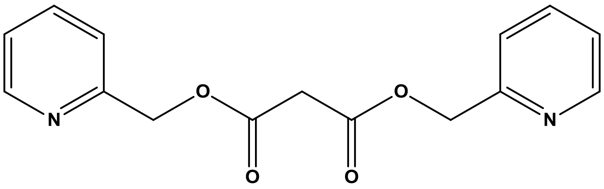
^{1}**H-NMR** (300 MHz, $CDCl_3$): d =6.82–6.69 (m, 2H, $–CH=CH–COCH_3$), 5.99–5.91 (d, 2H, $–CH=CH–COCH_3$), 2.2-2.0 (t, 6H, $–COCH_3$), 2.12–2.06 (m, 4H, $CH_2–CH=CH$), 1.39-1.04 (m, 2H, CH_2).

Cyclohexene yielded very little cross metathesis product under these reaction conditions while traces of polymers from cyclooctene were also observed.

Chapter 5 – Experimental

Studies of pyridine and poly ethoxy substituted diallyl substrate (**58** & **60**) were first time employed in our laboratory to analyse the RCM reactions.

Bis(pyridin-2-ylmethyl) malonate (57)[151]



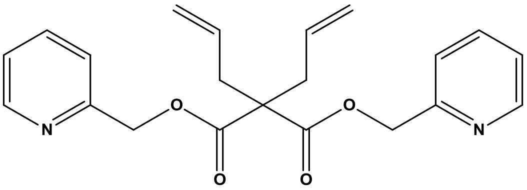
57

Pyridine-2-yl-methyl alcohol (1.10 g 10.17 mmol 2.04 eq.) and malonyl chloride A_2(0.70g, 4.97 mmol 1 eq.) with triethylamine **NEt_3** (1.10 g, 10.76 mmol, 2.16 eq.) yield dry residue (1.06 g). TLC indicated the presence of only 2 spots. The final product (1.2) was separated using column chromatography by pure Ethyl acetate dried in vacuum. Yield: 44.85% of slightly yellow oil.

^{1}H-NMR of 57. (300 MHz, $CDCl_3$): δ = 8.59−8.57 (d, 2 H, CH=C*H*N), 7.68-7.67 (t, 2H, CH=C*H*CH), 7.37-7.34 (d, 2 H, CHC*H*=C), 7.25-7.20 (t, 2 H, CHC*H*=CH), 5.31 (s, 4H, =CCH_2COO), 3.61 (s, 2H, COOCH_2COO).

^{13}C-NMR (75 MHz, CDCl3): 166.05 (s, –$COOCH_3$), 155.12 (s, –N=*C*CH) 149.51 (s, —N*CH*=CH), 136.88(s, –CH*CH*=CH), 123.05(s, –C*CH*=CH), 121.83 (s, –CH=CH–CH), 67.77 (s,O**C**H_2C=N), 41.41 (s, $COCH_2CO$).

Bis(pyridin-2-ylmethyl) 2,2-diallylmalonate (58)

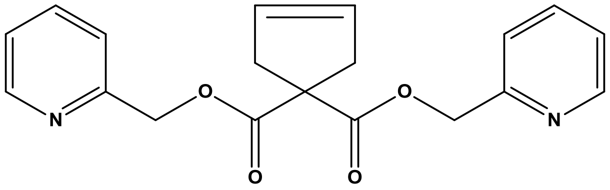


58

Pyridinyl malonic ester **57** (260 mg mmol 1 eq.) and allyl bromide (242mg, 4.97 mmol 1 eq.) with triethylamine **NaH** (100 mg, 10.87 mmol, 1 eq.) yield dry residue (1.06 g). TLC indicated the presence of 3 spots. The final product (1.12) was separated using column chromatography by pure ethyl acetate dried in vacuum. Yield: 77.3%

^{1}H-NMR of 58. (300 MHz, $CDCl_3$): δ = 8.55−8.53 (d, 2 H, CH=C*H*N), 7.64-7.57 (t, 2 H, CH=C*H*CH), 7.28-7.21 (d, 2 H, CHC*H*=C), 7.19-7.17 (t, 2 H, CHC*H*=CH), 5.75-5.61 (m, 2H, CH_2=C*H*CH_2), 5.26 (s, 2H, COOCH_2C=), 5.12-5.06 (d, 4H, CH_2=CHCH_2), 2.76-2.74 (d, 4H, CCH_2CH=C).

Bis(pyridin-2-ylmethyl) cyclopent-3-ene-1,1-dicarboxylate (59)

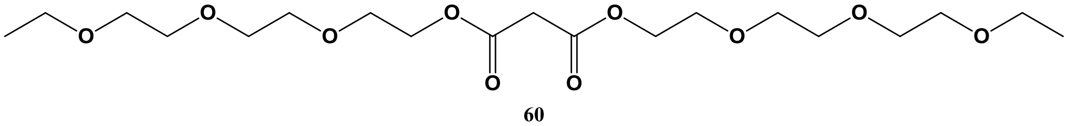


59

In an oven dried Schlenk flask 0.20 mmol of **58** was charged in DCM (0.2M) and 1mol% catalyst Neolyst **11** was added later on. Now the reaction was run for 4hrs at 45°C for DCM. The solvents were dried and sample was carried at different time intervals. When the reaction was complete two drops of ethyl vinyl ether were added to kill the excess catalyst and the reaction mixture was purified by column chromatography to get the pure cyclic products. Yield: 92%

^{1}H-NMR of 59. (300 MHz, $CDCl_3$): δ = 8.55−8.53 (d, 2 H, CH=C*H*N), 7.64-7.57 (t, 2 H,CH=C*H*CH), 7.28-7.21 (d, 2H, CHC*H*=C), 7.19-7.17 (t, 2H, CHC*H*=CH), 5.61 (s, 2H, CH_2=C*H*CH_2), 5.26 (s, 2H, COOCH_2C=), 5.12-5.06 (d, 4H, CH_2=CHCH_2), 2.96-2.88 (d, 4H, CCH_2CH=C).

Bis(2-(2-(2-ethoxyethoxy)ethoxy)ethyl) malonate (60)

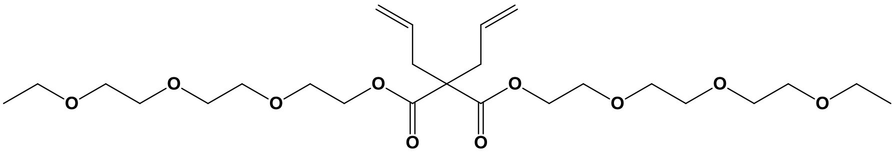


60

Triethylene glycol monoethyl ether alcohol (3.56 g 19.94 mmol 1.99 eq.) and malonyl chloride A_2(1.41g, 10 mmol 1 eq.) with triethylamine **NEt_3** (1.02 g, 10 mmol, 1 eq.) yield dry residue (4.86 g). TLC indicated the presence of only 2 spots. The final product (1) was separated using column chromatography by pure Ethyl acetate dried in vacuum. Yield: 3.11 g of slightly yellow oil (73.34%).

^{1}H-NMR of 60. (300 MHz, $CDCl_3$): δ = 4.31-4.28 (t, 4H, $COOCH_2CH_2$) 3.73-3.51 (m, 24 H, $CH_2OCH_2CH_2$), 3.45 (s, 2 H, $COCH_2CO$), 1.23-1.18 (t, 6 H, CH_2CH_3).

Bis(2-(2-(2-ethoxyethoxy)ethoxy)ethyl) 2,2-diallylmalonate (61):,

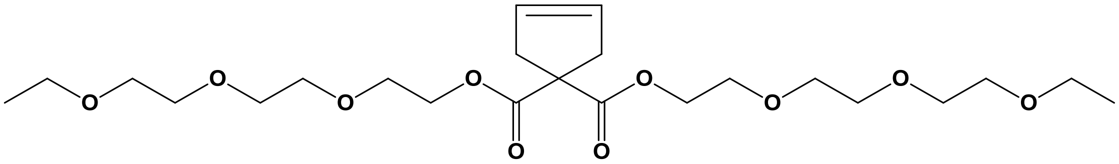


61

Triethylene glycol mono ethyl ether malonic ester X_1 (1.06 g mmol, 1 eq.) and allyl bromide (240mg, 4.97 mmol, 1 eq.) with triethylamine (200 mg, 10.87 mmol, 1 eq.) yielded a dry residue (1.06 g). TLC indicated the presence of 3 spots. The final product (1.12) was separated using column chromatography by 10% Ethyl acetate in cyclohexane and dried in vacuum. Yield: 0.48 g of a slightly yellow oil (69%).

^{1}H-NMR of 61. (300 MHz, $CDCl_3$): δ = 5.75-5.61 (m, 2H, CH_2=C*H*CH_2), 5.26 (s, 2H, $COOCH_2C$=), 5.12-5.06 (d, 4H, CH_2=$CHCH_2$), 4.31-4.28 (t, 4H, $COOCH_2CH_2$) 3.73-3.51 (m, 24 H, $CH_2OCH_2CH_2$), 3.45 (s, 2 H, $COCH_2CO$), 1.23-1.18 (t, 6 H, CH_2CH_3).

Bis(2-(2-(2-ethoxyethoxy)ethoxy)ethyl) cyclopent-3-ene-1,1-dicarboxylate(62)



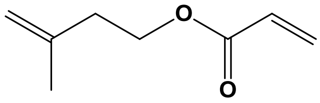
62

In an oven dried Schlenk flask 0.20 mmol of **61** was charged in DCM (0.2M) and 1mol% catalyst Neolyst **11** was added later on. Now the reaction was run for 4hrs at 45°C for DCM. The solvents were dried and sample was carried at different time intervals. When the reaction was complete two drops of ethyl vinyl ether were added to kill the excess catalyst and the reaction mixture was purified by column chromatography to get the pure cyclic products. Yield: 88%

In order to synthesize RCM products of various ring size various biolefinic substrates were used. Synthetic procedures of some of them is already mentioned in experimental section of previous chapter remaining are described here.

^{1}H-NMR of 62. (300 MHz, $CDCl_3$): δ = 5.62 (s, 2H, $CH_2=CHCH_2$), 5.22 (s, 2H, $COOCH_2C=$), 5.12-5.06 (d, 4H, $CH_2=CHCH_2$), 4.31-4.28 (t, 4H, $COOCH_2CH_2$) 3.73-3.51 (m, 24H, $CH_2OCH_2CH_2$), 3.45 (s, 2 H, $COCH_2CO$), 1.23-1.18 (t, 6 H, CH_2CH_3).

3-Methylbut-3-en-1-yl acrylate (63)

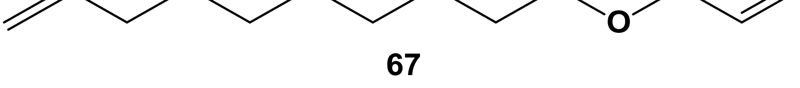


63

3-Methyl 3-ene 1-butanol O_3 (1.72 g 19.96 mmol 1 eq.) and acrolyl chloride A_3(1.80g, 19.88 mmol 1 eq.) with triethylamine **NEt_3** (2.10 g, 20.55 mmol, 1.03 eq.) yield dry residue (2.98 g). TLC indicated the presence of only 2 spots. The final product (1.3) was separated using column chromatography by 50% Ethyl acetate in cyclohexane dried in vacuum. Yield: 1.85g of a slightly yellow oil (66.07%).

^{1}H-NMR of 63. (300 MHz, $CDCl_3$): δ = 6.39-6.33 (d, 1H, $HCH=CH$), 6.12-6.02 (d, 1H, $CH_2=CH$),5.79-5.71 (t, 1H, $HCH=CH$), 4.77 (S, 1 H, $HCH=CMe$), 4.71 (S, 1 H, $HCH=CMe$), 4.26-4.21 (t, 2H, OCH_2CH_2) 2.36-2.32 (t, 2H, OCH_2CH_2CMe) 1.73 (s, 3H, CH_3).

1-Undecene allyl ether(67):

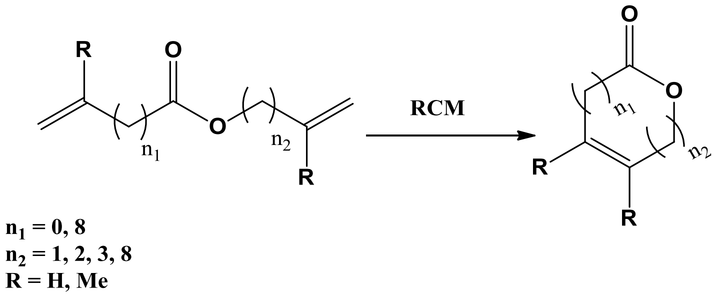


67

Undecenyl alcohol O_6 (3.16 g, 20.02 mmol, 1 eq.) and ally bromide A_4(1.18 g, 20.00 mmol, 1 eq.) with triethylamine **NEt_3** (3.00 g, 29.35 mmol, 1.49 eq.) yield dry residue (3.11 g). TLC indicated the presence of only 3 spots. Residue was dissolved in ethyl acetate EE and extracted H_2O/EE organic layer was three times washed with water and dried with Na_2SO_4. The final product allyl undec-10-enoate (5) was dried in vacuum. Yield: 3.62 g of a slightly yellow oil (85.17 %). final product was purified by column chromatography 10% ethyl acetate in cyclohexane.

After having a library of different diolefinic containing substrates their RCM was studied in different solvent concentration in presence of 1mol% of catalyst **11**. Only **63** gave high yields of RCM products remaining all olefins either substituted or ring forming of unfavorable size yielded only oligomers.

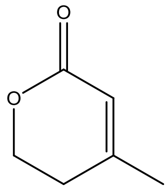
General Procedure of RCM for olefins 35-40, and 63-67



n_1 = 0, 8
n_2 = 1, 2, 3, 8
R = H, Me

In an oven dried Schlenk flask 0.20 mmol of one of the substrates **35-40** and **63-67** were charged in DCM or toluene (0.04-0.2M) and 1mol% catalyst Neolyst **11** was added later on. Now the reaction was run for 4hrs at 45°C for DCM and at 70°C for toluene. Solvents were dried and sample was carried at different time intervals. When the reaction was complete two drops of ethyl vinyl ether were added to kill the excess catalyst and the reaction mixture was purified by column chromatography to get the pure cyclic products. Cyclized products were only obtained from olefins **63** and **67**.

4-Methyl-5,6-dihydro-2H-pyran-2-one[155]



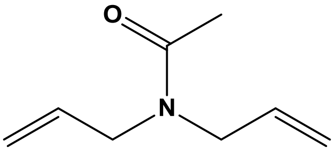
68

In an oven dried Schlenk flask 0.20 mmol of **63** were charged $CDCl_3$ (12M) and 1mol% catalyst Neolyst **11** was added later on. Now the reaction was run for 4hrs at 45^oC. The sample was carried at different time intervals. When the reaction was complete two drops of ethyl vinyl ether were added to kill the excess catalyst and the reaction mixture was purified by column chromatography to get the pure cyclic products.

^{1}**H-NMR of 68**. (300 MHz, $CDCl_3$): δ = 5.75 (s, 1H, $CH{=}C(CH_3)CH_2$), 4.33-4.29 (m, 2H, OCH_2CH_2) 2.33-2.9 (m, 2H, OCH_2CH_2CMe).

The ratio of RCM product to reacting substrate was calculated through NMR. RCM of **66** and **67** to yield **69** and **70** formed complex reaction mixture along with oligomers and polymers and was not separated from reaction mixture. The ratio of products was determined by NMR. Diallylamine was protected to yield the product **76** before using it in RCM.

N,N-Diallylacetamide (76)



76

In an oven dried Schlenk tube was charged with 0.01 mol of commercially available diallylamine was added and 0.012 mol of acetic anhydride and stirred the reaction for 5 minutes. Afterwards, the reaction mixture was poured in water and three times extracted with dichloromethane. The extracted fraction was dried to evaporate the excess solvent and 0.009 mol of acetylated diallylamine was formed. Yield: 92%

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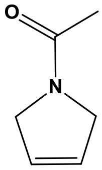
[155] White, J. D.; Avery, M. A.; Carter, J. P. J. Am. Chem. Soc. 1982, 104, 5486-5489.

^{1}H-NMR of 76. (300 MHz, $CDCl_3$): δ = 5.87-5.71 (m, 2H, CH_2=C*H*CH_2), 5.22-5.19 (m, 4H, NCH_2CH=CH_2), 3.87-3.71 (m, 4 H, CH_2NCH_2), 3.45 (s, 3 H, CH_3).

1-(2,5-Dihydro-1H-pyrrol-1-yl)ethanone (71)



71

In an oven dried Schlenk flask 0.20 mmol of **76** were charged $CDCl_3$ (12M) and 0.1 mol% catalyst Neolyst **14** was added later on. Now the reaction was run for 4hrs at 45°C. The sample was carried at different time intervals. When the reaction was complete two drops of ethyl vinyl ether were added to kill the excess catalyst and the reaction mixture was purified by column chromatography to get the pure cyclic products.

^{1}H-NMR of 71. (300 MHz, $CDCl_3$): δ = 5.75-5.62 (t, 2H, CH_2=C*H*CH_2), 3.27-3.22 (m, 4 H, CH_2NCH_2), 3.32 (s, 3 H, CH_3).

Chapter 6- Experimental

Typical procedure for synthesis of nanoparticles (72)

In a flame dried Schlenk tube silver nitrate (169.7mg, 1mmol) and oleylamine (2.81 g, 10mmol) were added under Argon and temperature was raised to 165 °C. After constantly stirring at this temperature for 30 minutes the reaction mixture was cooled down to room temperature and nanoparticles were precipitated in ethanol. Upon washing the nanoparticles three times with ethanol and drying in vacuum 230 mg of solid black nanoparticles were obtained.

Procedure for the preparation of nanoparticle containing pDCPD plates (73)

DCPD was heated to 30 °C in a water bath to melt it. 5 mg of the nanoparticles **(72)** were put into a glass vial and dissolved in 10 g of DCPD to give a homogenous brownish mixture. 4.7 mg **11** (0.005 mmol) were dissolved in 2 mL freshly degassed dichloromethane. 300 µL of the solution were put into a vial, 5 mL of the DCPD mixture were added with a syringe, thus perfectly mixing the batch. The prepared mould was filled with the mixture and left 10 min at room temperature to slowly start the polymerization. Then, it was put into a preheated oven at 60°C for 20 min. The mould was opened and the transparent, greyish pDCPD plate was removed and cut into 4x4 cm square.

Biological activities:

Antimicrobial studies performed at the ttz in Bremerhaven, according to Japanese industrial Standards (JIS)[136]

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Abbreviations

abs.	absolute
Ac	Acetyl
ADMET	Acyclic diene metathesis polymerization
ALARA	As low as reasonaboly acheivable
ALTMET	Alternating diene metathesis polycondensation
Ar	Aromatic
ax	axial
BHT	*ter*-butylated hydroxytoluene
Bn	Benzyl
Boc	*tert.*-Butyloxycarbonyl
Br	Bromo
Bu	Butyl
c	concentration
Cl	Chloro
°C	Degree Celsius
CM	Cross-metathesis
Cy	Cyclohexane or Cyclohexyl
d	dublett
DCPD	Dicyclopntadiene
DCM	Dichlormethane
DEDAM	Diethyl diallylmalonate
DMAP	4-Dimethylaminopyridine
DMF	*N*,*N*-Dimethylformamid
DMSO	Dimethylsulfoxid
EE	Ethyl acetate
ee	Enantiomeric excess
eq	equatorial
Et	Ethyl
Et_2O	diethyl ether
g	Gram
H	Hexane

hrs	hours
HR	High Resolution
Hz	Hertz
i	iso
I	Iodo
Imes	1,3-Bismesityl-dihydroimidazolidine-2-ylidene-carbene
IR	Infrared
J	Coupling constant
L	Ligand
m	multiplett
Me	Methyl
MeOH	Methanol
Mes	Mesityl
min	Minutes
Mn	Molecular weight
MOM	Methoxymethyl
MS	Mass spectrometry
MVK	methyl vinyl ketone
NHC	*N*-Heterocyclc Carbene
NMR	Nuclear Magnet Resonance
Np	Nanoparticles
NR	Natural Rubber
PCy_3	triphenyl cyclohexyl
pDCPD	poly(dicyclopentadiene)
PDI	poly dispersity index
PG	protecting group
Ph	Phenyl
ppm	parts per million
Py	Pyridine
q	Quartet
R	Rest
RCM	Ring closing metathesis
R*f*	Retention factor

RO/CM	Ring opening cross metathesis
ROIMP	Ring opening insertion metathesis polymerization
ROMP	Ring opening metathesis polymerization
Rt	Room temperature
RRM	Ring rearrangement metathesis
Ru	Ruthenium
s	Singulett
SHOP	Shell higher olefin process
SIMes	Saturated imidazolidine mesityl group
SIPr	Saturated imidazolidine *iso*-propoxy group
t	Triplett
tert	Tertiary
THF	Tetrahydrofuran
$Ti(i\text{-}OPr)_4$	Titanium isopropoxide
TON	Turn over number
Ts	Tosyl
-OEt	Ethoxy
-OMe	Methoxy
$\text{-O}^{i}\text{Pr}$	*iso*propoxy

Curriculam Vitae

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Current research

My current research interests lie in applying novel routes for the synthesis of nanoparticles using green chemical processes and in making olefin metathesis more sustainable. The main goal is to achieve environmentally benign reaction conditions with minimum cost implications. While working in these areas, I have contributed more than a dozen publications to international journals and in scientific meetings and conferences. A variety of organic molecules and polymers are developed in this regard and upon equipping selective polymers with silver nanoparticles valuable materials are also produced with special antimicrobial effects. Ruthenium based organometallic substrates are key precursors for olefin metathesis reactions. In this regard the studies have also been expanded to synthesis, characterization and application of such initiators.

Future prospective

For research and education current analysis would be applied in evaluation and understanding of advanced concepts in organic and material chemistry. Besides expanding our knowledge in synthesis and characterization of nanomaterials, their scope in medicinal, industrial and daily life use would also be considered. Similarly, metathesis reactions would be applied to olefins from natural and mineral resources like petro- and oleochemicals to produce valuable materials.

Technical skills

Followings are the major credentials of my previous work in the field of chemistry

- The synthesis of various organic and inorganic compounds with the help of both commercial and analytical grade chemicals by using *Schlenk technique* and other laboratory techniques. Completely neat, air and moisture free environment using *glove box technique* has also been applied for these syntheses.
- The qualitative and quantitative estimation of various components in a compound using various spectroscopic and other analytical techniques.
- Major spectroscopic techniques used for analysis like *UV-visible*, *Infra Red (IR)* and *FTIR* spectroscopy, *nuclear magnetic resonance (NMR)* and mass spectroscopic analysis using *MALDI* etc have also been used for the analysis of various substrates newly synthesized and already available in laboratory.
- The separation techniques like *sublimation*, *filtration*, *centrifugation* and various chromatographic techniques like *flash column chromatography* and *gel permeation chromatography (GPC)* for the separation of mixtures have also been used during the work in laboratory.

- For the detection of metal ions photometric techniques like flame photometry and UV-visible spectroscopic techniques have been used.
- A variety of techniques for the characterization of nanoparticles like *dynamic light scattering (DLS), Single electron microscopy (SEM)* and *transmission electron microscopy (TEM)* have also been applied.
- Advanced expertises are applied on personal computer applications like MS office. Besides literature searching tools like *Scopus* and scientific software like *Chemdraw* and for the evaluation of *NMR* spectra and other spectroscopic data evaluation available with equipments have also been used.

Projects and Fellowships

- **PhD fellowship** from *Higher education commission (HEC) Pakistan* under the program overseas phase II batch 1 for full study period.
- **Fellowship as research assistant** from E*uropean metathesis project (EUMET)* under FP7 program.

Teaching Experience

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- *TIU Institute, Lahore* (Affiliated with Riphah International University Islamabad), as **Lecturer** in pharmaceutical chemistry.
  The coaching of basic concepts of organic chemistry to the students especially the application of organic and pharmaceutical compounds in medicinal chemistry was part of my job in this lecture course. Analysis of various functional groups of organic molecules and synthesis of pharmaceutical drugs used in daily life was also established in laboratory.
- *Haleem Institute, Lahore,* as **Lecturer** in Chemistry.
  The teaching of chemistry to the students of secondary and higher secondary school certificate with local examination system and under examination system held by Cambridge has been conducted during this job.

Work Experience

Process Controller (Dyeing)	09-11-2004 to 01-08-2005	Angora Textile Pvt. Ltd. Lahore.

The maintenance of complete process of knitted fabric in dyeing section according to standard procedures including raw fabric testing, bleaching, washing, dyeing, and softening and after process the environmental control of waste was part of my job. The chemical addition and dyes recipe formation was also evaluated during my stay in Angora textile.

Academic Qualifications

2008- To date	PhD student Institute for Chemistry and Technology of Materials, Graz University of Technology, Graz, Austria
2004	MSc Chemistry University of the Punjab, Lahore, Pakistan
2002	BSc FC College, Lahore, Pakistan

Books and thesis

- MSc thesis with the title, *"Synthesis and studies of acid dyes and polyvinyl acetate"*.
- Editor of the book entitled *"Current objective chemistry for intermediate part II"* by Ghulam Nabi and Sons publishers, Urdu Bazar Lahore.

Membership in Professional Societies

Royal Society of Chemistry (RSC) with membership id.	486969
German Chemical Society (GDCh) with membership id.	100504
Austrian Chemical Society (GOeCh) with membership id.	27570
Chemical Society of Pakistan (CSP) with membership id.	P0380

Personal Information

Date of Birth	13 June 1983
Sex	Male
Marital Status	Single
Lingual Proficiency	English, German, Urdu
Nationality	Pakistani

List of Publications

1. Optimized reaction conditions for the cross-metathesis of methyl oleate and oleylamine with ethyl acrylate. Abbas, M.; Slugovc, C
 Monatsh. Chem. **2012**, *in press*.
2. "Alternating Diene Metathesis Polycondensation (ALTMET) – Opitimizing Catalyst Loading" Abbas, M.; Wappel, J.; Slugovc, C.: *Macromolecular Symposia*, **2012**, *311*, 122-125
 DOI: 10.1002/masy.201000095
3. "Optimization of cross metathesis reaction of oleochemicals with ethyl acrylate." Abbas, M.; Slugovc, C. *Chemické listy*, **2011**, *105*, S. s913 - s914.
4. "As low as reasonably achievable catalyst loadings in the cross-metathesis of olefins with ethyl acrylate."
 Abbas, M.; Slugovc, C. *Tetrahedron Lett.* **2011**, *52*, 2560-2562.
 DOI:10.1016/j.tetlet.2011.03.038
5. "Halide exchanged Hoveyda-type complexes in olefin metathesis."
 Wappel, J.; Urbina-Blanco, C. A.; Abbas, M.; Albering, J. H.; Saf, R.; Nolan S. P.; Slugovc, C. *Beilstein J. Org. Chem.* **2010**, *6*, 1091-1098. DOI: 10.3762/bjoc.6.125

Contribution in conferences for posters and oral presentations is also listed

6. Abbas, M.; Slugovc, C.:
 Synthesis of α-,β-unsaturated ketones by cross-metathesis of olefins with methyl vinyl ketone. - in: 10th International and 22nd National Chemistry Conference. Faisalabad on: 21.11.2011
7. Abbas, M.; Slugovc, C.:
 Designed Silver Nanoparticles as Key for Antimicrobially Equipping poly(Dicyclopentadiene). - in: Advances in Polymer Science and Technology (APST) 2 . Linz on: 28.09.2011
8. Abbas, M.; Slugovc, C.:
 Highly optimized catalyst loadings in cross metathesis of different olefins with ethyl acrylate. - in: 14. Österreichische Chemietage 2011. Linz on: 26.09.2011
9. Abbas, M.; Slugovc, C.:
 Reducing the environmental impact of olefin cross metathesis with acrylates. - in: 1st National Conference on Physical & Environmental Chemistry (PEC-2010). Peshawar on: 26.09.2010
10. Abbas, M.; Slugovc, C.:
 Optimization of cross metathesis reaction of oleochemicals with ethyl acrylate. - in: Chemistry and Life. Brno on: 14.09.2011
11. Abbas, M.; Slugovc, C.:
 Alternating Diene Metathesis Polymerization (ALTMET) – Optimizing Catalyst Loading. - in: 2nd Austrian Slovenian Polymer Meeting (ASPM). Leoben on: 08.09.2010
12. Abbas, M.; Slugovc, C.:
 New Polymerization by Alternating Diene Metathesis (ALTMET) With M2 Catalyst. - in: European Polymer Congress (epf'09). Graz on: 12.07.2009