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Ruthenium-based Catalysts for the Ring-Opening Metathesis Polymerization (ROMP) of Functionalized Cyclic Olefins

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SUMMARY: Recent developments in Ring-Opening Metathesis Polymerization (and copolymerization) of functionalized cycloolefins with well-defined ruthenium-based initiators are summarized and illustrated with synthesis of graft copolymers, telechelic and liquid crystalline polymers, glycopolymers and unsaturated ester-functionalized oligomers.

Historically, olefin metathesis has been studied extensively both in the context of polymer synthesis and from a mechanistic standpoint. Over the last decade, metathesis catalysts (or initiators) have evolved from poorly defined heterogeneous mixtures that characterized early systems to single component, single site initiators (no co-catalyst required) which react in a predictable way and can be fine tuned through simple ligand modification. Thanks to the emergence of these novel catalysts, olefin metathesis has recently emerged as a widely applicable synthetic method, both in polymer chemistry [1-3] and in fine organic synthesis.[4-7]

There are two types of polymerization process possible via metathesis. They both proceed via a [2 + 2] cycloaddition between a C=C double bond and a metal-carbene (or alkylidene) complex to give a metallacyclobutane intermediate. This step is then followed by a cycloreversion. When the C=C double bond is constrained within a ring, the newly formed C=C double bond remains attached to the metal center (Scheme 1).

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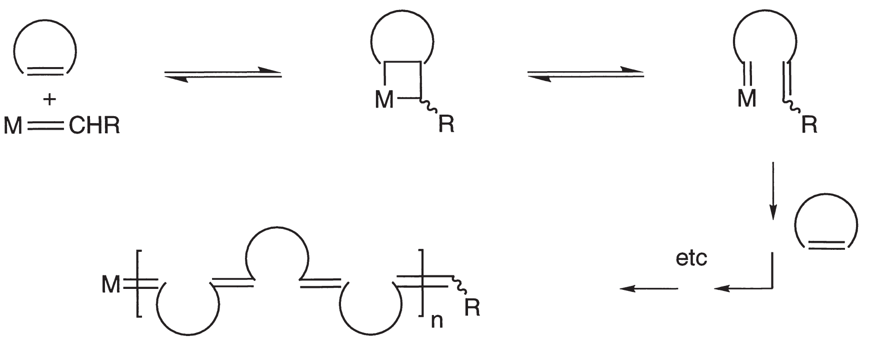
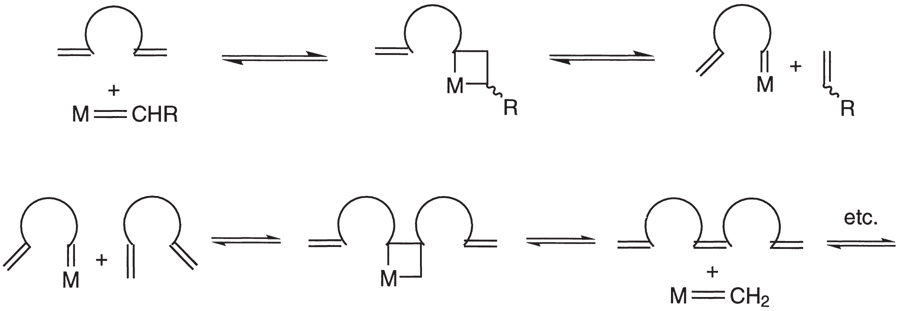


Scheme 1

This forms the basis of so-called *r*ing *o*pening *m*etathesis *p*olymerization (ROMP). With regard to monomers, the ability of cycloalkenes to undergo ROMP is primarily related to the difference in free energy between the ring and the chain structures. Thermodynamic datas indicate that for cycloalkenes from 3 to 8 and larger-membered compounds, the six-membered ring is the only one with a positive Δ*G*. Hence it does not undergo ROMP unless there is ring strain in the molecule due to bridging, as in the norbornene structure. As a rule, bicyclic and polycyclic olefins (e.g. dicyclopentadiene, DCPD), having a more negative Δ*G* of polymerization because of their increased ring strain, are especially prone to polymerize via ROM. Steric hindrance induced by substituents close to the double bond, and/or other geometric constrains are also important in determining the reactivity of a cycloolefin and the outcome of the polymerization.

The alternative reaction pathway, so-called *a*cyclic *d*iene *met*athesis or ADMET, involves a step-growth polymerization of α,ω-dienes with formation of a volatile olefin (usually ethene) as a by-product. Removal of this light product under vacuum drives the equilibrium towards



Scheme 2

the condensation process (Scheme 2).

Retention of unsaturation in the polymer backbone is one of the main features of metathesis polymerization, although there is usually little control of the double-bond stereochemistry. In many cases, the ROMP of strained cyclic olefins initiated by well-defined metal carbene complexes shows the characteristic features of a living polymerization and therefore block copolymers can be synthesized by sequential addition of different monomers.

In this short article which is in no way comprehensive, we illustrate some recent advances in the development of ROMP initiators with examples of applications from the literature and from our group.

The development of well-defined ROMP initiators has expanded the scope of the metathesis reaction, permitting the controlled polymerization of highly functionalized monomers. Historically, the first well-defined olefin metathesis initiators became available in the mid-1980s and were alkoxy imido complexes of tungsten and molybdenum of general formulaM(CHR)(NAr)$(OR')_2$.[8-9] The tungsten catalysts are more active than their molybdenum analogues but both type of initiators are very reactive towards polar functionalities, oxygen and water. Beside their thermal instability on storage and high cost of preparation, these early transition metal-based systems are therefore unsuitable for polymerizing monomers containing polar functional groups which results in the poisoning of the catalyst.

The search for catalysts more tolerant of polar functionalities involved a move towards late transition metals and culminated in the discovery of well-defined ruthenium-based initiators. The Ru-carbene complexes exhibit high reactivity (albeit lower than the best Mo- and W-based catalysts) in a variety of ROMP, RCM and ADMET processes while showing a remarkable tolerance towards many different organic functionalities. These initiators are stable for weeks and reactions can be carried out in the presence of air and humidity or even in water.

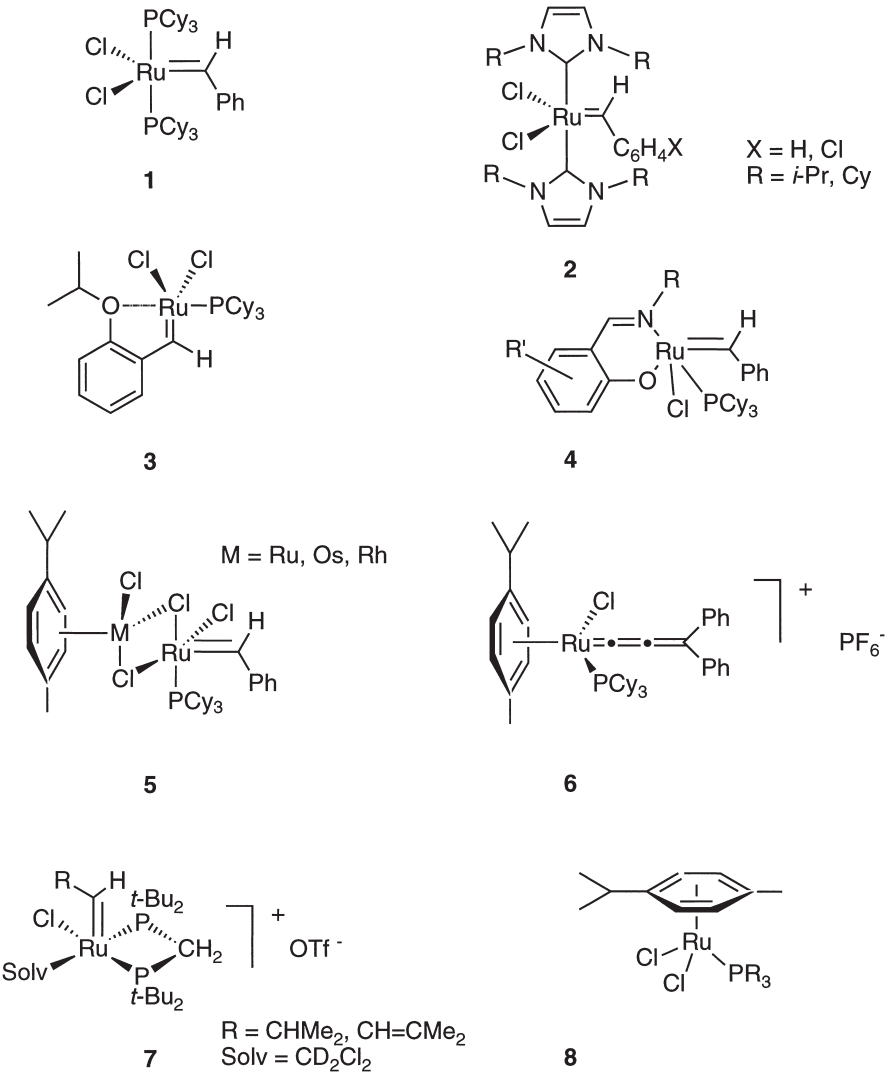
Grubbs-type square pyramidal Ru(II) carbene complexes with *trans*-phosphane ligands, of which commercially available ruthenium-benzylidene complex **1** (Scheme 3) is the archetype, have found numerous applications in ROMP and RCM. Mechanistic studies indicate that a phosphane reversibly dissociate from the metal center during metathesis. Attempts to improve catalyst performances have focused upon varying

- the carbene ligand, in order to improve the rate of initiation relative to propagation[10]

- the phosphane or/and the anionic ligands (chloride anions)[11]; by replacing one or both of the two *trans*-phosphines by Arduengo-type carbenes (**2** in Scheme 3).[12]

Further modifications of the parent structure **1** were accomplished

- by taking advantage of chelation, through formation of metal-oxygen bond (**3** in Scheme 3)[13] or with Schiff bases (**4** in Scheme 3)[14]
- by adding Lewis acids and by forming bimetallic (homo- and heterobimetallic) Ru-carbene complexes (**5** in Scheme 3)[15]



Scheme 3

Other variations were also made and the recently proposed cationic ruthenium-allenylidene complexes **6**[16], carbenes **7**[17] and carbynes[18] are certainly among the most promising ones.

Catalyst **7** is thermally stable in solution and appears to be the most active Ru(II) ROMP initiator described so far.

Related strategies for the generation of efficient ruthenium-carbene chemistry which have attracted attention due to potentially far reaching applications are the *in situ* preparation of well-defined species[19] and the development of one-component catalysts for thermal and photoinduced ring-opening polymerization (PROMP).[20-22] These two approaches take advantage of an arene displacement from ruthenium-arene complexes of type **8** (where PR_3 is usually tricyclohexylphosphine, PCy_3) to form highly coordinatively unsaturated species which promote the ROMP of cycloolefins. The scope of the reaction is however limited to strained olefins such as norbornene, as these species do not promote the polymerization of less strained cycloolefins such as cyclooctene. This drawback can be circumvented by addition of a catalytic amount of a diazocompound which acts as an activator, forming well-defined ruthenium carbene species *in situ.*[19] These polymerizations are however not living.

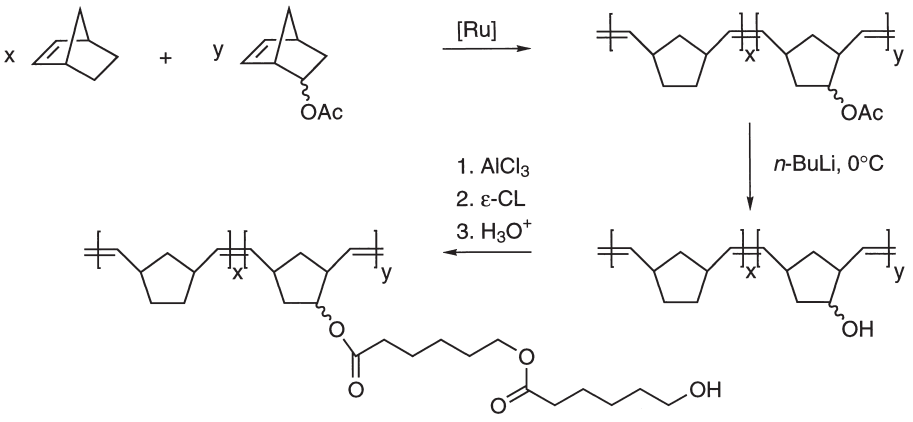
Other recent variations include ROMP in compressed carbon dioxide[23-24] and in water, including living polymerization using water-soluble aliphatic phosphanes.[25-26]

Selected applications

ROMP represents now a well-understood technique and the ruthenium-based systems often permit living polymerizations. "Living" in this context means that a controlled initiation takes place and that chain transfer as well as chain terminating reactions are absent (or more realistically are very limited) during propagation. This results in polymers with a low polydispersity and allows their stoichiometric design and the synthesis of block copolymers.

Synthesis of graft copolymers

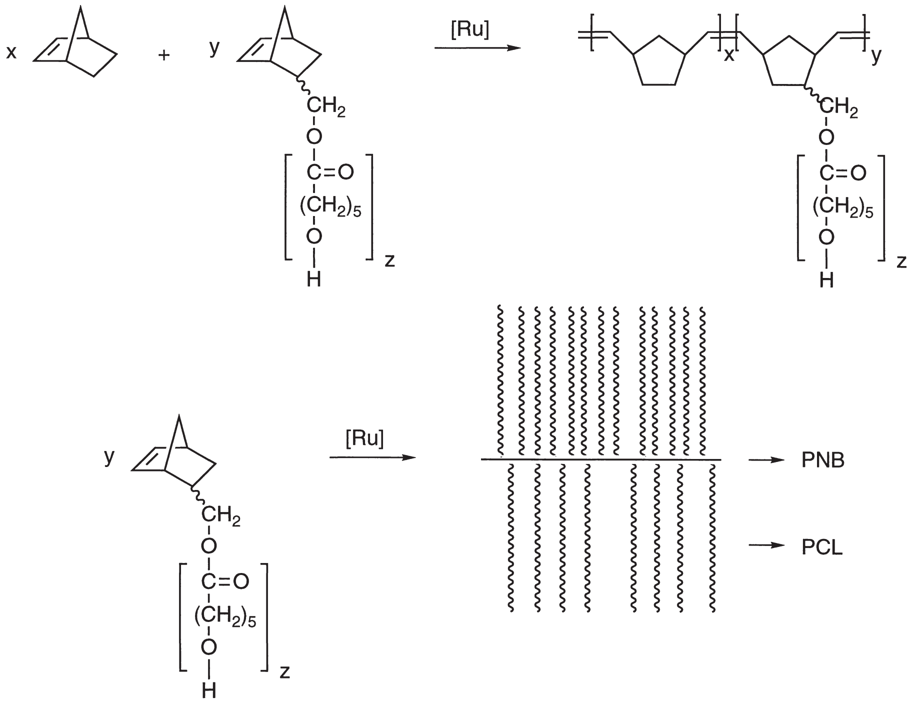
Poly(norbornene-g-ε-caprolactone) copolymers have been synthesized by the "grafting from" technique. Well controlled polynorbornene containing 5% acetate pendant groups was first prepared by ruthenium catalyzed ROMP, using the $RuCl_2$(*p*-cymene)PCy_3/TMSD catalyst system. The acetate groups were hydrolyzed and then derivatized into alkoxides with triethylaluminum. The aluminum alkoxide functionality is a well established catalyst for the living polymerization of ε-caprolactone (CL) (Scheme 4).[27]



Scheme 4

The two polymerization steps are under complete control and the graft copolymers were obtained with a narrow MW distribution and free of the parent homopolymers.[28-29]

Reversely, poly(ε-caprolactone) (PCL) macromonomers capped by a norbornene end-group were synthesized and (co)polymerized by ring-opening metathesis with the same catalytic system (Scheme 5).

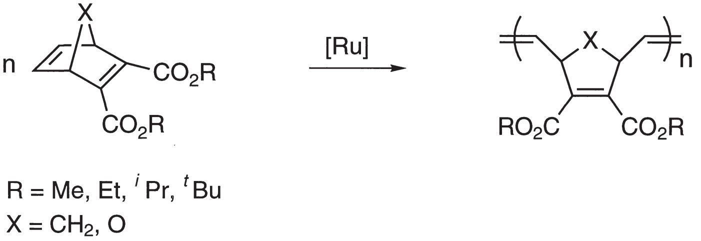


Scheme 5

Copolymerization of these macromonomers with norbornene or norbornene acetate has yielded a series of poly(norbornene)-graft-poly(ε-caprolactone) copolymers of well defined structures. Furthermore, PCL macromonomers were also homopolymerized in high yield into high MW comb chains of narrow MW distribution (Mw/Mn = 1.10).[29-30]
Such copolymers have potential applications as surface modifiers, polymeric surfactants, compatibilizers in polymer blends, and dispersion stabilizers.

Synthesis of tactic polynorbornadienes and of their 7-oxa analogues

Simple ruthenium complexes were found to be exceptionally useful for initiating the steroselective ROMP of diesters of norbornadiene and of their 7-oxa analogues. Commercially available, air stable [RuCl$_2$(*p*-cymene)]$_2$ dimer in the presence of TMSD yielded all-*trans*, highly tactic polymers, as illustrated in Scheme 6 for 2,3-dicarbalcoxynorbornadienes.[31]

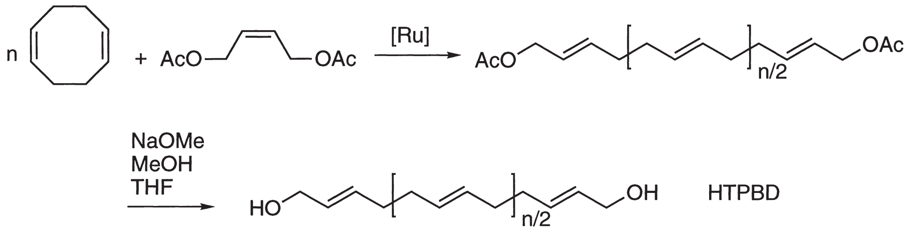


Scheme 6

Addition of tricyclohexylphosphine had a detrimental influence on the polymerization yield and stereoselectivity and an increase of the ester substituent size led to a decrease of the polymer *trans* content and tacticity, suggesting η^4-chelation of the monomer.

Synthesis of telechelic polymers

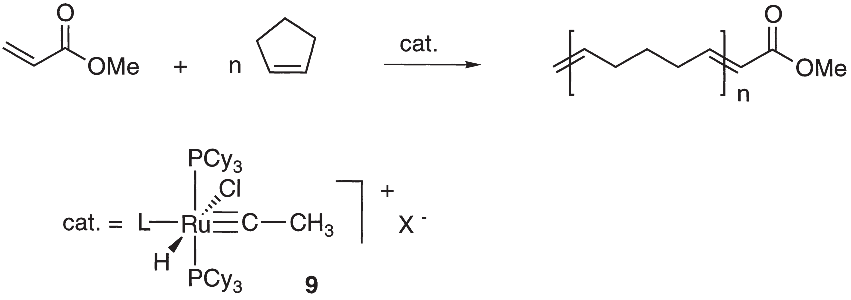
End-functionalized polymers can be prepared by ROMP in the presence of an appropriate chain transfer agent. For instance, a neat mixture of cyclooctadiene and of 1,4-diacetato-2-butene as chain transfer agent was polymerized using a ruthenium-based catalyst to yield difunctional 1,4-polybutadiene (Scheme 7). The acetate end groups could then be removed under mild conditions to give the commercially important hydroxytelechelic polybutadiene (HTPBD).[32]



Scheme 7

Synthesis of unsaturated ester-functionalized oligomers

Cationic carbynehydrido complexes of type **9** are not only highly efficient catalysts for olefin metathesis but they also promote the cross-olefin metathesis of cyclopentene with methyl acrylate (Scheme 8) to yield the first members of the homologous series of multiply unsaturated esters.[18]

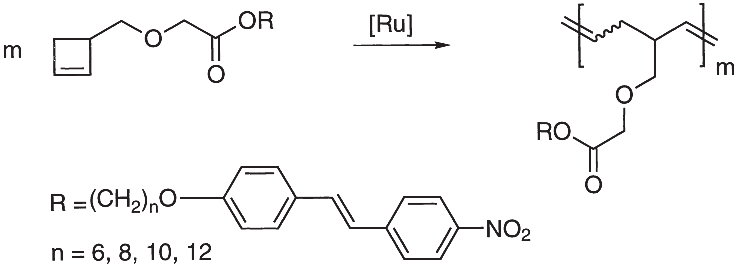


Scheme 8

These cationic complexes are among the rare ruthenium initiators able to catalyze the metathesis of electron-poor olefins; their lifetime is however lower than that of most other initiators.

Synthesis of liquid crystalline polymers

Recent advances have witnessed the use of "living" ROMP in the synthesis of a variety of side chain liquid crystalline polymers (SCLCPs) because of their potential applications in electrooptics. Polymers with well-defined structures where the mesogen is laterally attached to the polymer backbone are now available. For instance, polymerization of norbornene and cyclobutene monomers containing a *p*-nitrostilbene moiety as a mesogenic group produced SCLCPs with low polydispersities and defined MW, as illustrated in Scheme 9 for the cyclobutene derivative.[33]

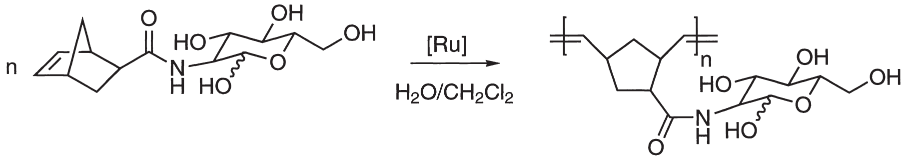


Scheme 9

Copolymerization of these two monomers into a diblock copolymer was also carried out. While ROMP opens the way to SCLCPs polymers, ADMET enabled the synthesis of main-chain liquid crystals.[34]

Synthesis of glycopolymers

The good tolerance of ruthenium-based catalysts to water also permitted the direct synthesis of unprotected, sugar-substituted polynorbornenes in an aqueous-organic two phase system (Scheme 10).[35]



Scheme 10

Conclusion

Olefin metathesis with ruthenium-based initiators has demonstrated vast potential both in organic synthesis and in polymer chemistry. Thanks to its good tolerance to many different functionalities, it has a bright future in the field of advanced material synthesis. Fundamentals have been established for the understanding of the reactions. Structure control, i.e. predicting and directing the stereoselectivities remains however quite often an unsolved problem. The rational design of the next generation of catalysts will have to tackle this issue.

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