



## Review

Reprint of: On metallocene-containing macromolecules and their applications<sup>☆</sup>Haibin Gu<sup>a</sup>, Roberto Ciganda<sup>b,c</sup>, Sylvain Gatard<sup>b</sup>, Feng Lu<sup>b</sup>, Pengxiang Zhao<sup>d</sup>, Jaime Ruiz<sup>b</sup>, Didier Astruc<sup>b,\*</sup><sup>a</sup> Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, PR China<sup>b</sup> ISM, UMR CNRS N° 5255, Univ. Bordeaux, 33405 Talence Cedex, France<sup>c</sup> Facultad de Química de San Sebastian, Universidad del País Vasco, Apdo 1072, 20080 San Sebastian, Spain<sup>d</sup> Science and Technology on Surface Physics and Chemistry Laboratory, PO Box 718-35, Mianyang 621907, Sichuan, PR China

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Dedicated to our distinguished colleague and friend Professor Heinrich Lang at the occasion of his 60<sup>th</sup> birthday and in recognition of his superb contribution to organometallic chemistry and molecular electronics.

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## ABSTRACT

A remarkable property of metallocenes, in particular those of the late first-row transition metals, is their redox function including the stability of two or several oxidation states. Recently our groups have introduced these compounds into precise dendrimers and polymers in view of sensing and catalytic applications. This short overview essentially focuses on the synthetic aspects and applications of our research conducted in this area.

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## 1. Introduction

The discovery of ferrocene and other metallocenes and  $\pi$ -complexes [1] has marked the very beginning of modern organometallic chemistry [1,2], and it has been rapidly followed by the introduction of ferrocene into polymers [3]. The redox aspects of transition metal organometallics [4,5], exemplified by the work of

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Professor Heinrich Lang's group in molecular electronics [6], are indeed essential for their applications, as shown with the early biomedical applications of ferrocene-modified pyrrole polymers as glucose sensors [7]. In the late first-row transition metal metallocenes, single electron transfer chemistry including stable 17- and 19-electron organometallic radicals dominate [8], which is not the case for the chemistry of second and third row counterparts [2]. These redox properties have been introduced in ferrocene- and cobalticinium-containing polymers for several decades with materials applications such as sensors [9–11]. More recently, specific topologies of precise metallocene-containing dendrimers [12,13] and ROMP polymers [14] have appeared, in particular with click metallodendrimers [15] and metallocene-containing living polymers and co-polymers synthesized by ring-opening metathesis polymerization (ROMP) using Grubbs' 3rd generation catalyst [16]. These new families and their properties that have been the subject of recent research in our laboratory will be discussed in this overview article.

## 2. Living polymers and copolymers containing late transition metal sandwich units

Metallopolymers have attracted considerable interest because of their physical properties that provide applications in catalysis [17] including electrocatalysis [18], sensing [7,19], responsive surfaces [20], capsules [21], photonic crystal displays [22], lithography [23], magnetism [24], electrochromism [25] and ceramic precursors [26], and these properties and applications have been recently reviewed [27]. Following a starting period marked by the syntheses of various ferrocene-containing polymers with poor definition and polydispersities [27a], the discovery by the Manner group in 1992 that strained ring-tilted ferrocenophane undergo, under a variety of stimuli (thermal, ionic, photolytic, catalytic), ring-opening polymerization (ROP) that can eventually be living, was a real breakthrough in metallopolymer chemistry, because these well-defined materials led to a variety of original electronic, mechanical, optic and magnetic properties, and the polymerization principle could be extended to a variety of metal-sandwich complexes [9,10,28]. Recently, we introduced a new effective method to introduce functional metal sandwich units in the main polymer chain using the well-known  $\text{Cu}^{\text{I}}$ -catalyzed alkyne azide cycloaddition (CuAAC), the best known among "click" reactions. With such a strategy, the polymerization is not living, but the presence of the 1,2,3-triazolyl groups in these metallopolymers offers the possibility to coordinate the cyclic nitrogen ligands to transition metal cations. This allows not only the possibility of redox recognition of these transition-metal cations by cyclic voltammetry but also the reduction of these coordinated cations to polymer-stabilized metal nanoparticles that disclose specific physico-chemical and catalytic properties [29]. For instance, the click reaction between bis(ethynyl)biferrocene and bis(azido) molecules yielded redox

polymers disclosing multiple properties including electrochromic, polyelectrolyte, sensor, electrode modifier, nanoparticle stabilizer and catalyst template [30].

Besides these metallopolymers containing metal-sandwich units in the main chain, there are numerous reports of polymers containing ferrocene or other metal-sandwich units in the side chain. These polymers are synthesized either by polymerization of a metallocene-containing monomer or by post-functionalization with a metallocene unit of a functional polymer, and the literature has been recently reviewed [27a]. Most remarkably, several modern polymerization techniques have provided well-defined polymers with predetermined molecular weights, low polydispersities and high functionalities by living polymerization: (i) living anionic polymerization (LAP) [31], (ii) ring-opening metathesis polymerization (ROMP) [32] using the most active group 6 and group 8 metal catalysts [16], and (iii) controlled radical polymerization (CRP) techniques [33] that include atom transfer radical polymerization (ATRP) [34], reversible addition-fragmentation chain transfer polymerization (RAFT) [35] and nitroxide-mediated polymerization (NMP) [36]. Although well-defined metallocene-containing polymers have been synthesized with all these techniques [27a], we focus here on ROMP following our interest for such olefin metathesis reactions [3,16c].

The most active catalysts for controlled living polymerization are Schrock's molybdenum and tungsten imido alkylidene complexes [37] and Grubbs' 3rd generation metathesis catalyst, namely ruthenium benzylidene *N*-heterocyclic carbene bis *m*-chloropyridine complex **1** (Fig. 1) [16,38].

The former complexes are air sensitive with limited tolerance to functional groups, whereas the latter complex **1** is more tolerant and is being generally used by polymer chemists for this purpose. Thus for instance various living ferrocene-containing polymers such as **2** and block copolymers have been synthesized using this ruthenium catalyst [11,14,39–41] (Scheme 1).

Cobalticinium that is isoelectronic with ferrocene [42] has been functionalized first by carboxy substituents [42b] then more recently with the very useful ethynyl substituent [43] for further click chemistry [43a,b] or reaction with amines [43b] (Scheme 2). These functional groups led to the synthesis of cobalticinium-containing polymers [40c,44].

For instance ROMP using Grubbs' 3rd generation catalyst allowed the synthesis of cobalticinium polymers either by ROMP of a cobalticinium-containing monomer or by functionalization with the cobalticinium monomer of a functional polymer [44c] (Scheme 3).

The cyclopentadienyl-iron-arene family is another series of metal sandwich complexes that has a rich functional chemistry [45–47] allowing its introduction into polymers by efficient nucleophilic substitution of one or two chloro substituents on the arene ligand of the 18-electron cationic form [45,47] that is thermally robust, but more or less sensitive to visible light [45,48]. Thus

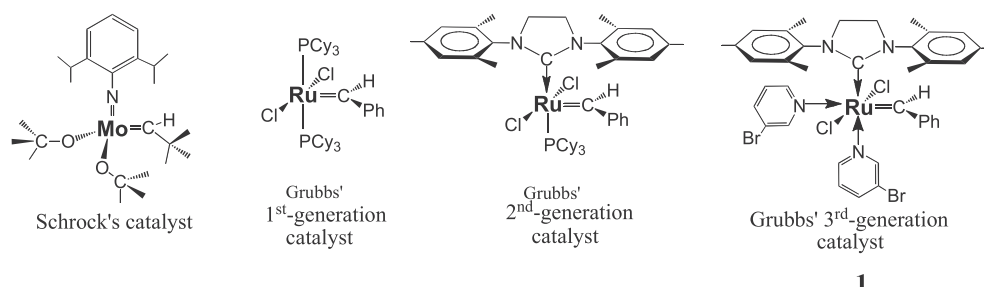


Fig. 1. ROMP metathesis catalysts.

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