Metal Catalyzed Polymerization: from Stereoregular Poly(α-olefins) to Tailor-made Biodegradable/Biorenewable Polymers and Copolymers

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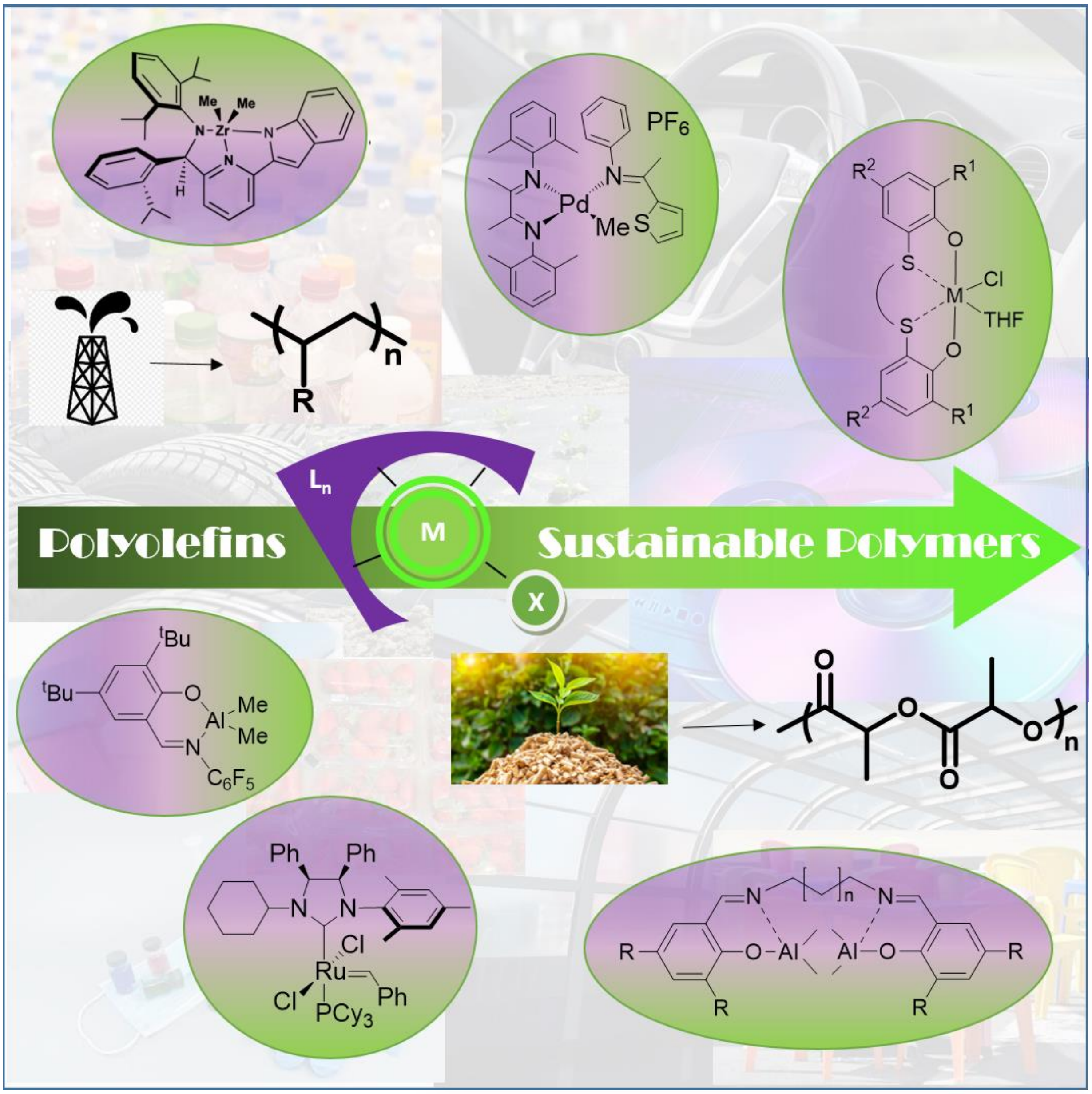

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ABSTRACT

Metal catalyzed polymerizations are among the most important chemical reactions, accounting for the production of about 400 million tons per year of polymeric materials, 50% of which are polyolefins. The CIRCC research units at the University of Salerno, founded by the late Professor Adolfo Zambelli, a coworker of Giulio Natta and a pioneer in the studies of stereospecific polymerization catalysts, has a consolidated expertise in this field. Although often considered a “mature” area of research, olefin polymerization catalysis continues to drive great interest of both industrial and academic scientists. On the other hand, strong political and economical pressure toward the development of “green” and possibly biodegradable alternatives to olefin-based polymers stimulated our group to direct increasing research efforts in the area of sustainable polymers. In this perspective, we focus on the most recent work from the CIRCC research units involved in homogeneous catalysis for polymerization of a variety of monomers, with the aim to address how the concepts and the expertise developed for olefin polymerization can be applied to the development of different metal-catalyzed polymerizations and copolymerizations. Of course, although the results are discussed in the frame of the most important literature contributions, a comprehensive review of such a wide and diversified topic is out of the scope of the paper. References to reviews covering the different types of metal catalyzed polymerizations are provided in each chapter.

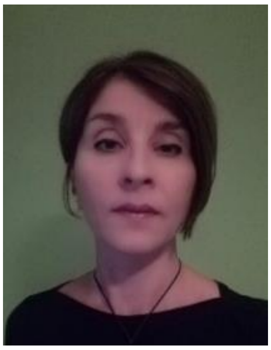
Biografical sketches

Carmine Capacchione

Carmine Capacchione received his M.Sc. and PhD degrees from the University of Salerno (Italy) under the supervision of Antonio Proto. He then held an Alexander von Humboldt post-doctoral fellowship working at the University of Heidelberg (Germany) in the group of Lutz H. Gade. He was appointed assistant professor in 2005 and promoted to associate professor in 2015 at the University of Salerno (Italy). From 2021 he is full professor at the same institute. His research interest is in the field of homogeneous polymerization catalysis with a focus on the valorization of bio-based feedstock and CO_2 utilization.

Fabia Grisi

Fabia Grisi is Associate Professor at the Department of Chemistry and Biology “Adolfo Zambelli” of the University of Salerno. After working at the Istituto di Chimica delle Macromolecole of CNR (Milano), she received her PhD in Chemistry 1999 and then became Assistant Professor at the University of Salerno. Her research activity is mainly focused on the synthesis and characterization of novel organometallic complexes for applications in homogeneous catalysis. She is also involved in the design of new partially biobased monomers for the preparation of functional materials via ring-opening metathesis polymerization.



Marina Lamberti

Marina Lamberti obtained her Ph.D in Chemistry in the 2003 and became Assistant Professor in the 2005. She is currently working as an Associate Professor at the Department of Chemistry and Biology "Adolfo Zambelli" of the University of Salerno. Her scientific studies concern essentially organometallic chemistry and homogeneous catalysis: from the synthesis and characterization of new metal complexes to their application in catalysis and the study of the involved mechanisms. Her current research interest mainly focuses on the fixation of carbon dioxide by reaction with epoxides and on the synthesis of sustainable polymers by ring-opening polymerization of cyclic esters.

Mina Mazzeo

Mina Mazzeo received her Ph.D in olefin polymerization catalysis in 2001 at the University of Salerno. From 2002 to 2016 she was Assistant Professor at Chemistry and Biology Department of the University of Salerno and in 2016 she became Associate Professor.

Her research interests include the synthesis of biodegradable polymers by ring opening polymerization of cyclic esters or ring opening co-polymerization of epoxides with cyclic anhydrides promoted by metal or organic catalysts and the chemical recycling of waste polymers.

Barbara Milani

Barbara Milani is Associate Professor of General and Inorganic Chemistry at the University of Trieste. She received her PhD degree at University of Trieste in 1994, where she became assistant professor in 1998 and in 2014 she was promoted associate professor. In 2017 she got the National Abilitation to Full Professor. She was member of the Advisory Board of European Journal of Inorganic Chemistry. Currently, she is member of the Advisory Board of Dalton Transactions. She is Rector Delegate for International Relationships and Mobility @UniTS. Her main research interests focus on organometallic chemistry and on development of homogeneous catalysts, based on late transition metals, for polymerization reactions.

Stefano Milione

Stefano Milione is Associate Professor at the Department of Chemistry and Biology of Salerno University. His research interest concerns the reactivity of highly electrophilic organometallic species in the polymerization of olefins and polar monomers. Principal aim of his studies is the understanding of the factors that control the insertion of monomer units in the growing polymer chain. Particular attention is devoted to polar monomers derived from renewable sources whose polymers have important properties of biocompatibility and biodegradability.

Daniela Pappalardo

Daniela Pappalardo received a PhD in Chemistry in 1998 at the University of Salerno (Italy). She was post-doc at the University of Leeds (UK). She became assistant professor and, since 2005, associate professor at the University of Sannio (Italy). She was a part-time guest professor at the KTH, Royal Institute of Technology in Stockholm (Sweden) during 2014–2017 and in the board of the academic spin-off Akira Science AB from 2019-2022. Her research interests are in the fields of organometallic chemistry and polymer chemistry, in particular homogeneous polymerization catalysis of olefins and polar monomers.

Cristiano Zuccaccia

Cristiano Zuccaccia received the Ph.D. degree in Chemical Science from the University of Perugia in 2000. After several years of post-doctoral fellow (Northwestern University, University of Perugia, University of Milano) he was appointed as Researcher in Physical Chemistry at the University of Perugia in 2008, where he holds the position of Associate Professor of General and Inorganic Chemistry from 2015. In 2006 he received the “Bonati” prize from the Italian Chemical Society. His recent scientific interests include application of NMR methodologies for the investigation of structure-reactivity relationships of organometallic catalysts.

Claudio Pellecchia

Claudio Pellecchia is Professor of General and Inorganic Chemistry at the University of Salerno. He obtained his doctorate (*summa cum laude*) in Industrial Chemistry at the University of Naples in 1984. After three years as a post-doctoral fellow with Professor Adolfo Zambelli and several periods at the USX Chemical (Pittsburgh, USA), he moved to the University of Salerno, where he was promoted researcher in 1992, associate professor in 1998 and Professor in 2001. He was Head of the Department of Chemistry and Biology (2010-2015), member of the Academic Senate (2009-2016) and of the Board of Directors (1999-2008). His current scientific interests focus on metal catalyzed polymerization of olefins and cyclic esters.

Introduction

Metal-catalyzed polymerizations are by far the largest industrial chemical processes, accounting for most of the 400 million tons/year of plastics produced worldwide. The "era of plastics" started with the discovery of Ziegler-Natta olefin polymerization catalysts, resulting in revolutionary developments in both industry and science, reaching a degree of mechanistic knowledge which has no comparison with any other chemical reaction.

The researchers affiliated to CIRCC operating at the University of Salerno (UNISA) have their scientific roots in the great tradition of the Natta's school, since the department of chemistry was established by the late Adolfo Zambelli, a former coworker of Giulio Natta at the times of the original discoveries and a pioneer of the mechanistic investigation of the stereospecific polymerization of olefins.[1] Over the years, research at UNISA has focused on the mechanism of steric control in the polymerization of α-olefins, conjugated dienes and styrene promoted by Ziegler-Natta, metallocene and “post-metallocene” catalysts, and on the synthesis and characterization of novel organometallic complexes and the study of their stoichiometric and catalytic reactions with unsaturated monomers. Following the increasing socio-economical pressure due to the concern for the end-of-life fate of non-degradable plastics, since 2007 researchers at UNISA have directed more and more efforts in the field of polymerization and copolymerization of monomers achievable from renewable sources, using different catalytic techniques (such as ring opening polymerization, ROP, or ring opening co-polymerization, ROCOP), to produce bio-based, bio-degradable alternatives to polyolefins.

Herein we review the results obtained mainly by researchers working at UNISA in metal-catalyzed polymerization, and the contributions in the field by the CIRCC research units at the University of Perugia (UNIPG) and at the University of Trieste (UNITS), from 2010 to now. The account consists of six chapters concerning catalysis studies for (i) olefin polymerization; (ii) polymerization of styrene and dienes; (iii) copolymerization of olefins with polar monomers; (iv) ROP of cyclic esters; (v) ROCOP of epoxides with CO_2 or organic anhydrides; (vi) ring opening metathesis polymerization (ROMP).

1. Olefin polymerization

As mentioned in the Introduction, studies of olefin polymerization catalysis were the core activity of research at UNISA since Adolfo Zambelli moved there in 1984: at that time, a seminal paper by John Ewen[2] inspired the extraordinary research efforts of many groups from both industry and academia worldwide opening the era of stereospecific metallocene catalysts.[3] In this respect, the UNISA group gave significant contributions to the elucidation of the stereochemical reaction mechanism, using techniques, previously developed by Zambelli for the traditional heterogeneous Ziegler-Natta catalysts,[4] based on the NMR analysis of suitably labelled polymers obtained by isotopically enriched catalysts or monomers.[5] The same approach was used to study the mechanism of stereospecific polymerization promoted by "post-metallocene" catalysts, such as late-transition metal Ni and Pd diimine and Fe bis(imino)pyridyl catalysts, and group 4 metal bis(phenoxyimine) catalysts. Other significant contributions were the identification of the true active species, with the isolation and characterization of new organometallic cationic complexes capable of reacting with olefins in catalytic and stoichiometric processes. While these results have been reviewed previoulsy,[6] here we discuss the most recent studies carried out at UNISA and UNIPG on the matter.

1.1. Structure and dynamics of ion pairs and the kinetic relevance of ionic aggregates.

Homogeneous olefin polymerization reactions are typically conducted in solvents of very low polarity, although the vast majority of available catalytic systems comprises highly electrophilic cationic complexes of group IV metals.[7] Under such conditions, ion pairs (IP) are considered the true active species and the strength of the cation-anion interaction is known to strongly modulate the catalytic performance.[8] Nevertheless, the specific mechanistic role played by IPs on catalytic elementary steps has been debated, mainly because it is difficult to dissect the intricate interplay of interactions between the cation, the anion, the solvent and the olefin substrate.

By using *ad hoc* engineered models and industrially relevant systems, the CIRCC research unit of UNIPG carried out a series of detailed NMR studies to investigate the general behavior of active IPs to shed some light on unsolved and interlaced disputes concerning the role of anion(s) and solvent(s) on the olefin insertion step, the dissociative[9] or associative[10] nature of the ion pair symmetrization (IPS) mechanism, and the possible kinetic relevance of homo- or mixed-ionic aggregates (IA) larger than IP.[11,12]

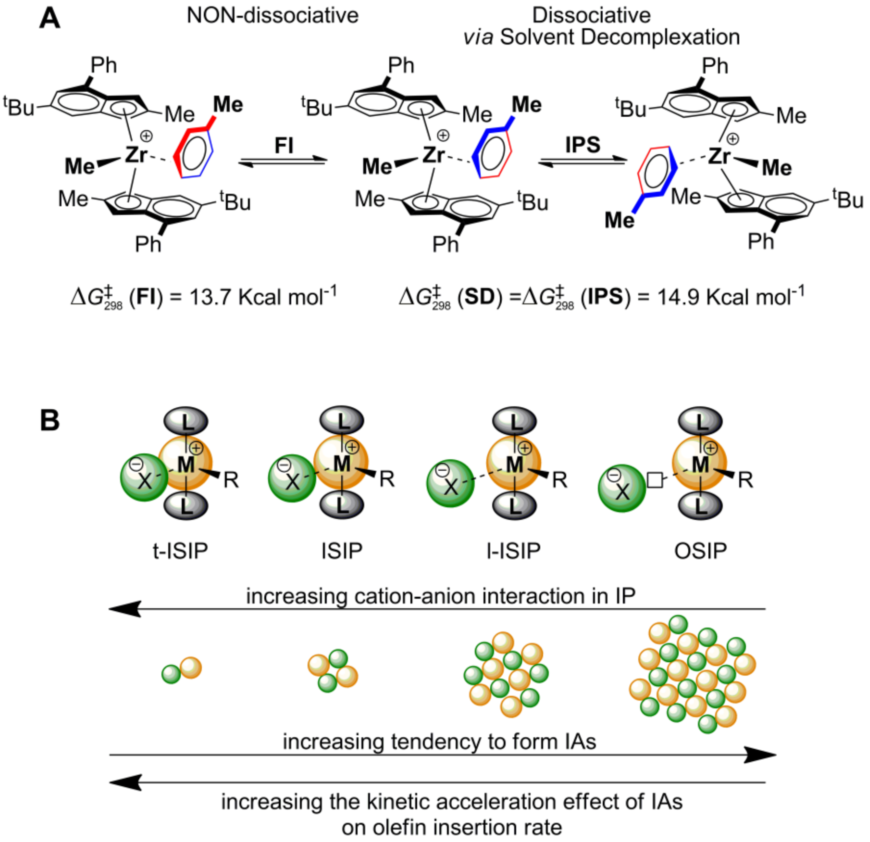
By accurately determining $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values for the insertion of a single olefin molecule into a Zr-C bond, we found that enthalpic barrier for olefin insertion is appreciably higher for IP bearing sticky counterions or in the presence of coordinating solvents, than for cations paired with non-coordinating anions.[13] However, the larger enthalpic penalty measured for the formers ($\Delta\Delta H^{\neq}$> 4 Kcal mol^{-1}) is partly compensated by a less negative entropic contribution associated with the displacement of the anion from the inner to the outer coordination sphere, or release of the coordinated solvent molecule into the bulk solution.

More recently, we confirmed the pivotal role of catalyst-solvent interaction by isolating and characterizing solvento-complexes of industrially relevant *ansa*-zirconocene systems.[14] Three distinct dynamic motions are operative in such IPs (Scheme 1A). Face inversion (FI) of coordinated toluene is the fastest process and is characterized by a near-zero entropic contribution to the activation barrier, indicating that it occurs in the first coordination sphere of the metal. The other two motions, solvent decomplexation (SD) and IPS, occurs with coincident rates, approximately 20x slower than FI, *via* a dissociative-like mechanism. Thus, solvent decomplexation triggers IPS and, differently from what proposed in the literature,[10] solvated alkyl cations do represent relevant intermediates, both for the IPS process and for the olefin uptake/insertion process as well.

Finally, we set out a comparative thermodynamic and kinetic study to correlate the tendency of IPs to self-aggregate into IAs[15] with the intrinsic ability of a given IP to insert an olefin into the M−C bond.[16] The results clearly shows that the two aspects are interlaced and strongly linked to the strength of cation−anion interactions, offering a general self-consistent picture (Scheme 1B) that also rationalizes apparently contrasting literature data.

When the cation-anion interaction energy is large, tight Inner Sphere Ion Pairs (t-ISIPs) form: such systems possess a small dipole moment and display a little thermodynamic tendency to form IAs.[15] Nevertheless, under conditions where (mixed) IAs form, a substantial weakening of the cation−anion interaction occurs due to close proximity of other ion pairs which are much more polar than the solvent molecules. This extra weakening of cation−anion interaction facilitates olefin insertion; for our systems a remarkable 15-28x enhancement of olefin insertion rate constants (k_{INS}) is observed when IAs containing an average of five IPs are mainly present in solution.

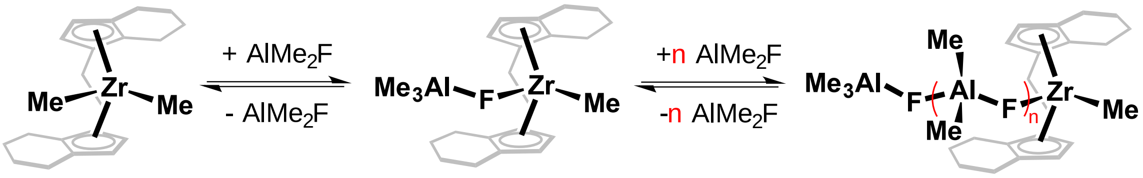
Progressively weakening cation-anion interactions lead to Inner Sphere Ion Pairs (ISIPs), loose Inner Sphere Ion Pairs (l-ISIPs) and Outer Sphere Ion Pairs (OSIPs) which possess increasingly larger dipole moments and display an higher tendency to form IAs in very low polar solvents, even at concentration approaching those used in catalysis.[15] Although k_{INS} can be even orders of magnitude faster than those measured for t-ISIPs, the (easy) formation of IAs does not alter significantly the already weak cation-anion interaction and k_{INS} are found to be independent of concentration or addition of external salts.



Scheme 1. (A) Schematic representation of the three dynamic motions operative in cationic *ansa*-zirconocene systems: face inversion of coordinated toluene (FI, left); ion pair symmetrization *via* solvent decomplexation (IPS and SD, right). The backbone $-SiMe_2$ bridging moiety is omitted for clarity. (B) Interplay between the strength of cation-anion interaction, the relative thermodynamic tendency of various kind of ion pairs (IP) to form larger ionic aggregates (IA) and the kinetic acceleration effect of IA on olefin insertion into the M-C bond.

1.2. Cation–anion interactions in metallocenium–methylalumoxane ion pairs

The serendipitous discovery of methylalumoxane (MAO) by Sinn, Kaminsky, and co-workers[17] was one of the key ingredients for the revolutionary development of the homogeneous metallocene stereospecific catalysis. Despite its enormous scientific and industrial importance, the structure and exact working principles of MAO "remain enshrouded by mystery”.[18] Recent studies suggested the relevance of “monomeric” AlMeO units in the equilibration of linear and cage-like structures of MAO oligomers, and/or of highly reactive $AlMe^{2+}$ cations.[19] In 1989 two papers by Zambelli's group reported that, similarly to MAO, $AlMe_2F$ is an efficient activator for metallocene catalysts for propene polymerization, at variance with other more common aluminum alkyls. The efficiency of $AlMe_2F$ in the catalysis was much higher in polar solvents, confirming the hypothesis that the role of the cocatalyst was to generate cationic active species. These findings were apparently overlooked in the following years, probably obscured by the disclosure of activators based on Lewis or Brønsted acidic boron compounds, resulting in the isolation and characterization of catalytically active metallocene and non-metallocene ion pair complexes.[20] With the aim to understand why $AlMe_2F$ behaves in catalysis more similarly to MAO than to other aluminum alkyls, the UNISA and the UNIPG research groups re-examined its solution structure as well as its reactivity with a prototypical ansa-metallocene by high resolution multidimensional NMR analysis.[21] Although $AlMe_2F$ was synthesized by K. Ziegler in the 1950's, the literature concerning its chemistry is surprisingly scarce: early studies based on cryoscopy and IR and Raman spectra suggested a tetrameric structure with 8-membered planar ring while gas phase electron diffraction studies proposed an Al_4F_4 puckered ring.[22] Advanced NMR experiments surprisingly showed that $AlMe_2F$ solutions consist of different oligomeric species in chemical equilibrium: in particular, an unprecedented heterocubane $[(Me_2Al)_4F_4]$ tetramer was observed and characterized. The reaction of $AlMe_2F$ with $[(ETH)ZrMe_2]$ (ETH = *rac*-[ethylene-bis(4,5,6,7-tetrahydro-1-indenyl)]) was investigated by 1D, 2D and PGSE variable temperature NMR experiments, indicating complex equilibria involving several $[(ETH)ZrMe^{\delta+}(\mu\text{-}F)(AlMe_2F)_nAlMe_3^{\delta-}]$ inner-sphere ion pairs, differing in the number of $AlMe_2F$ units, which were all characterized in solution (see Scheme 2).



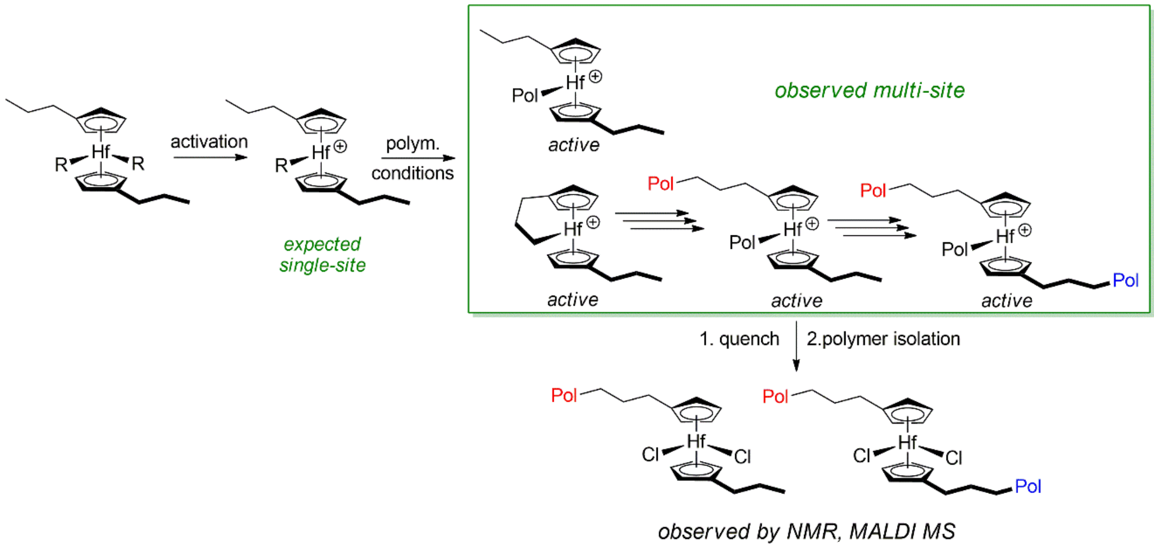
Scheme 2. Inner-sphere ion pairs produced in the activation of $[(ETH)ZrMe_2]$ with $AlMe_2F$.

Low temperature ^1H- and ^{19}F-EXSY NMR experiments suggested that equilibration occurs *via* a stepwise insertions/deinsertions in which $AlMe_2F$ units are added/removed from the zirconium center. The rate of incorporation/removal of $AlMe_2F$ units increases as the nuclearity of the associated $[F(AlMe_2F)_nAlMe_3]^-$ anion increases. Consistently, ^{19}F NMR chemical shift values of the Zr-(μ-F) moiety gradually move to lower frequencies as the number of $AlMe_2F$ unit increases, indicating a progressive decrease of cation-anion interaction. These results highlighted the potential of $AlMe_2F$ to properly mimics AlMeO units in metallocenium/MAO ion pairs, likely characterized by an M···O-Al motif. Also, oligomers in MAO mixtures have been shown to equilibrate via the addition/removal of monomeric AlMeO units,[18] similarly to our findings for $AlMe_2F$.

1.3. Ligand modification by monomer as a source of multisite behavior in metallocene catalysts

Well defined molecular catalysts typically produce polyolefins with narrow molecular weight distribution (MWD) and chemical composition distribution (CCD).[23] However, under industrially relevant conditions, some of these catalysts, including metallocenes, may display non-single site behavior, affording polymers and copolymers with broad and/or multimodal MWD and CCD. Explanations based on mass and/or heat transfer phenomena,[24] presence of trace metal impurities,[25] and/or specific interactions with the support, seem inconsistent with the observation that multimodality appears to be far more pronounced for systems bearing alkyl-substituted Cps, provided the alkyl chain(s) is long enough.

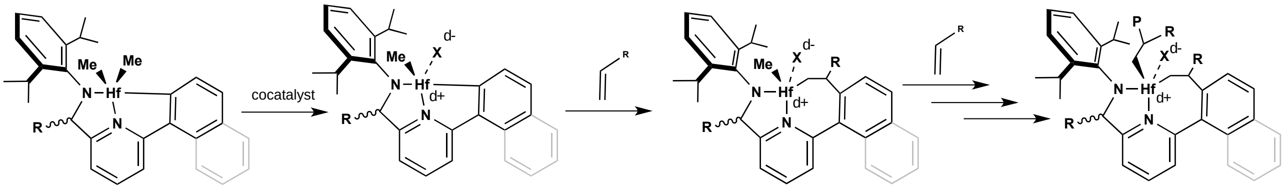
Within the framework of an academic/industry partnership, the UNIPG CIRCC unit investigated the activation chemistry, reactivity, and polymerization behaviour of propyl-substituted hafnocenes $(Cp^{Pr})_2HfR_2$ (R = Me or Bu, Scheme 3). It was found that the cationic species, obtained after reaction with $[CPh_3][B(C_6F_5)_4]$, undergo a clean Cp-propyl activation affording the corresponding metallacycle $[(Cp^{Pr})(\eta^5,\kappa^1\text{-}C_5H_4CH_2CH_2CH_2\text{-})Hf][B(C_6F_5)_4]$. (Scheme 3). Comparative NMR kinetic studies indicated that cyclometallation is slow for R = Me but occurs much faster than typical catalyst residence time for R = Bu; thus it represents a competitive catalyst transformation pathway as soon as a polymer chain start to regularly grow on the metal site. In contrast with previous conclusions, which proposed cyclometallated species as deactivation byproducts,[26] the isolated metallacycle catalyses 1-hexene polymerization as efficiently as the starting non-metallated cationic species, consistently producing polymers with slightly higher MW. Ad hoc polymerization at low 1-hexene/catalyst ratio, followed by controlled HCl hydrolysis, allowed to isolate polymeric material suitable for end-group analysis. Multinuclear, multidimensional and diffusion NMR investigations, in combination with *in situ* and *ex-situ* MALDI-TOF MS and collision-induced dissociation (CID) studies,[27] indicate that a measurable fraction of poly-1-hexene chains consist of $(Cp(CH_2)_3\text{-}(Poly\text{-}1\text{-}hexene)_2HfCl_2$ species. Data demonstrate that ring expansion via olefin insertions onto the Hf-C bond occurs through repeated 2,1-insertions of 1-hexene, irreversibly modifying the catalyst architecture via the incorporation of (different) polymeryl chain(s) into Cp-ligand(s).[28] Different molecular species can then be formed as a consequence of chain termination/cyclometallation events; the latter modified species can reinitiate catalysis via the conventional polymerization mechanism, thus offering an alternative rationale for the observed multisite behaviour (Scheme 3).



Scheme 3. Proposed explanation of multisite behavior *via* formation of polymer-appended hafnocene catalysts under catalytic conditions.

1.4. N-heteroaryl-pyridylamido group 4 metal catalysts.

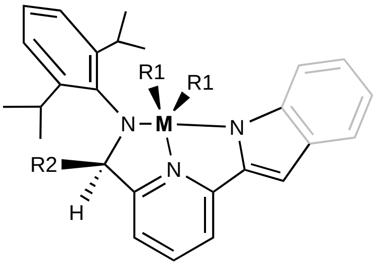
C_1-symmetric arylpyridylamido Hf(IV) complexes $(N^-,N,C_{Aryl}^-)HfR_2$ (Scheme 4) were discovered and optimized through high-throughput parallel screening by Dow and Symyx researchers and then introduced in the industrial production of a variety of ethylene-α-olefin copolymers.[29] The performance of these catalysts, yielding highly isotactic, high MW polypropylene at high temperature, was shown to depend on arylcyclometallation reactions, changing a $[N,N^-]$ monoanionic bidentate ligand into a $[^-N,N,C^-]$ dianionic tridentate one, and by further ligand modification in the activation process with MAO or $[CPh_3][B(C_6F_5)_4]$ cocatalyst, *via* monomer insertion into a Hf-C_{aryl} bond in the cationic active species (see scheme 4).[30]



Scheme 4. Arylpyridylamido $(N^-,N,C_{Aryl}^-)Hf(IV)R_2$ complexes and proposed active species deriving by activation with MAO or $[CPh_3][B(C_6F_5)_4]$ cocatalyst.

With the aim to further investigate the proposed active species of this class of catalysts, the UNISA CIRCC unit designed dianionic N-heteroaryl-pyridylamido (heteroaryl = pyrrolyl or indolyl) tridentate ligands and synthesized the corresponding $[(N^-,N,N^-)M^{IV}(NMe_2)_2]$ pentacoordinate complexes (M = Ti, Zr, Hf, see Figure 1, complexes **1**-**8**), which apparently were not amenable to the above mentioned *in situ* arylcyclometallation and ligand modification *via* monomer insertion.[31] Complexes **1**-**8**, after activation with MAO/Al^iBu_2H, resulted in highly active polymerization catalysts, affording ultra-high MW polyethylenes and highly isotactic polypropylenes. Interestingly, isotactic polypropylene with an "*enantiomorphic site*" type microstructure was also produced by the achiral C_s-symmetric complexes **3**[31a] and **5**,[31c] as previously observed for the corresponding C_s-symmetric arylpyridylamido Hf(IV) catalysts.[32] In the latter case, reduction to C_1-symmetry because of propene insertion into the Zr-C_{aryl} bond was hypothesized to explain the stereospecifity.[33] In our case, a similar modification would imply monomer insertion into a Zr-$N_{heteroaryl}$ bond, which appears unlikely (*v. infra*).

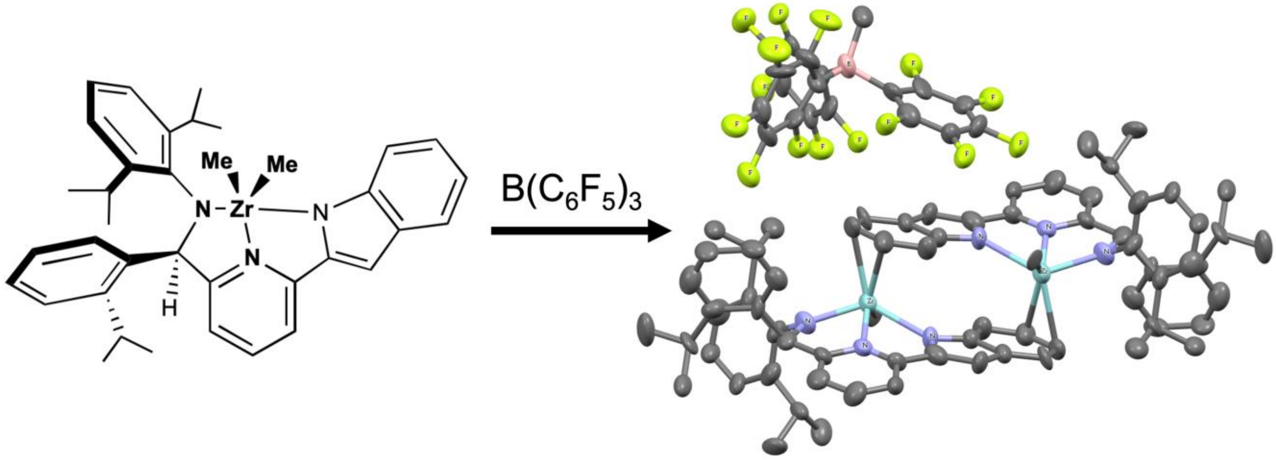
Subsequently, we synthesized the related $[(N^-,N,N^-)MR_2]$ dialkyl complexes, (M = Zr or Hf; R = Me or CH_2Ph, see Figure 1, complexes **9**-**11**). Multidimensional NMR analysis, performed in collaboration with the UNIPG CIRCC Unit, allowed us to obtain the three-dimensional structure in solution of the ionic species formed upon activation of the latter dialkyl complexes with $B(C_6F_5)_3$ or MAO or $[HNMe_2Ph][B(C_6F_5)_4]$, suggesting the formation of "out-of-sphere" (OSIP) species, consisting of dimeric cations in which the pyrrolyl or indolyl moiety of one unit coordinates to the metal center of the other unit, while the counterions are out of the first coordination sphere.[34]



1 R1= NMe_2; M = Ti; R2=H; heteroaryl=pyrrolyl
2 R1= NMe_2; M = Ti; R2=1-isopropylphenyl; heteroaryl=pyrrolyl
3 R1= NMe_2; M = Zr; R2=H; heteroaryl=pyrrolyl
4 R1= NMe_2; M = Zr; R2=1-isopropylphenyl; heteroaryl=pyrrolyl
5 R1= NMe_2; M = Hf; R2=H; heteroaryl=pyrrolyl
6 R1= NMe_2; M = Hf; R2=1-isopropylphenyl; heteroaryl=pyrrolyl
7 R1= NMe_2; M = Zr; R2=H; heteroaryl=indolyl
8 R1= NMe_2; M = Zr; R2=1-isopropylphenyl; heteroaryl=indolyl
9 R1= Me; M = Zr; R2=1-isopropylphenyl; heteroaryl=pyrrolyl
10 R1= CH_2Ph; M = Zr; R2=1-isopropylphenyl; heteroaryl=pyrrolyl
11 R1= Me; M = Zr; R2=1-isopropylphenyl; heteroaryl=indolyl

Figure 1. N-heteroaryl-pyridylamido (heteroaryl = pyrrolyl or indolyl) $[(N^-,N,N^-)M^{IV}(NMe_2)_2]$ (M = Ti, Zr, Hf) and $[(N^-,N,N^-)Zr^{IV}R_2]$ (R = Me or CH_2Ph) complexes.[31]

The species deriving from the reaction of the N-indolyl-pyridylamido Zr(IV) dimethyl complex **11** was isolated and single crystals suitable for X-ray diffraction were obtained: the solid state structure (see Scheme 5) confirmed the formation of a dinuclear complex consisting of two indolyl-pyridyl-amidomethylzirconium $[(N^-,N,N^-)Zr^{IV}R]^+$ units, with each Zr atom having a square pyramidal geometry, where the tridentate ligand and one methyl group occupy the base of the pyramid, while the apical position is occupied by a η^n-indolyl unit belonging to the other unit. Two out-of-sphere $[B(C_6F_5)(CH_3)]^-$ anions are present in the cell, allowing for electroneutrality.

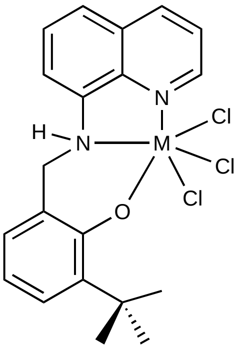


Scheme 5. Synthesis and X-ray crystal structure of dimeric $\{[(N^-,N,N^-)Zr(Me)]_2\}^{2+}$; only one of the two out-of-sphere $[MeB(C_6F_5)_3]^-$ anions is shown.

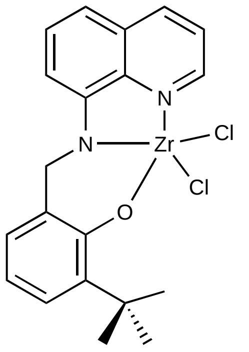
Interestingly, activation of the $[(N^-,N,N^-)ZrR_2]$ dialkyl complexes with 1 equivalent of either $[Ph_3C][B(C_6F_5)_4]$, $B(C_6F_5)_3$, or $[HNPhMe_2][B(C_6F_5)_4]$) did not give active polymerization catalysts. NMR monitoring of the reaction of the ionic species with propene showed no evidence of carbon metallation and/or ligand modification by monomer insertion. Only the addition of mixtures of MAO/Al^iBu_2H as the co-catalyst resulted in high activity for propene polymerization, again without evidence of ligand modification. We hypothesized that monomer binding is hampered by the η^n-indolyl coordination in the dimeric OSIP species and that addition of Al^iBu_2H is crucial to split the homodimers, e. g. via homobinuclear ⇆ heterobinuclear equilibria, resulting in $[(N^-,N,N^-)Zr(\mu\text{-}H)_nAl{}^iBu_2]^+$ species, as observed in some zirconocene-Al^iBu_2H mixtures.[35] Subsequent theoretical studies by Talarico et al.[36] showed that the formation of such Zr-μ-H-Al dimeric species in these systems is energetically feasible, and, more importantly, that it can explain the origin of stereospecificity of propene polymerization also for C_s-symmetric complexes of this class, via an unusual direct ligand monomer interaction in a square pyramidal intermediate.

1.5. Other post-metallocene group 4 catalysts

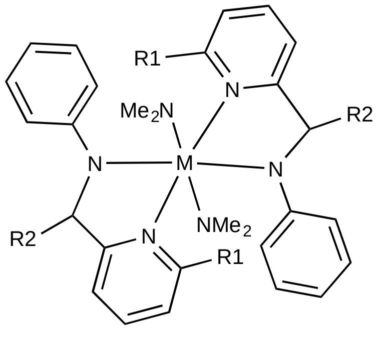
After the "metallocene era", olefin polymerization catalysis moved to the search of different coordination environments and different metals, resulting in the discovery of a huge number of new catalysts, often referred to as "non-metallocenes"[7b] or "post-metallocenes", some of which have also entered in industrial processes.[37] In this respect, in addition to the N-heteroaryl-pyridylamido catalysts cited in section 1.4, the UNISA CIRCC unit synthesized Zr and Hf complexes bearing either a tridentate monoanionic 2-tert-butyl-6-[(quinolin-8-ylamino)methyl]phenolate or a dianionic 2-tert-butyl-6-[(quinolin-8-ylamido)methyl]phenolate ligand (Figure 2, complexes **12**-**14**).[38] Moderately active catalysts were obtained from all the complexes after activation with MAO, producing high molecular weight linear polyethylene and prevailingly isotactic poly(α-olefins), with stereospecificity increasing while the size of the monomer increases (the content of isotactic pentads ranges from 50% for polypropylene up to 99% for poly(1-hexene). *In situ* NMR monitoring of the activation reaction by MAO suggested the hypothesis that similar active species are formed from the amino $[N,N,O^-]ZrCl_3$ complexes **12** and **13**, and the amido $[N,N^-,O^-]ZrCl_3$ complex **14**, due to abstraction of the NH proton by a Zr-Me as shown by the evolution of methane.



12 M = Zr
13 M = Hf



14



15 M = Zr; R1=R2=H
16 M = Hf; R1=R2=H
17 M = Zr; R1=CH_3; R2=H
18 M = Hf; R1=CH_3; R2=H
19 M = Zr; R1=Br; R2=H
20 M = Hf; R1=Br; R2=H
21 M = Zr; R1=H; R2=CH_3

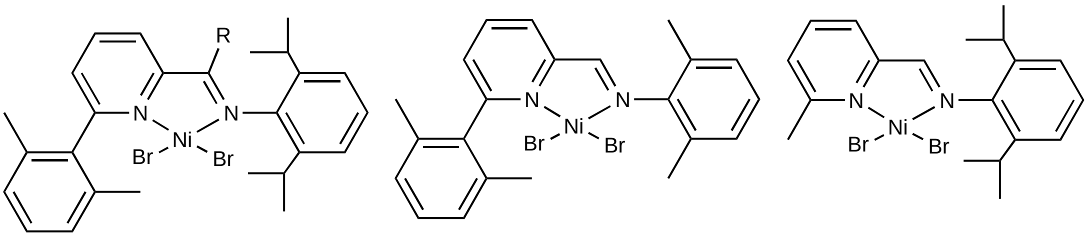
Figure 2. 2-tert-butyl-6-[(quinolin-8-ylamino)methyl]phenolato [N,N,O^-]MCl_3 (M = Zr or Hf), 2-tert-butyl-6-[(quinolin-8-ylamido)methyl]phenolato [N,N^-,O^-]$ZrCl_2$, and bis(2-anilidomethylpyridine) $[N,N^-]_2M(NMe_2)_2$ complexes (M = Zr or Hf).

In another study, bis(chelate) zirconium and hafnium $[N,N^-]_2M(NMe_2)_2$ complexes **15**-**21** bearing different 2-anilidomethylpyridine ligands were synthesized and characterized in solution as more or less fluxional octahedral species, depending on the steric and electronic features of the ligands (Figure 2).[39] All the complexes were activated using Al^iBu_2H /MAO as the co-catalyst, resulting in efficient polymerization of ethylene, producing polymers with more or less broad molecular weight distributions, paralleling the complex fluxionalities.

1.6. Ni(II) catalysts

The discovery of α-diimine Ni(II) catalysts by Brookhart and coworkers opened the era of late-transition metal olefin polymerization catalysts.[40] Brookhart's catalysts promote a "chain-walking" polymerization of ethylene, resulting in the production of branched macromolecules, with a branching degree depending on temperature, monomer pressure and catalyst structure.[40] Early work by the UNISA group reported that the degree of branching is also significantly influenced by co-catalyst effects,[41] but this finding was apparently overlooked, although some contrasting results on the matter were reported in the following years.[42] More recently, the relationships between the mode of activation and the resulting polyethylene structure were re-examined, confirming that a proper choice of the mode of activation is a powerful tool to modulate the polymer microstructure.[43] In fact, comparison of the performance of the prototypical Brookhart catalyst bis(N-(2,6-diisopropylphenyl)imino)acenaphthene dibromo nickel(II) activated by either $AlEt_2Cl$ or MAO under a variety of conditions indicated that polymers prepared using $AlEt_2Cl$ instead of MAO have a higher content of long chain branches and of "branches on branches". Consequently, high molecular weight amorphous PE's displaying excellent elastomeric properties could be produced under suitable conditions. Full characterization of these materials by thermal, X-ray diffraction and mechanical analyses provided insight in the relationships between the microstructure and the crystallization behavior and the elasticity of the polymers. The most relevant conclusion was the achievement of amorphous ethylene polymers displaying the ability to reversibly crystallize under stretch (a feature of natural rubber) and an elastic performance comparable to that of conventional ethylene-propylene copolymers, but with a significantly lower number of tertiary carbons in the chain. The latter feature implies (i) reduction of the glass transition temperature, and (ii) more efficient radical crosslinking with reduction of degradation reactions.

Another important class of late-transition metal catalysts was discovered by the groups of Brookhart and Gibson, who independently reported 5-coordinate 2,6-bis(arylimino)pyridyl Fe(II) and Co(II) complexes as catalyst efficiently producing polyethylenes with interesting features, e. g. bimodal molecular weight distributions, and suitable for use in existing industrial plants.[44] Following the success of the arylimino-pyridyl moiety in these catalysts, complexes of bidentate iminopyridine ligands with Fe(II), Co(II), Ni(II) and Pd(II) were also tested for ethylene homo-polymerization[45] and co-polymerization with polar monomers (*v. infra*). While most of the previously reported iminopyridine ligands lack substituents at the pyridine moiety, the UNISA group reported the synthesis of Ni(II) dibromo complexes **22**-**25** bearing iminopyridine ligands with bulky substituent in the 6-position of pyridine (Figure 3).[46] These complexes were initially tested in the polymerization of ethylene after activation with $AlEt_2Cl$ under 1 - 50 atm monomer pressure and at T = 20 - 50 °C, resulting in the production of hyperbranched, methanol soluble, low molecular weight polyethylene oils (which may find applications as synthetic base stocks in the formulation of high performance synthetic lubricants). On the other hand, polymerization at sub-ambient temperature and high pressure resulted in the production of solid polymers, in some cases consisting of different fractions. Analysis of the catalyst residues after the reaction showed partial reduction of the imino functionality. This finding prompted us to synthesize and test some corresponding aminopyridine Ni(II) complexes. The results suggested the formation of multiple active species owing to ligand structure modification in the activation process under certain conditions.[46b]



22 R = H
23 R = CH_3

24

25

Figure 3. Structures of Ni(II) complexes bearing iminopyridine ligands with bulky substituents at both the imine and the pyridine moieties.

2. Polymerization of styrene and dienes

2.1 Styrene-dienes copolymerization

Styrene-butadiene copolymers (SBR) represent, by far, the most important commodity in the field of copolymers and, with high *cis*-polybutadiene, the most important synthetic elastomer. Commercial SBR are obtained by anionic-living polymerization initiated by alkyl-lithium with a scarce control on the stereoregularity of the resulting copolymers.[47] Indeed, the tool to obtain an higher control in the stereoselectivity during the polymerization reaction is the use of heterogeneous or homogeneous Ziegler-Natta catalysts operating through a coordination-insertion mechanism.

Notwithstanding the efficient stereoregular polymerization of 1,3-butadiene[48] and stereoregular polymerization of styrene[49] are both possible, the systems able to efficiently copolymerize these monomers are rather rare. On one hand, the renewed interest in the stereoregular polymerization of styrene (**S**) sparked by the discovery of syndiotactic polystyrene (*s***PS)** by Ishihara in 1986[50] also stimulated the search of homogeneous titanium catalysts for the stereoregular styrene-butadiene copolymerization.[51],[52] On the other hand, although isotactic polystyrene (i**PS**) was the first stereoregular polymer structurally characterized,[53] the synthesis of this material was for a long time neglected because of its low rate of crystallization hampering commercial applications.

With the exception of a report on a C_1 bridged zirconocene,[54] the isospecific **S** polymerization by using homogeneous group 4 complexes became possible by using the [OSSO]-type metal complexes **26-29** (Figure 4) that produced i**PS** with a high degree of isotacticity, as evidenced by the value of T_m (217 - 223 °C) and the ^{13}C NMR analysis.[55] In the case of the titanium compound **26** high molecular weight (up to 2 654 000 g/mol) and narrow dispersity ($Đ$ = 1.7 - 2.0) were also obtained.

32

26 R1 = R2 = *t*Bu; M = Ti; X = Cl
27 R1 = R2 = *t*Bu; M = Ti; X = O^iPr
28 R1 = R2 = *t*Bu; M = Zr; X = CH_2Ph
29 R1 = R2 = *t*Bu; M = Hf; X = CH_2Ph
30 R1 =$C(CH_3)_2Ph$; R2 = CH_3; M = Ti; X = Cl
31 R1 = R2 =$C(CH_3)_2Ph$; M = Ti; X = Cl

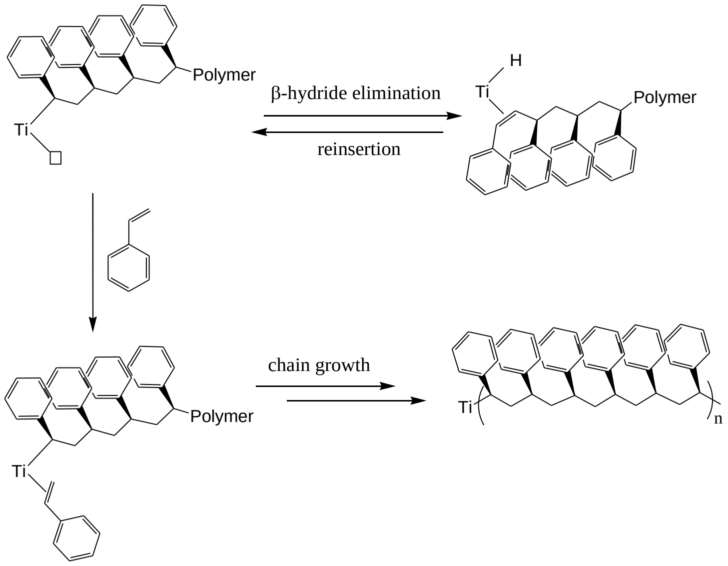
Figure 4. [OSSO]type group 4 complexes (**26-31**) and titanium monocyclopentadienyl complex **32**.

After this first finding a systematic study on the structure-reactivity relationship for the titanium compounds was performed by varying the length of the bridge between the two sulfur atoms and the steric bulk of the substituents on the aromatic rings.[56]

In particular, in 2010 we observed that the titanium compound **30** activated by MAO promoted the living, isospecific polymerization of styrene with a linear increase of the molecular weight with conversion and narrow dispersity (*Đ* = 1.05 - 1.19) at room temperature.[57] The same complex also promote the 1,4-*trans*-selective(≥ 95%) polymerization of 1,3-butadiene (**B**) at 0 °C in a controlled fashion (*Đ* = 1.28 - 1.77). Such behavior allowed the synthesis of diblock isotactic polystyrene-block-1,4-*trans*-polybutadiene (i**PS**-*block*-1,4-*trans***PB)** by sequential monomer addition. The length of both blocks can be adjusted simply regulating the feed composition with the resulting copolymers displaying narrow dispersity (*Đ* = 1.08 - 1.10). The DSC thermograms highlight that both blocks are crystalline displaying the typical transitions of i**PS** (224.5 °C) and 1,4-*trans*-**PB** (46.9/87.8 °C).

A living behavior for the catalyst **30**/MAO was also observed in the isoselective polymerization of 4-methyl-1,3-pentadiene,(**MPD**) 4-methylstyrene,(**MS)** and 4-tert-butylstyrene(**TBS**), allowing the synthesis of a series of new diblock and triblock copolymers: isotactic polystyrene-block-poly-(4-methyl-1,3-pentadiene), poly(4-methylstyrene)-block-polystyrene, poly(4-methylstyrene)-block-1,4-trans-poly(1,3-butadiene), poly(4-methylstyrene)-block-polystyrene-block-poly(4-methylstyrene),poly(4-methylstyrene)-block-polystyrene-block-poly(4-methyl-1,3-pentadiene), and poly(4-methylstyrene)-block-polystyrene-block-poly-(4-tert-butylstyrene).[58]

The living behavior in the polymerization of **S** also allowed the synthesis of low molecular weight polystyrene showing the polymer chain ends, as expected the insertion into the Ti-CH_3 bond is secondary (i.e. 2,1) in both the initiation and the termination steps, but the signals relative to an unsaturated terminal due to β-hydride elimination reaction with *cis* configuration are clearly visible in the spectrum. This observation coupled with the absence in the spectrum of the terminal due to the insertion into the Ti-H bond suggest that the β-hydrogen reaction does not represent an irreversible event but the unsaturated polymer chain is rather a resting state in equilibrium with chain growth state (Scheme 6) similarly to the mechanism depicted for the syndiospecific polymerization of styrene promoted by $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$.[59]



Scheme 6. Proposed mechanism for the formation of unsaturated chain ends. Reproduced from ref. [58], Copyright with permission (2011) from ACS

Later, the complex **26**/MAO and the monocyclopentadienyl titanium complex **32**/MAO were used in the binary polymerization of **MS** with **B** and isoprene(**I**).[60]

Complex **26**/MAO produces copolymers in a wide range of compositions (**MS** = 29-93% in mol) with a molecular weight distribution compatible with material being copolymeric in nature($Đ$ = 1.7 - 2.6), the $\boldsymbol{T_g}$ increase by increasing the styrene content from -23 °C to 98 °C. ^{13}C NMR study show a random structure with the **MS** units enchained in isotactic way (maximum MS block lengths from 2 to 7 units) and the **B** unit mainly present as 1,4-*trans* with lower amount of 1,4-*cis* units. The **MS**-**B** copolymers (**MS** = 19-70% in mol) obtained in the presence of **32**/MAO display slightly broader molecular weight distribution ($Đ$ = 2.9 - 3.8), and two values of two T_g at -89 and 66°C as expected for a phase separated polymeric material consisting of long s**PMS** homosequences (MS block lengths from 4 to 25 units) and 1,4-*cis*-**PB** segments. A similar trend is observed in the case of **MS**-**I** copolymerization with on one hand the catalyst system **26**/MAO affording copolymers with *i***PMS** segments and **I** mainly enchained with 1,4-*trans* streochemistry and on the other hand **31**/MAO pruducing coplymer with *s***PMS** blocks and 1,4-*cis*-**PB** segments.

The titanium catalyst **26** and **31** activated by MAO were also used in the **S-I** copolymerization and **S**-1,3-pentadiene (**PD**) copolymerization.[61] The microstructure in the case of the **S-I** copolymers obtained in the presence of catalyst **26** is similar to that observed in the case of the **MS-I** copolymers with isotactic polystyreneblocks and 1,4-trans-isprene. Notably by using the catalyst **31** an increase of the **I** 1,4-*cis* (up to 28% of the **I**) and 3,4 units (up to 28% of the **I**) was observed in the copolymer microstructure.

In the case of the **S**-**PD** copolymers both catalysts give copolymers with similar microstructural features with **PD** preferentially enchained ad 1,2-units as already observed for the homopolymerization.[62]

4MPD was also copolymerized with **S**, **B** and **I** in the presence of catalyst **31**/MAO obtaining copolymers with preferentially alternating microstructure.[63]

2.2 Polymerization and copolymerization of acyclic terpenes

More recently, terpenes emerged as valuable building blocks for bio-based polymers.[64,65] Indeed, catalysts **26** and **32** promote the homo-polymerization of myrcene (**M**) and ocimene (**O**) (Figure 5).[66] In particular, in the case of M the catalysts **26** give a polymer with prevalently 1,4-*trans* streochemistry (up to 92%) and catalyst **32** with 1,4-*cis* units as observed in the case of **B** and **I**. In addition, catalyst **26**/MAO also promote the , **S**-**M** and the **S**-**O** copolymerization giving the desired copolymers in a wide range of compositions (11 - 96% mol of **M** and 13 - 85% mol of **O**) and with narrow molecular weight distribution (*Đ* = 1.1 - 1.9). For the **S-M** copolymers, the reactions were performed in toluene at 70 °C ([Al]/[Ti] =500, [**M**+**S**]/[Ti] = 1 000) giving a copolymer with **M** incorporated mostly as 1,4-*trans* units (89 - 62% mol) with a lower amount of 3,4-vinyl units, with isolated **S** units in the case of the copolymers with a lower amount of **S** and short *i***PS** blocks in the copolymers with higher **S** content.

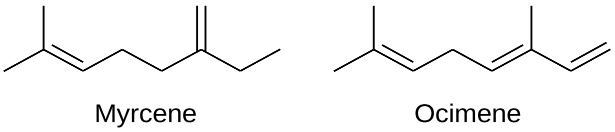


Figure 5. Structures of acyclic terpenes myrcene and ocimene.

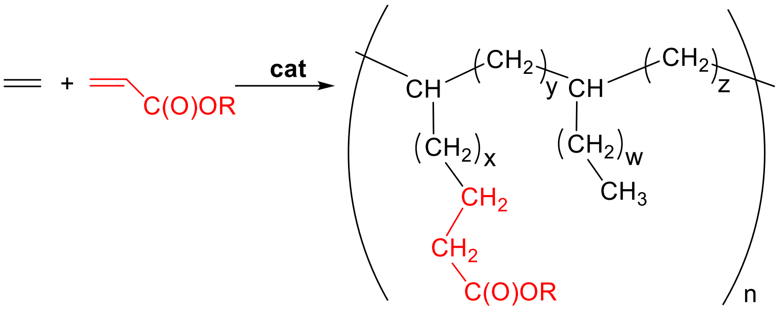
Intriguingly the stereochemistry of **O** in the homopolymerization promoted by **26** and **31** is temperature dependent giving at 70 °C for the catalyst **26** an high content of 1,4-trans units (70%) and a 1,2-isotactic-polymer at 0 °C for the catalyst **31**. Such behavior is observed also in the **S-O** copolymerization at 25 °C or 70 °C ([Al]/[Ti] = 500, [**O**+**S**]/[Ti] = 1 000). As a matter of fact, in the first case the **O** units were exclusively incorporated as vinyl 1,2-segments, in the second case an almost equal amount of 1,4-trans and 1,2-units (43 - 47% mol and 53 - 57% mol, respectively) were detected by using the catalyst **31**/MAO. The multiblock nature of the resulting copolymers was evidenced by an AFM study of the polymer thin film morphology, highlighting the presence of small i**PS** domains.

By using **31**/MAO it was also possible to copolymerize **B** with **M** and **O** obtaining copolymers with a wide range of compositions (up to 85% mol for **O** and 47% of **M**) with high degree of stereoselectivity (up to 95% of 1,4-*trans* for **B** and 92% of 1,2 insertions in the case of **O** and up to 90% and 71% of 1,4-trans insertion for **B** and **M**, respectively) and narrow dispersity ($Đ$ = 1.1 - 2.0).[67]

The **B**-**O** copolymer showed better behavior in a model tread compound with respect to the commercial 1,4-*cis*-polybutadiene suggesting that these copolymers could in principle be used in substitution of standard *cis*-BR in a tire tread without major alteration of the compound properties.

3. Copolymerization of olefins with polar monomers

Brookhart's discovery of highly efficient ethylene polymerization catalysts based on Ni(II) and Pd(II) complexes with α-diimine (N-N) ligands[40a] represented a breakthrough in the field of catalysis for controlled polymerization because the same complexes are also able to catalyze the copolymerization of ethylene with polar vinyl monomers, such as acrylic esters, to yield functionalized polyolefins (Scheme 7).[68] The latter macromolecules are highly desirable materials because, thanks to the presence of polar functional groups into the otherwise apolar polyolefin skeleton, they should show enhanced surface properties and have access to easier recyclable pathways than polyolefin themselves.



Scheme 7. The ethylene/acrylic ester copolymerization.

A few years later, Drent, Pugh et al. reported a catalytic system for the ethylene/methyl acrylate (MA) copolymerization always based on palladium(II) complexes but differing for the spectator ligand that belongs to the class of phosphino-sulfonate (P-O) derivatives.[69] The two catalytic systems led to very different macromolecules: the copolymers obtained with the α-diimines are made of branched macromolecules with an MA content around 5 mol %, inserted exclusively at the end of the branches, whereas those produced with the P-O based catalysts are made of linear macromolecules with an almost 1:1 ratio of the two comonomers inserted into the main chain.[70] In addition, the latter class of catalysts demonstrated to be quite versatile being able to copolymerize ethylene with a variety of polar vinyl monomers, like vinyl acetate,[71] acrylonitrile,[72] allyl monomers,[73] alkyl vinyl ether,[74] vinyl fluoride,[75] and nitrogen-containing polar monomers.[76] Moreover, they were also found to be active for emulsion copolymerization.[77]

These two classes of catalysts remained those preferentially investigated for almost two decades. Afterwards new molecules started to be applied as chelating ancillary ligands for both Pd(II) and Ni(II) catalysts.[78] In addition to determine catalyst activity, content of polar monomer incorporation and copolymer molecular weight and polydispersity, the nature of the spectator ligand was found to affect the way of polar monomer incorporation. As an example, bisphosphino monoxide derivatives led to linear copolymers with MA randomly distributed into the main chain.[79] An analogous way of incorporation was found for the copolymers obtained with phosphino-(diethyl phosphonate) ligands, whereas when the bis(diethyl phosphonate) counterparts were used, the obtained linear macromolecules have MA inserted both into the main chain and as terminating end-groups.[80] Pd(II) catalysts having molecules belonging to the family of phosphine-phosphonic amide[81] or diamide[82] resulted to be very active in the production of E/MA copolymers with higher molecular weight than those obtained with the P-O derivatives. Finally, as an alternative to the phosphine molecules, NHC carbenes were also investigated, and the corresponding Pd-catalysts led to copolymers of MA with both ethylene and propene, with moderate yields, molecular weight and amount of inserted polar monomer.[83,84]

Among the different families of ligands investigated till now, α-diimines appear to be the most promising and versatile,[78c] thus as a consequence of Brookhart's discovery an impressive number of molecules of this class has been developed, and the contribution of UNITS unit to the field is, indeed, focused on α-diimine Pd(II) catalysts.

From a general point of view the investigated α-diimines can be grouped into three classes depending on ligand variation with respect to the parent compounds that are α-diimines with either a 1,4-diaza-2,3-butadiene (DAB) or an acenaphthene (BIAN) skeleton and bearing aryl rings substituted in 2 and 6 positions with either isopropyl or methyl groups. The considered variations involve: i. ligand desymmetrization meaning at having different substituted aryl rings on the iminic nitrogen atoms (class 1); ii. ligand skeleton meaning at increasing the bulkiness of the backbone (class 2); iii. ligand bulkiness meaning at remarkably enhance the steric congestion around the catalytic center (class 3).

As for ligand desymmetrization, the UNITS unit was among the first research groups applying nonsymmetric α-diimines (N-N') as ancillary ligands for Pd(II) catalysts for ethylene/methyl acrylate copolymerization. We initially investigated Pd-complexes with α-diimines having either a BIAN (**Pd-BIAN**, **33**; Figure 6) or a DAB skeleton (**Pd-DAB**, **36**; Figure 6) and one aryl ring 2,6-dimethyl substituted and the other bearing a trifluoromethyl group on positions 3 and 5, thus creating a subtle electronic and steric unbalance on the two nitrogen-donor atoms.[85,86] In general the synthesis of the nonsymmetric ligands was not trivial at all and in a few cases the ligand itself was not obtained as an isolated molecule, but the desired palladium complex was directly synthesized by following a template synthesis based on the use of [Pd(cod)(Me)Cl] as templating agent (cod = *cis*,*cis*-1,5-cyclooctadiene).[86]

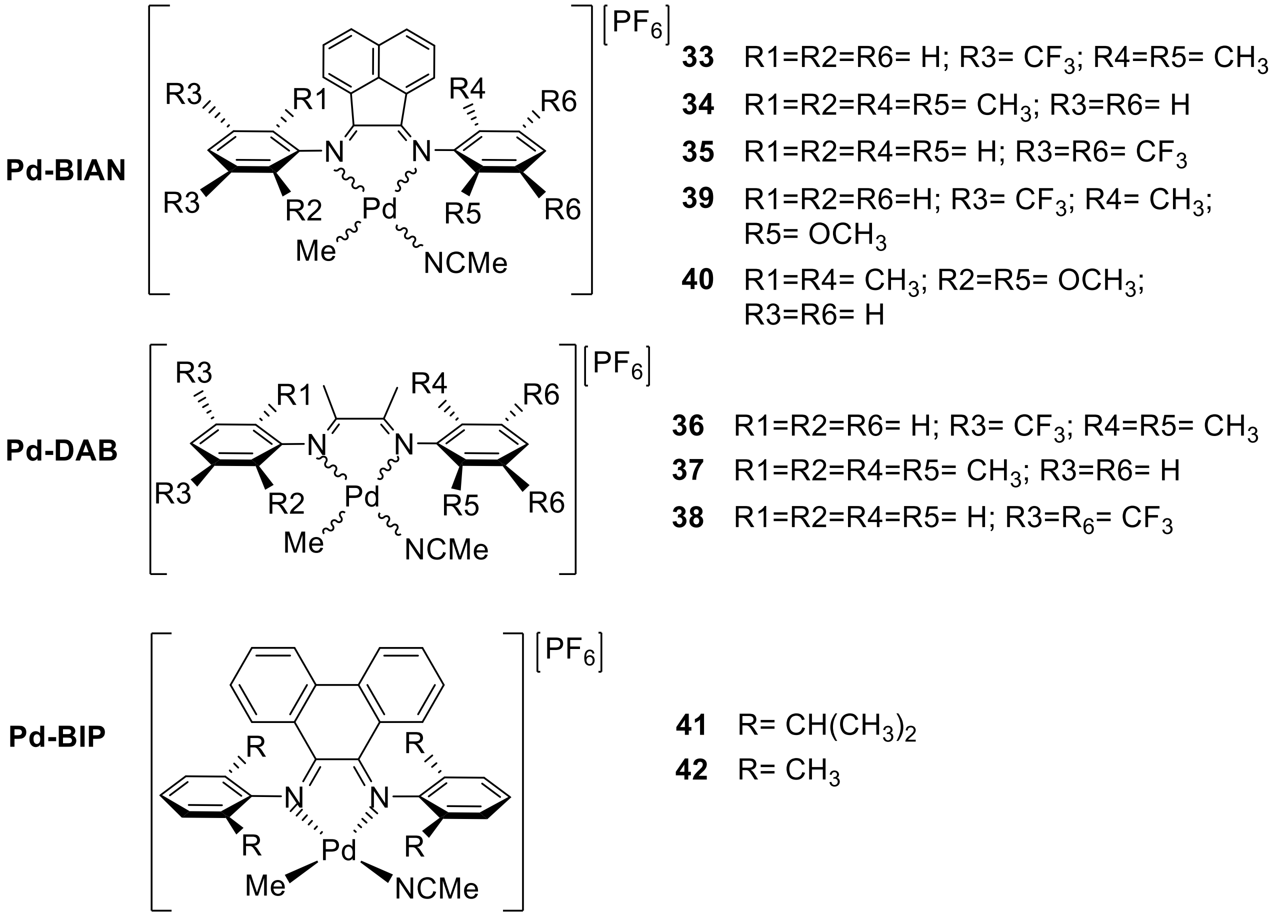


Figure 6. The investigated Pd(II) complexes with either nonsymmetric, N-N', or symmetric, N-N, α-diimines.

The cationic Pd(II) complexes of general formula [Pd(Me)(N-N'/N-N)(NCMe)][PF_6] (**33-40**, Figure 6) were tested as precatalysts for the ethylene/methyl acrylate copolymerization, under mild reaction conditions of temperature and ethylene pressure (T = 298 – 308 K; P_E = 1.5 – 7 bar), and in 2,2,2-trifluoroethanol (TFE) as a solvent. The isolated catalytic products obtained with precatalysts **33**, **36**, **39**, having the nonsymmetric ligands, were oils made of highly branched (≈ 100 branches per 1000 carbon atoms) ethylene/MA co-oligomers having the polar monomer inserted at the end of the branches, which is, in agreement with literature,[68,87] the result of the chain walking mechanism. Moreover, the GC-MS analyses of the reaction mixtures, performed at the end of the catalytic runs, also indicated the production of higher alkenes in the range C_4-C_{16}. The latter result and the formation of co-oligomers instead of copolymers are reasonably ascribed to the decrease of steric hindrance on one of the two aryl rings of the nonsymmetric ligands.

The effect of ligand desymmetrization on productivity is somehow related to ligand nature. In particular, precatalyst **33** showed a productivity higher than that found for the derivatives with the corresponding symmetric BIANs (**34**, **35**), leading to ethylene/MA co-oligomers with a higher content of inserted MA**.**[85] Instead when precatalysts **36** or **37**, having the ligands with DAB backbone, were used, an increase in the productivity was achieved with respect to the BIAN analogues, but for precatalyst **36**, with the nonsymmetric DAB**,** the increment was not as pronounced as expected, and its productivity resulted to be lower than that of precatalyst **37** with the corresponding symmetric ligand.[86] For both series of compounds, complexes **35** and **38**, with the symmetrically CF_3-substituted ligands, were found practically inactive due to fast decomposition to palladium metal.

The use of precatalysts **39** and **40**, whose ligands can be considered as formally derived from the replacement of one or more methyl groups with methoxy substituents on position 2 of either one or both aryl rings, respectively, resulted in a remarkable decrease in productivity.[88] In all cases the ethylene/MA co-oligomers produced with catalysts having the nonsymmetric ligands have a higher content of inserted MA (a value up to 38 % was reached for co-oligomers produced with **39**) than those obtained with the corresponding symmetric derivatives. This data might be another effect of the lower steric hindrance created around palladium by the nonsymmetric derivatives with respect to that of the ortho symmetrically substituted molecules.

The negative effect of the methoxy substituent on the productivity is in contrast to literature data, where the introduction of this group resulted in much better performing catalysts both for phosphino-sulfonate derivatives,[69] and for α-diimine ligands having it either in *para* position of the aryl rings[89] or on the BIAN skeleton.[90] Kinetic studies about the rate of the migratory insertion reaction of methyl acrylate into the Pd-Me bond for complexes **39** and **33**, together with the higher content of inserted MA suggest that the catalysts with the methoxy-substituted ligands have a high affinity for the polar monomer and its insertion into the growing co-oligomer chain might be favored with respect to that of ethylene leading to a highly stable species that represents a deactivated form of the catalyst.

Other relevant contributions to ligand desymmetrization dealt with both the modulation of the steric hindrance around palladium by remarkably increasing the steric congestion on one imminic nitrogen atom through the introduction of a dibenzyhydryl-aryl fragment,[91] and the enhancement of the electronic differentiation of the two donor atoms moving from an α-diimine to an imino-amine ligand. The relevant Pd(II) catalyst was able to insert MA preferentially into the main chain.[92]

The UNITS unit also contributed to class 2 of ligands, by studying Pd(II) complexes having α-diimine molecules with a phenanthrene skeleton (BIP) and aryl rings substituted in 2,6 positions with either iso-propyl (**41**) or methyl groups (**42**) (Figure 6).[93]

The comparison of the structure in solid state of the corresponding neutral complexes **43** and **44**[94] points out that in **43** the ligand is stronger coordinated to palladium than that one in **44** (Figure 7). Moreover, whereas in **44** the coordinated BIAN molecule is almost perfectly planar, in **43** the BIP derivative is markedly twisted. Both differences positively reflected on the performances of the catalysts with the BIP ligands that generated active species, having a good thermal stability, for the ethylene/MA copolymerization leading to real copolymers with a content of inserted MA up to 5.3 % and Mn values up to 37 kDa. Moreover, it was discovered that the polar monomer was inserted both at the end of the branches (**T(MA**)) and into the main chain (**M(MA)**), with a more selective enchainment than that found in the copolymers obtained with the Pd-BIP catalysts but in dichloromethane instead that in the fluorinated solvent.

Another important variation of the ligand skeleton was related with the introduction of a dibenzobarrelene backbone,[95] and when this backbone was also associated to pentiptycenyl-based substituents on the iminic nitrogen atoms (a ligand of class 3) the resulting Pd(II) catalysts led to the synthesis of a ultrahighly branched copolymer with MA inserted into the main chain.[96]

The effect of the solvent used for the catalytic reactions on the way of MA enchainment was even much more pronounced when the copolymerization reactions were performed in trifluoroethanol with the simple Brookhart's precatalyst **37**. In this case the **M(MA)**:**T(MA)** ratio was 40:60, whereas for the copolymer produced in dichloromethane was 12:88. The value of the ratio was raised up to 45:55, when the precatalyst has a tiophenimine (N-S) in place of acetonitrile in the palladium coordination sphere (Figure 7).[97]

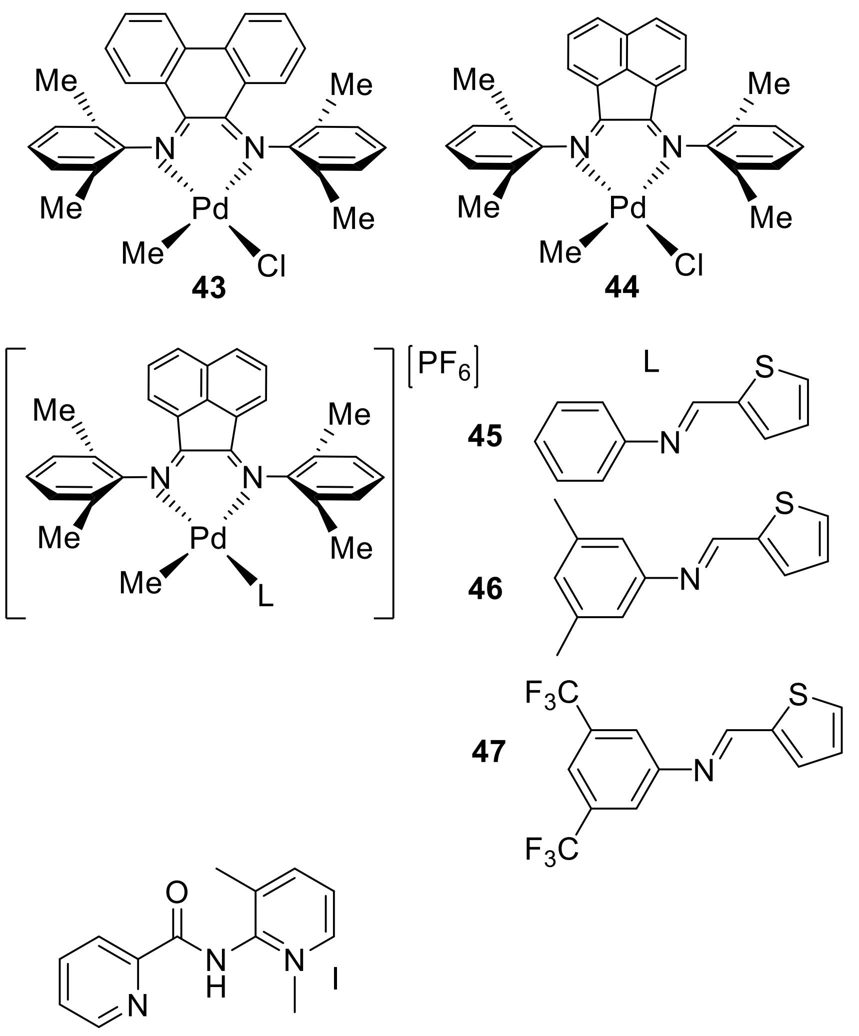


Figure 7. Some neutral and cationic Pd(II) complexes, together with investigated thiophenimines, N-S, and the pyridyl-pyridylidene amide molecule.

An accurate mechanistic investigation on the reactivity of precatalysts **37** and **45** with both comonomers, ethylene and methyl acrylate, carried out by in situ NMR spectroscopy, both in TFE-d_3 and in CD_2Cl_2, at room temperature, pointed out some remarkable differences with respect to the typical reactivity of the Pd-α-diimine catalysts.[85,86,87,93] In particular, we demonstrated that in TFE-d_3 the migratory insertion reaction of MA into the Pd-Me bond led to the formation of the expected six-membered palladacycle **MC6**, as the result of the chain walking phenomenon, together with the open-chain intermediates, **OC1** and **OC2**, having both the organic fragment, originated by the insertion of MA into the Pd-alkyl bond, and either acetonitrile or N-S coordinated to palladium (Figure 8). The open-chain intermediates were detected for the first time in this study. They are stabilized by a network of hydrogen bonds involving trifluoroethanol and the oxygen atoms of the ester group of inserted MA. In these intermediates, MA is trapped into the main chain and the further reactivity with ethylene leads to the growing of the copolymer having the M(MA) enchainment. These NMR findings, combined with DFT calculations, allowed to identify the open-chain species as novel catalyst resting states.

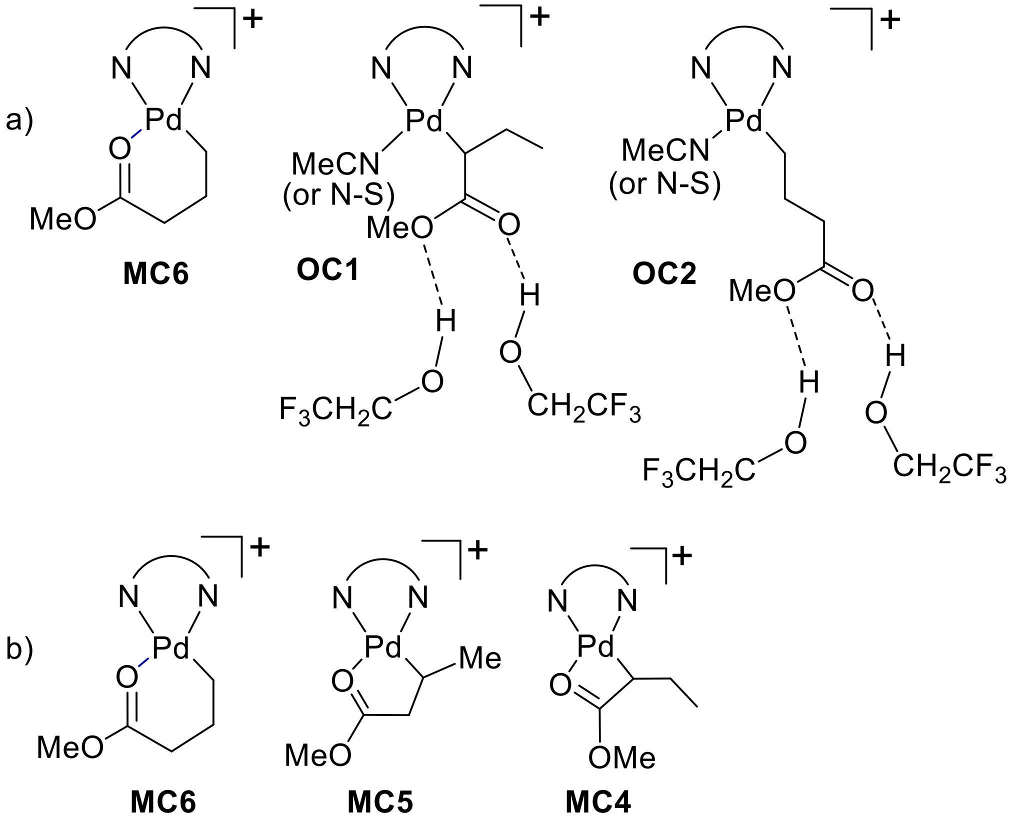


Figure 8. Detected intermediates in the reactivity of **37** and **45** with MA, at room temperature, in: a) TFE; b) CD_2Cl_2.

In addition, the study of the reaction between MA and the acetonitrile precatalyst **37** in CD_2Cl_2, at room temperature, allowed to detect, in addition to the six-membered metallacycle **MC6**, both the five- and the four-membered intermediates (**MC5** and **MC4**, respectively; Figure 8). This was the first experiment where **MC4** was observed at temperature higher than 213 K for Pd-α-diimine precatalysts. The main differences between the complex under investigation and the typical Brookhart's catalysts refer to the counterion and to the presence of acetonitrile that might remain close to the metal center during catalysis thus favorably hampering the chain walking process. This hypothesis is in agreement with our findings about the reaction between MA and the palladium complex [Pd(Me)(N-N')(MeCN)][PF_6] with N-N' = pyridyl-pyridylidene amide ligand (Figure 7).[98] Even in this case the studies carried out by in situ NMR spectroscopy allowed to detect the corresponding **MC4** species that resulted to be stable enough for at least 10 h at room temperature. In this case no formation of the possible six-membered metallacycle was observed thus pointing out that the chain walking process was significantly slowed down.

During the last five years, some investigations on the application of nickel(II) complexes as catalysts for the copolymerization of ethylene with polar vinyl monomers started to appear.[99] Thanks to the experience of the UNISA unit in the use of Ni(II) complexes with iminopyridine ligands as catalysts for polyethylene synthesis,[46] four of them (complexes **22**-**25**, Figure 3) were also tested in the copolymerization of ethylene with methyl acrylate in a collaboration between UNISA and UNITS units.[100] They led to the formation of low molecular weight, hyperbranched ethylene/MA copolymers with a content of polar monomer in the range 0.5 – 38 mol % and incorporated in a variety of modes, some of them never observed before (Figure 9).

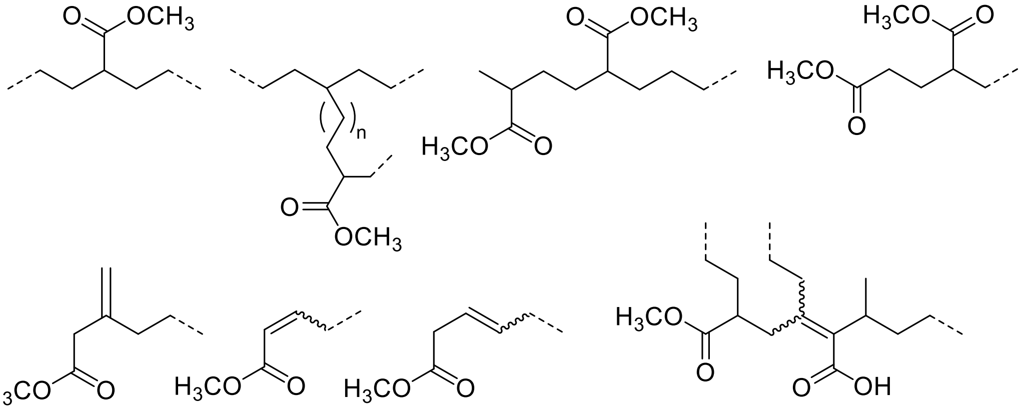


Figure 9. Molecular fragments of inserted MA in the ethylene/MA copolymers obtained with Ni(II) catalysts **22**-**25** (Figure 3).

The main conclusion was that the nature of the iminopyridine affects catalyst productivity, polymer molecular weight and amount of inserted MA, but not the way of MA incorporation, that is dictated by both the activating agent and the solvent used.

4. Ring-opening polymerization of cyclic esters

Linear aliphatic polyesters as degradable thermoplastic polymers constitute the green alternative to fossil-fuel based polymers and can be obtained by polycondensation reactions from a diol and a diacid and ring-opening polymerization (ROP) of cyclic esters. The polycondensation is however difficult to control, and moreover it is difficult to achieve high molecular weight polymer with this process. The ROP of cyclic esters is traditionally promoted by homoleptic metal alkoxide complexes, such as tin (II) octanoate ($SnOct_2$). The latter is an efficient catalyst for the ROP of a wide range of cyclic esters, and it is used in the industrial process for the production of 300 kTons/year of poly(lactide) (PLA). However, the potential toxicity of Sn residues in the polymer is a matter of concern, especially for biomedical and food packaging applications, spurring intensive academic research toward the development of novel catalysts.

A large synthetic effort has been directed towards the development of efficient metal-based initiators and the studies of their reactivities. The *first generation* of active initiators were mainly constituted by simple homoleptic metal complexes, such as zinc(II) lactate and aluminium(III) isopropoxide[101], and constituted the playground where the understanding of three step coordination-insertion mechanism for the ROP of cyclic esters was developed.[102] In this mechanism, the first step is the coordination of the monomer to the metal center through the carbonyl oxygen, followed by the insertion of the monomer in the metal-initiating group bond, typically an alkoxide.

The homoleptic complexes, however, presented several drawbacks; first, due to complex equilibrium and the multinuclearities of the active centers, deleterious transesterification reactions with broadening of the polymers dispersities were achieved; in addition, no control of stereochemistry was obtained. Subsequently, a *second generation* of catalysts with well-defined structure and fine tuning of the ligand structure was developed, with the aim to reach better control, activity and selectivity in the ROP. Properly designed metal complexes played an important role not only for the control of molecular weight and molecular weight distribution, but also for the production of stereoregular polyesters. It is worth noting that the industrial production of isotactic poly(L-lactide) and poly(D-lactide) does not use a stereoselective catalyst, but only a catalyst that does not produce monomer epimerization, since optically pure either L or D lactic acid is currently produced by fermentation processes using suitable bacterial strains. The important advances and current trends in the stereocontrolled ring-opening polymerization of lactide have been largely discussed in the literature. Readers interested to this topic are addressed to eminent literature reviews. [103]

In the presence of proper catalyst and conditions, the ROP could also proceed in a "*living*" fashion, enabling the preparation of materials with predictable molecular weights, narrow dispersities, as well as the synthesis of block copolymers by sequential addition of different monomers.[104] Moreover, "*immortal*" polymerization could be achieved in the presence of proper catalysts and large amounts of alcohols as chain transfer agents and large loadings of monomer for the rapid formation of polyesters. [105]

To date, not only metal complexes, but also enzymes or simple organic molecules have been reported as ROP catalysts or initiators.[106] Depending on monomers, catalytic system, nature of active species, the ROP can proceed as a coordinative, anionic or cationic polymerization mechanism. Between these methods, the coordinative ROP by metal-based catalysts allows a better control on the polymer microstructure.

Research at the UNISA CIRCC units in the field of ROP of cyclic esters started 15 years ago,[107] focusing on the development of *second generation* novel catalysts based on main and transition metals, bearing bi-dentate, tridentate or tetradentate ligands with hard and/or soft donor atoms.

Cyclic diesters and lactones, such as glycolide (GL), lactide (LA), ε-caprolactone (CL) and rac-β-butyrolactone (rac-BL) have been the most investigated monomers (Figure 10). The ROP of large ring-size lactones, such as pentadecalactone (PDL), and the ω–6-hexadecenlactone (6HDL), and of a novel thio-functionalized lactide has been also developed.

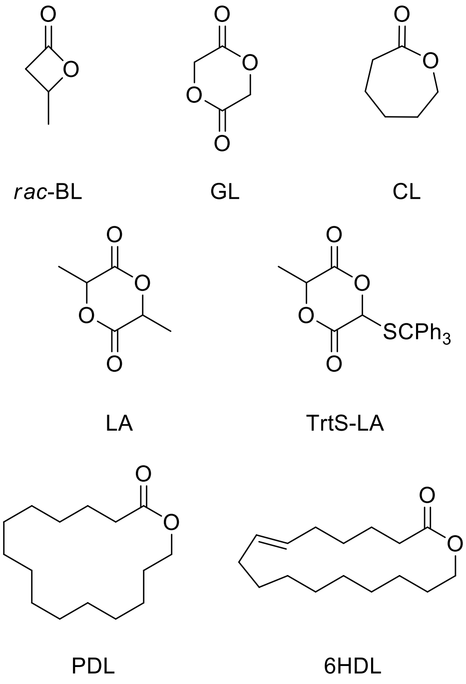


Figure 10. Monomers for ring opening polymerization: rac-β-butyrolactone (rac-BL), glycolide (GA), ε-caprolactone (CL), lactide (LA), 3-methyl-6-(tritylthiomethyl)-1,4-dioxane-2,5-dione (TrtS-LA), pentadecalactone (PDL) and ω–6-hexadecenlactone (6HDL).

4.1. Al-based ROP catalysts

Aluminum based organometallic complexes have traditionally a leading position as efficient catalysts for this polymerization process.[108] After the discovery of the stereoselective polymerization of *rac*-LA by chiral binaphthyl Schiff base aluminum complexes,[109] a large synthetic effort has been devoted to the preparation of achiral and chiral aluminium Schiff-base systems five-coordinate *salen* aluminum complexes and their use in the ROP of lactones and lactides. Some of the most significant advances in stereo controlled polymerization of *rac*-LA have been achieved using aluminum alkyls or alkoxides derivatives stabilized by *salen*- or *salan*-type ligands.[110] Polydentate phenolate-based ligands, previously used for the preparation of group 4 metal complexes for olefin polymerization with high performances, were applied for the preparation of ROP catalysts. In addition to tetradentate ONNO *salen*, aluminum derivatives of tetradentate *salalen* and *half-salen* bidentate phenoxy-imine ligands were shown to be effective initiators in the ROP of cyclic esters. The CIRCC research was also devoted to expand the ROP initiators to coordination environment other than salen and its modification, such as dianionic [$^{-}$N,N,N^{-}] tridentate pyrrolylpyridylamido ligands and phenoxy-thioether (OS) ligands.

Half-salen. Previous reports disclosed the use of various Al-salicylaldimine complexes, prepared *in situ* by mixing two equiv. of salicylaldimine ligand with $AlEt_3$ and benzyl alcohol, for the polymerization of CL.[111] Following these studies, we described and used dimethyl(salicylaldiminato)aluminum compounds not only for the ROP of CL, but also of LA (Figure 11, **48**).[112] Interestingly, the polymerization showed a controlled and *living* behavior, when the phenyl substituent on the phenoxyimine ligand of the catalyst was perfluorinated, allowing the preparation of block copolymers by sequential polymerization. In addition, random copolymers of CL and LA were obtained, while transesterification reactions were not observed.[113] Extending the expertise in the co-polymerization of CL and LA, the homo-and copolymerization of GL and *rac*-LA were also carried out in the presence of dimethyl(salicylaldiminato)aluminum compounds. Diverse microstructures in the copolymerization of GL and rac-LA, from random to block to microblocks, were achieved, by varying the experimental conditions.[114] The same catalytic approach was subsequently exploited in copolymerizations of GL with CL and in the terpolymerizations of GL, CL and *rac*-LA, producing random copolyesters.[115] This family of catalysts were very versatile; indeed, they were active not only in the ROP of traditional cyclic esters, but also of large ring-size macrolactone and of novel synthetized thiol-functionalized lactide. Macrolactones, i.e. cyclic esters having more than 14 atoms ring size, have low polymerizability, due to the lack of ring strain. Dimethyl(salicylaldiminato) aluminum compound (Figure 11, **48**) resulted active catalysts for the ROP of 6HDL and the polymerization showed a *pseudo-living* character.[116] The synthesis of linear block copolymers of 6HDL with CL and/or *rac*-LA was achieved by sequential copolymerizations, while the copolymerization of a 50/50 mixture of 6HDL and CL produced a random copolymer.

Dimethyl(salicylaldiminato)aluminum complex was also used for the ROP of a lactide-type monomer bearing a thiol-protected group as trityl thioether, the 3-methyl-6-(tritylthiomethyl)-1,4-dioxane-2,5-dione (TrtS-LA). This latter was copolymerized via ROP with LA and CL in the presence of complex **48** in Figure 11 and 1 equivalent of MeOH as initiator, to give thiol-functionalized and further editable polyesters main chain.[117]

An aluminum complex featuring two salicylaldimine was also investigated in the ROP of cyclic esters. In this complex the absence of the bridge between the two salicylaldimine units induces a more flexible coordination environment compared to that imposed by the tetradentate ONNO ligands. It was found to be highly active in the ROP of β-butyrolactone.[118]

Readers wishing to explore deeper in Al-salicylaldimine complexes used in the ROP of cyclic esters are referred to a recent review on the topic.[119]

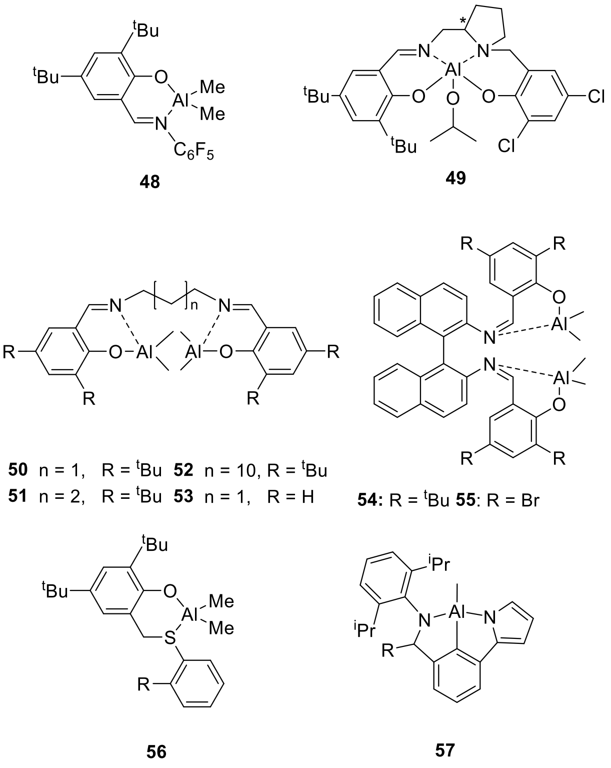


Figure 11. Aluminum-based ROP catalysts.

Salalen. Salalen ligands have been first synthesized by Kol,[120] while salalen aluminum complexes as catalysts in the ROP of *rac*-LA were introduced by Jones,[121] showing their ability to furnish different PLA microstructures by varying the salalen structure. Subsequently, we described enantiomerically pure aluminum complexes bearing aminomethylpyrrolidine-based salalen ligands (Figure 11, **49**) which were active in the polymerization of *rac*-lactide with a selectivity depending on the substituents on the ligand skeleton. Interestingly, isoselective catalysts furnished a polylactide with a new microstructure, the gradient isotactic multiblock PLA, by a combination of enantiomorphic-site and chain-end control mechanisms.[122] Non-chiral salalen ligands, having one imine functionality of the traditional salen ligand reduced to amine, were used for the preparation of aluminum complexes. The complexes were able to polymerize L-, D-, rac- and meso-lactide, and showed moderate productivities. rac-LA gave rise to isotactic polylactides (with Pm up to 72%), while meso-LA gave rise to heterotactic polylactides (with a Pm of 79%). Evidences for polymeryl exchange between propagating species were reported.[123]

Dinuclear salen. Dinuclear salen aluminum complexes with alkyl backbone of different length between the two phenoxy imine coordinative pockets have been developed as efficient catalysts for the ROP of lactide, lactones and macrolactones (**50-52**, Figure 11).[124] All complexes, activated by an alcohol, promoted controlled polymerization of rac-LA showing different activities depending on the distance between the two metal centers as consequence of cooperativity between the metal centers. The dinuclear complex **50** was the most active in the ROP of LA producing isotactic enriched PLA. Otherwise, the complexes in which the two metal centers were remote (**51**-**52**) produced atactic PLA with inferior activity. Analogous differences in terms of activity emerged in the ROP of epoxides. These results suggested the possibility of cooperation between the two reactive centers of the dinuclear species in which these are close together. The same beneficial effect was observed also in the ROP of macrolactones (PDL), ethylene brassilate (EB) and HDL.[125]

The cooperation between the aluminum reactive centres was influenced also by their spatial orientation. When a dinaphthaleneimine bridge was introduced to allocate the reactive metals in rigid coordinative pockets (rac **55**-**56**), even higher activities were observed above all toward less encumbering monomers and/or more flexible growing chains.[126]

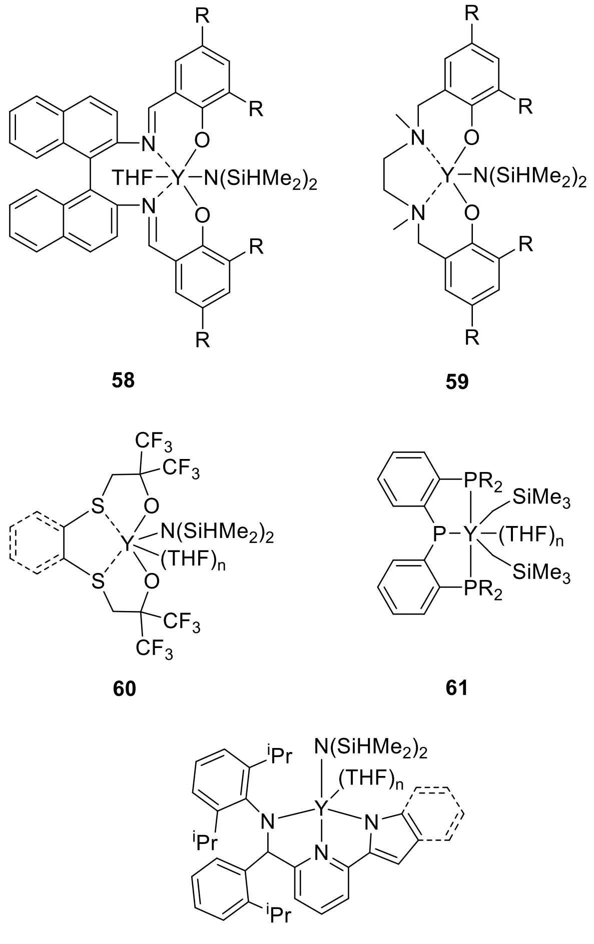
Phenoxy-thioether. Bidentate phenoxy-thioether (OS) ligands, which combine a hard phenoxide donor with a soft sulfur donor, were used for the preparation of aluminum complexes (Figure 11, **56**), which resulted active catalysts in the ROP of CL, L-LA and rac-LA with immortal behavior in the presence of methanol. The introduction of a substituent at the ortho position of the thiophenol aryl ring showed an opposite effect on the catalytic activities of the two different cyclic esters, increasing the activity in the ε-caprolactone polymerization and decreasing it in the polymerization of lactide.[127]

***NNN*.** Dianionic [$^{-}$N,N,N^{-}] tridentate pyrrolylpyridylamido ligands with general formula [NNN]AlMe (Figure 11, **57**), were synthesized and used as initiators in the ROP of CL, L-LA, and rac-LA, in the latter case with moderate isoselectivity (P_m = 76 %). More interestingly, this class of catalysts promoted the random copolymerization of ε-caprolactone and rac-lactides.[128]

4.2. Y-based ROP catalysts

After the discovery by Dupont researchers of homoleptic yttrium alkoxides as highly active initiators for the ROP of LA,[129] several well defined group 3 metal complexes have been reported. Coates and Ovitt studied the catalytic behavior of a new heteroleptic yttrium alkoxide complex, using the same chiral Schiff-base ligand that enabled aluminum complex to produce isotactic poly(lactide).[130] However, although the activity was relatively higher than the parent aluminum derivative, no stereoselectivity was observed for the polymerization of rac-LA.

In this ambit, we described a series of yttrium amido complexes bearing tetradentate binaphthyl-bridged salen and diamine-bisphenolate salan ligands (Figure 12, **58** and **59**) as efficient initiators for the ROP of CL, rac-LA and L-LA. In THF solution, the polymerization of rac-LA produced highly heterotactic polymers with Pr up to 0.91.[131] The same complexes resulted active initiators in the polymerization of rac-BL under mild conditions. The obtained poly(3-hydroxybutyrate) were syndiotactic enriched, with probability of racemic linkages P_r up to 0.81.[132]



58 59 60 61 62

Figure 12. Yttrium-based ROP catalysts

ONNO. A salan-based yttrium isopropoxide catalyst, previously described by Thomas *et al.*[133] and the analogous aluminum complex bearing the same tetradentate ligand were used in the copolymerization of rac-BL and LA. The salan-yttrium compound was a more effective catalyst compared to the aluminum compound; the formation of a gradient BL/LA copolymer was proposed.[134]

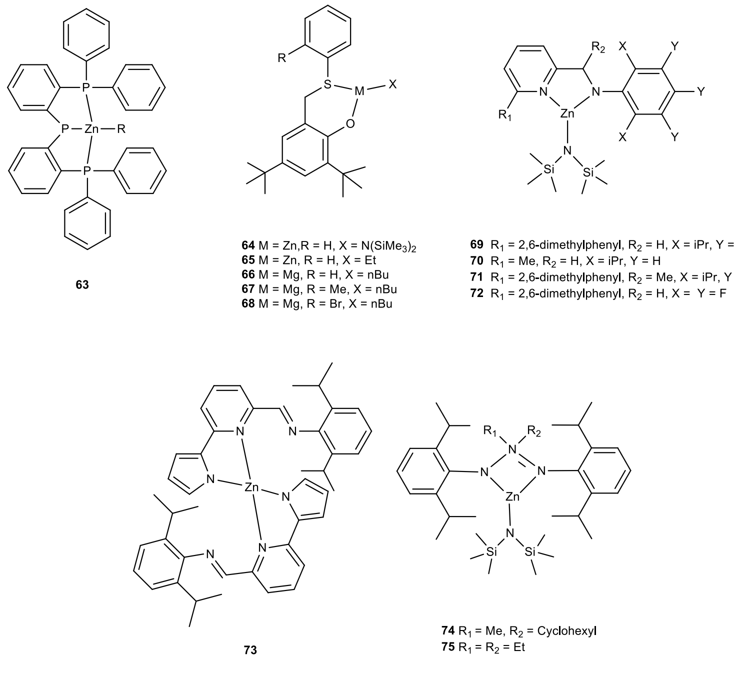
OSSO. Dithiodiolate ligands that feature different bridges between the sulfur atoms (Figure 12, **60**) were used to prepare new yttrium and aluminium complexes. Yttrium complexes promoted controlled polymerization of ε-CL and rac-LA in the presence of isopropyl alcohol, whereas in the absence of the alcohol these complexes were highly active in the production of high molecular weight PCLs.[135]

PPP. Phosphido-diphosphine pincer yttrium and scandium complexes (Figure 12, **61**) were investigated in the ring-opening polymerization of cyclic esters. Yttrium complexes were found to be highly active initiators. Immortal and living ROP of CL and L-LA was obtained, while the ROP of rac-BL produced oligomers.[136]

***NNN*.** Novel Y and Sc metal complexes, bearing anilidopyridyl-pyrrolide and anilidopyridyl-indolide dianionic [−NNN−] tridentate ligands, were synthesized and characterized (Figure 12, **62**). The yttrium complexes resulted in highly active catalysts (TOF up to 104 mol lactide molY $^{-1}$ h^{-1}), even in solvent-free condition, whereas the scandium complex showed moderate activities. Heterotactic PLAs were obtained, with Pr values in the range of 0.57−0.84.[137]

4.3. Zn and Mg-based ROP catalysts

In the search of catalytic systems based on non-toxic and biocompatible metals, zinc and magnesium emerged as highly desirable in the synthesis of polyesters, in particular when the target application is in biomedical field. Different ligand frameworks were investigated for the development of new single-site neutral catalysts based on these metals.


63

64 M = Zn,R = H, X = N(SiMe$_3$)$_2$
65 M = Zn, R = H, X = Et
66 M = Mg, R = H, X = nBu
67 M = Mg, R = Me, X = nBu
68 M = Mg, R = Br, X = nBu

69 R$_1$ = 2,6-dimethylphenyl, R$_2$ = H, X = iPr, Y = H
70 R$_1$ = Me, R$_2$ = H, X = iPr, Y = H
71 R$_1$ = 2,6-dimethylphenyl, R$_2$ = Me, X = iPr, Y = H
72 R$_1$ = 2,6-dimethylphenyl, R$_2$ = H, X = Y = F

73

74 R$_1$ = Me, R$_2$ = Cyclohexyl
75 R$_1$ = R$_2$ = Et

Figure 13. Zinc-based ROP catalysts.

***PPP*.** New zinc complexes bearing a diarylphosphido di-phosphine ligand (Figure 13, **63**) have been synthesized and tested in the ring-opening polymerization of ε-caprolactone and L- and rac-lactide. Polyesters with controlled molecular parameters and low polydispersities were obtained under mild polymerization conditions.[138]

OS. A series of homeleptic and heteroleptic Mg(II) and Zn(II) complexes coordinated by phenoxy-thioether ligands (Figure 13, **64-68**) resulted effective single-site initiators for the well-controlled polymerization of cyclic esters to give high molecular weight polymers with narrow polydispersities. Magnesium complexes showed better catalytic performances respect to those observed for zinc complexes.[139]

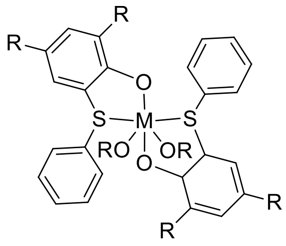
NN. A family of 3-coordinated Zn(II) complexes bearing sterically encumbered bidentate monoanionic pyridylamido ligands (Figure 13, **69-72**) was used for the ROP of LA and CL with high turnover frequencies at room temperature, allowing the synthesis of stereodiblock, stereotriblock and stereotetrablock copolymers of L-LA, D-LA and rac-LA, as well as diblock copolymers L-LA and CL, by one-pot sequential addition of the monomers in short reaction times.[140] A catalyst of this class was used also for the ROP of two large ring size lactones, the ω-6-hexadecenlactone (6HDL) and the ω-pentadecalactone (PDL).[141] Random copolymers of the two macrolactones and of CL with 6HDL were prepared. These latter copolymers were functionalized with a novel thiol derivative of eugenol and the antimicrobial properties were evaluated.[142] A homoleptic bis(pyrrolylpyridiylimino) Zn(II) complex (Figure 13, **73**) and its Mg(II) analogue were also successfully tested in the ROP of CL and L-LA, resulting in moderate (Zn) and high (Mg) activity under mild conditions after activation with 1 equiv of alcohol. NMR studies led to the conclusion that the polymerization proceeds *via* an “activated-monomer” mechanism assisted by an "arm-on" "arm-off" equilibrium of the imine moiety.[143] While a plethora of well performing complexes have been tested under mild laboratory conditions (i. e. at T = 25-100 °C, in solvents such as CH_2Cl_2, THF or toluene, using recrystallized monomer and low LA / catalyst molar ratios of 100-1000), reports of catalysts active under conditions close to those of the industrial processes (i. e. T = 180-200 °C, technical grade monomer at L-LA/catalyst ratio 5000-10000 : 1, excess of alcohol) are rare.[144] In this respect, we reported new guanidinate Zn(II) complexes (Figure 13, **74-75**) as very efficient catalysts for ROP of technical grade L-LA under the just mentioned industrially relevant conditions. A variety of either block or random copolymers of L-LA and CL could be also obtained, depending on the reaction conditions.[145]

4.4. Group 4 metal ROP catalysts

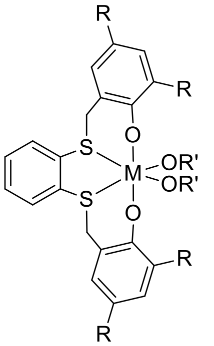
Group 4 metal are relatively inexpensive and earth-abundant and the corresponding heteroleptic complexes are active, stable, robust, and, in some cases, exert a good control over the polymerization process. In most of the group 4 metal complexes reported in literature, the metal atom is coordinated by a bi- or tetradentate phenoxo-type chelating ligands in which the anionic oxygen atoms are paired with neutral immine or amino groups.[146] An example is the complexes with ONNO ligands by Jones et al. in which a 2,2′-bipyrrolidine-derived salan ligand was used to develop zirconium or hafnium compexes which were able to afford highly isotactic enriched polylactides.[147]

Catalysts developed at UNISA are based on octahedral complexes featuring bi- or tetradentate ligands featuring hard phenoxo or amide donors and soft sulfur donors. The use of ligand with second-row atoms as neutral donors was found to be advantageous for the catalytic activity, as matter of fact one of the most active group 4 complexes is the hafnium complex bearing the tetradentate dithiodiolate ligand reported by Kol et al., this complex is able to convert in melt 300 equiv. of monomer in 1 min.[148]

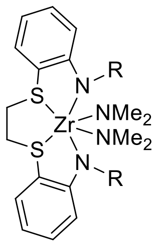
It is also worth citing the group 4 complexes with tetradentate OSSO ligands which were able to stereochemically control the polymerization of meso-lactide[149] and the complexes with mixed sulfur and nitrogen donors, the ONSO lignads, which, depending on the substituents of the phenolate ring, were able to produce heterotactically inclined or isotactically inclined polylactide.[150]



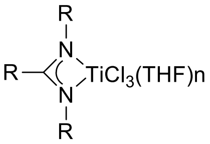
76 M = Ti, R' = *i*-Pr, R = *t*-Bu
77 M = Zr, R' = *t*-Bu, R = *t*-Bu
78 M = Hf, R' = *t*-Bu, R = *t*-Bu
79 M = Zr, R' = *t*-Bu, R = CMe$_2$Ph



80 M = Zr, R' = *t*-Bu, R = *t*-Bu
81 M = Zr, R' = *t*-Bu, R = Cum
82 M = Ti, R' = *i*-Pr, R = Cum
83 M = Hf, R' = *t*-Bu, R = Cum



84 R = iPr
85 R = Cyclohexyl
86 R = Mes



87 R' = Ph R = SiMe$_3$ n = 0
88 R' = Ph R = iPr n = 1
89 R' = Ph R = Me n = 0
90 R' = Me R = iPr n = 1
91 R' = Me R = iPr n = 0

Figure 14. Group 4 metals ROP catalysts

Octahedral complexes featuring two thioether phenolate ligands (Figure 14, **76-79**) were active catalysts in the ROP of cyclic esters such as lactide, ε-caprolactone and rac-β-butyrolactone, giving polymers with predictable molecular weights and narrow dispersity indexes.[151] In presence of isopropanol, effective "immortal" polymerizations were achieved. These complexes were also active in copolymerization of lactide with ε-caprolactone or rac- β-butyrolactone. In the caprolactone/lactide copolymerization, gradient copolymers with a continuous change in composition of the two monomers along the polymer chain were obtained, whereas, in the butyrolactone/lactide copolymerization, block copolymers were obtained.[152] The zirconium complexes with thioether phenolate ligands (**77**) was one of the rare examples of group 4 metal complexes active in the homo and copolymerization of β-butyrrolactone. Group 4 metal complexes featuring o-phenylenebridged bis(phenolato) ligands (Figure 14, **80-83**) were used in the ROP of rac-lactide. In absence of exogenous alcohol, the activities were moderate, while in the presence of exogenous alcohol higher activities were obtained, but the reaction proceeds according to an activated monomer mechanism.[153] With the aim of exploring new coordinative environments, zirconium and hafnium complexes coordinated by tetradentate tioether-amide ligands (Figure 14, **84-86**) were prepared and tested in the ring opening polymerization of cyclic esters.[154] The complexes were highly active, their activities were superior to those displayed by analogous complexes coordinated by OSSO ligands and well compare with that of the most active group 4 complexes. Finally, titanium amidinate complexes (Figure 14, **87-91**) were used as catalysts for the controlled polymerization of cyclic esters under industrially attractive melt conditions. These complexes were also active in the caprolactone/lactide copolymerization: depending on the initiator architecture, polymers with microstructures ranging from gradient to truly random were obtained.[155]

5. Ring-Opening COPolymerization of epoxides with CO_2 and anhydrides

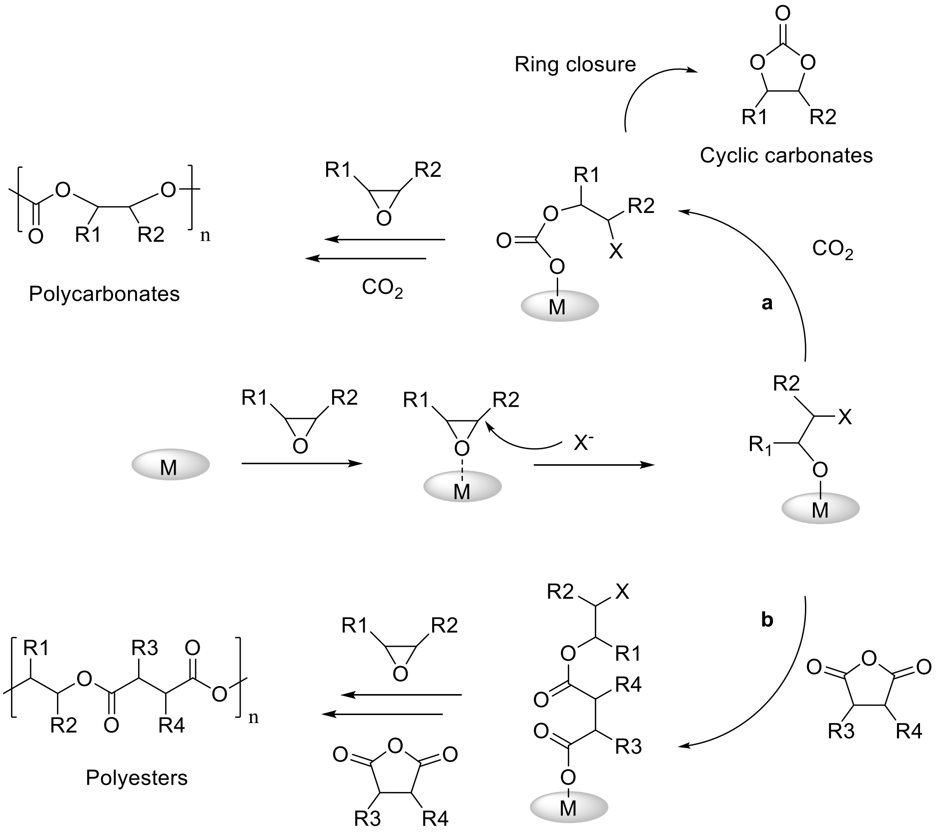
Polyesters and polycarbonates are among the most widely applied oxygenated polymers, with poly(ethylene terephthalate) and polycarbonate (from bisphenol A) as the most representative examples. Thanks to their properties, they find disparate applications from packaging to engineering materials. However, both materials come from petrochemical and in some cases toxic sources and are not biodegradable. The recently emerging Ring-Opening COPolymerization (ROCOP) of energy-rich substrates such as epoxides with CO_2 or anhydrides[156] (Scheme 8) allows the preparation of aliphatic polycarbonates and polyesters, respectively. This synthetic strategy has some noteworthy advantages with respect to typical polycondensation reactions. First, these are 100% atom efficient reactions, a crucial aspect to save materials and reduce waste production; moreover the properties of the resulting materials can be easily manipulated by changing the structure of the epoxide, through reactions which generally proceed under similar conditions. The large potentiality of ROCOP of epoxides with CO_2 or anhydrides has been also expressed in the possibility to combine the two catalytic processes with each other and/or with the ROP of lactones in switching catalysis strategies to produce block polymers by one pot procedures.[157,158]

Among the catalytic systems able to promote ROCOP reactions in controlled manner, the most significant examples are salen complexes of trivalent metals such as Al(III), Cr(III) and Co(III) and complexes of bivalent metals such as Zn (II) and Mg(II) with nitrogen- or oxygen-based ligands.[156] Generally, they are used in combination with neutral or ionic nucleophilic species as cocatalysts for the formation of binary catalyst/cocatalyst pairs.

According to the general mechanism reported for the ROCOP reactions, in the first step the epoxide is activated by coordination to the Lewis acidic metal center, afterwards the nucleophilic attack of the initiating species (X) ring-open the activated monomer. The initiating species may be a labile ligand coordinated at the metal and/or the external nucleophilic species added as cocatalyst in the polymerization medium.

In the case of the ROCOP with CO_2 (Scheme 8, **a**) the resulting metal alkoxide insert a CO_2 molecule generating a metal carbonate, then repetitive and sequential insertion of epoxides and CO_2 leads to the formation of the polycarbonate products, while intramolecular ring closure may produce five-membered cyclic carbonates.

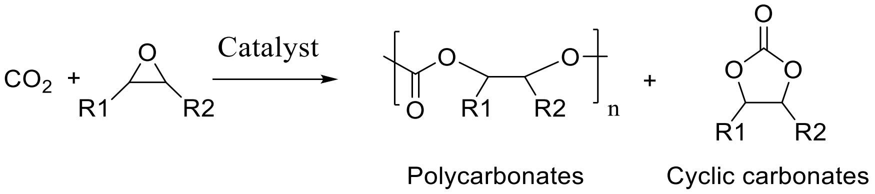
In the ROCOP of anhydrides and epoxides (Scheme 8, **b**) after the formation of the alkoxide derivative, the propagation proceeds with the coordination and the insertion of an anhydride unit with the consequent formation of a carboxylate intermediate. The alternated insertions of the two monomers account to produce polyesters with perfectly alternated structures. In both cases, a possible side reaction is the homo-polymerization of the epoxides with the consequent formation of polyether sequences englobed in the polymer chains.



Scheme 8. Proposed reaction mechanism for the reaction of epoxides with **a**) CO_2 yielding either polymeric or cyclic carbonates, and **b**) anhydrides. The metal center (M) activates the epoxide while the Lewis base (X^-) acts as nucleophile.

5.1. Polycarbonates synthesis

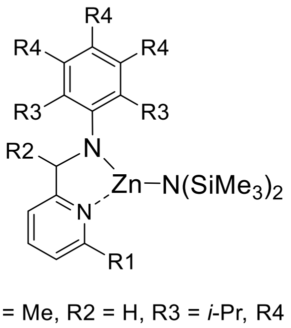
Aliphatic polycarbonates are the sustainable alternative to conventional polycarbonates. They can be obtained by using CO_2 as renewable, nontoxic, and abundant C1 resource and typically are biodegradable,[159] both substantial aspects in the context of carbon neutrality and of a circular economy. On the other hand, CO_2 is a kinetically inert molecule and the reaction of CO_2 with epoxides can provide two classes of products, namely cyclic carbonates and polycarbonates (Scheme 9). For these reasons, the choice of an appropriate catalyst that is selective towards the formation of polymers and sufficiently active to ensure environmentally friendly process conditions, is of fundamental importance.



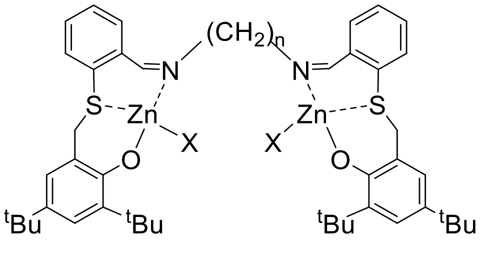
Scheme 9. General scheme of the reaction of an epoxide with CO_2.

In the past few decades, numerous homogeneous catalyst systems able to promote the synthesis of polycarbonates by ROCOP have been developed, with some of them turning out to be highly active and selective.[160] From the β-diiminate (BDI) zinc complexes reported by Coates,[161] a milestone for this catalysis, to the tethered BDI bimetallic zinc complexes reported by Rieger,[162] which represent the most active catalysts in the ROCOP of CO_2 and CHO to date, zinc based complexes are playing a key role in these polymerization reactions. Efficient and selective dizinc catalysts for the copolymerization of cyclohexene oxide and carbon dioxide have been also reported by other authors. In particular, Williams disclosed dinuclear zinc structures bearing macrocyclic ancillary ligands, which showed remarkable activity at only 0.1 MPa CO_2 and even with post-combustion captured CO_2,[163] while Castro-Osma and Lara-Sánchez described heteroscorpionate-based dizinc catalysts for the synthesis of polycyclohexene carbonate with high molecular weights.[164]

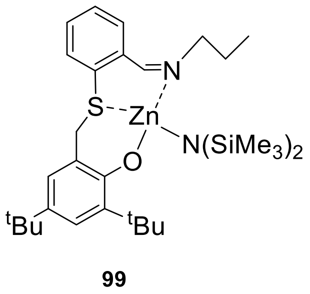
In this context, we reported pyridylamido zinc(II) amido complexes **92**-**96** (Figure 15) which acted as "single component" catalysts for the alternating copolymerization of carbon dioxide and cyclohexene oxide also under rather mild conditions.[165] The effect of the substituent variation in the coordination environment of the zinc catalysts was evaluated for this class of complexes, with complex **96** showing a TOF of 30 h^{-1} and selectivity towards polycarbonate products of 98%. Both experimental and theoretical data suggested the involvement of different active species, including dimeric species, analogous to those invoked by Coates for the β-diiminate complexes.



92 R1 = Me, R2 = H, R3 = *i*-Pr, R4 = H
93 R1 = 2,6-Me$_2$Ph, R2 = Me, R3 = *i*-Pr, R4 = H
94 R1 = 2,6-Me$_2$Ph, R2 = H, R3 = *i*-Pr, R4 = H
95 R1 = 2,6-Me$_2$Ph, R2 = Me, R3 = Me, R4 = H
96 R1 = 2,6-Me$_2$Ph, R2 = H, R3 = F, R4 = F



97 n = 2, X = N(SiMe$_3$)$_2$
98 n = 3, X = N(SiMe$_3$)$_2$

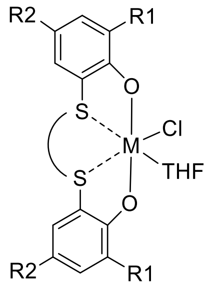


99

Figure 15. Monometallic and bimetallic zinc complexes active as single component catalysts in the synthesis of polycarbonates by ROCOP

Bimetallic zinc complexes **97** and **98** supported by new hexadentate bis(aldimine-thioether-phenolate) ligands were reported by Lamberti.[166] These purposely designed ligands resemble salen ligands, one of the most versatile class of ligands, yet present two additional sulphur atoms as neutral donors, thus ensuring two coordinative tetrahedral pockets for the zinc atoms. Complex **97** was able to convert CO_2 and CHO in the corresponding polycarbonate product with a good selectivity (up to 97 %) and a moderate activity (TOF up to 36 h^{-1}) without requiring the use of an external nucleophile and/or of a solvent. When PPNCl was added as a cocatalyst, the selectivity diverted towards the formation of cyclic carbonates (up to 94 % of *cis*- and *trans*-CHC) with a slightly higher activity (TOF = 50 h^{-1}). The comparison with the analogous monometallic species, complex **99**, indicated that the two zinc centers act independently, reasonably because of the fluxionality of the alkyl bridges.

The beneficial role of sulphur atoms in the ligand skeleton has been widely highlighted by Capacchione *et al.* who developed numerous bis-thioether-diphenolate [OSSO]-ligands showing their great versatility in catalysis, as ancillary ligands of different metals.[167] Among the different metals used in catalysis, iron is one of the most abundant and less toxic. Active iron catalysts in the ROCOP of CO_2 with epoxides have been reported both as bimetallic complexes bearing a macrocyclic phenolate ligand[168] and as monometallic amino triphenolate-based complexes.[169] Interestingly, for both families of catalysts, a shift in selectivity between cyclic and polymeric carbonates was realized by tuning the relative amount of organic halide used as cocatalyst. In this framework, Capacchione reported iron(III) complexes **100**-**105** (Figure 16) resulted active in the ROCOP of CO_2 with cyclohexene oxide,[170] with complex **101** reaching TOF up to 400 h^{-1} in the selective production of the polycarbonate product, under 10 atm of CO_2 pressure. On the other hand, when other variously mono- and di-substituted epoxides were used as substrate, the corresponding cyclic carbonates were obtained with excellent activity and selectivity. Kinetic measurements identified a different order with respect to the Fe(III) concentration in the formation of propylene carbonate and in the formation of poly(cyclohexene carbonate), suggesting that different catalytic species may be active in the two different processes.



100 M = Fe, ⌒ = $(CH_2)_2$, R1 = CPh_3, R2 = CH_3
101 M = Fe, ⌒ = $(CH_2)_2$, R1 = $C(CH_3)_2Ph$, R2 = $C(CH_3)_2Ph$
102 M = Fe, ⌒ = $(CH_2)_2$, R1 = CH_3, R2 = CH_3
103 M = Fe, ⌒ = c-Hex, R1 = $C(CH_3)_3$, R2 = $C(CH_3)_3$
104 M = Cr, ⌒ = $(CH_2)_2$, R1 = $C(CH_3)_2Ph$, R2 = $C(CH_3)_2Ph$
105 M = Cr, ⌒ = c-Hex, R1 = $C(CH_3)_3$, R2 = $C(CH_3)_3$

Figure 16. Bis-thioether-diphenolate based iron and chromium complexes active in the coupling of CO_2 with epoxides.

The bis-thioether-diphenolate ligand with α-cumyl substituents in the *ortho* and *para* positions of the phenolate moieties was tested also as coordinative environment for the chromium metal center.[171] Complex **104**, in combination with an ammonium based cocatalyst, catalyzed the formation of polycarbonates from propylene oxide, cyclohexene oxide and hexene oxide (with selectivity from 93 % upwards) and even with the challenging substrate styrene oxide, the corresponding polymer was obtained, although with a lower selectivity of 32 %. For the CO_2/CHO copolymerization TOF value up to 19 h^{-1} was calculated at 80 ° C and 20 bar of CO_2. Interestingly, the catalytic system was also able to promote the formation of terpolymers of CO_2 and propylene oxide with either cyclohexene oxide or hexene oxide, with the experimental data suggesting a blocky structure.

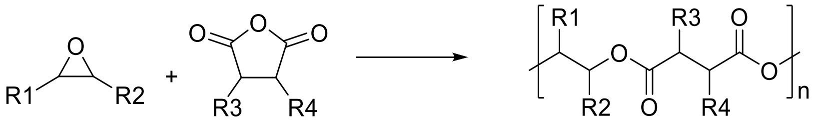
Subsequently, a systematic study of the structure-reactivity relationship for the [OSSO]-chromium complexes revealed that complex **105** with a more rigid C-Hex bridge show even superior performances in the copolymerization of CO_2 with CHO with TOF values up to 26 h^{-1}.[172]

Both in the case of the iron complexes and the chromium complexes, DFT-based calculations explained the formation of the polymer instead of cyclic carbonates by identifying a lower energy barrier of the chain propagation step with respect to that of the ring closing of the cyclic product.

5.2 Ring Opening Co-Polymerization of epoxides and anhydrides.

In 2007 Coates reported for the first time the production of high molecular weight polyesters with perfectly alternating microstructures by ring-opening co-polymerization (ROCOP) between epoxides and cyclic anhydrides by using a zinc 2-cyano-β-diketiminato complex.[173]

After this discovery the ROCOP between epoxides and cyclic anhydrides emerged as a powerful synthetic strategy for the synthesis of polyesters (scheme 10).



Scheme 10. Ring Opening CO-Polymerization of epoxides and anhydrides

As alternative to ring opening polymerization of cyclic esters (ROP), this methodology offers the additional advantages of the availability of two large libraries of monomers, some of which obtained from renewable resources, and of a good tolerance toward monomers that contain aromatic moieties or functional groups. This makes ROCOP an extremely versatile tool for the synthesis of polyesters with tunable properties.

In the last ten years, several catalytic systems have been developed based both on metal complexes,[156] and organic systems.[174]

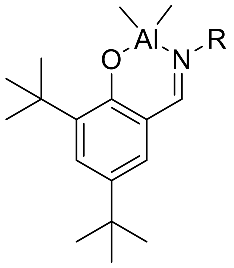
Among these, bimetallic catalysts showed enhanced abilities in terms of activity and stereoselectivity. Stereoregular polyesters with main-chain chirality were achieved for the first time by asymmetric copolymerization of meso-epoxides and cyclic anhydrides with dinuclear enantiopure aluminum or chromium catalysts.[175] The same authors reported the first highly enantioselective resolution copolymerization of racemic cis-internal epoxides with anhydrides via multi-chiral synergistic catalysis by enantiopure dinuclear aluminum catalysts for which the steric hindrance of the substituents on the phenolate ring of the ligand and the axial chirality significantly affected both the catalytic activity and enantioselectivity. [176]

Motivated by the interest to explore the potentiality of cooperative phenomena for bimetallic catalysts in the copolymerization of epoxides with anhydrides, the researchers of UNISA extended the use of bimetallic aluminum salen ligands with flexible alkyl or rigid binaphthyl bridges (see Figure 11, **50**-**55**) to this catalysis. All complexes (Figure 11, **50**-**55**) revealed to be effective catalysts in ring opening copolymerization of cyclohexene oxide and limonene oxide with succinic and phthalic anhydrides producing copolymers with completely alternating microstructures.[177,178]

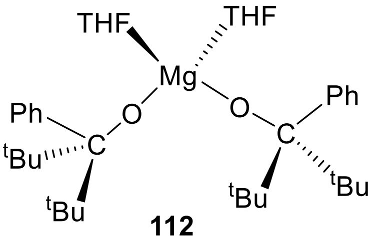
A good control of the molecular masses that showed low dispersities and linear relationships toward the conversion of the monomer were observed. The choice of cocatalyst revealed to be crucial in terms of selectivity and activity: non-ionic co-catalysts, such as 4-(N,N-dimethylamino)pyridine(DMAP), showed higher selectivity in apolar media while ionic co-catalysts were revealed to be more efficient in polar solvents.

Differently from that observed in ROP of cyclic esters, the ROCOP followed a monometallic pathway thus no cooperative phenomenon was involved.[156] Nevertheless, all bimetallic complexes showed better performances in comparison to those of the related monometallic salen complexes, thus suggesting that complexes in which the reactive aluminum centers have a lower coordination offer valid alternatives to the classic pentacoordinate salen complexes.

Thus, ROCOP studies were extended to simple phenoxy-imine aluminum complexes (Figure 17) that were found to be highly active towards different combinations of monomers among them LO and phthalic anhydride (PA) resulting in the production of partially renewable semi-aromatic polyesters.[179]



106 R = *n*-propyl
107 R = Ph
108 R = 2,6-diisopropylphenyl
109 R = 2,6-dimethylphenyl
110 R = 4-methoxyphenyl
111 R = C_6F_5



112

Figure 17. Phenoxy-imine aluminum complexes and a bis(alkoxide) magnesium complex

Taking advantage from the good performance of bimetallic catalysts in the ROP of lactones as well as in the ROCOP of different couples of epoxides and anhydrides, the syntheses of several block polyesters, by combination of two distinct processes were performed.

These one-pot procedures have been recently introduced by Williams for the synthesis of block polymers from mixtures of monomers by using a single catalyst with the ability to “switch” between different catalytic cycles to produce selectively block polymer sequences.[180]

From a mixed monomer feedstock comprising cyclohexene oxide, succinic anhydride, and a cyclic ester (ε-CL or LA), block copolymers polycyclohexene succinate-co polyester were obtained. [125,126]

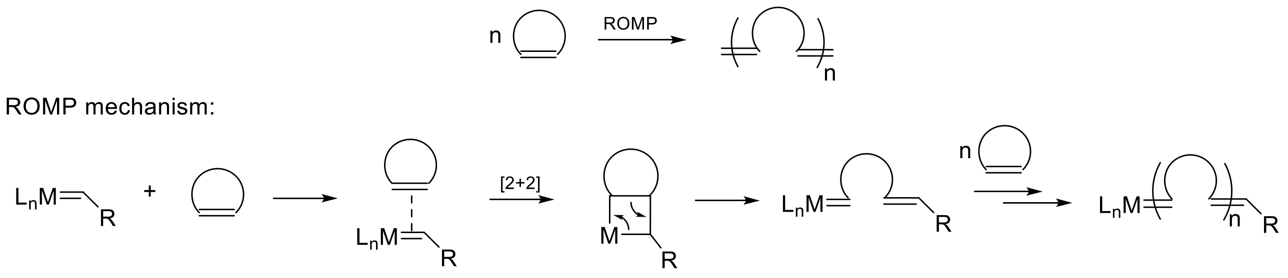
From a combination of macrolactones (PDL and HDL), phthalic anhydride and cyclohexene oxide block polyesters were produced containing a first semi-aromatic chain segment followed by a segment produced by ROP of macrolactones. These copolymers are the first examples described in the literature of di-block copolymers with one polyethylene-like block and a semi-aromatic polyester as a second block. The semi-aromatic polyester block was formed first, followed by the polyethylene like portion produced by ROP of macrolactone.[181]

A fully bio-renewable novel copolymer was obtained for the first time by copolymerization of two bio-renewable monomers, namely limonene oxide and dihydrocumarin, by using a mononuclear bis(alkoxide) magnesium complex (Figure 17, complex **112**).[182]

6. Ring-Opening Metathesis Polymerization (ROMP)

ROMP of cyclic olefins is a versatile and well-established methodology for the synthesis of macromolecular materials mediated by transition metal-carbene complexes ($L_nM{=}CHR$).[183]

The mechanism of the polymerization is based on the olefin metathesis reaction, which is a process of carbon–carbon double bond exchange. As a result, any unsaturation associated with the monomer is retained along the main chain of the polymer. This feature represents an important difference of ROMP from other typical olefin addition polymerizations. According to Chauvin's mechanism,[183b] the initiation step involves coordination of a cyclic olefin to a metal alkylidene complex. Subsequent [2+2] cycloaddition produces a metallacyclobutane intermediate that undergoes a cycloreversion to afford a new metal alkylidene containing the first unit of a growing polymer chain. Analogous steps occur during the propagation stage until polymerization ceases (Scheme 11). Like most olefin metathesis reactions, all the individual steps in the catalytic cycle of ROMP are generally reversible. The reaction is driven from monomer to polymer by the release of the ring strain associated with the cyclic olefin, which determines the irreversible nature of ROMP, as the pathway back to the cyclic compound(s) is not thermodynamically favored.



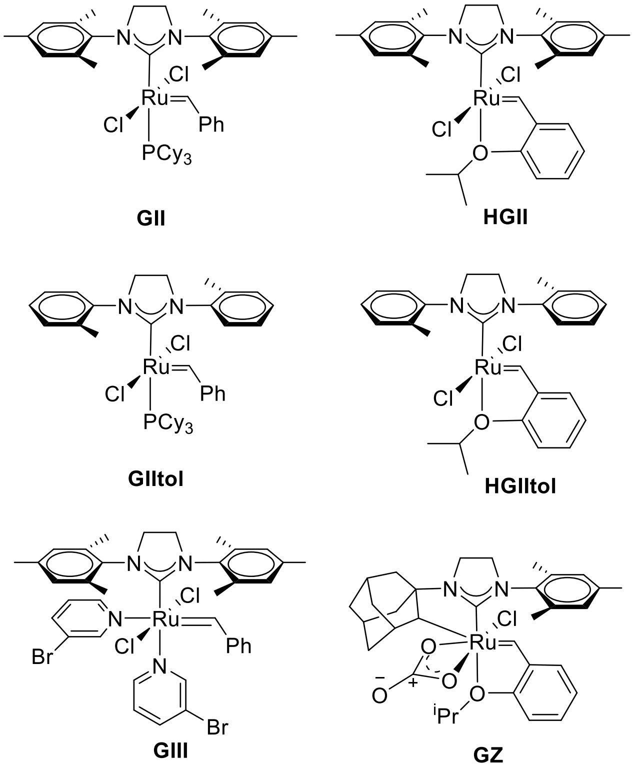
Scheme 11. A general ROMP reaction.

The increasing popularity of ROMP as polymerization technique is mainly related to the introduction of easily accessible, highly efficient ruthenium-based olefin metathesis catalysts that enabled for the preparation of polymers with tunable sizes and unique molecular architectures, including cyclic, star, dendronized and brush polymers,[184] as well as for the synthesis of functional polymers for diverse applications in chemistry, biology, physics, and biomedicine.[185]

In this framework, we describe our recent contribution to the development of new ruthenium catalysts for the preparation of precision hydrocarbon polymers, and to the synthesis of new polymers functionalized with fluorescent moieties.

6.1 Ruthenium catalysts with backbone-substituted unsymmetrical NHC ligands

The introduction of ruthenium-based catalysts stabilized by N-heterocyclic carbene (NHC) ligands has led to significant advancements in the field of olefin metathesis (Figure 18).[186]



GII HGII

GIItol HGIItol

GIII GZ

Figure 18. Commercial ruthenium catalysts with NHC ligands.

Most of the improvements in stability, activity, and selectivity of this class of catalysts have been achieved through manipulation of the NHC scaffold, including modifications of the steric and electronic properties of substituents on the backbone and/or the nitrogen atoms.[186,187,188]

In particular, the unsymmetrical substitution at the nitrogen atoms of the NHC ligand has been found to have a strong impact on the reactivity and selectivity of the corresponding ruthenium catalysts, as a result of the different steric and/or electronic environment created in close proximity of the reactive metal-carbene fragment.[187b,188]

With the aim to investigate the combined effect of different backbone configuration (*syn* or *anti*) and unsymmetrical substitution at the nitrogens of the NHC ligands (*N*-alkyl, *N'*-aryl), we synthesized catalysts **113**-**120** (Figure 19).[189] Their capability to accomplish ROMP reactions was evaluated in the polymerization of 1,5-cyclooctadiene (COD),[189b] employed as the model substrate, as proposed by Grubbs which introduced a set of standardized olefin metathesis transformations as a tool for the comparison and evaluation of new metathesis catalysts.[190]

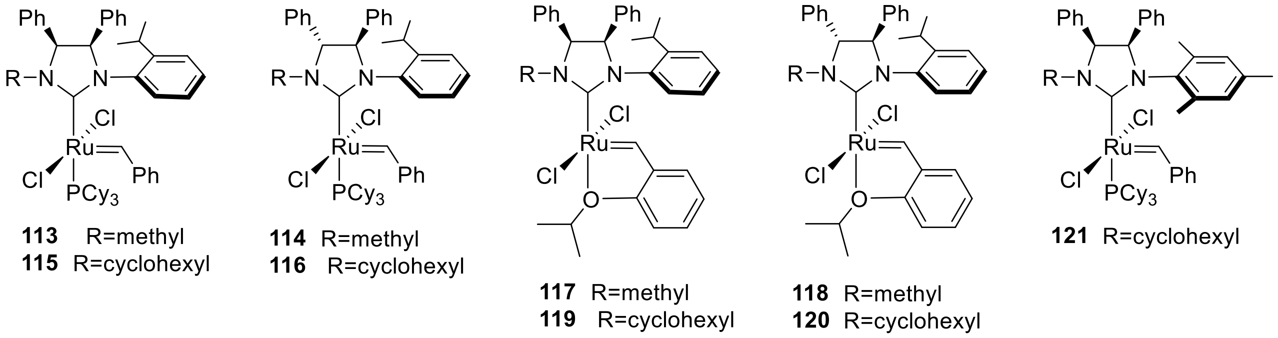
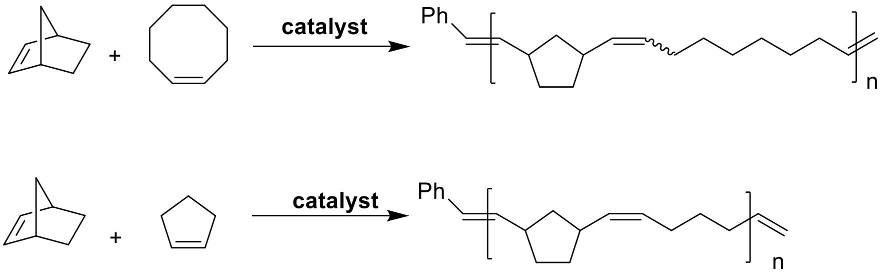

113 R=methyl
115 R=cyclohexyl
114 R=methyl
116 R=cyclohexyl
117 R=methyl
119 R=cyclohexyl
118 R=methyl
120 R=cyclohexyl
121 R=cyclohexyl

Figure 19. Ru catalysts with backbone-substituted unsymmetrical NHC ligands.

The catalytic performances of Grubbs' and Hoveyda-Grubbs' second generation type catalysts **113**-**120** were compared with those of commercial *N*-*o*-tolyl catalysts **GIItol** and **HGIItol** (see Figure 18). Grubbs-type catalysts **113-116** were all found to be highly efficient in the ROMP of COD, with the *anti* isomers outperforming the corresponding *syn* isomers. However, both *anti* catalysts **114** and **116** displayed activities inferior to that of the benchmark catalyst **GIItol**. In general, we observed that less encumbered *N*-methyl catalysts (**113** and **114**) displayed higher activities. *Anti* and *syn* isomers of Hoveyda-type catalysts **117**-**120** showed a similar reactivity trend, even if with less accentuated differences, and worse catalytic performances than the reference catalyst **HGIItol**. As for *E/Z* selectivity, all the catalysts furnished polymers with *E/Z* ratios lower than those registered for polymers obtained with **GIItol** and **HGIItol**. An increased *Z* olefin content was achieved with *N*-methyl catalysts which possess NHCs showing a high level of dissymmetry.

As already underlined, ruthenium complexes coordinated with unsymmetrical NHC ligands offer new opportunities for several metathesis applications, including those in which their symmetrical counterparts fail or are scarcely efficient.[187b,188] One of these applications is the synthesis of precision polymers by alternating ROMP copolymerization of two different monomers, such as norbornene (NBE) with *cis*-cyclooctene (COE) or cyclopentene (CPE). Indeed, their alternating copolymers are of high interest as they possess a polymer skeleton that can hardly be realized from one single monomer. To achieve high chemoselectivity in the synthesis of poly(NBE)-alt-poly(COE) or poly(NBE)-alt-poly(CPE), a large excess of the less reactive monomer (COE or CPE) is required.[191,192,193] Blechert and Buchemeiser reported the copolymerization of NBE with COE and CPE in the presence of several second-generation ruthenium catalysts bearing unsymmetrically substituted NHCs.[191] A remarkable selectivity was observed in both copolymerization, reaching 97% of alternating diads in the copolymerization of NBE and COE and 91% in the copolymerization of NBE with CPE. A similar chemoselectivity (>97%) was obtained by Togni in the ROMP copolymerization of NBE and COE promoted by ruthenium complexes having unsymmetrical NHCs with an *N* -trifluoromethyl group.[192] In both cases, high comonomers ratios (NBE:COE 1:50 and NBE:CPE:1:7) were used. Plenio introduced a new family of unsymmetrical *N*-alkyl,*N*′-pentiptycenyl NHC ruthenium catalysts able to afford alternating copolymers of NBE with COE with up to 98% of alternating diads at low NBE/COE ratio (1:10). However, the synthesis of the catalysts is not trivial, involving a multi-step procedure, and the obtained alternating copolymer exhibits a low molecular weight and a high dispersity value.[193]

In this context, we thought to investigate the propensity of complexes **115** and **116**, differing only in the NHC backbone configuration (*syn* and *anti*, respectively), to promote the alternating copolymerization via ROMP of NBE with COE or CPE (Scheme 12) (Scheme 12).[194]

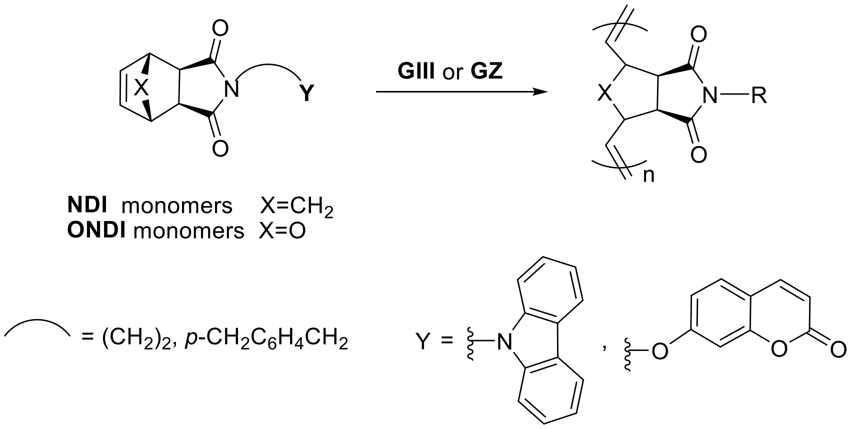


Scheme 12. Alternating ROMP of NBE with COE and CPE.

In the copolymerization of an equimolar mixture of NBE with COE, *syn* complex **115** displayed a more pronounced chemoselectivity than *anti* complex **116**, giving up to 88% of alternating diads for a low NBE:COE ratio (1:10). Taking into account the major tendency of *syn* complex **115** to give alternating sequences, we focused on steric differences between *N*-alkyl and *N*-aryl substituents of the NHC ligand to further improve the selectivity of the resulting catalysts. To this end, we prepared *syn* complex **121**, presenting a bulkier mesityl group in place of an isopropylphenyl group (Figure 19). As hypothesized, **121** produced copolymers of NBE with COE or CPE with a high degree of chemoselectivity (up to 98% and 95% of alternating diads, respectively) at low comonomers ratios (NBE:COE 1:10 and NBE:CPE 1:6), proving to be the most selective catalyst reported so far for these transformations. Moreover, the alternating copolymers possessed high molecular weights with unimodal molecular weight distributions.

6.2 Synthesis of fluorescent polymers

One of the greatest advantages offered by ROMP as polymerization technique is the facile access to advanced functional polymers.[184,185] Given the increasing interest in developing fluorescent polymers for applications in fields ranging from materials to life science,[195] recently we focused on the ROMP of new (oxa)norbornene dicarboximide (**NDI** or **ONDI**) monomers functionalized with fluorophore groups (carbazole or coumarin) linked to the polymerizable unit through an ethylene or *p*-xylene bridge (Scheme 13).[196]



Scheme 13. ROMP of **NDI** and **ONDI** monomers functionalized with carbazole or coumarin groups.

The ROMP behavior of these fluorescent monomers was investigated in the presence of commercial Grubbs' non-stereoselective (**GIII**) and *cis*-selective (**GZ**) catalysts (see Figure 18), to evaluate the influence of polymer stereochemistry on the optoelectronic properties of the resulting polymers.[196b]

While **NDI** monomers were all efficiently polymerized by both the catalysts, **ONDI** analogues showed very low reactivity in the ROMP promoted by **GZ**. This finding was attributed to the coordination of the ether oxygen of the **ONDI** monomers to the ruthenium center, which hampers productive metathesis reaction. No influence of the nature of the bridge (ethylene or *p*-xylene) between the **NDI** unit and the fluorophore on the monomer reactivities was appreciated. In the presence of **GIII**, polymers with approximatively an equal content of *cis* and *trans* double bonds were obtained, while in the presence of **GZ**, polymers of **NDI** with a high amount of *cis* double bonds (82-89%) was produced, providing the first example of *cis*-selective ROMP of fluorescent monomers.

As for photoluminescence properties, the obtained polymers exhibited only characteristic carbazole or coumarin fluorescence in both solution and solid state. A significant excimer emission due to the stacking of carbazole groups was observed for the film of the carbazole polymer having a *p*-xylene bridge and a *cis* double bonds content of 83%. Excimer formation could be reconducted to the combined effect of the stiffness of the bridge (*p*-xylene) and the high stereoregularity degree of the main chain that favors the overlap of carbazole groups. The result suggested that polymer optoelectronic properties can be modulate through appropriate monomer design and high stereoregularity degree of the main chain.

Summary and Outlook

The discovery of the Ziegler-Natta catalysts for olefin polymerization was the base for the incredible growth of the production of plastics and the consequent revolutionary change in the economy and everyday life worldwide. Progress in heterogeneous Ziegler-Natta catalysts allowed the development of simplified, extremely efficient, and economically convenient industrial processes to produce polyethylene and polypropylene commodities, which now account for about 50% of the 400 million tons of plastics produced every year. The advances in homogeneous metallocene and post-metallocene catalysts lead to an unprecedented understanding of the detailed reaction mechanism and of the relationships between catalyst structure and polymer properties, allowing the synthesis of "tailor made" macromolecules, and becoming a paradigmatic example of the power of metal catalysis. Significant contributions in the field have been provided by the Italian research groups affiliated to CIRCC following the tradition of the Natta's school: some of the most recent ones have been reviewed here, trying to show how the competences developed for olefin polymerization catalysts can be used as well to respond to the current challenge of plastic sustainability, requiring, e. g., the development of bio-based and/or biodegradable polymers.

Metal catalysis is expected to be a powerful tool also for the management of end-of-life plastics through chemical recycling to monomers, emerging as a strategic approach to alleviate the negative impact of polymers on the environment in the context of a circular economy. Successful chemical recycling to monomers must achieve a delicate balance between the polymerization and depolymerization energetics: polyesters, polyurethanes and polyamides are more easily

depolymerized with respect to polyolefins. The design of suitable catalysts for specific depolymerization leading to defined products, either monomers or useful oligomers, is the next challenge for the catalysis research.

Keywords: homogeneous catalysis; olefin (co-)polymerization; ring-opening polymerization; ROCOP; ROMP.

Table of contents

Homogeneous catalysis plays an important role in a variety of polymerization processes. This review covers the contributions of the research units of CIRCC in the last decade, involving studies of catalysts for the polymerization of olefins, styrene and dienes, the copolymerization of ethylene with acrylates, the ring opening polymerization of cyclic esters, the copolymerization of epoxides with CO_2 or organic anhydrides, the ring opening metathesis polymerization.

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