Werner Prize

Recent Developments in Ring-Opening Metathesis Polymerization (ROMP)

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Abstract. Properties and applications of newly developed homogeneous Ring-Opening Metathesis Polymerization catalysts as well as Photo-induced Ring-Opening Metathesis Polymerization catalysts are discussed. In contrast to well-defined, one-component metal-carbene catalysts, the aqueous ROMP with simple Ru^{II} salts is a chain reaction and not a living polymerization. One-component Photo-ROMP initiators were developed with good thermal latency and are either based on early-transition-metal alkyl complexes or on $[Ru(arene)_2]^{2+}$ complexes. Mechanistic aspects of the photochemically induced solvation of Ru^{II} complexes are presented.

Andreas Hafner born in 1956 received his doctorate at the University of Zürich (Department of Organic Chemistry, Prof. *W. von Philipsborn*). After 18 months of post-doctoral studies with Prof. *L.S. Hegedus* (Colorado State University) he joined Central Research at *Ciba*, Basel and took part in the development of novel enantioselective titanium reagents and their applications. In 1992 he has been nominated as group leader to the materials research department of *Ciba*, Marly. In 1994 he received the *Werner Prize* of the Swiss Chemical Society and in 1995 he was a *Fluka Prize* winner 'Reagent of the Year 1995'. His current research interests involves the development of (photo)catalysts and functional chromophores in the field of materials science.

Introduction

The metathesis of olefins is a reaction in which an interchange of C-atoms takes place between pairs of double bonds. In 1967 it was realized by *Calderon* and coworkers that *Eqns. a* and *b* in *Scheme 1* were examples of one and the same chemical reaction [1]. Today this general reaction has been divided into four categories (see *Scheme 1*): Olefin Metathesis (exchange, disproportionation; *Eqn. a*) [2], Ring-Opening Metathesis Polymerization (ROMP) (*Eqn. b*) [2], Ring-Closure Metathesis (*Eqn. c*) [3], and Degradative

Metathesis (*Eqn. d*) [2]. The Acyclic Diene Metathesis Polymerization, a combination of (*b*) and (*c*), was just recently discovered [4].

In 1957, *Eleutorio* described in a patent the ROMP reaction of cyclopentene and norbornene with an Al_2O_3 catalyst activated by $LiAlH_4$ [5]. In 1960, the first metathesis reaction of linear olefins were reported by *Banks* and *Bailey* using an Al_2O_3-supported $Mo(CO)_6$ catalyst [6]. In 1970, *Herisson* and *Chauvin* postulated that metal carbenes [7] are the active sites in this type of reaction [8]. In this mechanism a metal-carbene species forms with an alkene a metallacyclobutane. When this complex decomposes in a productive metathesis step, a new olefin is formed together with a new metal-carbene species. If this new olefin and the carbene function remain in the same molecule (*e.g.* by reaction with cyclic olefins), excess olefin leads to polymer formation.

Early-Transition-Metal Catalysts

Catalyst systems based on early-transition-metal halides, oxides or oxychlorides with alkylating reagents as cocatalyst such as R_4Sn or Et_2AlCl together with promoters, *e.g.* O_2, EtOH, PhOH, dominated the field from the beginning (*e.g.* the famous *Calderon* catalyst $WCl_6/Et_2AlCl/$ EtOH). In the mid-1980's, the first well-

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Scheme 1
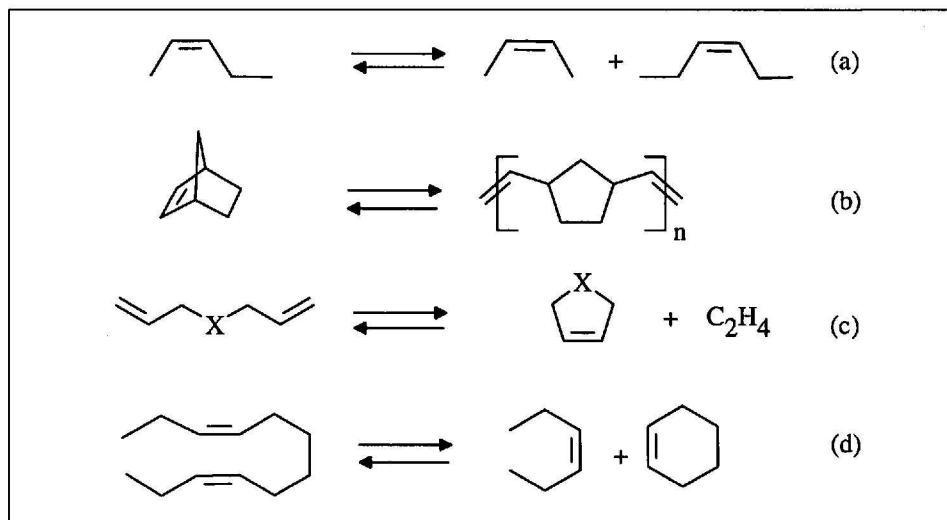
defined, single-component catalysts were developed by *Osborn* (*e.g.* 1) [9] and *Schrock* (*e.g.* 2) [10][11] using a thermally induced H_α-abstraction reaction for the carbene formation. Other efforts have been directed to the synthesis of metal-carbon double bonds by ring opening of cyclopropene [12] or using carbene-transfer reactions from phosphoranes [13].

Complexes of type 1 are five-coordinated, whereas those of type 2 contain large ligands which protect them from inter- or intramolecular decomposition reactions. The catalytic activity towards linear olefins is in both cases dramatically decreased when stronger π-donating alkoxides are introduced, *e.g.* $W(=CHCMe_3)(=NAr)(OR)_2$ with $OR = OCMe(CF_3)_2$ is very active with *cis*-pent-2-ene, where as

a similar complex with $OR = OCMe_3$ is virtually inactive.

These types of complexes act as initiators in the ROMP reaction in a living manner. A polymerization reaction is called a 'living polymerization', if each catalyst molecule acts as a catalytic site to form the growing polymer chain, and the initiation is faster compared to the propagation. The advantages of living-polymerization catalysts are, that polymers can be obtained with very narrow molecular-weight distributions and that block copolymers can be prepared by sequentially adding two, or more, different types of monomers [14]. Such polymers are expected to be useful in highly specialized applications, *e.g.* in optical, electro-optical, and electrochemical devices [15].
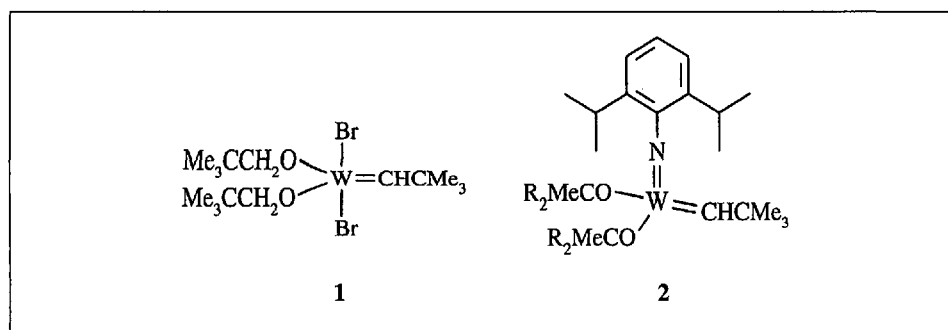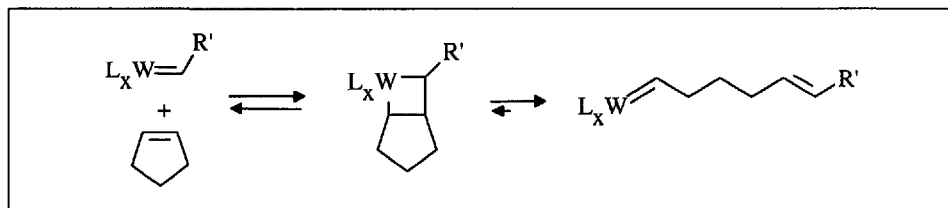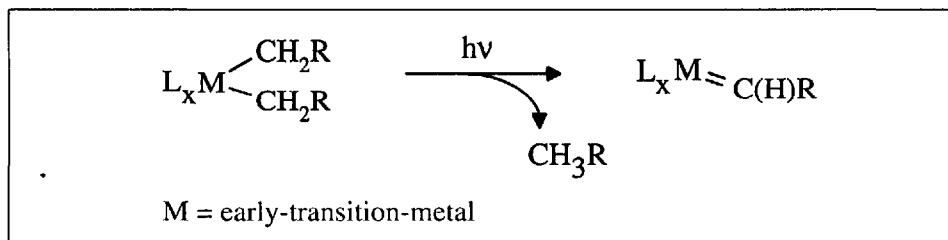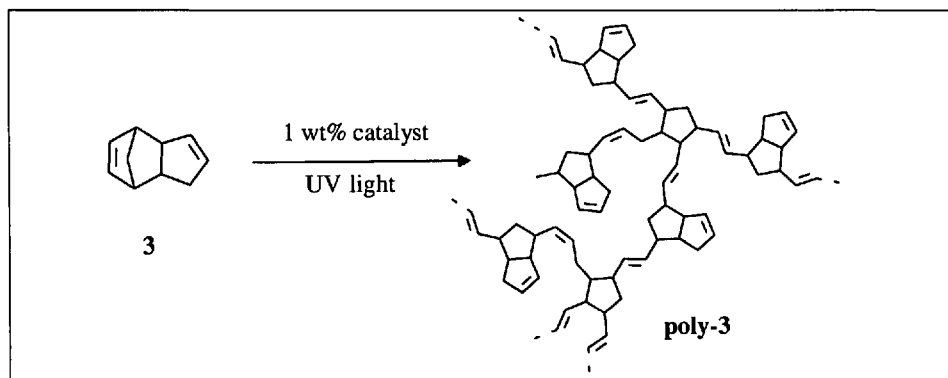
Early-Transition-Metal Photocatalysts

The main disadvantage of conventional early transition-metal catalysts is their lack of latency in pure monomers, and the long and difficult preparation routes. Although some indications are given in the literature that early-transition-metal alkyl complexes can be light-sensitive and even that irradiation can accelerate an H_α-abstraction reaction [16], no examples are known, besides our own work, using the principle of Photo-induced Ring-Opening Metathesis Polymerization (PROMP) with well-defined, one-component metal complexes [17]. This is even more surprising taking into account that photo-processes are known for almost all other polymerization reactions and widely applied in a broad range of commercial applications [18]. Active ROMP initiators can be generated *in situ* using simple early-transition-metal alkyl complexes and light (see *Scheme 3*). Such photo-induced H_α-abstraction reactions can only proceed, if the two alkyl groups are in a *cis*-position with respect to each other, and do not have any β-hydrogens. Catalysts with good thermal latency and high photoactivity were developed [19].

This new class of catalysts can be successfully applied for UV curing of strained cyclic olefins like DCPD (3) to form **poly-3** (see *Scheme 4*) and derivatives or oligomers containing cyclo-olefin side groups.
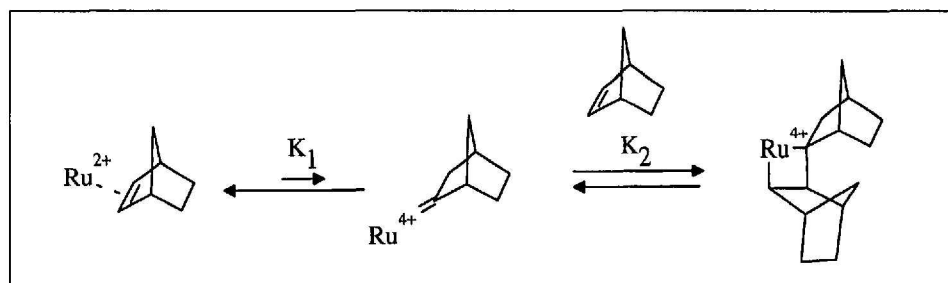
Late-Transition-Metal Catalysts

In contrast to the high oxidation-state early-transition-metal carbenes, Ru- and Os-catalysts possess a remarkable tolerance to most functional groups including protic species such as water and have, therefore, attracted much attention over the past seven years [20]. This extraordinary stability to water displayed by normally highly reactive organometallic intermediates (metal carbenes and metallacyclobutanes) suggests that the application range of such catalyst systems goes far beyond the classical application range of olefin-polymerization reactions. Unfortunately, catalysts based on Ru and/or Os salts, *e.g.* $[RuCl_3(H_2O)_3]$ (4), $[Ru(II)(\eta^6\text{-benzene})(H_2O)_3]tos_2$ (5), and $[Ru(H_2O)_6]tos_2$ (6) (tos = *p*-toluenesulfonate), show normally a lower reactivity compared to the early-transition-metal carbene catalysts [21]. It is shown that the aqueous ROMP with these catalysts is not a living polymerization since molecular weights (M_w) and polydispersities (PDI =

1 2

Scheme 2

Scheme 3

M = early-transition-metal

Scheme 4

3 poly-3

M_w/M_n) were in the range 100 000–700 000 and 1.5–3.0, respectively, and almost invariable from the nature of the catalysts and variation of the reaction conditions. Yields depend strongly on both the monomer and the catalyst concentration, are difficult to reproduce and seldom reach values above 80–90%. These observations imply that both the carbene and the metallacycle formations are rather unfavorable and associated with a substantial activation energy (see *Scheme 5*). Therefore, only a very small amount of active catalyst is present at any time. The propagation is fast in comparison with the initiation [21].

Very recently, *R.H. Grubbs* and coworkers succeeded in preparing such a postulated carbene intermediate (starting from phenyldiazomethane and [RuCl$_2$(PPh$_3$)$_3$] followed by a phosphine exchange reaction). Even the synthesis of substituted carbene complexes is possible *via* cross-methathesis (see *Scheme 6*) [22].

These catalysts are highly reactive and produce nearly monodisperse polynorbornene. They fulfill, in contrast to Ru-salt catalysts, the criteria for living systems. In addition to the high ROMP activity, **7** is also an efficient catalyst for metathesis of acyclic olefins [22].
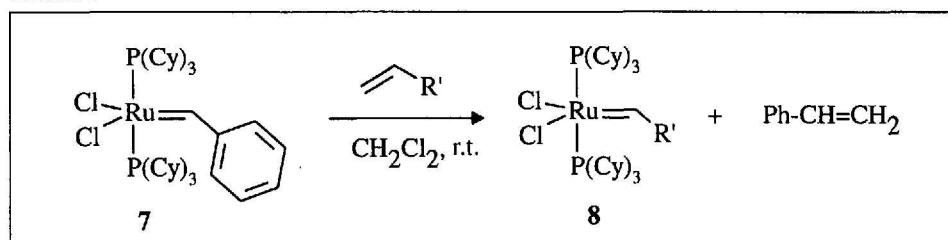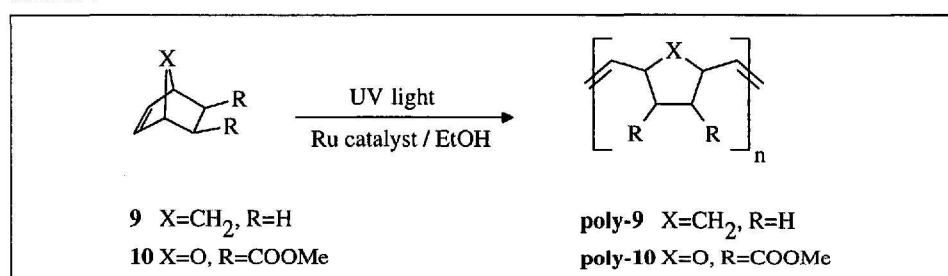
Late-Transition-Metal Photo-Catalysts [17]

[Bis(arene)Ru(II)] and [Ru(NC–R)$_6$]$^{2+}$ complexes belong to the most stable and inert complexes known for divalent ruthenium. In the absence of light [bis(arene)Ru(II)] complexes are completely inactive in ROMP and only few [Ru(NC–R)$_6$]$^{2+}$ complexes show some very low activity. If these complexes are irradiated with UV light ROMP activity was observed.

The *Table* shows results of comparative studies on the activity of ruthenium complexes in ROMP (thermal reaction) and with irradiation of UV light (PROMP) reaction. For example a concentrated solution of **9** or **10** in EtOH containing 1% of catalyst [(C$_6$H$_6$)Ru(biphenyl)]tos$_2$ (**15**) is almost quantitatively polymerized within a few minutes upon irradiation with an argon laser (364 nm, 150 mW) at 70° (*Scheme 7*). The influence of light on the initiation of the polymerization shows a pronounced dependence on wavelength with a maximal effect around 360 nm for the sandwich complexes. Irradiation above 420 nm usually does not start the polymerization reaction except for catalysts having shifted their lowest-energy absorption band into the visible region of the spec-

Scheme 5

Scheme 6

Scheme 7

9 X=CH$_2$, R=H

10 X=O, R=COOMe

poly-9 X=CH$_2$, R=H

poly-10 X=O, R=COOMe

Table. *Activity of Different Ruthenium Catalysts for ROMP and PROMP of* **9** *and* **10** *to form* **poly-9** *and* **poly-10** [17][a])

No.	Compound	Thermal activity	Photo activity[b])	Quantum yield $\sigma_p \times 10^2$
6	[Ru(H$_2$O)$_6$](tos)$_2$	very high	–	–
11	[Ru(CH$_3$CN)$_6$](tos)$_2$	weak	high	5
5	[(C$_6$H$_6$)Ru(H$_2$O)$_3$](tos)$_2$	medium	high	1.4
12	[Hexamethylbenzene)Ru(H$_2$O)$_3$](tos)$_2$	very weak	very weak	–
13	[(C$_6$H$_6$)$_2$Ru](tos)$_2$	none	high	10
14	[(C$_6$H$_6$)Ru(mesitylene)](tos)$_2$	none	weak	7.8
15	[(C$_6$H$_6$)Ru(biphenyl)](tos)$_2$	none	very high	2.0

[a]) Monomer concentrations, 50–200 mg/ml; catalyst, 1 wt% relative to monomer. [b]) Irradiation with a 200-W-Hg lamp for 15 min prior to addition of monomer.

trum (*e.g.* **15**). In general, irradiation into the energetically lowest absorption band of the catalyst precursor leads to very efficient initiation.

The characteristics of the PROMP activity are the same for [(η^6-arene)Ru(η^6-arene)]$^{2+}$ and [Ru(NC–R)$_6$]$^{2+}$ complexes and comparable to the thermal ROMP reaction using [Ru(solvent)$_6$]$^{2+}$ complexes. The same is true for the polymer properties like the observed broad molecular-weight distributions, the high molecular weights, and the strong influence of the

initial starting concentration of monomer on final yields [17].

Investigations by ^{1}H-NMR and UV spectroscopy show that the photochemical activation of [bis(arene)Ru(II)] complexes by irradiation into the UV region leads to solvation in two steps [23] (*Scheme 8*).

The so formed intermediate species [(η^6-arene)Ru(solvent)$_3$]$^{2+}$ as well as the fully solvated complexes [Ru(solvent)$_6$]$^{2+}$ are both ROMP catalysts for strained cyclic olefins, with the former showing only mod-

erate activity [17]. Therefore, the active species is mainly related to the fully solvated complexes [Ru(solvent)$_6$]$^{2+}$. Irradiation of unsymmetrical sandwich complexes of the type [(η^6-C$_6$H$_6$)Ru(η^6-C$_6$H$_{6-n}$-R$_n$)]$^{2+}$ where R is a σ-donating substituent, selectively leads to [(η^6-C$_6$H$_{6-n}$-R$_n$)Ru(solvent)$_3$]$^+$ complexes. Quantum yields for further solvation of these complexes are low and decrease sharply with increasing number of substituents. Accordingly, a low activity is observed for these complexes (e.g. 12).

Also the ruthenium-nitrile complexes like [Ru(NCCH$_3$)$_6$]$^{2+}$ (11) in D$_2$O show upon irradiation a release of acetonitrile and the formation of [Ru(NCCH$_3$)$_{6-x}$(D$_2$O)$_x$]$^{2+}$, as seen by ^{1}H-NMR spectroscopy. A rough estimation of the quantum yield for this photochemically activated ligand-exchange reaction gives a value of 0.05 which is comparable to quantum yields for the photochemically activated solvation process in sandwich complexes.

Conclusions

Photo-induced Ring-Opening Metathesis Polymerization (PROMP), recently discovered in our laboratories, and Ring-Opening Metathesis Polymerization (ROMP) are versatile tools for the preparation of a wide variety of speciality polymers. The catalyst systems discussed are based on early- as well as on late-transition-metals. In general the former catalysts are more active, but in contrast to late-transition-metal catalysts they tolerate only nonprotic solvents and a limited variety of functional groups.

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Scheme 8