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CYCLOLEFIN COPOLYMERS VIA CHAIN  
SHUTTTLING

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# **ABSTRACT**





The insertion of co- and ter-monomers in polyethylene chain synthesized with Ziegler-Natta catalysts allows tailoring physical and chemical properties in a wide range. The insertion of cyclic comonomers, possible with metallocene catalysts, allowed a modulation of glass transition temperature ( $T_g$ ) to obtain copolymers with increased  $T_g$  and to increase mechanical and thermal properties of the material

In particular, ethylene-norbornene copolymers (E-co-N) by metallocene synthesis have high thermal resistance, high resistance to solvent dissolution, high gas barrier properties and high optical transparency (I. Tritto, L. Boggioni, D. R. Ferro, *Coordination Chemistry Reviews*, 250, 212 – 241, (2006)). High norbornene content copolymers still have this characteristics but they become brittle. To overcome this limitation we decided to explore a new synthesis strategy, introduced by Dow Chemical Company (D.J. Arriola, E.M. Carnahan, P.D. Hustad, R.L. Kuhlman, T.T. Wenzel, *Science*, 312, 714 (2006)) in 2006 the so-called, “Chain Shuttling Polymerization” (CSP) strategy. CSP allows to obtain multiblocks microstructure copolymers where different microstructures are bonded together in an alternate sequence in the same polymeric chain. The catalytic system of CSP is composed by three fundamental components: two catalysts with different propensity to incorporate the comonomeric units and one chain transfer agent (CTA) that “shuttle” the growing chain from one catalytic center to another catalytic center.

In the investigations on ethylene-norbornene copolymerizations via CS, we selected: i) one catalyst with high norbornene incorporation, ii) one catalyst with low norbornene incorporation, iii)  $ZnEt_2$  as chain shuttling agent (CSA).

We explored two different catalytic systems: i) two zirconocenes with different ligands, to evaluate the influence of the ligands on the final polymer properties; ii) two metallocenes with different metal atom and the same ligands. The activation of the catalyst was performed by dimethylanilinium tetrakis(pentafluorophenyl)borate for both systems (M. Bochmann, *Organometallics*, 29, 4711 - 4770 (2010)).

All the synthesis were performed in autoclave at high pressure (1-19 bar) at different N/E feed ratio of 1,3; 4.8 and 26,0. All the E-co-N copolymers were characterized with  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopy, GPC exclusion chromatography and thermal analysis DSC.

An initial screening was performed to find out the best polymerization conditions for keeping the N conversion lower than 15%. Subsequently, the E-co-N copolymerizations with a single metallocene in the presence of  $\text{ZnEt}_2$  have been performed at three different concentration of Zn in solution to evaluate CSA effect on the final properties of the copolymers. Finally, a set of E-co-N copolymers via CSP have been performed with both catalytic systems in the presence of  $\text{ZnEt}_2$ .

The thermal analysis of E-co-N copolymers obtained via CS shows a unique  $T_g$  event with values intermediate between those of E-co-N copolymers obtained without CSA and they are not affected by the concentration of  $\text{ZnEt}_2$  in solution. Conversely, the molecular weights of E-co-N copolymers obtained via CS decrease by increasing the  $\text{ZnEt}_2$  concentration in solution for all the catalysts selected. Narrow molecular weight distributions are obtained and termination pathways occur in a negligible way. These characteristics are clues that the polymerization proceeded via a chain shuttling mechanism. The results obtained in this work suggest the possibility of application of “chain

shuttling mechanism” to obtain blocky ethylene-norbornene copolymers.



# **CHAPTER 1**

## **INTRODUCTION**



Since 1963, when Natta and Ziegler were awarded the Nobel Prize, the study of macromolecules have raised in an exponential way due to the broad range of polymer applications. Every aspect of life can be correlated to a product of polymeric industry: from cosmetic and sanitary applications to synthesis of plastic materials. For example in literature the number of publications increased of 100% from 1990 to 2010. These two trends give us information about the constantly importance of research on the synthesis and characterization of new polymeric materials.

The discovery of Ziegler-Natta catalysts has been of fundamental relevance for industrial growth. The low energy demand for catalytic synthesis and the relative low temperature of polymer processing were good characteristics for industrial investments. Furthermore, the monomers (ethylene and propylene are the most commonly used) are obtained from a single-step treatment of crude oil (cracking). Products of polymerization (polyolefins) are materials that can be recycled or used for obtaining thermal energy by combustion; thermal degradation of these kind of materials produces low-impact chemicals (mainly water and carbon dioxide)<sup>(1)</sup>. Since 70s the global demand for polyolefins has been constantly increasing. The global demand in 2014 is estimated to be between 100 to 120 million metric tons and for next 10 years the trend is constantly increasing due to the arising of Asian countries markets.

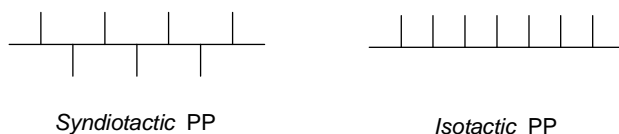
## Ziegler-Natta catalysts

Ziegler and Natta received a Nobel prize for the discovery of catalysts that can polymerise olefins with low activation energy and in high yields. Ziegler-Natta catalysts consist in titanium based-organometallic complexes obtained by reaction of titanium halide with alkylated aluminum<sup>(2)</sup>. Nowadays, the main industrial application of catalytic synthesis of polyolefins is based on Ziegler-Natta heterogeneous catalysis.

catalysis.

The polymerization reaction of prochiral monomers, *e.g.* propylene, introduced the concept of stereoselectivity and of “tacticity”, a new concept in chemical science<sup>(3)</sup>. Insertion mechanism of prochiral  $\alpha$ -olefins can be described using the concept of *meso* and *racemic* (*m* and *r*). With these two concepts, stereochemical configuration can be described on local scale: *meso* structures are those where the substituent group (in case of propylene is a methyl group) on a carbon atom has the same steric configuration of the nearest carbon atom substituent. In *isotactic* polymers all the substituents have the same steric configuration along the macromolecular backbone. In *racemic* structures the substituent group on a carbon atom has the opposite steric configuration of the nearest carbon atom. In *syndiotactic* polymers all the substituents have an alternate steric configuration along the macromolecular backbone. In atactic macromolecules the substituents are placed randomly along the chain.





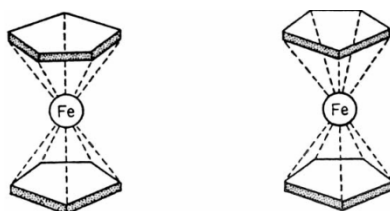
**Figure 1** Examples of tacticity on polypropylene (propylene is the simplest prochiral monomer)

Heterogeneous catalysis leads to high comonomer content in short copolymer chains and low content of comonomer in copolymer chains with high molecular weight. Instead, high comonomer incorporation in long polymer chains can be obtained by metallocene-based technology<sup>(8)</sup>.

This characteristic allowed to perform polyolefin synthesis for a wide range of applications: from films and packaging polymers to elastomers. Evolution of metallocene technology is focused on tuning the microstructure of the macromolecule. The new frontiers of research in polymer science are co- and ter-polymerisation reactions with metallocenes, chain shuttling polymerization and post-metallocene copolymerization<sup>(4)</sup> to obtain polymers with improved performances such as sealing, optical properties, elasticity along with improved mechanical performance and processability. Metallocenes are a class of chemical compounds that were discovered in 1951 by Pauson and Kealy<sup>(5)</sup> from an unsuccessfully reaction. The aim of the reaction was the synthesis of dihydrofulvalene by catalysis with  $\text{FeCl}_3$ ; the product was an unexpected yellow powder with formula  $\text{C}_{10}\text{H}_{10}\text{Fe}$  from elemental analysis. The structure of the compound, resolved by X-ray diffraction; consists of two planar, five-membered rings sandwiching an iron atom between them.

Robert Burns Woodward and Geoffrey Wilkinson deduced the structure based on its reactivity. Independently Ernst Otto Fischer also came to the conclusion of the sandwich structure and started to synthesize other metallocenes such as nickelocene and cobaltocene.

This led to the synthesis of a wide range of chemicals and to the birth of organometallic chemistry; from IR and UV analysis it was clear the “sandwich” structure<sup>(6)</sup>. The high stability of the compound in air and against chemical led to the conclusion that each 5-member ring participates with six electrons in the bonding the central Iron atom. Assuming the iron atom to be in the oxidation state of II, the total number of electrons involved in the “coordination” bond is 18 (6 electrons from Fe II atom and 6 electrons from each aromatic ring). From a reactivity point of view, the ferrocene maintains the aromaticity; it was demonstrated by reaction of acetylation (Friedel-Crafts acylation on aromatic rings) on the substrate.



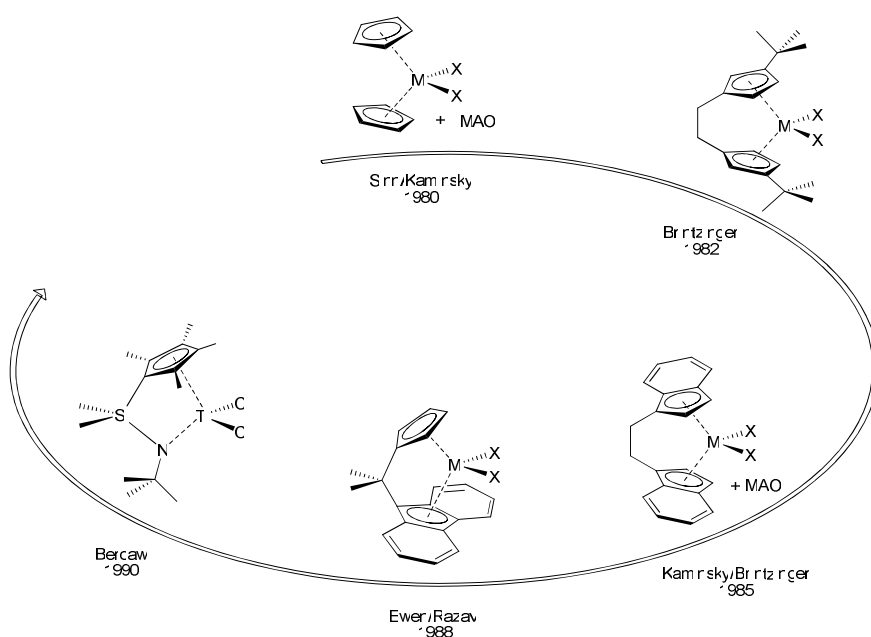
**Figure 2.** Sandwich-like structure of Ferrocene in two conformational modes

This was the first prototype sandwich compound and, after the discovery of this substrate, a great number of compounds with many transition metals with a great variety of ligands were synthesized<sup>(7)(8)(9)(10)(11)</sup>. Nowadays, the Wilkinson discovery of ferrocene is considered the beginning of modern organometallic chemistry.

Shortly after the synthesis of the first Group IV metallocenes by Wilkinson et al. in 1953<sup>(8)</sup>, the use of these complexes as

polymerisation catalysts was tested. Mixtures of  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$  in combination with aluminiumalkyls such as  $\text{AlClEt}_2$ , were found to polymerize ethylene with comparatively moderate activity, while no activity toward higher  $\alpha$ -olefins was reported<sup>(12)(13)</sup>. This kind of substrate did not reach industrial application because of its reduction to Ti(III) and deactivation. The field remained inactive for decades until an unexpected discovery. Metallocene catalysts were found to be sensitive to hydrolysis, traces of water actually increased the rate of polymerisation of titanocene catalysts, and the formation of aluminoxanes by partial hydrolysis of the aluminium alkyl components was reported<sup>(14)</sup>. This phenomenon was investigated in detail by Sinn and Kaminsky who showed that low active system  $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]/\text{AlMe}_3$  becomes highly active upon addition of significant quantity of water (Al:H<sub>2</sub>O ratio = 1:2), producing polyethylene with narrow molar masses distributions typical for single-site catalysis<sup>(15)</sup>. From further experiments and characterization it was clear the action of the cocatalyst on the titanium complex: in 1977 it was discovered that the cocatalyst was methylaluminumoxane (MAO), a mixture of molecules in which Al and oxygen atoms are bonded in an alternate way with methyl groups on free valences. The real turning happened when Brintzinger et al. synthesized the first “*ansa*” metallocene in 1982 providing the basis for the homogeneous polymerization<sup>(16)</sup>. Moreover, the synthesis worked not only with ethylene but with  $\alpha$ -olefins and was stereospecific. The principal characteristics of these catalysts are the two cyclopentadienyl ligands bonded with a bridge that brings rigidity to the structure which means a retaining of the configuration to guarantee stereospecificity during the polymerization<sup>(17)</sup>.

First evidence of stereospecificity was found in Ewen's group: in a mixture of *rac*- and *meso*-ethylenebis(indenyl)titanium dichloride in presence of MAO cocatalyst, the species *rac*- was the one that catalyses the polymerization of propylene only in isotactic fashion<sup>(18)</sup>. From then on, a variety of metallocenes with different ligands, bridges and central metal atoms have been synthesized. By changing the ligands structure it is possible to modify the symmetry of the catalyst and the stereoregularity of the final polymer chain<sup>(19)</sup>.



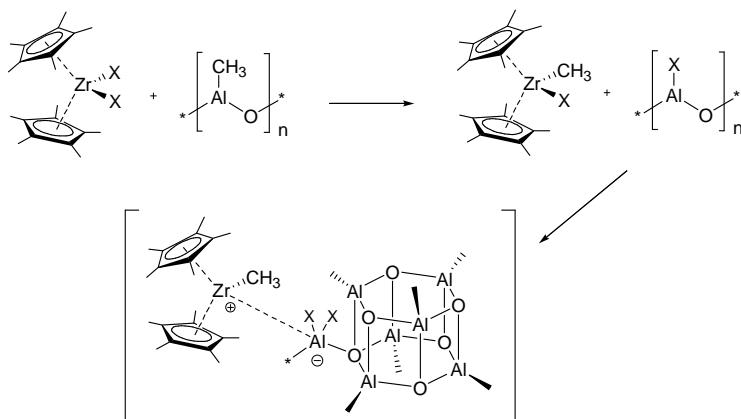
**Figure 3.** Historical evolution of catalysts for homogeneous polymerisation<sup>(29)</sup>

## The cocatalyst

As anticipated, Ziegler-Natta catalysis consists of two different “actors” acting synergistically: the cocatalyst is important as much as the precatalyst because the activity of the catalytic system is affected

by some parameters correlated only to the cocatalyst. The first cocatalyst was methylalumoxane (MAO) which is produced by controlled hydrolysis of  $\text{AlMe}_3$ . The molecular formula reported  $\text{AlOCH}_3$  represents only the internal ratios between the atom obtained by the hydrolysis. The real formula is  $[\text{Al}(\text{Me})\text{O}]_n$  ( $n = 5 - 20$ ) and the structure includes one-dimensional chains, two dimensional polycyclic and even three-dimensional clusters<sup>(20)</sup>. The molecular weight of the clusters was cryoscopically measured and found to be 1200-1600 g/mol. Organic solvents, such as toluene, were found to be good solvents due to the ligand exchange in aluminum complexes. Samples from commercial sources are not pure: a certain percentage of  $\text{AlMe}_3$  remains as impurity. From deep studies and publications<sup>(21)</sup>, it was demonstrated that the real active species in metallocene-MAO systems are the metallocene alkyl cations, that are  $d^0$  14-electrons species of  $[\text{L}_n\text{MR}]^+$  (with M a metal of IV Group) that form an ion pair with an anion which is complexed to the cage-like MAO structure.

The activation reaction proceeds in two steps: *i*) a rapid ligand exchange reaction with the metallocene dichloride forms a metallocene methyl and a dimethylaluminum compounds an *ii*) a  $\text{Cl}^-$  or  $\text{CH}_3^-$  is abstracted from the metallocene compound by an Al-center in MAO, thus forming a bulky cocatalyst anion and a metallocene cation with a weak back-donation. It is generally assumed that the lower the ion interaction, the higher the catalyst activity. (Figure 4).



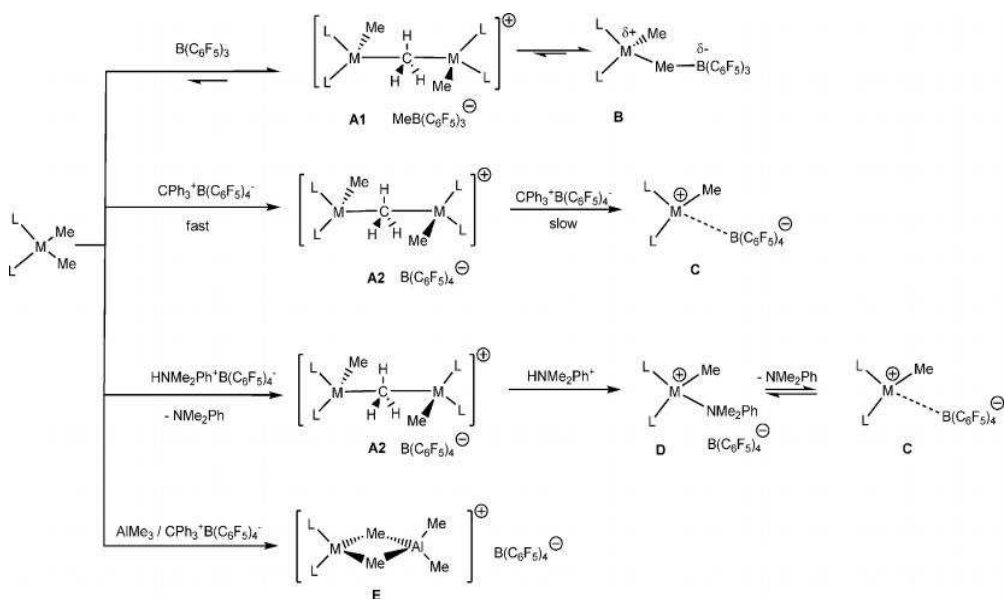
**Figure 4.** Activation mechanism of MAO on metallocene

Bulky ligands at the transition metal can produce metallocene monomethyl cations which dissociate more easily from the MAO anion. As a consequence, the activity can be increased by factors of 5 or 6<sup>(22)</sup>. The high excess of MAO is required to provide sufficiently bulky MAO cages. The cocatalyst has to be employed usually at [Al]/[M] ratios of 103 – 104/1, so that in such catalysts the cost of MAO by far outstrips that of the metallocene complex. There are additional possible roles of MAO that explain the large amount required for high activity and selectivity. Firstly, MAO undoubtedly acts as a scavenger for impurities such as water and oxygen from the reaction medium. Moreover, the metallocene is probably surrounded by MAO even in the outer-sphere and thus prevents catalyst deactivation by bimolecular processes between two metallocenes through either reductive elimination of polymer chains or oxidative coupling forming hydrocarbon bridges between two transition metal atoms. In addition, coordination of MAO to some metallocenes can lead to improved stereochemical control of catalysts<sup>(23)</sup>. One of the major obstacles to the commercialization of metallocene catalysts was

the need for large amounts of the expensive cocatalyst MAO, hence there is a large interest to find alternative activators.

Recently, MAO-free activators such as perfluoroarylboranes and trityl and ammonium borates as well as new supported activators were developed. These bulky cocatalysts can be used for the activation of single-site catalysts in low amount. In contrast to MAO, borates, especially the perfluorinated tri- or tetraaryl derivatives, can be applied stoichiometrically to give activities that can be compared with those obtained from MAO. The disadvantage of this class of cocatalysts is their sensitiveness to decomposition, high price, and the incorporation of fluorine into the polymer which can cause decomposition during polyolefins thermal processing.

Borates represent a new frontier in activation of metallocene catalysts. As is well established<sup>(24)</sup>, activation can be achieved by reaction of  $L_nMMe_2$  (M from IV Group) with suitable Lewis acids such as  $B(C_6F_5)_3$  and its congeners, trityl salts of noncoordinating anions or Bronsted acids capable of generating weakly coordinating counteranions. Among the last class of activators, anilinium salts such as  $[HNR_2Ph][B(C_6F_5)_4]$  (R=Me, Et) have been largely used. Aluminum activators (like MAO) also act as scavengers for background polar impurities; thus mixture of organic activators with  $AlMe_3$  or, much more effectively,  $AlBu^i_3$  are often used (TIBA). However, the addition of aluminum alkyls certainly complicates the chemistry of generating the active species, as its structure and reactivity, and the  $R_2AlCl$  by product has to be considered. Mechanism of activation reaction is reported in the scheme below:

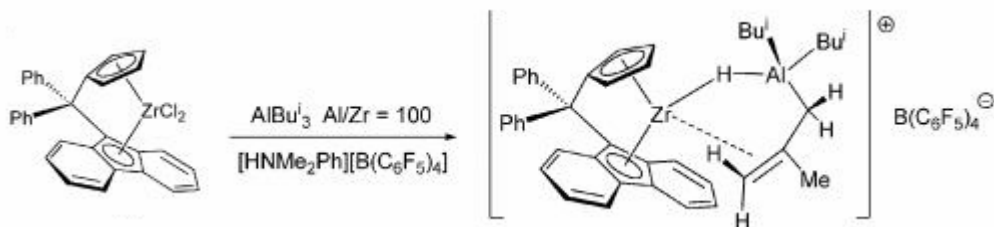


**Figure 5.** Activation reaction pathways with boranes and borates

The product of the reaction with  $[\text{HNR}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  is an aniline complex (reported in Figure 5 as complex D), and although the assumption is usually made that such complexes are very labile (if they exist in solution at all), this may or may not be true depending on the metal and the ligands. The main factor that determines the Lewis acidity and consequent olefin binding capacity of a metal alkyl complex is the counterion. The “Anion engineering” led to remarkable activity improvements; main design principle is to increase the delocalization of the negative charge over a larger volume as possible. A second consideration is to ensure that the anion is not polarizable and has either no or a minimal dipole moment. The size of the counteranions correlates with catalytic activity, provided the anion is not polar and contains no sterically accessible donor heteroatoms. In most cases the volumes are substantially larger than volumes of the metallocene cations<sup>(25)</sup>. Presence of TIBA (triisobutyl aluminum



Al<sup>i</sup>Bu<sub>3</sub>) in catalytic activator system has usually remarkable beneficial effects. The reasons for this are not entirely clear. In MAO-activated ethylene/norbornene copolymerizations with *ansa*-metallocenes, TIBA has low or no tendency to undergo exchange of Zr-polymeryl chains. In this case the beneficial effect may be due to the removal of AlMe<sub>3</sub> acted by TIBA. Interaction of TIBA with group 4 metallocenes under catalyst activation conditions but in absence of monomer has led to the isolation of a number of species that can be regarded as resting states, or possibly deactivation products, for cationic metal alkyl species<sup>(25)</sup>. Götz et al.<sup>(26)</sup> found that Cp<sub>2</sub>-ZrCl<sub>2</sub> gives TIBA adducts of zirconocene hydrides [Cp<sub>2</sub>Zr-(μ-H)(HAlBu<sup>i</sup><sub>3</sub>)]<sub>2</sub>, probably via Cp<sub>2</sub>ZrBu<sup>i</sup><sub>2</sub>. Activation of zirconocene Ph<sub>2</sub>C(Cp)(Fluorenyl)ZrCl<sub>2</sub> with TIBA/[HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] at an Al/Zr ratio of 100 gave the unusual hydride-bridged cation reported in Figure 6<sup>(25)</sup>.

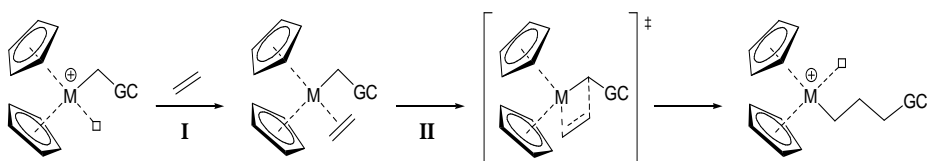


**Figure 6.** Activation of Zr complex with organic borate in presence of TIBA

## The mechanism

Compared to conventional heterogeneous systems, homogeneous catalysts give very uniform catalytically active sites which possess a well-defined chemical scaffold surrounding. Several investigations

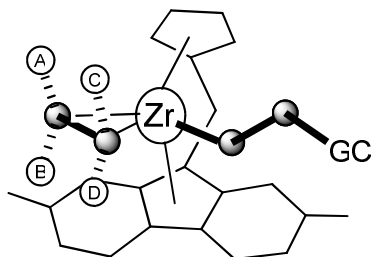
have confirmed that the real active species in polymerization reaction is a ion pair  $[L_nMR]^+[X]^-$  formed by metallocene alkyl cations and a weakly coordinating anion (in this case a borate). From an accurate observation on the cationic species, the electronic configuration is  $d^0$  and the total number of valence electrons is 14; according to the 18 electrons-rule, this is an electron-deficient species. For this reason, the cation exhibits a strong tendency to coordinate with the weak Lewis base olefin molecules. Studies based on Molecular Orbital (MO) Theory indicated that once an olefin is coordinated to the metallocene alkyl, the insertion of the olefin into the alkyl-metal bond would proceed rapidly. The driving force of this reaction is the energy gain on converting a  $\pi$  bond into a  $\sigma$  bond, with energy release of 20 Kcal/mol<sup>(27)</sup>. The mechanism of polymerization of an  $\alpha$ -olefin proceeds according to the Cossee-Arlman mechanism<sup>(28)</sup>, that was reported in Figure 7.



**Figure 7.** Migration and insertion mechanism of olefin on alkyl metallocene

According to the scheme, the active site of the catalyst incorporates both the growing chain (GC) and a vacancy; the importance of the vacancy is that it permits the  $\pi$ -coordination of the monomer (Figure 7; Step D). Step II is the cis-opening of the  $\pi$ -bond of the olefin via 4-member cyclic transition state; this mechanism is simultaneous with

the chain migration (GC) to the olefin ligand that leaves a new vacancy. The new vacancy provides the conditions for the next propagation step. This is the general mechanism of polymerization reported for this kind of metallocene; but the good potential of metallocene polymerization is that the presence of the ligand guarantees a good stereochemical control. When the olefin that is polymerized is prochiral (e.g. propylene), the introduction of an asymmetric element must be considered and the stereochemistry plays an important role.



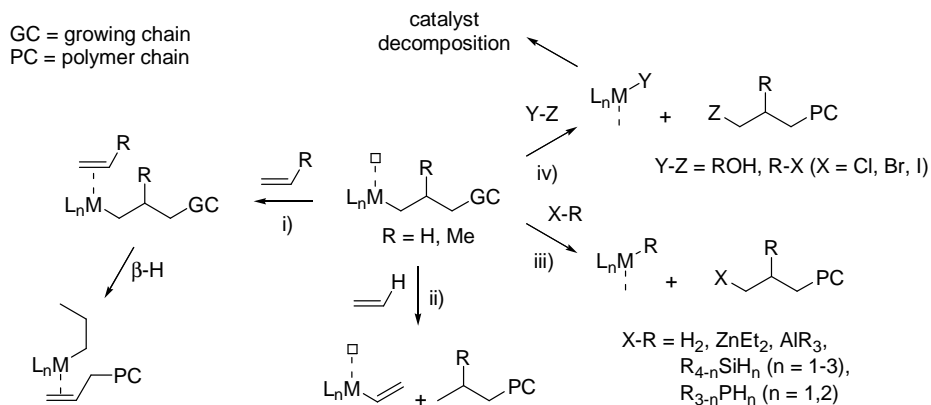
**Figure 8.** Different positions of migration of growing chain to prochiral olefin

The growing chain (GC) can migrate in four different positions (A,B,C,D in Figure 7). Preferential pathways depend on steric interactions of the ligand that surrounds the catalytic center and the incoming olefin building block. Changes in ligand structure lead to changes in polyolefin microstructure: isotactic, syndiotactic and atactic microstructures can be obtained only by tailoring the structure of the local symmetry of the metallocene<sup>(29)</sup>. Different positions of migration (A,B,C,D in Figure 8) are all different in energy and the favoured species is the one with the lowest energy content. To give stereospecificity, the energy gap between the preferential position and

the other possible position has to be sufficiently high. Local symmetry influences the stereospecificity of propylene (the simplest chiral  $\alpha$ -olefin) polymerization: a catalyst with  $C_s$  symmetry produces syndiotactic polypropylene and a  $C_2$  symmetry catalyst produces isotactic polypropylene. This is due to the mechanism explained: it is well known that if the chain migration is blocked by a bulky substituent, the polymer chain cannot undergo the inversion step and as a consequence an originally syndiotactic polypropylene can switch to an isotactic polypropylene. If the substituent is smaller, the precursor catalytic form produces hemitactic polypropylene, which exhibits a random configuration only on every second monomer unit.

Stereocontrol can be achieved in two different ways: by enantiomorphic site (the mechanism explained before) or chain-end control<sup>(30)</sup>. For polyolefin production, mechanisms of chain propagation and chain termination are competitors; the length of a single chain is determined by the relative rates of these two mechanisms.

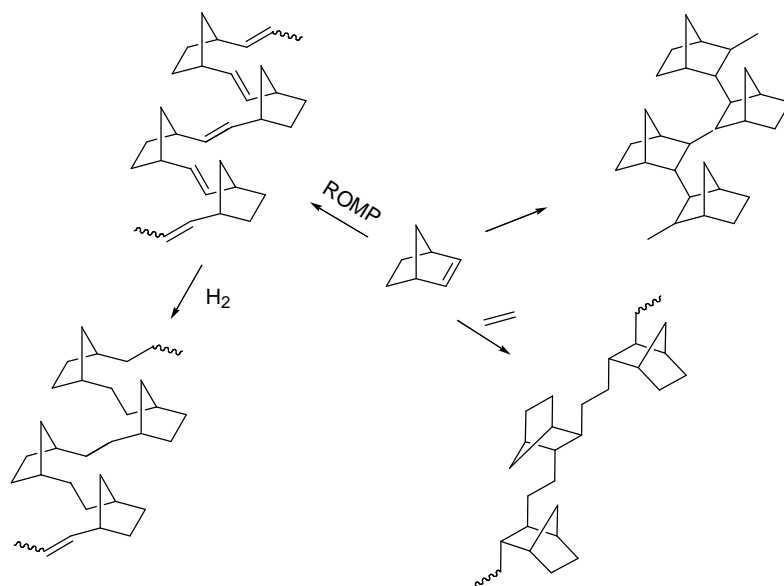
Most of the physical properties of the final polyolefin material is influenced by the length of the polymer chains and the homogeneity of the polymer chain lengths (these two concepts are well expressed by  $M_w$  and  $M_w/M_n$  parameters). Mechanism of chain termination is preferentially via  $\beta$ -hydrogen elimination pathways, a process that is about three orders of magnitude slower than insertion and produces terminal olefin function<sup>(31)</sup>.  $\beta$ -hydrogen elimination is not the only mechanism of chain termination: all mechanisms are reported in Figure 9. The monomer and cocatalyst used for polymerization influence the termination pathway.



**Figure 9.** General scheme of chain termination reactions i) H-transfer to monomer and chain release; ii) C-H bond activation and transfer from monomer to chain; iii) metathesis with cocatalyst or chain transfer agents; iv) poisoning of catalyst

## Homo- and copolymers based on cyclo olefins

Cyclo Olefin Homopolymers are a family of specialty and engineering polymers derived from ring shaped molecules that express different characteristics from linear co-monomer macromolecules. There are several cyclic monomers that can be used like cyclobutene (CB), cyclopentene (CP), norbornene (N), 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphtalene (DMON) and 1,4,5,8,9,10-trimethano-1,2,3,4,4a,5,8,8a,9,9a,10,10a-dodecahydroanthracene (TMDA). Cyclic olefins can follow two different pathways of polymerization: while the polymerization with heterogeneous Ziegler-Natta catalysts is accompanied by ring opening (ROMP) featuring elastomeric materials<sup>(32)</sup>, the homopolymerization of cyclic olefins by double bond opening can be achieved by several transition metal catalysts, namely late-metal Ni<sup>(33)</sup> or Pd<sup>(34)</sup> catalysts and metallocenes<sup>(35)</sup>. ROMP involves the breaking and reforming of the double bond with opening of the structure (Figure 10). The driving force of this kind of reaction is the release of ring strain because the change in entropy is unfavourable. The other way of polymerization of cyclic olefin monomers is by vinyl addition, that is by opening only the  $\pi$  component of the double bond maintaining the cyclic structure. The vinyl addition of norbornene by “naked” late transition metal catalysts gives a specialty polymer, developed and commercialized under the trade name Avatrel<sup>(36)</sup>. Poly(norbornene) possesses high glass transition and decomposition temperature, and excellent transparency as main properties, and is applied as cover layer for liquid-crystal displays and as electro- optical material.



**Figura 10** Mechanism of ring opening (ROMP) vs mechanism of insertion-migration on norbornene based polymeric materials

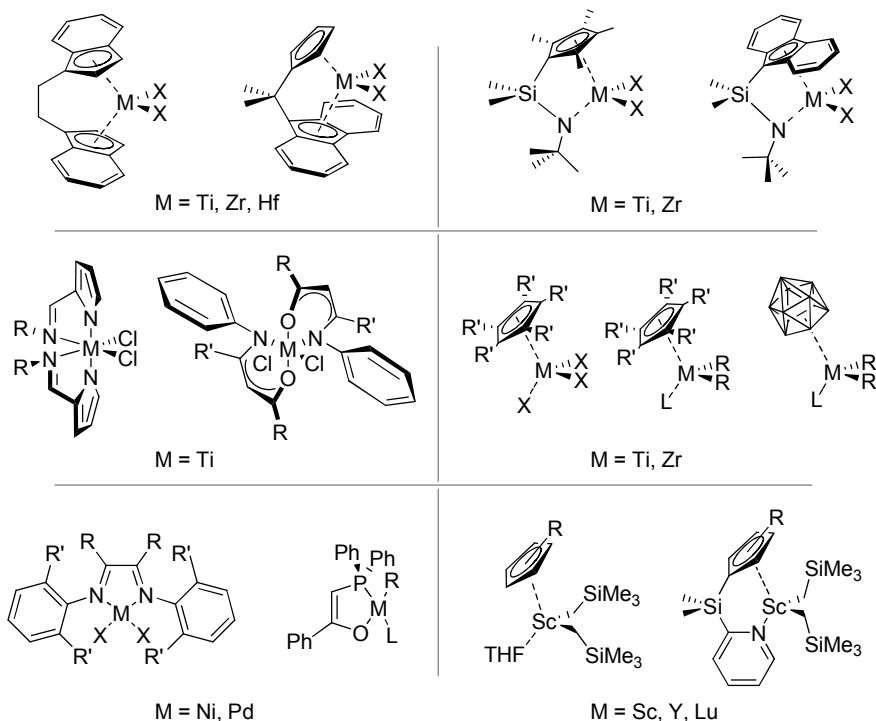
Metallocenes are the first class of catalysts able to polymerize cyclic olefins without ring opening<sup>(35)</sup>. Reactivity of cyclic olefins depends from two factors: the dimension (in terms of volume) of the comonomer and the intrinsic reactivity. Higher the volume of the cyclic olefin, higher the stress created in the active site of the catalyst: this is only due to steric interactions between the olefin and the ligand that surround the metal center. Intrinsic reactivity works in an opposite way to the steric factors and it is determined by two factors: firstly the olefin strain, which may be quantified by the difference in energy between the olefin and the corresponding alkane as calculated by force field methods and, secondly, by the non-planarity of the reacting double bond which can be described by symmetric or asymmetric deformation. On the basis of these considerations it turns out that cycloolefins with symmetric out-of-plane bending of the double bond

protons, such as norbornene, DMON and cyclopentene, can be polymerized; indeed this kind of bending makes the coordination of the monomer to the transition metal and the insertion easier owing to the lower barrier for the geometric changes occurring when the  $sp^3$  hybridization develops. Conversely, cycloolefins with antisymmetric out-of-plane bending cannot be polymerized. Typical examples are cyclohexene or cyclooctene. The reactivity of cycloolefins with planar double bonds is determined by the olefin strained. However, polycycloalkenes from a vinyl polymerization showed extremely high melting points which lie above their decomposition temperatures (in air). Under vacuum the melting points were found (by DSC) to be 485 °C for polycyclobutene, 395 °C for polycyclopentene, and over 600 °C for polynorbornene<sup>(38)</sup>. Therefore, such polycycloolefins are generally difficult to process, due to their high melting points and their insolubility in common organic solvents, and are of little commercial interest. Copolymers based on cycloolefin and  $\alpha$ -olefins (COC) overcame all these issues for their good processability, good thermal, optical and mechanical properties that made COCs a new class of engineering plastics with potential applications in various commercial areas.

One of the most interesting COCs are the ethylene-*co*-norbornene copolymers. They are versatile and interesting for technical uses and for the easy supply of monomer: ethylene is the most abundant chemical compound obtained by cracking of crude oil and norbornene is obtained by Diels-Alder reaction of cyclopentadiene and ethylene. The first experiment of copolymerization ethylene/norbornene was reported by Kaminsky et al. with catalyst *rac*-[Et(Ind)<sub>2</sub>]ZrCl<sub>2</sub>/MAO<sup>(39)</sup>. Since then, many efforts have been made by academic and industrial



research groups to deeply understand the microstructure and properties of ethylene/norbornene copolymers<sup>(41)</sup>.

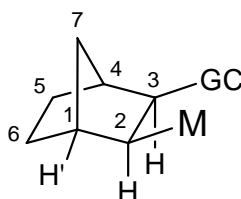


**Figure 11.** Different generations of metallocene catalysts for ethylene-norbornene polymerization

By changing the metal centre and the ligands scaffold of metallocenes, it is possible to fine tune the copolymers microstructure and to synthesize a variety of poly(E-co-N) copolymers with a wide range of N contents and controlled N distributions. Several catalysts of  $C_2$ - and  $C_5$ -symmetry allowed to develop copolymers with different microstructures and incorporation ratios of the cyclic olefin. Statistical copolymers are amorphous for comonomer incorporation beyond 15-20 mol % of cyclic olefin. The glass transition temperature of poly(E-co-N) varied over a wide range: copolymers containing more than 50

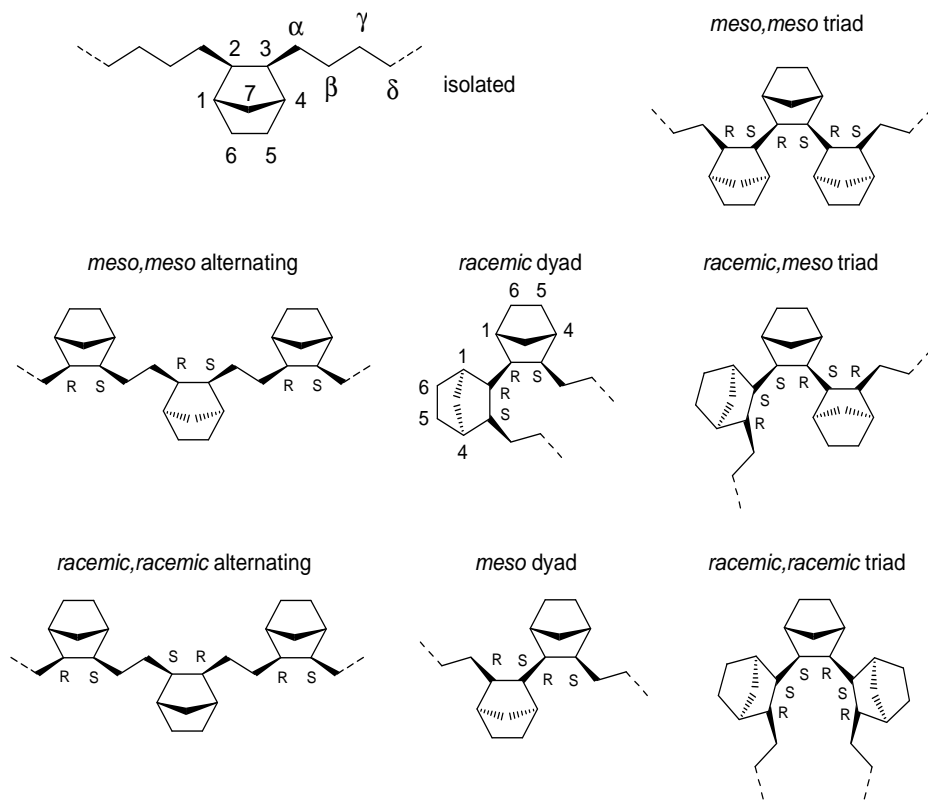
mol-% of norbornene can have glass transition temperatures up to 220 °C<sup>(40)</sup>.

The determination of the microstructure is fundamental for its influence on all the physical and mechanical properties of the final material. Metallocene catalysts incorporate norbornene in *cis-2,3-exo* fashion. One of the consequences is that norbornene cannot undergo  $\beta$ -hydrogen elimination as one  $\beta$ -H is located on the *endo* side and *trans* to the M-C bond, whereas elimination of the  $\beta$ -H' would result in the formation of an anti-Bredt olefin (like illustrated in Figure 10).



**Figure 12.** *Cis-2,3-exo* insertion of norbornene, which impedes  $\beta$ -hydrogen elimination reaction

The polymer microstructure of poly(E-co-N), evaluated by means of <sup>13</sup>C-NMR spectroscopy, is quite complex<sup>(41)</sup>. Copolymers having high amounts of norbornene incorporated display a large number of possible comonomer sequences. Depending on catalysts structure, norbornene units can be arranged in alternating fashion (*ENEN*) or in short norbornene homosequences such as dyads (*ENNE*) and triads (*ENNN*)<sup>(42)</sup>. Moreover, due to the presence of two chiral centers per norbornene unit carbon atoms, C2/C3 can be either S/R or R/S, so the relationship between two subsequent norbornene units can be either erythrodiisotactic (*meso*) or erythrodisyndiotactic (*racemic*). Possible arrangements of norbornene units (N) are reported in Figure 13



**Figure 13.** Isolated (EENE), alternated (ENEN), dyads (ENNE), triads (ENNN) norbornene sequences along with the relative configuration of stereogenic carbon atoms.

The polymer microstructure is tightly connected with metallocene symmetry and the nature of the ligands. For example copolymers obtained with a catalyst such as the Constrained Geometry  $[\text{Ti}(\eta^5:\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NtBu})\text{Cl}_2]$  are atactic<sup>(43)</sup>, thus containing both *meso* and *racemic NENE* sequences, whereas metallocene complexes containing ligands with higher steric demand, such as the  $C_2$  metallocene  $[\text{Zr}\{(\eta^5\text{-2-Me-[e]-benzindenyl})_2\text{SiMe}_2\}\text{Cl}_2]$ , can generate mainly *isotactic* alternating copolymers<sup>(44)</sup>.

Alternating stereoregular E-N copolymers can also be achieved by means of catalysts with heterotopic sites. For example, copolymers obtained by the  $C_1$ -symmetric complex  $[\text{Zr}(\eta^5:\eta^5\text{-}(3\text{-R}'\text{C}_5\text{H}_4)\text{CR}_2\text{C}_{13}\text{H}_8)\text{Cl}_2]$  [ $\text{R} = \text{Me}$  or  $\text{Ph}$ ,  $\text{R}' = \text{Me}$  or  $t\text{-Bu}$ ] in the presence of an excess of norbornene are highly alternating isotactic poly(E-co-N). Interestingly these copolymers resulted to be crystalline if the N content is higher than 37 mol-%, showing melting points from 270 to 320 °C<sup>(45)</sup>.

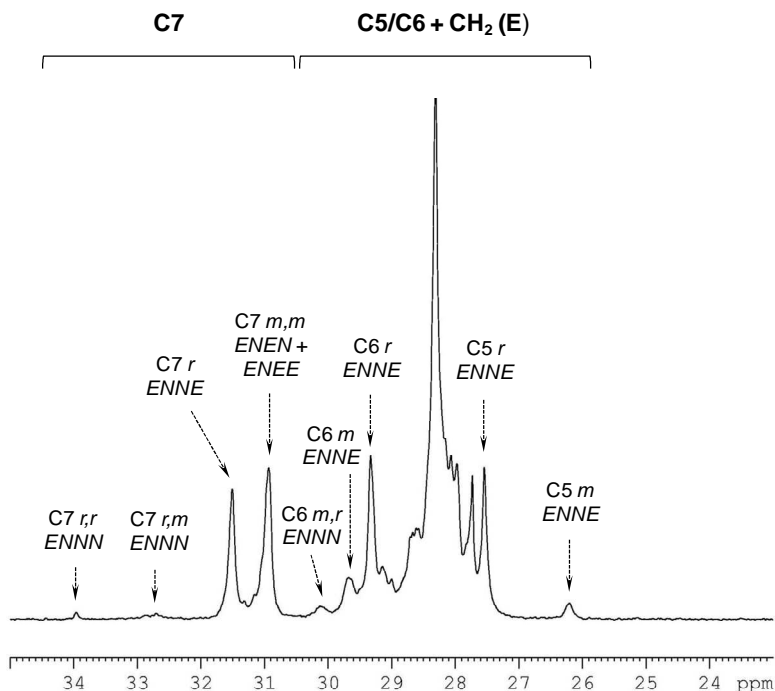
*Ansa*-metallocenes of  $C_2$  and  $C_s$  symmetries could also generate random poly(E-co-N) containing short norbornene homosequences (dyads and triads), allowing the synthesis of copolymers having more than 50 mol-% of norbornene incorporated and thus materials with glass transition temperatures up to 220 °C<sup>(46)</sup>. Constrained Geometry Catalysts allowed the synthesis of alternating poly(E-co-N) copolymers; the stereochemistry of subsequent units of norbornene produced mainly atactic sequences (no stereocontrol on prochiral olefins)<sup>(44)</sup>. By using cyclopentadienyl-free catalysts a high control on molar masses was achieved, whereas by exploiting catalysts with late-transition metals, functionalized norbornene derivatives were introduced<sup>(47)</sup>.

Recent developments of single-site catalysis brought cationic rare earth metal half-sandwich catalyst to show excellent activity for the copolymerization of various cyclic olefins. This family of catalysts led to the exclusive formation of alternating poly(E-co-N) and, if a relative small amount of norbornene was used, an poly(E-co-N) with an ethylene block poly(E-co-N)-b-PE can be obtained<sup>(48)</sup>.

## Microstructural analysis of COC copolymers

In general, the  $^{13}\text{C}$ -NMR resonances of poly(E-co-N) fall into four areas that can be assigned as methylene C5/C6 and C7 carbon atoms or methine C1/C4 and C2/C3 resonances of norbornene<sup>(46)</sup>. The region of C5/C6 carbon atoms of N ranges from 26.2 to 30.6 ppm. Within the same interval ethylene (E) resonances are also to be found. The signals at 26.2 and 29.7 ppm and at 27.5 and 29.3 ppm are assigned to *meso* and *racemic* ENNE dyads, respectively. The signals of carbons C5/C6 in ENNN triads sequence might be overlapped with the signals of *meso* and *racemic* dyads, while the weak peak located at 30.1 ppm should be corresponding to the *meso*, *racemic* triad of carbon C6.

The resonances of carbon C7 of norbornene are located in the region of the spectra between 30.6 and 34.3. The peak at 30.9 corresponds to the *meso meso meso* alternating (ENEN) and isolated (ENEE) sequences. The peak at 31.5 ppm is assigned to *racemic* dyads of carbon C7 while the weak signals at 32.7 and 33.9 should be corresponding to the *meso*, *racemic* and *racemic, racemic* ENNN sequences, respectively.



**Figure 14.** Example of expansion between 24-35 ppm of a  $^{13}\text{C}$ -NMR for a E-N copolymer

In the region of the spectrum between 42.5 and 34.8 ppm resonances attributed to C1/C4 methine carbons of norbornene are observed. The weak signals located between 38.5 and 37 ppm are ascribed to *racemic, racemic* triads. The peaks at 39 and 39.8 ppm correspond to carbons of *racemic* ENNE sequences, while the peak at 39.5 ppm and part of the signal at 40.1 ppm are ascribed to *meso* and *racemic* alternating (ENEN) and isolated (ENEE) sequences. Finally, resonances ranging between 42.5 and 53.8 ppm are attributed to the C2/C3 resonances of N. The peaks at 45 and 45.8 ppm are assigned to carbons C2 and C3 in isolated and *racemic* and *meso* alternating units, respectively. The signals at 45.6 and 48 ppm correspond to *racemic* dyads, while signals ascribed to *meso* dyads are located at 46.5 and

47.1 ppm. In the region of the spectrum between 47.2 and 47.7 ppm are expected the resonances of *meso,racemic* and *racemic,racemic* ENNN triads. Detailed assignments of the complex spectra of these copolymers have been achieved. Quantitative data concerning the structural characteristics of poly(E-*co*-N) from the relative intensities of the respective peaks make possible to reach a complete description of the copolymer microstructure at tetrad level or even at pentad level<sup>(49)</sup>.

Ethylene-*co*-norbornene copolymers (commercially TOPAS: Transparent Olefin Polymer Amorphous Structure) are transparent thermoplastic resins very attractive for a wide range of applications. Table 1.1 reports the basic physical properties of poly(E-*co*-N)s compared to those of other transparent amorphous plastics, while in Table 1.2 the major applications of these materials are presented.

The outstanding feature of this new class of polymer is their ability to tailor the glass transition temperature ( $T_g$ ) simply by varying the norbornene/ethylene ratio in the copolymer. With increasing the norbornene content increases the stiffness of poly(E-*co*-N) along with the glass transition temperature and the heat deflection temperature (HDT) of the material, that is the temperature at which a polymer or plastic sample deforms under a specified load. As shown in Table 1.1, commercial grades have typically  $T_g$  values from 80 to 185 °C, and HDT from 75 to 170 °C. Poly(E-*co*-N) with glass transition temperature below 100 °C became more flexible and give much higher elongation at break at the expense of lowering tensile strength and HDT. Notably, the flowability of the material is adjusted by controlling the molar mass ( $M_w$ ) characteristics.

## Optical properties

Poly(E-*co*-N)s are glass-clear materials successfully applied for the production of high-quality optical components. Their light transmittance, which extends through the visible spectrum into the near UV, exceeds that of polystyrene (PS) and polycarbonate (PC), and nearly equals that of polymethylmethacrylate (PMMA), as shown in Table 1.1. Because of its aliphatic structure poly(E-*co*-N) has inherently low birefringence, which is a critical factor in a wide range of applications from lenses to films. Worth mentioning is the birefringence of poly(E-*co*-N) under the effect of an applied tensile strength, which remains rather stable, in contrast to many other transparent plastics like PC. These copolymers also have a high Abbé number, that is a measure of the change of refractive index with wave length. This number is high for poly(E-*co*-N), indicating low chromatic aberration (Table 1).



**Table 1.** Properties of poly(E-*co*-N) in comparison with other transparent amorphous plastics.

<b>General</b>	<b>P(E-<i>co</i>-N)</b>	<b>PS</b>	<b>PC</b>	<b>PMMA</b>
Density (g/cm <sup>3</sup> )	1.02	1.05	1.2	1.2
Flexural modulus (Msi)	0.5	0.45 - 0.5	0.34	0.45
Tensile strength (ksi)	9	6.4 - 8.2	9	10
Elongation (%)	3 - 10	2 - 4	80	5
Water absorption (%)	0,01	0.1 - 0.3	0.04	0.1
Heat deflection temperature - HDT (°C)	75 - 170	75 - 94	142	92
Glass transition temperature - $T_g$ (°C)	80 - 185	95	150	85 - 165
<b>Optical</b>				
Luminous transmission (%)	92	91	88	92
Haze (%)	1	3	1	1
Index of refraction	1.53	1.59	1.59	1.5
Abbé Number	56	31	34	61
Birefringence	Low	Variable	Variable	Low

P(E-*co*-N) = Ethylene/norbornene copolymers; PS = Polystyrene; PMMA = Poly(methylmethacrylate); PC = Polycarbonate.

Interestingly, the density of poly(E-*co*-N)s is very low compared to classical transparent amorphous resins such as PC and PMMA that are about 20 % higher in density, and have less than half the density of glass. These properties, along with a lower brittleness, make E-N copolymers suitable for replacing glass in optical components where weight and durability are needed such as video camcorder, hard-disk drives and flat panel displays. On the other hand, the optical properties of poly(E-*co*-N)s combined with their very low moisture absorption give them advantages in applications such as projection TVs and

computer displays, and other applications where heat or humidity can deform acrylic or PC lenses such as higher capacity DVDs and lenses for LEDs. Other potential optical elements include applications as toner binder resin for laser print engines (Table 2).

**Table 2.** General applications of poly(E-co-N).

<b>Applications</b>	
<b>Precision Optics</b>	<ul style="list-style-type: none"> <li>- Video camcorders, hard disk drives, flat panel displays, light guides for automotive</li> <li>- Projections and computer displays, lenses</li> <li>- DVDs, lenses for LEDs prints, diffractive optics, lighting, metalized reflectors, mirrors</li> <li>- Toner binder in colour printers</li> </ul>
<b>Electrical</b>	<ul style="list-style-type: none"> <li>- Thin-film capacitors</li> </ul>
<b>Medical and Diagnostic</b>	<ul style="list-style-type: none"> <li>- Syringe, serum vials, blood containers, petri dishes, test tubes, diagnostic and biomedical container</li> <li>- Cuvettes (spectrophotometer readings)</li> <li>- Microtiter plates, contact lens tooling, inhaler and dialysis parts</li> </ul>
<b>Packaging</b>	<ul style="list-style-type: none"> <li>- Flexible films for food, drugs, cosmetics, personal care</li> <li>- Bags and pouches for drinks and food.</li> <li>- Blister packaging, shrink films.</li> </ul>

## **Electrical applications**

Poly(E-co-N)s are good electrical insulators, with relatively constant electrical properties over a wide range of temperatures and frequencies. Properties such as low electron mobility and non-polarity could generate high resistivity and low dissipation factor that render the copolymer particularly useful in thin-film capacitors. Poly(E-co-N)s-based capacitors can be smaller and more energy efficient than those of polypropylene (PP) in applications as AC motor starter and high-frequency semiconductor circuits.

## **Medical and diagnostic applications**

Properties such as high transparency, excellent moisture barrier and chemical resistance to hydrolysis, acids and alkali, as well as to polar organic chemicals, enable E-N copolymers to be suitable for medical and diagnostic applications. Pharmaceutical and biomedical containers made of poly(E-co-N) can withstand all common sterilization regimes and displays excellent shatter resistance. Consequently, they can replace glass in several application from syringe to pharmaceutical bottles as shown in Table 1.2.

Poly(E-co-N) can also be employed to manufacture cuvettes and microtiter plates. These devices provide high light transmission through the near UV and low chromatic aberration for sensitive and accurate spectrophotometer readings.

## **Packaging applications**

Poly(E-co-N)s are of particular interest for primary packaging of pharmaceuticals and medical devices. Moreover, they are suitable for

direct food contact applications and are largely used in flexible packaging for food, drugs, cosmetics, and consumer products (Table 1.2). Poly(E-*co*-N) combined with polyethylene (PE) in blend films enhances the stiffness and sealability of the material, by keeping moisture out or preventing moisture loss during storage. They can be combined with PE in monolayer blend films or used in multilayer structures with layers of other resins. Typical uses for these blends include blister packaging, shrink films, and further packaging applications where improved moisture barrier and sealability are needed.

Finally, poly(E-*co*-N)s are processable by all commonly used methods for thermoplastics including injection molding, cast and blown film extrusion and coextrusion, injection blow-molding, and injection-stretch blow molding.

## **Recycling**

Most of the poly(E-*co*-N)s packaging applications involve mixed structures with other polymers, hence the post-consumer recycling depends on the polymers which are combined with. Although many blends and multilayered structures should be coded with the recycling number “7” under the SPI system (Society of the Plastics Industry), certain PE combinations may use the code of the majority PE component. For instance, a LDPE structure having a minor amount of poly(E-*co*-N) may retain a SPI recycle code of “4”.

If it is not practical to recycle a poly(E-*co*-N)s-containing product, it may be incinerated in waste disposal systems; when combusted completely it yields only carbon dioxide and water by releasing about 23000 kJ/kg.

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**CHAPTER 2**  
**EXPERIMENTAL SECTION**

## Materials and Chemicals

Metallocene catalysts are sensible to presence of polar impurities like oxygen and humidity; the collateral reactions with these impurities produce deactivation of the catalyst. Because of this high affinity to polar substances, all synthesis experiments were conducted with Schlenk techniques. It consists in using Schlenk-type glassware and high vacuum lines ( $10^{-6}$  Torr) with atmospheric pressure nitrogen and glove-box systems. All glassware is stored in an oven instead of the flaming procedure.

Gaseous chemicals (high pressure and atmospheric pressure ethylene, nitrogen) are purified by fluxing through columns of BTS-catalysts,  $\text{CaCl}_2$  and molecular sieves (4 Å and 4-8 mesh). This sequence of fluxing removes oxygen and humidity from the stream of chemical gas that flows at pressure higher than atmospheric pressure.

The main solvent used for polymerization reactions is toluene. This solvent, that is purchased from Sigma-Aldrich, is 99% pure by GC analysis. This high purity is not sufficient for the polymerization reaction because of its role of solvent (it is the reagent most present in the reaction environment). Toluene is stored on anhydrous  $\text{CaCl}_2$  for three days; then it is distilled on sodium in a special apparatus for distillation.

All catalysts and the cocatalyst have been purchased by TOPAS Advanced Polymers GmbH and stored in glove-box under controlled inert atmosphere (anhydrous nitrogen).

Triisobutyl aluminum (TIBA) is purchased by Crompton and by Sigma-Aldrich (in both cases it was purchased pure 100%). This chemical compound, as other aluminium alkyl compounds, is sensitive to oxygen

and very sensitive (flammable) to humidity so it has been manipulated using the Schlenk technique.

The comonomer used in this thesis is norbornene. Norbornene, which IUPAC name is bicyclo[2.2.1]hept-2-ene, is a chemical compound of the cyclic olefins category. It is a white solid with a melting point of 44-46°C. It was purchased pure from Sigma-Aldrich. It was purified by distillation on sodium in inert atmosphere. It is soluble in toluene in concentration up to 90% in mass. Because of this characteristic, it is more convenient to manipulate it in toluene solution than in solid state. To quantify the norbornene in the reactor, the Schlenk-type round bottom flask for the recovery of norbornene was previously weighted with the magnetic stirrer after flaming (this weight registered as  $W_1$ ); after inert atmosphere distillation, the round bottom flask containing purified norbornene was weighted again (reported as  $W_2$ ). Then, again under nitrogen atmosphere, toluene was added and the flask weighted again (reported as  $W_3$ ). In this way, it is possible to calculate the weight percentage of norbornene in solution by the following mathematical relationship:

$$\text{Norbornene\% in solution} = (W_2 - W_1) / (W_3 - W_1) * 100$$

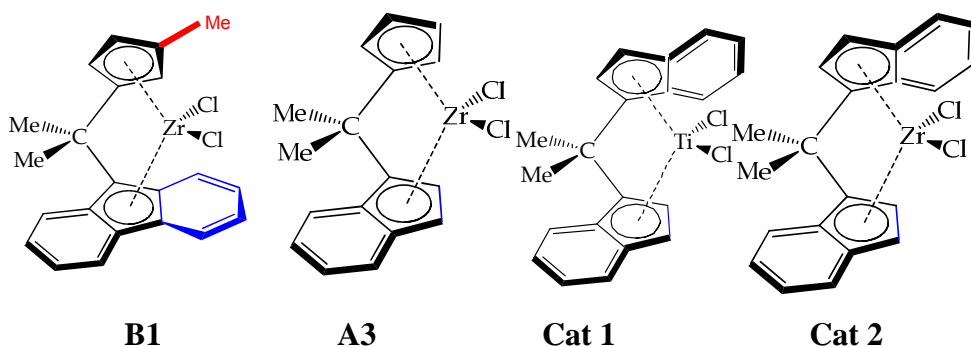
Having an information about the density of the norbornene solution it is possible to correlate the volume of solution with the weight of norbornene manipulated. In this group, it is common to use an empirical mathematical equation to correlate the weight percentage of norbornene in toluene and the density of this solution. The empirical equation is reported below:

$$\rho \text{ (g/mL)} = 9 * 10^{-5} * \text{wt(\%)} + 0,8652$$

This empirical equation is validated from 30 to 90% weight. Using these two equations it is possible to calculate the amount of comonomer added to the reactor for the copolymerization reaction.

All catalysts, reported below, have been purchased by Dr. Udo Stehling from TOPAS Advanced Polymers GmbH.

The organometallic compounds that were used as metallocene catalysts for copolymerization of ethylene and norbornene are the following:



First one is isopropylidene(3-methylcyclopentadienyl)(Fluorenyl)Zirconium dichloride reported as catalyst B1 in this thesis. It has  $C_1$ -symmetry which means that it has the tendency to form an alternating isotactic copolymer.

The second catalyst is isopropylidene(cyclopentadienyl)(Indenyl)Zirconium dichloride, reported as A3. This catalyst has also a  $C_1$ -symmetry but the absence of sterically hindered groups that prevent the migration of the growing chain in a random way produces a copolymer with a random stereochemistry (but with  $m$  NN dyads more abundant than  $r$  dyads).

The other two catalysts are isopropylidene(indenyl)<sub>2</sub>Titanium dichloride (Cat1) and isopropylidene(indenyl)<sub>2</sub>Zirconium dichloride (Cat2): these  $C_2$ -

symmetric catalysts can produce random copolymers with prevailingly *m* NN dyads. The difference of the two copolymers is in norbornene content due to the steric interactions between the ligand scaffold and the bulky cyclic olefin. All these organometallic compounds are sensitive to polar impurities: presence of water, oxygen and polar solvent traces. Manipulation of all these chemical compounds has to be conducted in inert atmosphere using Schlenk lines. These chemical compounds have to be weighted under inert atmosphere: they were weighted in a glove box. The procedure for weighting in glove box is to insert flamed Schlenk flask with magnetic stirrers in the anti-chamber of the glove box and make 3 cycles of vacuum and refilling with nitrogen. Terminated this first step for eliminating polar impurities, the Schlenk flask is placed into the glove-box and chemical compounds (catalysts and cocatalyst) are weighted in the Schlenk flask by difference: all chemical compounds that are stored in the glove box in vials and the amount of chemical compound is calculated as the final weight subtracted by the initial value (the weight of the taken chemical is reported as negative value because is registered as weight loss). Before exiting the glove box, all caps and taps have to be closed with grease to prevent the contamination by air.

## **Polymerization procedures**

Polymerization reactions can be conducted in two different ways: batch process at atmospheric pressure and batch process at high pressure (in autoclave).

**Batch process at atmospheric pressure** is the first step for studying new catalysts or new strategies of synthesis. In this phase of the research, it is possible to obtain information about the catalytic system activity during polymerization: the main target is to obtain information about the microstructure of the copolymer synthesized (by NMR spectroscopy), about the activity of the catalytic system (with the possibility to modify the conditions of the reaction), studying the variation of cocatalyst/catalyst ratio on the final macromolecule. Batch atmospheric pressure copolymerization is the preliminary step for approaching a new problem in polymer science research. It is useful to have information about the homopolymerization reaction to have information about the main affinity by monomer or co-monomer during the polymerization. Copolymerization procedure starts with connection of a 250 mL Schlenk-modified round bottom flask to Schlenk line to perform 3 steps of vacuum with refilling of nitrogen to remove air from the reaction environment. In the meantime, in glove box, catalyst and cocatalyst are weighted in two Schlenk flasks in inert atmosphere; the amount of these two chemical compounds is variable depending on the reaction condition of the copolymerization. Both compounds are dissolved in a precise volume of toluene to calculate with accuracy its concentration in solution. Next step is the introduction of the reaction solvent in the round bottom flask: fresh-distilled toluene is stored in a 100 mL Schlenk flask and then transferred to the round bottom flask with a siphon. After the introduction of the solvent, the solution of cocatalyst (MAO in toluene) is added with a syringe to the round bottom flask; the amount of MAO solution that is added to the reaction environment depends on the reaction conditions decided for the polymerization. Then, the comonomer (in solution of toluene) is added with a syringe to the round bottom flask; the amount of



comonomer is previously calculated from the equations reported in this section for norbornene. All quantities of solvent, cocatalyst and comonomer solutions are calculated to reach a certain total volume (usually 100 mL for atmospheric reaction in batch). Next step is the removal of nitrogen from the reaction ambient: this operation is important because the presence of nitrogen dissolved in toluene reduces the ethylene solubility in toluene. Nitrogen is removed by Schlenk-line by applying vacuum repeatedly for short gap of time. After the removal of nitrogen, ethylene is added to the round bottom flask: to calculate the amount of ethylene that is dissolved in toluene, Henry's law is used. Henry's law is a function that can calculate the concentration of a gas by controlling temperature and pressure. For this system, Henry's law is calculated as:

$$C(\text{mol/L}) = P_E * K_H * e^{(\Delta H/RT)}$$

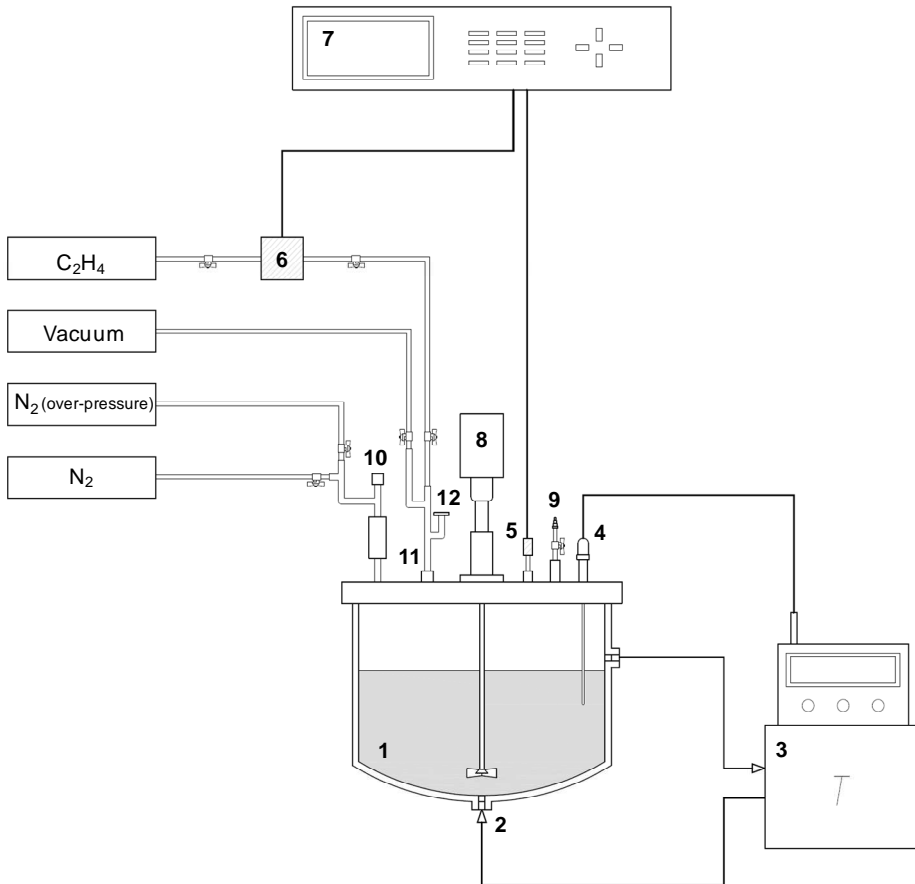
This is the general equation of Henry's law that expresses the behaviour of gases in solution: higher the pressure higher the concentration, higher the temperature lower the solubility of the gas. For ethylene in toluene, the parameters are  $\Delta H = 2569 \text{ cal/mol}$ ,  $K_H = 0,00175 \text{ mol*L/atm}$ ,  $R = 1,989 \text{ cal/K*mol}$ . Ethylene saturation of reaction solution is guaranteed by exposure of solution with gaseous monomer for almost 15 minutes. Addition of catalyst by syringe is the last step of the polymerization procedure: the amount of catalyst, in terms of volume of solution, is relative to the amount of catalyst decided to introduce in the reaction environment. The duration of the reaction is fixed from experimental problems related to the batch process: in a batch process, the incorporation of comonomer in the polymeric chain induces a reduction in the comonomer/monomer ratio that can cause inhomogeneity in

composition of the copolymer obtained. So the main adopted strategy consists in using a standard time (15 minutes) and to adjust the amount of catalyst to have a consumption of comonomer lower than 15% in mol. After 15 minutes, the reaction is stopped by introducing in the round bottom flask 2 mL of a mixture of ethanol and hydrochloric acid; this operation deactivate the catalyst. Then the reaction mixture is added to 1 L of distilled ethanol with hydrochloric acid to precipitate the polymer. The purification consists in solubilization of the solid (after filtration) in toluene and a second precipitation in pure acetone. This step is essential to remove the product of reaction of aluminum alkyls with acidic ethanol (mainly alumina).

**Synthesis at high pressure in autoclave.** The synthesis strategy is different because the apparatus include a high pressure reactor (Figure 1). The reactor (1) is a steel Buchi reactor of 600 mL with jacket for temperature control connected to a Buchi thermostat (3) that guarantees the temperature control by recirculation of a mixture of water and glycerine. The reactor has a thermocouple (4) that registers and controls the temperature during all operations and is connected to a Schlenk line (11) (vacuum and nitrogen). It is also connected to a high-pressure ethylene line and multigas controller (7) to provide the monomer to the reactor. In the end the reactor has a connection with a high-pressure nitrogen line. The first operation consists in removing air from the reactor: the different material (stainless steel) and the higher volume lead to a different treatment. First step consists in application of three cycles of vacuum and refilling with nitrogen at a higher temperature (85°C) and for one hour, 30 minutes and 15 minutes. The solution that has to be charged in autoclave in this case consists in a mixture of solvent (toluene), TIBA

and the comonomer (norbornene). In all high pressure synthesis the catalyst has been activated with borate before entering in the reactor. The catalyst solution is prepared completely in glove box: 25 mL of fresh-distilled toluene are mixed with 0,1 mL of pure TIBA and stirred for 30 minutes in a 25 mL Schlenk. Then the Schlenk is brought into the glove box and the calculated amount of catalyst is added. Then for completely dissolution of catalyst, the solution is stirred for 3 hours. Then the cocatalyst (dimethylanilinium tetrakis(pentafluorophenyl)borate) is added in 1,5 molar ratio. The suspension is stirred for 45 minutes and then the active species of the catalyst is ready. Meanwhile, in a special glass flask for autoclave, fresh-distilled toluene is added in inert atmosphere. The second step is the addition of norbornene with a syringe: the amount of norbornene depends on the feed requested by the reaction conditions decided for the experiment. TIBA is introduced with a syringe in the glass flask as scavenger agent for impurities. This solution is introduced into the autoclave by application of stationary vacuum to the autoclave: solution migrate from the flask to the autoclave only by difference of pressure. Then the system is brought to the exercise temperature (the chosen temperature for the experiment) and the mechanical stirring (8) is set to 750 rpm. This step is important because the solution, that is in stationary state of vacuum, tends to evaporate to a fixed value of pressure; this value is similar to the vapour pressure of toluene (which is the substance more abundant in the system) and depends on the amounts of norbornene and TIBA that are introduced in the solution. This step requires different time intervals from 30 minutes to 45 minutes depending on the composition of the feed: higher amounts of norbornene in solution need longer time to reach this equilibrium state between the solution and its vapour. The pressure inside the reactor is registered by a Baratron (5):

a Baratron is a transducer that can measure the pressure of a system from the conductivity alteration of a semiconductor membrane due to the geometric deformation caused by the pressure activity. The transducer is connected to the multigas controller as reported in Figure 1:



**Figure 1** High pressure reactor scheme

Then, the ethylene is introduced into the reactor: the system for introduction of ethylene is composed by an automatic valve (6) and a parallel manual valve with the multigas controller. The manual valve is used for introducing ethylene and bring the pressure close to the target: the pressure is read on the multigas controller screen. To reach the target pressure, the automatic valve is turned on: this kind of valve is connected

to the multigas controller. When the pressure registered by the Baratron-multigas controller system is lower than the target, the controller sends an electric signal to the automatic valve and let it open and flow ethylene to the autoclave. When the pressure reaches the target, the multigas controller let the automatic valve close and stop the flow of ethylene to the autoclave. With this system the autoclave reaches a precise value of pressure for polymerization. With this operation, the gaseous monomer starts to dissolve into the reaction solvent until saturation: the maximum concentration of ethylene in toluene is calculated with the Henry's law reported before. For experiments at high pressure the automatic system is essential: in fact the automatic valve-multigas controller guarantees an accurate and reproducible value of pressure equal to the setpoint. To reach saturation status of the system, the amount of ethylene, in terms of moles, is higher. Multigas controller is useful to observe the saturation of the system because it allows the control of two parameters: the first is the pressure registered in the autoclave and the second is the volume (expressed in std liter) of ethylene that flows through the valve. When the valve is opened, the indicator of pressure starts raising and the value of the volume is different from zero. When the pressure reaches the set point, the value of the flow reaches zero (closed valve). Saturation status is reached when the pressure is equal to the setpoint and the value of the ethylene flow is zero. This operation requires almost 20-30 minutes because ethylene have to dissolve in solution at a pressure higher than the atmospheric: according to Henry's law, higher the pressure higher the concentration of ethylene in solution. After saturation, the system is ready for introduction of the catalyst: this is the real start of the polymerization process. Catalyst is introduced in the reactor in solution: this solution is prepared in same conditions as the atmospheric pressure polymerization.

The introduction of catalyst solution is different from normal addition: in this case the catalytic species are prepared in the same way as for the polymerization at atmospheric pressure. Because of the high pressure of the reactor, catalyst solution is introduced by applying a high pressure nitrogen push. Catalyst solution is introduced with a syphon (or with a syringe) in an antichamber (11) through an opening (10). High pressure nitrogen is introduced into the antichamber to reach an internal pressure higher than the pressure requested for the reaction. By opening the tap that connects the antichamber and the reactor, solution is completely introduced into the reactor (for this reason an accurate amount of catalyst solution have to be introduced into the antichamber). Activated species catalyst start the polymerization reaction by the usual mechanism described in the previous chapter. Ethylene and norbornene are consumed to form the copolymer; ethylene is connected in continuous with the line so the amount of gas (in terms of mol) is constant in the reaction environment. The consumption of ethylene can be observed during the reaction by the value reported on the online screen that express the volume (in standard liter) of gas that passes through the automatic valve: if the pressure is stable and the volume is zero, this indicates that the reaction does not occur in the autoclave. On the contrary, if the reaction occurs the volume reported on the online screen is higher than zero and the pressure is stable. During the reaction, the amount of norbornene decreases because norbornene is in batch condition. For this reason, the co-monomer/monomer ratio decrease during the reaction carry on. A single-site polymerization catalyst (like metallocene) has the main characteristic to produce uniform copolymers in terms of microstructure and molecular weight; this characteristic is true at a fixed co-monomer/monomer ratio. If this ratio changes during the reaction,

polymer chains obtained from the reaction are not homogeneous in composition and molecular weight. For having an homogeneous composition, the consumption of norbornene has to be controlled during the polymerization. The consumption of norbornene depends mainly from the incorporation of co-monomer in the polymeric chain and the catalyst activity (capability of production of copolymer). Higher the activity, higher the consumption of norbornene; if the catalyst produces high-norbornene content copolymer the consumption of norbornene is higher. Consumption of norbornene can be easily expressed by the “Conversion” parameter: it express the amount of norbornene that is consumed as percentage of the initial amount (in terms of mol). After 15 minutes (standard time for polymerization), distilled ethanol (few milliliters) is introduced into the autoclave using the same strategy as the catalyst solution; introduction of ethanol destroys the catalyst species and immediately stops the reaction. Then the pressure is reduced to the atmospheric pressure and the reaction solution is poured into 1 liter of distilled ethanol added with few milliliters of hydrochloric acid; this step is the precipitation of the copolymer. The copolymer is then purified by dissolution in toluene and re-precipitation in acetone under vigorous mechanical stirring.

## **Copolymer Characterization**

Co-polymers obtained are characterized by  $^{13}\text{C}$ -NMR to evaluate the microstructure and to calculate the content of co-monomer in the polymeric chain, by Differential Scanning Calorimetry analysis for observing the thermal behaviour (observation of  $T_g$  and eventually  $T_m$ ) and by Size Exclusion Chromatography for evaluation of molecular weight and distribution.

**Size Exclusion Chromatography technique** consists in a chromatographic separation of a sample by molecular weight. This technique, called Gel Permeation Chromatography, consists in separation of the sample through a nanoporous gel material that permits the separation of a mixture of molecules with different molecular weight. Separation is based on a different pathway of the macromolecules through the nanoporous gel: this material is characterized by the presence of tunnels of different length and radial dimension that allow the passage through by macromolecules with lower molecular weight; these macromolecules have a higher pathway into the gel material and macromolecules with low molecular weight have a high elution time. Macromolecules with high molecular weight cannot enter into the pores of the gel material and have a lower pathway. Elution time for macromolecules with higher molecular weight is lower. Detection system is composed by multiple elements: a UV spectrofotometer, a refractometer, a light scattering detector and a viscometer. UV spectrofotometer is the detector for conjugated polymers (that have an UV absorption); ethylene-*co*-norbornene does not have conjugated double bonds so this detector is not useful for these samples. Refractometer is a detector that register the presence of a macromolecule into a fraction exiting from the column by calculating the variation of the refraction index between the sample and the pure solvent. For this system, E-*co*-N macromolecules in *o*-dichlorobenzene at 165°C have problems of isorefractivity with solvent when norbornene molar content is between 21 and 22%. Light scattering detector is a detector that correlates the amount of an analyte in solution with the concentration by the intensity of the light scattered from macromolecules in solution state. This detector is very sensitive to the presence of macromolecules with high molecular



weight because light is scattered with higher intensity by these kind of macromolecules instead of lower molecular weight macromolecules. The last detector used for molecular characterization is the viscometer. This detector is able to identify the presence of a macromolecule in solution exiting from the column by the modification of the viscosity of the solution. Viscosity is a property of a liquid phase (molten polymers or macromolecules in solution) that is correlated with the concentration of the macromolecules and the hydrodynamic volume of the macromolecule in solution (that depends directly from the microstructure and the degree of polymerization). From elaboration of the output of these three detectors, molecular weight profiles are obtained.

Copolymer sample (about 15-20 mg) are dissolved in o-dichlorobenzene and injected into the instrument (GPCV2000). Separation system is composed by a system of columns: the column set was composed of three mixed TSK-Gel GMHXL-XT columns from Tosohaas. All the SEC system was calibrated with a set of standards. The universal calibration was constructed from 18 narrow MM Distribution polystyrene standards, with the molar mass ranging from 162 to  $5.48 \times 10^6 \text{ g mol}^{-1}$ .

**$^{13}\text{C}$ -NMR characterization technique:** this is a spectroscopic technique that gives information about the microstructure using a magnetic field and an excitation produced with radiofrequencies.  $^{13}\text{C}$  nuclei with different chemical environment consist in absorptions in different region of the spectrum (in terms of MHz or ppm). Using this technique it is possible to obtain information about the amount of co-monomer incorporated in the macromolecular chain, the kind of connection (in terms of regio and stereochemistry). All the spectra were recorded on a Bruker NMR Advance 400 MHz Spectrometer operating in PFT mode at high

temperature (103°C). For all spectra, chemical shifts are referred to hexamethyldisiloxane (HMDS). Samples are prepared weighting 80-100 mg of dry copolymer and dissolve in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> in a 10 mm NMR tube and transferred to the spectrometer with the probehead pre-equilibrated at exercise temperature (103°C). Settings used for analysis are the following: 10 mm probe, 90° pulse angle (12.50 μs); 64K data points; acquisition time 0.93 s; relaxation delay 16 s; 3-4 K transient.

The quantitative determination of norbornene (N) content in poly(E-co-N)s was calculated from the observed integrals (I) in <sup>13</sup>C-NMR spectra of ethylene and norbornene carbons:

$$N(\text{mol} - \%) = \frac{[N]}{[N] + [E]} \times 100$$

$$= \frac{\frac{1}{3}(I_{C_{2/3}} + I_{C_{1/4}} + 2I_{C_7})}{I_{CH_2}} \times 100$$

where IC<sub>2/3</sub>, IC<sub>1/4</sub>, and IC<sub>7</sub> are the peak intensities of C<sub>2</sub>/C<sub>3</sub>, C<sub>1</sub>/C<sub>4</sub>, and C<sub>7</sub> carbons in norbornene units, and ICH<sub>2</sub> indicates the total area of peaks from 26.2 to 34.3 ppm. From the relative peak intensities of the carbons C<sub>5</sub>/C<sub>6</sub>, it was possible to estimate the content of *racemic* and *meso* NN dyads sequences. The signals at 28.6 and 32.5 ppm were assigned to carbons C<sub>5</sub>/C<sub>6</sub> of *meso* NN sequences, while signals at 29.9 and 31.7 ppm were assigned to the *racemic* NN dyads.

**Differential Scanning Calorimetry (DSC)** is a thermal analysis technique that permits to evidence the changing of the matter state by studying thermal properties of a sample. The basic principle underlying

this technique is the following: when the sample undergoes a physical transformation such as a phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle physical changes, such as glass transitions. It is well known that polymeric materials can be crystalline or amorphous: crystalline solids change their matter status by melting and amorphous solids changes to elastomeric form by glass transition. Both these transitions can be registered by the instrument because melting happens at a single temperature instead of a glass transition that happens in a range of temperatures. So DSC scanning can discriminate a crystalline polymer instead of an amorphous polymer. With DSC analysis, it is possible to obtain information about the characteristic structure and thermal behaviour (if crystalline or amorphous); for cyclic olefins (like E-co-N copolymers) higher the cyclic olefin content higher results the glass transition temperature. Measurements were performed on a Pyris 1 Perkin-Elmer instrument. The samples (around 8 mg) were heated from 50 to 200 °C at 20 °C/min, with a nitrogen flow (30 mL/min), using heating and cooling rates of 20

°C min<sup>-1</sup>. A first scan was realized to erase the thermal history of each polymer. Glass transition temperature ( $T_g$ ) was then recorded during a second thermal cycle.

**CHAPTER 3**  
**RESULTS AND DISCUSSION**

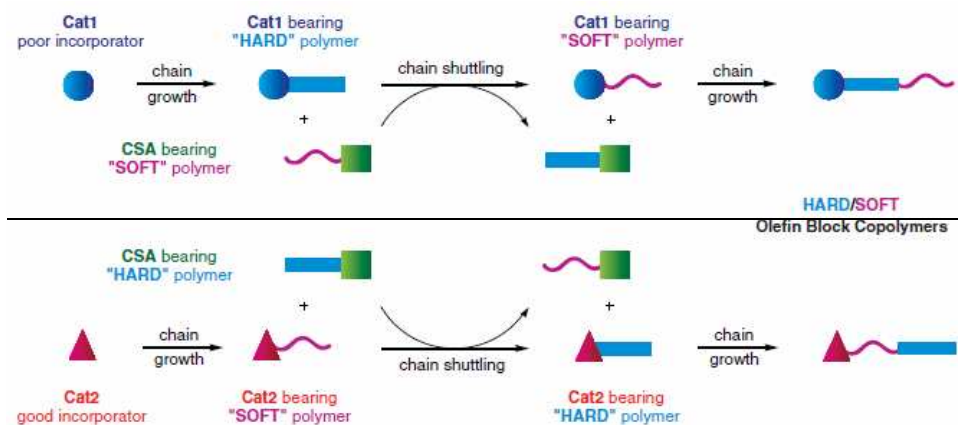
## Introduction

Tailored block copolymers, that consist of sequences of one unit followed by long sequences of another, often perform better than homopolymer blends or random copolymers, but their large scale production has been hindered by the fact that living polymerization catalysts are required to synthesize polymers block by block.<sup>(1)</sup>

Living coordination polymerization allows to produce block copolymers with high control on stereochemistry of prochiral olefins and extremely high control on blocks length. These two characteristics can be achieved by sequential monomer addition strategies with a living coordination polymerization catalyst. However, this class of catalysts can produce only one chain per catalyst molecule. In addition, these catalysts can operate as “living” only at low temperature and this inhibits the synthesis of materials containing more than one semicrystalline block because of the premature precipitation of the polymer.

To circumvent the problems connected to the living polymerization strategy, a new strategy called “chain shuttling polymerization” (CSP) was introduced recently,<sup>(2)</sup> that enables production of multiblock copolymers<sup>(3)(4)(5)</sup> on a commercial viable scale. It is defined as the transfer of a growing polymer chain between catalyst sites, through at least two different catalysts. This mechanism can be performed only by the presence of a Chain Shuttling Agent (CSA) that can facilitate this transfer. In the absence of CSA, a polymer blend is produced with none of the advantageous properties of block copolymer architecture. In the presence of an effective CSA polymer chains are swapped between catalysts before chain termination. To understand this

swapping phenomenon, it is instructive to follow the life-time of a representative polymer chain. The chain may begin growing on Cat1 as a hard polymer. The chain is then exchanged onto a CSA, where it is held for some period of time without growing (dormant polymer chain). The dormant polymer chain may then return to another molecule of the same catalyst and lengthen the hard segment or it may shuttle to a molecule of Cat2, from which subsequent chain growth results in formation of a polymer chain with both soft and hard blocks. The process may be repeated any number of times during the lifetime of the chain before chain termination occurs via a usual mechanism. (Figure 1).



**Figure 15.** Scheme of the mechanism of Chain Shuttling <sup>(6)</sup>

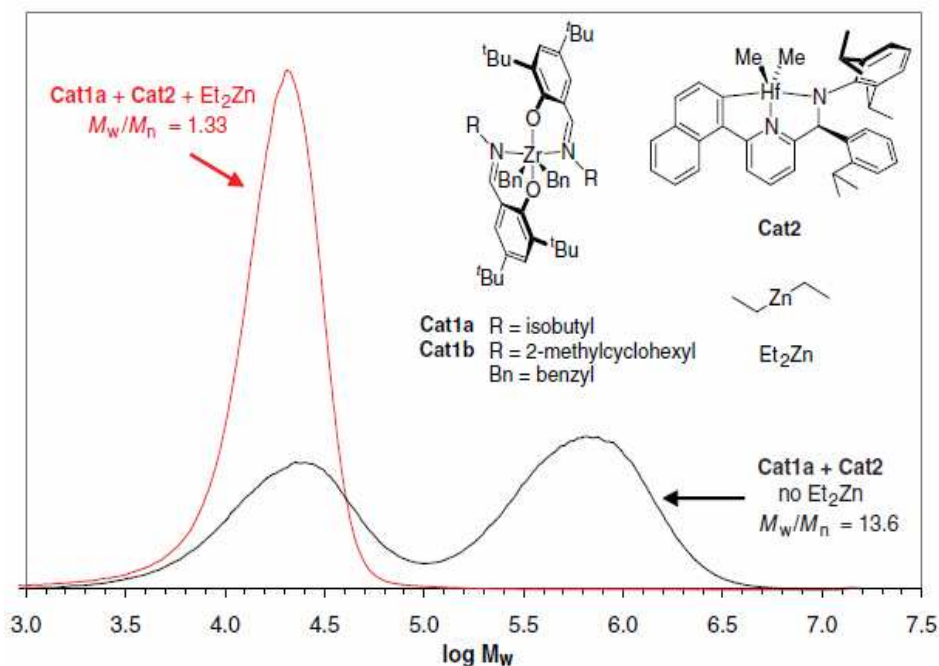
A statistical analysis of this chain shuttling phenomenon reveals multiblock copolymers with a most probable distribution of block lengths and number of blocks per chain. This microstructure is distinctly different from materials made with living polymerization techniques, which ideally have a Poisson distribution of block lengths and a precise number of blocks. Furthermore, the synthesis of these

olefin block copolymers is not stoichiometrically limited by Cat1, Cat2 and CSA<sup>(6)</sup>. Furthermore, this approach enables precise control over polymer microstructure. Despite the differences in monomer selectivity between the two catalysts, fast rates of chain shuttling and judicious selection of process variables produce copolymers with homogeneous molecular weight and composition distributions. The overall composition (like hard-to-soft polymer ratio), can be easily controlled by the relative amount of the catalyst used. The comonomer content of the individual hard and soft blocks can be tailored by reactor feed or catalyst modifications. Finally, the average length of the blocks, which is a function of the relative rates of chain growth and shuttling, can be controlled simply by adjusting the ratio of concentrations of CSA and monomer ( $[CSA]/[C_2H_4]$ ). It is well established in olefin polymerization that growing chains can be transferred from the catalyst to an added main-group metal in exchange for an alkyl group (for example chain transfer to metal)<sup>(7)</sup>. This transfer is most often irreversible, leading to the termination of the growing chain and the initiation of a new polymer chain. However, the synthesis of block copolymers via chain shuttling requires a reversible polymer chain transfer. The main-group centres cannot act as a final “repository” for “dead” polymer chains. Instead, they must serve as a reservoir of “live” chains that are intermittently reattached to catalysts centres for further growth. For single-catalyst system, this process has been used to prepare long-chain metal alkyls and has been described as “catalyzed chain growth”. Given the multitude of olefin polymerization catalysts, it was daunting to identify a pair of catalysts with substantially different monomer selectivity that are also capable of chain shuttling. Furthermore, the chosen system also needs to



operate at a high solution-reaction temperature ( $T > 120^\circ\text{C}$ ) to prevent undesired polymer precipitation.

To begin the selection process, Arriola <sup>(6)</sup> selected representative examples from a broad variety of catalyst structure types known to have high polymerization rates. First step was ethylene polymerization in combination with various CSAs using high-throughput screening technique. Catalyst efficiency, estimated by polymer yield, eliminated several of the potential CSAs due to their inhibition of polymerization. For combinations that produced sufficient amount of polymer for characterization, the molecular weight distribution of the polyethylene was then compared with that of a polymer obtained without CSA. A reduction in  $M_n$  in combination with a narrowing of the molecular weight distribution ( $M_w/M_n$ ) indicated a “hit” for chain shuttling behaviour.



**Figure 2.** Example of catalytic system for chain shuttling<sup>(6)</sup>

A zirconium bis(phenoxyimine) catalyst (Cat1a) and a hafnium pyridylamide (Cat2) displayed significant differences in monomer selectivity and also showed characteristics of chain shuttling using diethylzinc as the CSA. After this dual-catalyst/CSA combination was identified, a secondary screening process was conducted to further validate the shuttling capability of these hits. This process involved evaluation of both individual catalyst/CSA combinations, as well as mixed catalyst experiments in the high-throughput reactor. Individual catalysts were screened to evaluate the effect of different catalyst/CSA ratios on  $M_n$  and  $M_w/M_n$ . Dual-catalysts experiments provided further confirmation of the shuttling behaviour of this system. A mixture of Cat1 and Cat2 produced a blend of copolymers with a 1-octene content intermediate between those afforded by the single catalysts, indicating that both catalysts are active during the polymerization. The resulting product has a high molecular weight and a broad, bimodal molecular weight distribution ( $M_w/M_n=13,6$ ), indicating a different behaviour of the two selected catalysts in termination reactions. The introduction of the CSA resulted in levelling the tendency of termination of the two catalysts and can be observed by the narrow molecular weight distribution ( $M_w/M_n=1,33$ ). The composition of the resulting copolymer is intermediate in terms of incorporation of comonomer; this is important, because it is the confirmation that both catalysts are active during the polymerization. The observation of narrow molecular weight indicates fast rates of chain shuttling with a dual-catalyst/CSA system.

Due to the ability of the CSA strategy to produce multiblock copolymers, we thought CSA could be a good methodology for the

synthesis of E-*co*-N block copolymers with segments with modulated norbornene content. The presence of a component rich in ethylene and a component rich in norbornene bonded in an alternate multi-block sequence could impart elastic properties to E-*co*-N copolymers and concur to solve the brittleness problem of the high norbornene content copolymers.

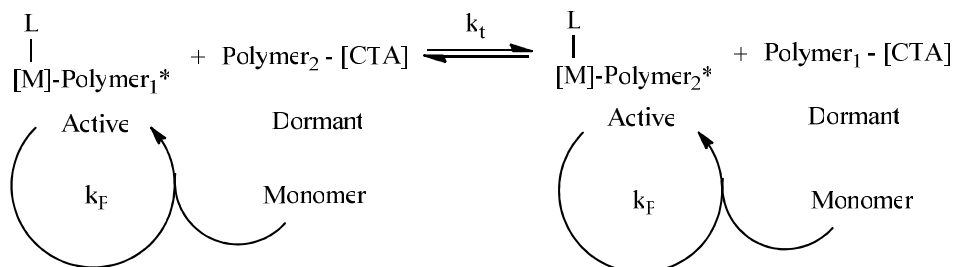
**Aim of this work is the synthesis of E-*co*-N block copolymers by CSA technique to obtain copolymers with both low and high norbornene content amorphous multiblocks in the same polymeric chain to obtain copolymers with more elastic properties.**

Before starting the exploration of the CSP and apply it to the synthesis of E-*co*-N block copolymers, we undertook a detailed evaluation on the known studies of coordinative chain transfer polymerization (CCTP).

CCTP consists of a copolymerization with a single transition metal based catalyst and a chain transfer agent (CTA), usually a metal alkyl<sup>(8)-(17)</sup>. CCTP has been developed in order to reduce the consumption of high expensive transition metal based catalysts, to control the molecular weight of the polymer and enabling growth of several macromolecular chains per catalyst.

Mechanism of CCTP (**Scheme 1**) involves the transfer of the macromolecular growing chain from the catalytic species to the chain transfer agent via transalkylation. The catalytic species is considered the “active species” because propagation of polymerization can occur only on this species; the “dormant species” is the zinc-polymeryl species that cannot undergo the propagation step of polymerization. Early CCTP studies were motivated by beneficial effects for catalyst economy, control over molecular weight and end-functionalization of

the resulting polymer. In recent years, CCTP experiments are oriented to catalytic systems able to finely control the microstructure and the architecture of the polymer, in order to obtain materials with new performances.

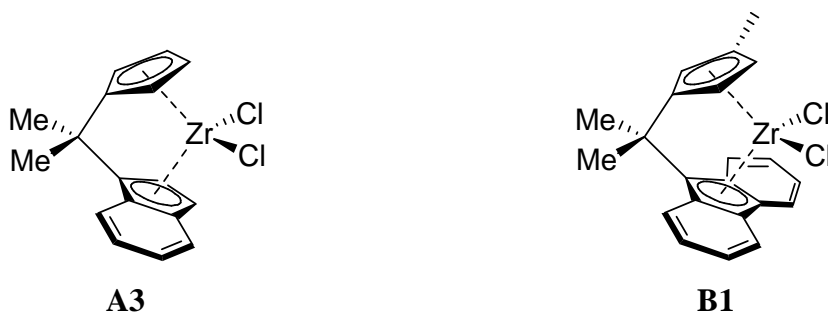


**Scheme 1.** General mechanism of Coordinative Chain Transfer Polymerization

## Results and Discussion on Coordinative Chain Transfer Polymerization

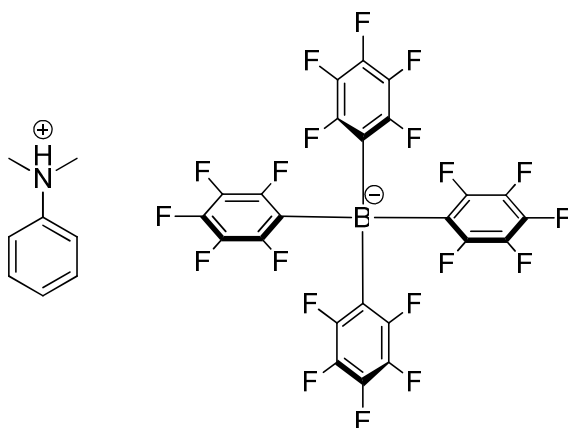
We focused on two *ansa*-metallocene catalysts, *rac*- $[\eta^5, \eta^5$ -Isopropylidene(cyclopentadienyl)(indenyl)]zirconium dichloride (A3) and *rac*- $[\eta^5, \eta^5$ -Isopropylidene(3-Methylcyclopentadienyl)(fluorenyl)]zirconium dichloride (B1) as candidates for Chain Shuttling Copolymerization with ethylene and norbornene. Both catalysts (A3 and B1) are  $C_1$ -symmetric catalysts but with different ligands, so they have different behaviour in presence of prochiral monomers and produce copolymers with different microstructures. The  $C_1$ -symmetric catalyst class includes organometallic catalysts in which the two coordination sites are diastereotopic. Because of this property, and depending on the size of the substituent on the cyclopentadienyl ligand,  $C_1$ -symmetric catalysts can vary in stereoselectivity from hemiispecific to partially

isospecific to isospecific. Catalyst A3 is the simplest  $C_1$ -symmetric complex that has been extensively investigated<sup>(18)-(26)</sup>; it is well known from the literature that this catalyst produces atactic polymers in presence of prochiral monomers. Catalyst B1 is also a  $C_1$ -symmetric complex with a higher steric environment. In presence of propylene, catalyst B1 produces a hemiisotactic polypropylene<sup>(27)(28)(29)</sup>. The presence of a methyl group brings a more isoselective character to catalyst B1, even more for bulky olefinic monomers as norbornene. This work consists of studying the effect of a variable amount of  $Zn(Et)_2$  as chain transfer agent (CTA) on the synthesis of ethylene-*co*-norbornene copolymers at three different concentrations of norbornene in the feed. Zn is among the most efficient chain-transfer reagents for single-site catalysts across the transition series, because the metal carbon bond energies of the zinc alkyl closely match those of transition-metal alkyl species, the polarities of the Zn–C and M–C bonds are similar, and the mononuclear dicoordinated Zn centers are uncrowded<sup>(9)</sup>. All copolymers synthesized have been characterized to evaluate microstructure and comonomer content (by  $^{13}C$ -NMR),  $M_w$  and molecular weight distribution (by GPC) and thermal properties (by DSC).



**Figure 1.** *Ansa* – zirconocene based precursors studied for CCTP

All catalysts were activated with *N,N*-Dimethylaniliniumtetrakis(pentafluorophenyl)borate (Figure 2). This cocatalyst is well known in literature <sup>(30)</sup> to form not-coordinating species in the activation process and thus it is suitable in the studies of the diethylzinc interactions with activated catalyst species, where the presence of an intimate ion pair with a coordinating anionic species should be reduced or even suppressed.



**Figure 2.** Lewis structure of *N,N*-Dimethylanilinium tetrakis(pentafluorophenyl)borate

All polymerization reactions were performed at 70°C at three different feeds expressed as N/E ratio of 1.3, 4.8, and 26.0. Ethylene pressure inside the autoclave was kept constant during the polymerization by an automatic system valve (see Experimental section), and varied for the three N/E ratios ( $P_E=19$  bar for N/E=1.3,  $P_E=10$  bar for N/E=4.8 and  $P_E=4$  bar for N/E=26.0).

### Poly(ethylene-*co*-norbornene) with catalysts A3 and B1.

A set of preliminary experiments was performed to select the best polymerization conditions to guarantee good catalytic activities and a norbornene conversion below 20 mol % (Table 1).

**Table 1.** Poly(Ethylene -*co*- Norbornene) using Catalysts A3 and B1.

Entry <sup>a</sup>	N/E <sup>b</sup>	P <sub>E</sub> (bar)	Cat.	Cat. ( $\mu$ mol)	Activity <sup>c</sup>	M <sub>w</sub> <sup>d</sup> (10 <sup>-3</sup> )	D <sup>d</sup>	N <sup>e</sup> (mol%)	T <sub>g</sub> <sup>f</sup> (°C)
1	1.3	19	A3	8	242	30	1,8	32	89
2	1.3	19	B1	8	213	128	2,9	20	23
3	4.8	10	A3	10	436	103	2,7	45	120
4	4.8	10	B1	12	196	296	2,7	33	81
5	26.0	4	A3	20	330	135	2,2	62	182
6	26.0	4	B1	30	70	275	5,4	44	133

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>N/E is expressed as molar ratio.

<sup>c</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>d</sup>Molar characterization is obtained by SEC.

<sup>e</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

<sup>f</sup>T<sub>g</sub> are obtained by DSC.

Increasing the norbornene amount in the feed, the polymerization activities with catalyst A3 tend to slightly increase; this behaviour can be explained to the high affinity of this catalyst for norbornene. Instead, catalyst B1 activities evidently decrease. Moreover, catalyst A3 shows higher activity than catalyst B1 for all feed ratios.

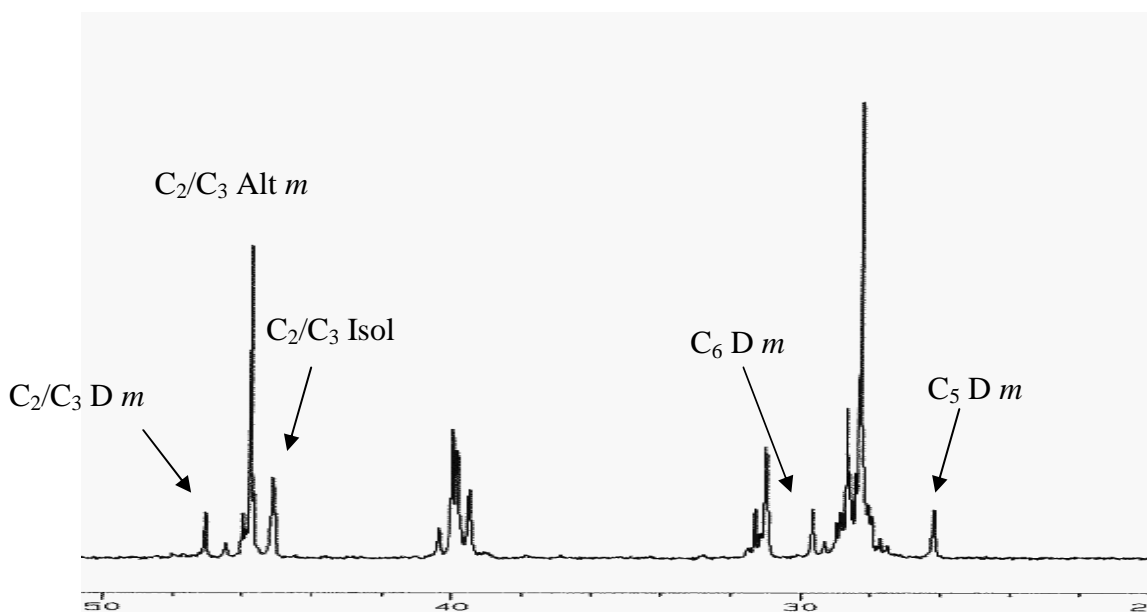
Catalyst A3 can incorporate higher amount of norbornene than catalyst B1 for the same feed ratio (see entry 1 vs 2, 3 vs 4 and 5 vs 6). The glass transition temperature (*T<sub>g</sub>*) values registered for copolymers obtained with catalyst A3 are higher than those obtained by catalyst B1. Conversely, catalyst B1 forms copolymers with higher *M<sub>w</sub>* than the ones obtained with catalyst A3.

The poly(ethylene-*co*-norbornene) samples were analyzed by <sup>13</sup>C NMR spectroscopy to evaluate the monomer content and eventually



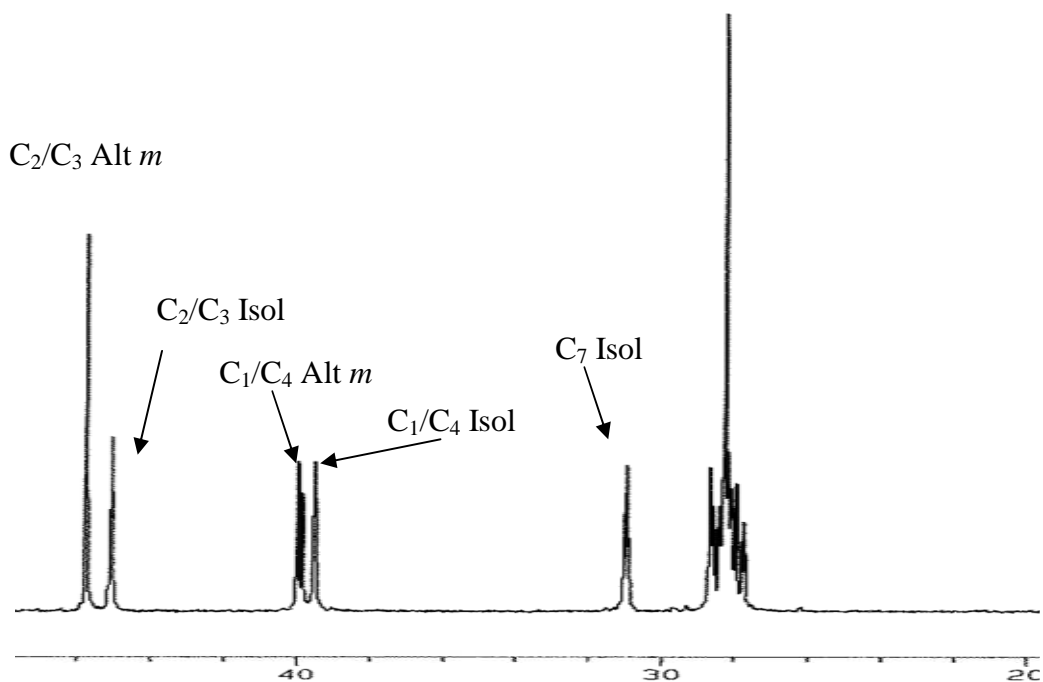
the microstructure. In case of ethylene-*co*-norbornene copolymers, the assignment of stereosequences allows to determine the polymer microstructure, which is dominated by metallocene symmetry and ligand type.

Ethylene-*co*-norbornene copolymers, prepared with catalyst A3, performed at a [N]/[E] molar feed ratio of 4.8, showed an N incorporation of 45 mol % (Figure 3). The complete analysis of the spectra at tetrad level revealed that catalyst A3 has a marked selectivity for producing poly(E-*co*-N ) copolymers with EEEE units (17 mol%), isolated norbornene units ENEE (30 mol%) and NEEE (16 mol %), alternated NENE (28.0 mol%) sequences and gave a low amount of NNEN (0.05 mol%) and NNNE (0.4 mol%) *meso* tetrads stereoblocks.



**Figure 3.** Spectra of E-*co*-N produced with catalyst A3 at N/E feed ratio of 4.8

Ethylene-*co*-norbornene copolymers prepared with catalyst B1 performed at a [N]/[E] molar feed ratio of 4.8 showed an N incorporation of 33 mol % containing high amount of EEEE sequences (34.0 mol %), isolated norbornene units ENEE (27 mol%) and NEEE (19 mol %), alternated NENE (16.0 mol%), while the NNEN and NNNE tetrads are not present. From the stereochemical point of view, norbornene units are oriented in an isotactic way. This catalyst can be characterized as an alternating isotactic copolymer catalyst (Figure 4).



**Figure 4.** NMR spectra of typical copolymer produced with catalyst B1 at N/E molar feed ratio of 4.8

**Ethylene-*co*-norbornene copolymerization with catalysts A3 and B1 in the presence of diethylzinc.**

Syntheses performed with catalysts A3 and B1 were replicated with variable amount of diethylzinc to evaluate the effect of a Chain Transfer Agent on copolymerization reactions. Diethylzinc was introduced into the polymerization reaction at three different Zn/Zr ratios of 100, 200 and 400. Because the degree of chain transfer is affected by several factors—including the concentration of chain-transfer reagent, the concentration of monomer, and the temperature of the polymerization—it is necessary to find a set of conditions optimal for the chain shuttling.

**Table 2.** Poly(Ethylene *–co–* Norbornene) Using Catalysts A3 and B1 in the presence of Zn(Et)<sub>2</sub> at N/E feed ratio of 4.8.

Entry	Cat	Zn mmol	Zn/Zr	Yield(g)	Activity <sup>b</sup>	N mol % <sup>d</sup>	Conv	$T_g^f$ (°C)	$M_w^c$ (10 <sup>-3</sup> )	D <sup>c</sup>
3	<b>A3</b>	---	---	10,9	436	45	15,4	120	103	2,7
4	<b>B1</b>	---	---	5,9	196	33	7,1	81	296	2,7
7	<b>A3</b>	1,0	100	1,7	68	46	2,4	113	61	1,9
8	<b>B1</b>	1,2	100	5,9	197	34	7,2	82	309	1,7
9	<b>A3</b>	2,0	200	11,0	440	45	16	115	64	2,0
10	<b>B1</b>	2,4	200	1,5	50	34	1,8	76	170	2,9
11	<b>A3</b>	4,0	400	0,7	28	46	1,0	113	47	2,0
12	<b>B1</b>	4,8	400	3,9	130	34	4,8	76	97	2,6

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

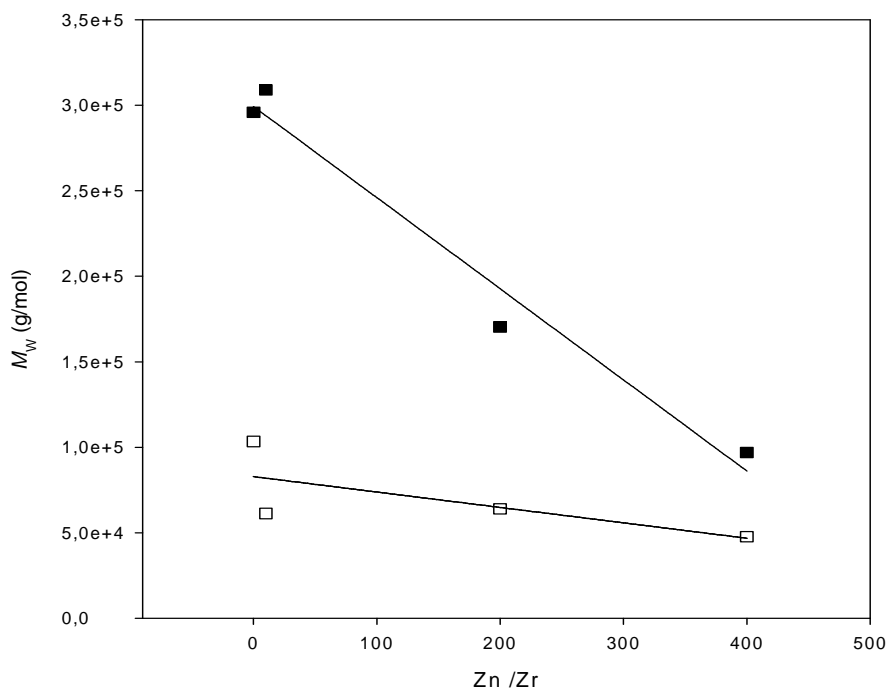
<sup>e</sup> $T_g$  are obtained by DSC.

For N/E molar ratio 4.8, concerning catalyst A3, the polymerization activity seems to decrease dramatically with the introduction of diethylzinc (except entry 9), conversely with catalyst B1 the activities remain almost constant with increasing zinc in the reaction system (except entry 10). The norbornene incorporation is not affected by the

presence of diethylzinc. As expected, the molecular weight decreases with the increasing diethylzinc with both catalysts while the molecular weight distribution remains narrow and decreases with respect to the Poly(E-*co*-N) obtained in absence of ZnEt<sub>2</sub>.

Thermal properties are not affected much by the presence of a CTA because the  $T_g$  increase or decrease depends mainly on the norbornene content in the copolymer chain.

As reported in Figure 5, molecular weight of copolymers obtained by both catalysts decrease by increasing the amount of Chain Transfer Agent. From the trends reported, catalyst B1 seems more affected by the presence of diethylzinc. In absence of diethylzinc, ethylene-*co*-norbornene copolymers produced by catalyst B1 have a  $M_w$  higher than those by catalyst A3 so diethylzinc affects more a copolymer with high  $M_w$  than one with lower  $M_w$ .



**Figure 5.** Trends of molecular weight vs Zn/Zr of poly(Ethylene-co-norbornene) obtained with catalysts A3 and B1 at N/E feed ratio of 4.8. (Black squares B1, White squares A3)

A similar set of experiments was performed with N/E ratio of 26.0 to study the effect of diethylzinc as chain transfer agent when in presence of high comonomer content. Results of copolymerization and characterization are reported in Table 3.

**Table 3.** Poly(Ethylene *-co-* Norbornene) Using Catalysts A3 and B1 in the presence of Zn(Et)<sub>2</sub> at N/E feed ratio of 26.0.

Entry	Cat	Zn mmol	Zn/Zr	Yield(g)	Activity <sup>b</sup>	N mol % <sup>d</sup>	Conv	T <sub>g</sub> <sup>e</sup> (°C)	M <sub>w</sub> <sup>c</sup> (10 <sup>-3</sup> )	D <sup>c</sup>
13	A3	2,8	140	15,8	790	64	12,1	195	146	5,4
14	B1	2,8	93	1,0	133	37	0,6	132	---	---
15	A3	5,5	275	1,7	340	60	1,3	177	54	2,0
16	B1	5,5	183	2,0	267	36	1,2	134	122	2,0
17	A3	11,0	550	0,2	40	62	0,2	169	40	3,1
18	B1	11,0	367	0,4	53	32	0,2	115	77	4,8

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

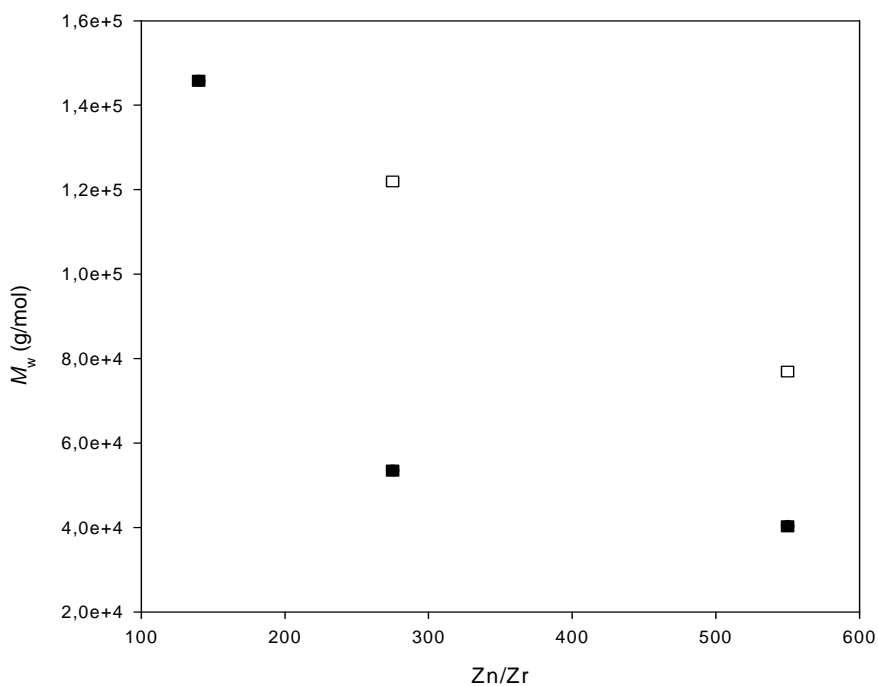
<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

<sup>e</sup>T<sub>g</sub> are obtained by DSC

Catalyst A3, which is the catalyst that presents higher affinity for norbornene, has higher activity than catalyst B1. For this feed also, activity becomes lower when increasing the amount of diethylzinc in the reaction environment; this behaviour could be correlated to formation of dormant or inactive species in the presence of high amount of diethylzinc. Polydispersion becomes lower for both catalysts (A3 and B1) for an optimal amount of diethylzinc (5,5 mmol of Zn), while for a lower and a higher amount of Zn in solution polydispersion raises. This behaviour can be probably explained by the not effective chain transfer at low diethylzinc concentration and by the presence of dormant or inactive species at high diethylzinc concentration. When there is no equilibrium between the propagation step and the chain transfer step, polydispersion becomes broader.

For N/E feed ratio of 26.0, plots of M<sub>w</sub> of copolymers with both catalysts versus Zn/Zr are reported (Figure 6); for both catalysts (A3 and B1) M<sub>w</sub> decreases with increasing the amount of diethylzinc which is connected to the activity of diethylzinc as chain transfer agent.

Norbornene contents become slightly lower when increasing the amount of chain transfer agent. For catalyst A3,  $T_g$  values decrease noticeably (about 30°C); this behaviour can be correlated to the very high decrease of  $M_w$  that reaches values in a non-linear correlation zone between a generic physical property and the molecular weight.



**Figure 6.** Trends of molecular weight vs Zn/Zr of poly(Ethylene-co-norbornene) obtained with catalysts A3 and B1 at N/E feed ratio of 26.0. (Black squares A3, White squares B1).

In Figure 6 the  $M_w$  of  $M_w$  versus the amount of diethylzinc in solution for both catalysts are reported. The graphical representation shows that for both catalysts the chain transfer mechanism in presence of a chain transfer agent at this N/E feed ratio is active. From observation of polydispersion, it results clear that chain transfer mechanism is

reversible (polydispersions are not high as reported in literature). The optimal amount of diethylzinc is near Zn/Zr ratio of 200 (in this case 5,5 mmol of diethylzinc) when propagation step rate and chain transfer rate are optimized for CCTP.

Similar experiments were conducted for N/E feed ratio of 1,3 for studying CCTP in presence of high amount of ethylene. Results and characterizations are reported in Table 4.

**Table 4.** Poly(Ethylene *-co-* Norbornene) Using Catalysts A3 and B1 in the presence of Zn(Et)<sub>2</sub> at N/E feed ratio of 1.3.

Entry	Cat	Zn mmol	Zn/Zr	Yield(g)	Activity <sup>b</sup>	N mol % <sup>d</sup>	Conv	T <sub>g</sub> <sup>e</sup> (°C)	M <sub>wc</sub> (10 <sup>-3</sup> )	D <sup>c</sup>
19	<b>A3</b>	0,8	99	9,3	245	35	23	67	30	1,9
20	<b>B1</b>	0,8	99	9,7	255	22	18	29	---	---
21	<b>A3</b>	1,6	198	7,2	189	35	17,5	53	29	1,9
22	<b>B1</b>	1,6	198	9,5	250	21	17,1	28	---	---
23	<b>A3</b>	3,2	396	5,3	139	31	12	37	29	1,8
24	<b>B1</b>	3,2	396	9,8	258	22	18	20	---	---

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

<sup>e</sup>T<sub>g</sub> are obtained by DSC

For N/E feed ratio of 1.3, as expected, the amounts of norbornene incorporated are lower than those at higher N/E feed ratios. In these conditions also, catalyst A3 is still the catalyst with higher norbornene incorporation (see entries 19, 21, 23 vs 20, 22, 24). For the norbornene content and T<sub>g</sub>s correlation, copolymers obtained with catalyst A3 have higher T<sub>g</sub> than copolymers obtained with catalyst B1. At these reaction conditions, copolymerization reactions are favoured; for this reason both catalysts have high activity (B1 activity becomes more similar to A3 activity in these conditions). This behaviour is confirmed by the amount of catalyst injected in the autoclave for copolymerization



reactions: for N/E 4.8 and 26.0 catalyst A3 was always used in lower concentration; for N/E equal to 1.3 both catalysts (A3 and B1) were used in same concentration in the reaction environment (both 8  $\mu\text{mol}$  in 150 mL).

As expected, in these experiments with lower amount of norbornene the activities of both catalysts are higher and the norbornene incorporated becomes lower. Norbornene content is not affected in a significant way by an increasing amount of diethylzinc but the  $T_g$  becomes lower: this effect is related to the low molecular weight of the copolymer obtained. For catalyst B1 it was not possible to obtain the molecular weight distribution, because polymer solutions in *o*-dichlorobenzene have an isorefractivity similar to pure *o*-dichlorobenzene for norbornene contents of 21-22 mol %. This means, for all B1 copolymers of this series it was not possible to determine the molecular weight distribution. Polydispersities for catalyst A3 are very narrow ( $D$  is between 1.8 and 1.9). This characteristic is fundamental to confirm diethylzinc as an efficient chain transfer agent with this catalyst at this conditions.

On the basis of the Gibson calculation<sup>(11)</sup>, we succeeded in the determination of  $Zn_{\text{ext}}$  by using the following equation:

$$(Zn - Et)_{\text{ext}} = \frac{\text{yield}(\text{polymer})}{M_n} + \sum \frac{\text{yield}(\text{oligomer})}{M(\text{oligomer})}$$

In our case, due to the high molecular weight obtained, the contribution due to oligomers has been ignored.

$(Zn-Et)_{\text{ext}}$  species represent the amount of diethylzinc, that participated in chain transfer reactions, bearing a polymeryl chain (that already underwent chain transfer mechanism). If chain transfer

mechanism does not occur in a reaction environment, the percentage of Zinc-Et extended structures will be equal to zero. If the Zinc-Et extended percentage is high, it is the signal that chain transfer mechanism has a rate lower than the propagation step rate. In this case, the polymeryl chain has more affinity to zinc atom than to zirconium atom.

**Table 5.** Zinc-extended calculated values

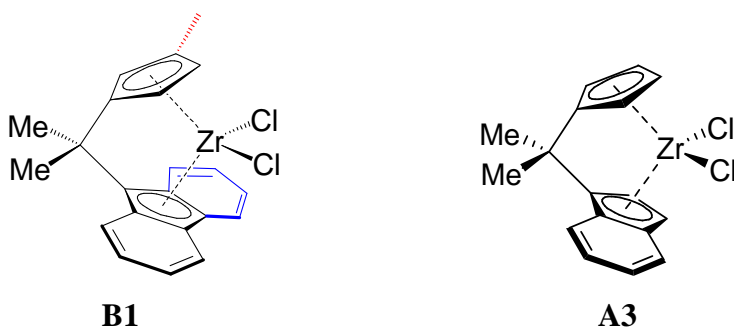
Entry	Cat	[N]/[E]	D ( $M_w/M_n$ )	Mn (kg/mol)	Yield (g)	ZnEt <sub>2</sub> (mmol)	(Zn- Et) Ext mmol	(Zn- Et)ext (mmol%)
<b>19</b>	<b>A3</b>	1.3	1.9	16	9.3	0.8	0.59	36.6
<b>21</b>	<b>A3</b>	1.3	1.9	15	7.2	1.6	1.47	14.7
<b>23</b>	<b>A3</b>	1.3	1.9	16	5.3	3.2	0.33	5.1
<b>7</b>	<b>A3</b>	4.8	1.9	32	1.7	1	0.05	2.6
<b>9</b>	<b>A3</b>	4.8	2.0	32	11.0	2	0.34	8.6
<b>11</b>	<b>A3</b>	4.8	2.0	24	0.7	4	0.03	0.4
<b>13</b>	<b>A3</b>	26.0	5.4	27	15.8	2.8	0.59	10.4
<b>15</b>	<b>A3</b>	26.0	2.0	27	1.7	5.5	0.06	0.6
<b>17</b>	<b>A3</b>	26.0	3.1	13	0.2	11	0.02	0.1
<b>8</b>	<b>B1</b>	4.8	1.7	181	5.9	1.2	0.03	1.3
<b>10</b>	<b>B1</b>	4.8	2.9	587	1.5	2.4	0.03	0.5
<b>12</b>	<b>B1</b>	4.8	2.6	37	3.9	4.8	0.10	1.1
<b>16</b>	<b>B1</b>	26.0	2.0	61	2.0	5.5	0.03	0.3
<b>18</b>	<b>B1</b>	26.0	4.8	16	0.4	11	0.02	0.1

From an analysis of the data of Zinc-Et extended percentage, it is clear that in all copolymerization reactions, in presence of diethylzinc, chain transfer mechanism occurs to some degree. It is also possible to identify the different behaviour of the two catalysts: in fact the amount of Zinc-Et extended structures in presence of catalyst A3 is always higher than in presence of catalyst B1. In presence of catalyst B1, diethylzinc has a lower chain transfer rate than propagation step rate

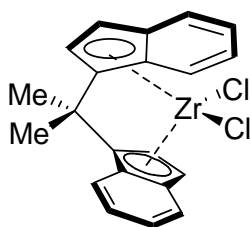
(in fact zinc atom is bearing a lower amount of chains) while the opposite occurs for catalyst A3 and zinc atom bears a higher amount of chains in solution. This characteristic can be correlated to the lower steric interactions between the zirconium atom and the zinc atom when zirconium atom is embedded in the A3 catalyst structure. In addition, when a zirconium atom is embedded in the A3 catalyst structure, it has a higher electron density, because the  $\pi$ -electrons of the indenyl ligand are delocalized over a smaller number of carbon atoms compared to the larger fluorenyl ligand (present in B1 catalyst). So, diethylzinc, which can be classified as a Lewis acidic species, has a higher affinity for catalyst A3 than for B1. From analysis of the zinc-extended chains, it is clear that for ethylene-norbornene copolymers the chain transfer mechanism is optimized when the feed is richer in ethylene content. This behaviour can be explained with higher steric interactions whenever transalkylation between polymeryl chains and last inserted norbornene units is needed.

## Results and discussion on Chain Shuttling Polymerization

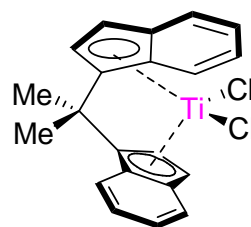
For the CSP investigation on E-co-N copolymerization we focused on two couples of catalysts: one couple is formed by two zirconocenes with different scaffold and the other by metallocenes with same ligand structure but different metal atom. First couple of catalysts is formed by B1 and A3: B1 formula is  $\text{Me}_2\text{C}(\text{3-methylcyclopentadienyl})(\text{fluorenyl})$  zirconium dichloride.



B1 catalyst has a  $C_1$ -symmetry and its tendency is to form isotactic polymers with prochiral monomers. In E-co-N copolymerization reaction, catalyst B1 affords alternating isotactic ethylene-norbornene copolymers. Catalyst A3 (its formula is  $\text{Me}_2\text{C}(\text{cyclopentadienyl})(\text{indenyl})$  zirconium dichloride) is also a  $C_1$ -symmetric catalyst: lower steric interactions between the ligand and growing chain during propagation step permit the synthesis of random copolymers with NN dyads (both *m* and *r* dyads). The other couple of catalyst is formed by two *ansa*-bridged bisindenyl metallocenes:



**Cat1**



**Cat2**

In this case the symmetry of the two catalysts is the same: both have  $C_2$ -symmetry and the tendency is to form random E-co-N copolymers with *meso* NN dyads. The difference in the catalytic system is caused by different characteristics of the central metal atom: Ti has a smaller dimension and a higher electron density than zirconium. Therefore, the active site of the zirconocene, which has a greater radius than the titanocene, has more affinity to norbornene, which is a large sterically hindered olefin.

All copolymers obtained by catalytic polymerization via chain shuttling mechanism were characterized by thermal, molecular weight and microstructural analysis. For understanding the differences between copolymers obtained by combined catalyst systems and single catalyst systems all characterizations have been compared with reference copolymers. Samples obtained by single catalyst ethylene-norbornene copolymerization in presence of diethylzinc have been used as references for combined catalyst system (chain shuttling copolymers); this means, experiments for CCTP studies have been used as references for comparison for the characterization of chain shuttling copolymers.

All syntheses were performed in autoclave at high pressure (4-19 bar) at different N/E feed ratio of 1,3, 4.8 and 26,0.

Table 6 presents the results obtained at the N/E feed ratio of 4.8 at three different Zn/Zr ratios .

**Table 6.** Characterization of copolymers via chain shuttling (N/E 4.8)

Entry	Cat	Zn mmol	Zn/Zr	Yield(g)	Activity <sup>b</sup>	N mol % <sup>d</sup>	Conv	T <sub>g</sub> <sup>e</sup> (°C)	M <sub>w</sub> (10 <sup>-3</sup> ) <sup>c</sup>	D <sup>c</sup>
<b>25</b>	<b>B1+A3</b>	<b>1,2</b>	<b>55</b>	<b>16,0</b>	<b>290</b>	<b>37</b>	<b>20,6</b>	<b>93</b>	<b>239</b>	<b>2,9</b>
7	<b>A3</b>	1,0	100	1,7	68	46	2,4	113	61	1,9
8	<b>B1</b>	1,2	100	5,9	197	34	7,2	82	309	1,7
<b>26</b>	<b>B1+A3</b>	<b>2,4</b>	<b>109</b>	<b>15,9</b>	<b>289</b>	<b>38</b>	<b>21</b>	<b>91</b>	<b>155</b>	<b>2,7</b>
9	<b>A3</b>	2,0	200	11,0	440	45	16	115	64	2,0
10	<b>B1</b>	2,4	200	1,5	50	34	1,8	76	170	2,9
<b>27</b>	<b>B1+A3</b>	<b>4,8</b>	<b>218</b>	<b>9,7</b>	<b>176</b>	<b>35</b>	<b>12</b>	<b>81</b>	<b>113</b>	<b>2,9</b>
11	<b>A3</b>	4,0	400	0,7	28	46	1,0	113	48	2,0
12	<b>B1</b>	4,8	400	3,9	130	34	4,8	76	97	2,6

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

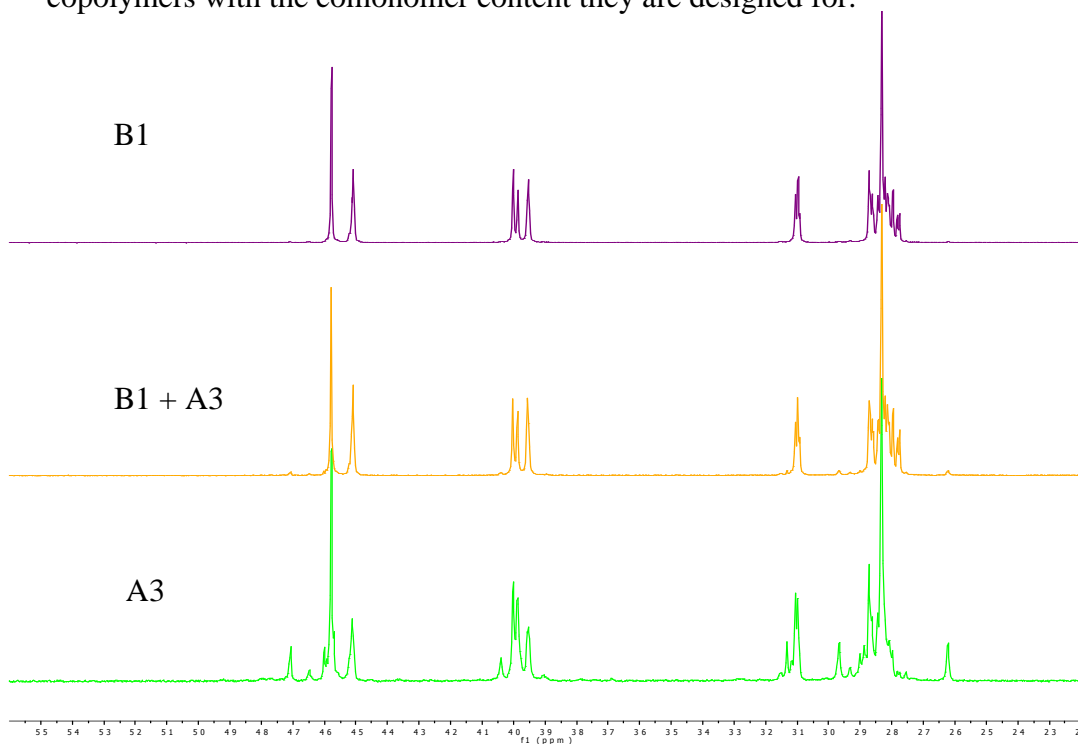
<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

<sup>e</sup>T<sub>g</sub> are obtained by DSC

As reported for CCTP studies with single catalytic systems (see previous chapter *Studies of Coordinative Chain Transfer Polymerization*), diethylzinc acts on M<sub>w</sub> and molecular weight distribution (D parameter) reducing the M<sub>w</sub>, while maintaining molecular weight distribution narrow. All copolymers obtained by chain shuttling copolymerization have been compared with their references in terms of M<sub>w</sub>, D, norbornene content and T<sub>g</sub>s.

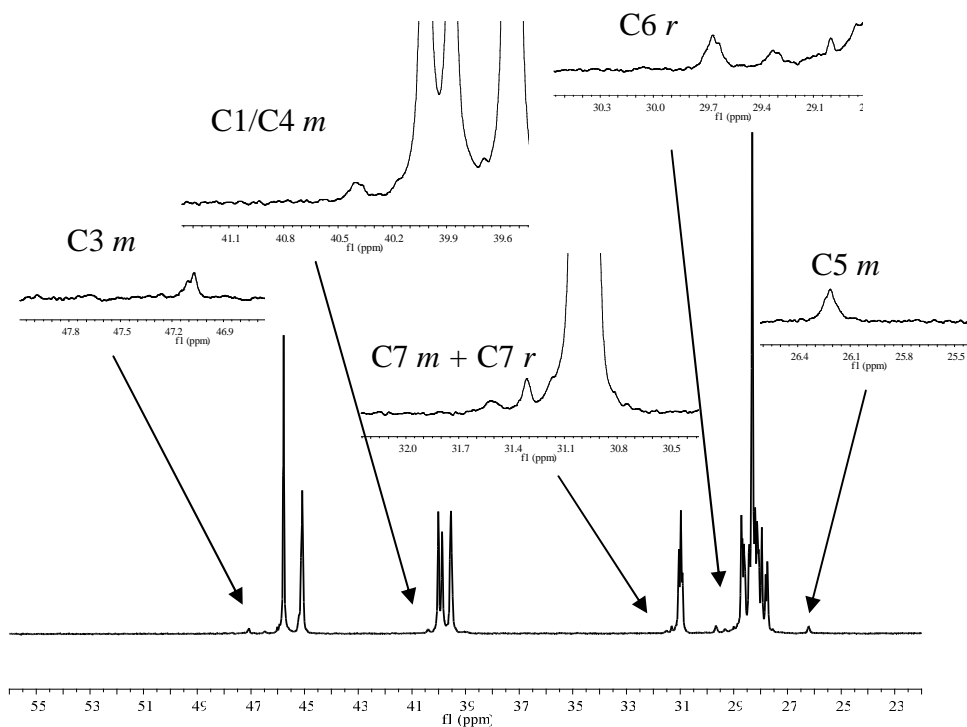
An indication of the simultaneous catalytic activity of B1 and A3 is provided by the value of norbornene content in the copolymers prepared by B1+A3 combined catalytic system (entries 25, 26 and 27). It is worth noting that this value is different from both references and this indicates

that both catalysts are active in the reaction environment and produce the copolymers with the comonomer content they are designed for.



**Figure 7.** Comparison of  $^{13}\text{C}$ -NMR spectra of entry 25(B1+A3) against entry 7 (A3) and entry 8 (B1)

As reported in Figure 7, the  $^{13}\text{C}$ -NMR spectrum of the copolymer (entry 25) obtained by chain shuttling is similar to those obtained with catalyst B1. However, this  $^{13}\text{C}$ -NMR spectrum presents some peaks, ascribed to NN dyads, that are not present in NMR spectra of copolymers obtained with B1 but are characteristics of copolymers obtained by catalyst A3.



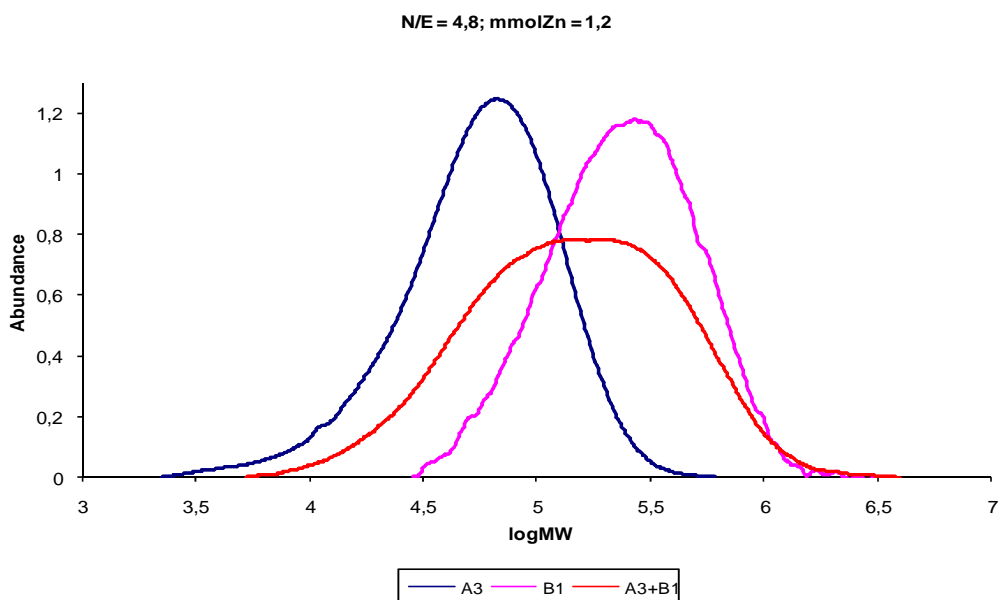
**Figure 8.**  $^{13}\text{C}$ -NMR spectrum, with expansions, of entry 25 (B1+A3).

The B1+A3 combined catalytic systems are in general more active than the reference ones except for entry 26. DSC analysis of chain shuttling copolymers show a single event and the  $T_g$  values are intermediate between the references.



The presence of a single  $T_g$  event as well as an intermediate N content, seems to be a good indication of the presence of homogenous copolymer chains and not of a blend of copolymers.

$M_w$  of entry 25 is between the  $M_w$  of the reference ones (entries 7 and 8) as shown in Figure 9.



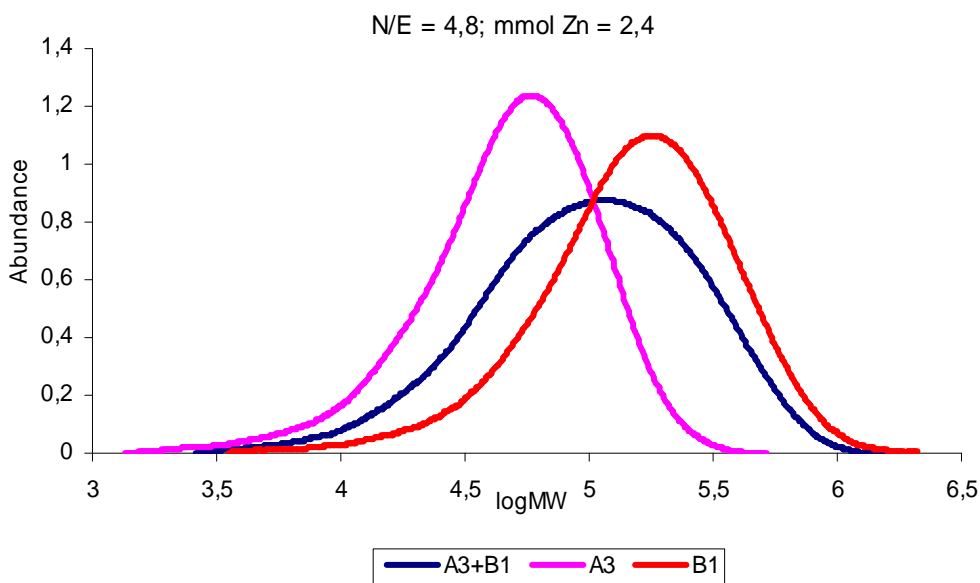
**Figure 9.** Molecular weight profiles for N/E 4.8 and Zn 1,2 mmol

Molecular weight distribution (D in Table 6) becomes broader than the references (D is 2,9 instead of 1,7 and 1,9), but it is still compatible with reversible chain transfer processes (in fact in literature<sup>(31)</sup> polydispersion of irreversible chain transfer processes reaches values higher than 10.0).

For Zn/Zr equal to 109 (entry 26 vs 9 and 10) results of characterizations have a similar behaviour. Norbornene content is in between those of references, and DSC characterization of the copolymer obtained by chain

shuttling experiment shows a single  $T_g$  event in the range of  $T_g$ s references.

$M_w$  also is intermediate to those of references (Figure 10) and this behaviour is connected to the copolymerization with a combined catalytic system (A3 and B1) in presence of a chain shuttling agent.



**Figure 10.** Molecular weight profiles for N/E 4.8 and Zn 2.4 mmol

For the N/E feed ratio of 4.8 (Zn/Zr equal to 218) the results of NMR and thermal analysis characterizations have the same behaviour than those of previous experiments (25 and 26).  $T_g$  value is intermediate to those of references; a single event of glass transition temperature is recorded for this copolymer in the range of the reference ones.

In contrast, SEC analysis shows that  $M_w$  of the copolymer obtained by chain shuttling experiment (entry 27) is slightly higher than those of

reference copolymers. Also for this Zn/Zr ratio, the molecular weight distribution (D in Table 6) becomes slightly broader than the references (D is 2,9 instead of 2,0 and 2,6); however this increase is compatible with reversible chain transfer processes, being not too high to indicate irreversible chain transfer processes.

**Table 7.** Characterization of copolymers via chain shuttling (N/E 4.8)

Entry	Cat	Zn mmol	Zn/Zr	Yield(g)	Activity <sup>b</sup>	N mol % <sup>d</sup>	Conv	T <sub>g</sub> <sup>e</sup> (°C)	M <sub>w</sub> <sup>c</sup> (10 <sup>-3</sup> ) <sup>c</sup>	D <sup>c</sup>
25	<b>B1+A3</b>	1,2	55	16,0	290	37	20,6	93	239	2,9
26	<b>B1+A3</b>	2,4	109	15,9	289	38	21	91	155	2,7
27	<b>B1+A3</b>	4,8	218	9,7	176	35	12	81	113	2,9

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

<sup>e</sup>T<sub>g</sub> are obtained by DSC

By comparing results of characterization of chain shuttling copolymers, it is evident that the presence of diethylzinc affects the activities of the dual catalytic systems (increasing the amount of diethylzinc the activity slightly drops) as in the experiment with single catalysts, while T<sub>g</sub> values and norbornene contents are quite similar. Conversely, M<sub>w</sub> becomes lower increasing the amount of diethylzinc as observed for CCTP.

A similar set of experiments was performed at a different N/E molar ratio feed equal to 26.0 to study the effect of diethylzinc as chain shuttling agent in presence of a high amount of comonomer.

**Table 8.** Chain shuttling copolymers and references for N/E 26.0 molar ratio

Entry	Cat	Zn mmol	Zn/Zr	Yield(g)	Activity <sup>b</sup>	N mol % <sup>d</sup>	Conv	T <sub>g</sub> <sup>e</sup> (°C)	M <sub>w</sub> (10 <sup>-3</sup> ) <sup>c</sup>	D <sup>c</sup>
<b>28</b>	<b>B1+A3</b>	<b>2,8</b>	<b>56</b>	<b>7,9</b>	<b>158</b>	<b>51</b>	<b>5,5</b>	<b>140</b>	<b>99</b>	<b>2,2</b>
13	A3	2,8	140	15,8	790	64	12,1	195	146	5,4
14	B1	2,8	93	1	33	37	0,6	132	---	---
<b>29</b>	<b>B1+A3</b>	<b>5,5</b>	<b>110</b>	<b>21,6</b>	<b>432</b>	<b>64</b>	<b>16,6</b>	<b>192</b>	<b>53</b>	<b>1,9</b>
15	A3	5,5	275	1,7	85	60	1,3	177	54	2,0
16	B1	5,5	183	2	67	36	1,2	134	122	2,0
<b>30</b>	<b>B1+A3</b>	<b>11,0</b>	<b>220</b>	<b>8,8</b>	<b>176</b>	<b>59</b>	<b>6,5</b>	<b>160</b>	<b>27</b>	<b>2,0</b>
17	A3	11,0	550	0,2	10	62	0,2	169	40	3,1
18	B1	11,0	367	0,4	13	32	0,2	115	77	4,8

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

<sup>e</sup>T<sub>g</sub> are obtained by DSC

For N/E ratio equal 26.0 copolymerization experiments were performed at three Zn/Zr ratios (entries 28, 29, 30). All copolymers obtained by chain shuttling copolymerization have been compared with their references in terms of M<sub>w</sub>, D, norbornene content and T<sub>g</sub>s. As reported for CCTP studies with a single catalytic system (see previous chapter *Studies of Coordinative Chain Transfer Polymerization*), diethylzinc acts on M<sub>w</sub> and molecular weight distribution (D parameter) by reducing the M<sub>w</sub> and maintaining narrow molecular weight distribution.

For Zn/Zr ratio equal to 56 (entries 28, 13 and 14 as references; Figure 11) the activity of the combined catalytic systems is intermediate to those

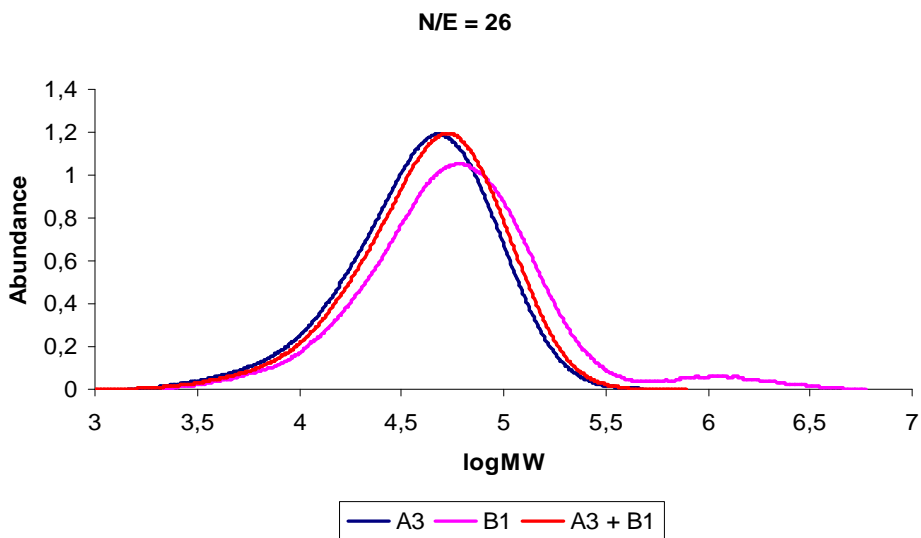
of references but much lower than those obtained by A3.  $M_w$  is slightly lower than  $M_w$  reported for copolymer obtained by catalyst A3 (which is the catalyst that produces lower  $M_w$  copolymers). The copolymer obtained by catalyst B1 was not soluble in *o*-dichlorobenzene and SEC characterization was not possible. This could be explained by the semicrystalline alternating isotactic microstructure of copolymers obtained by catalyst B1 for high norbornene incorporation.

DSC of chain shuttling copolymer shows a single event and the  $T_g$  value is intermediate between the reference ones.

Molecular weight distribution (D in Table 7) is 2.2 and this value is similar to the polydispersion of single metallocene (typically Schulz-Flory distribution with polydispersion equal to 2.1).

For Zn/Zr equal to 110 and 220 (entry 29 vs 15 and 16 and entry 30 vs 17 and 18) the activities of the combined catalytic systems are much higher than references. Norbornene content of chain shuttling copolymers are quite similar to those obtained by catalyst A3 and higher than those obtained by B1. For Zn/Zr equal to 110 the  $T_g$  value of the chain shuttling copolymer is higher than the references while for Zn/Zr equal to 220 is similar to the  $T_g$  of A3 copolymer.

$M_w$  is lower than the references  $M_w$  (Figure 10) for both Zn/Zr ratio possibly due to the high norbornene content that decreases the propagation step rate of the catalytic system. Molecular weight distribution (D) becomes narrower (polydispersion equal to 1,9) than the references; for this set of experiments also the narrow polydispersion suggests the formation of multiblock microstructure of ethylene-*co*-norbornene copolymers.



**Figure 11.** Molecular weight profiles for N/E 26.0 and Zn 5.5 mmol

For N/E feed ratio of 26, the principal effect of diethylzinc is on the molecular weight that decreases by increasing the amount of zinc in solution. For this feed ratio, the molecular weight distribution remains narrow for all Zn concentration explored and very close to the Schulz-Flory distribution (Table 9).

**Table 9.** Copolymers by chain shuttling N/E = 26.0

Entry	Cat	Zn mmol	Zn/Zr	Yield(g)	Activity <sup>b</sup>	N mol % <sup>d</sup>	Conv	$T_g^e$ (°C)	$M_w$ ( $10^{-3}$ ) <sup>c</sup>	$D^c$
28	<b>B1+A3</b>	2,8	56	7,9	158	51	5,5	140	99	2,2
29	<b>B1+A3</b>	5,5	110	21,6	432	64	16,6	192	53	1,9
30	<b>B1+A3</b>	11,0	220	8,8	176	59	6,5	160	27	2,0

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

<sup>e</sup> $T_g$  are obtained by DSC

The last N/E feed ratio explored for CSP studies for this couple of catalysts (A3 and B1) is N/E molar ratio of 1.3. This feed ratio was explored to study effect of diethylzinc as chain shuttling agent when the catalyst system composed by A3 and B1 produces copolymers with low norbornene content.

**Table 10.** Copolymers by chain shuttling and references N/E = 1.3

Entry	Cat	Zn mmol	Zn/Zr	Yield(g)	Activity <sup>b</sup>	N mol % <sup>d</sup>	Conv	$T_g^e$ (°C)	$M_w$ (10 <sup>-3</sup> ) <sup>c</sup>	D <sup>c</sup>
<b>31</b>	<b>B1+A3</b>	<b>0,8</b>	<b>50</b>	<b>18,4</b>	<b>242</b>	<b>31</b>	<b>42</b>	---	<b>27</b>	<b>1,8</b>
19	A3	0,8	99	9,3	244	35	23	67	30	1,9
20	B1	0,8	99	9,7	255	22	18	29	---	---
<b>32</b>	<b>B1+A3</b>	<b>1,6</b>	<b>99</b>	<b>16,8</b>	<b>221</b>	<b>31</b>	<b>36</b>	---	<b>25</b>	<b>1,8</b>
21	A3	1,6	198	7,2	189	35	17,5	53	29	1,9
22	B1	1,6	198	9,5	250	21	17,1	28	---	---
<b>33</b>	<b>B1+A3</b>	<b>3,2</b>	<b>396</b>	<b>8,4</b>	<b>110</b>	<b>29</b>	<b>18</b>	---	<b>23</b>	<b>1,7</b>
23	A3	3,2	396	5,3	139	31	12	37	29	1,8
24	B1	3,2	396	9,8	258	22	18	20	---	---

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

<sup>e</sup> $T_g$  are obtained by DSC

For N/E 1.3, data analysis from all characterizations is similar to previous cases. In this set of experiments it was not possible to obtain the  $M_w$  value because of similar isorefractivity of the copolymer produced by B1 (with a 21-22 mol % of norbornene) and the SEC solvent. Norbornene content is found between the references for each Zn concentration. For the chain shuttling copolymers (entries 31, 33, 33)  $M_w$  decreases with increasing the concentration of diethylzinc. It is worth noting that  $M_w$  decreases but the molecular weight distribution is still very narrow (from 1.7 to 1.9), lower

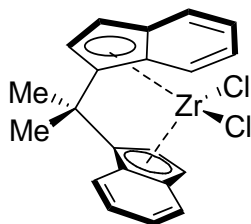
than a theoretical Schulz-Flory distribution and tends to a theoretical Poisson distribution. This is a clear indication that diethylzinc acts as chain shuttling agent for this feed ratio and with Zn/Zr of 99. For entries 31, 32, and 33, norbornene content seems not to be affected by the variation of diethylzinc in the medium.

Chain shuttling made ethylene-norbornene copolymers obtained at a N/E feed ratio of 1.3 do not present a  $T_g$  in the range explored with the DSC analysis. This characteristic can be explained by a highly disordered microstructure of the multiblock copolymer synthesized; in a high ethylene environment, the chain shuttling mechanism has a high rate. It is assumed that polymer blocks with a short length are produced and the thermal response of these short blocks cannot be registered by a DSC scan.

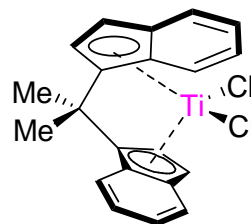


## Studies of CSP on zirconium/titanium catalytic system

A second series of experiments was performed with a second couple of catalytic systems: *rac*-[ $\eta^5$ ,  $\eta^5$ -Isopropylidene(bis-1-indenyl)zirconium dichloride (Cat1) and *rac*-[ $\eta^5$ ,  $\eta^5$ -Isopropylidene(bis-1-indenyl)titanium dichloride (Cat 2).



Cat 1



Cat 2

Both catalysts have  $C_2$ -symmetry, so they have a tendency to form isotactic polymers with prochiral olefins. For comparison with the other couple of catalysts (A3 and B1), both catalysts have been tested separately on three different N/E feed ratios. Cat 1 was active at all three N/E feed ratios (1.3, 4.8 and 26.0). However, for each ratio there is a different optimal amount of catalyst in the reaction environment (increasing the amount of norbornene decreases the activity). No copolymerization reaction occurred with Cat 2 (titanocene) in presence of 4.8 and 26.0 N/E feed ratios. So only results relative to low-norbornene content (N/E 1.3 and 19 bar) have been reported in this thesis.

### Copolymerization with catalytic systems Cat1 and Cat2 at N/E feed ratio 1.3

Optimized experiments for N/E ratio 1.3 are reported in Table 9 along with copolymer characterization by NMR, GPC, and DSC analysis.

**Table 9.** References for Cat1 and Cat2 catalyst system

Entry	Cat	$\mu\text{mol}$	Al/Metal	Yield (g)	Activity <sup>b</sup>	N mol% <sup>d</sup>	Conv	$T_g^e$	$M_w$ ( $10^{-3}$ ) <sup>c</sup>	$D^c$
34	2	20,1	598	3,2	34	21,8	3,0	24	470	1,3
35	1	5,8	2075	20,6	750	29,6	23,3	31	73	2,4

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

<sup>e</sup> $T_g$  are obtained by DSC

As reported in Table 9, the behaviour of Cat1 and Cat2 is different for the synthesis of ethylene-*co*-norbornene copolymers. Cat1 (zirconocene) has a higher activity than Cat 2 (titanocene) (entries 34 and 35). Because of the low activity of Cat2, the amount of catalyst had to be increased to obtain enough material for characterization. Cat1 has a higher norbornene incorporation and a higher  $T_g$  than Cat2 (norbornene content and  $T_g$  are directly correlated). From molecular weight characterization, Cat1 gives low molecular weight copolymers with polydispersion similar to Schulz-Flory distribution (2.4 instead of 2.1); Cat2 gives higher molecular weight with extremely narrow molecular weight distribution close to a Poisson distribution (polydispersion equal to 1.3).

## Effect of diethylzinc on Cat1 and Cat2 as single catalyst systems

**Table 10.** Effect of diethylzinc on Cat1

Entry	Cat	mmol	mmol Zn	Zn /Metal	Yield (g)	Activity <sup>b</sup>	N mol% <sup>d</sup>	Conv	$T_g^e$	$M_w$ ( $10^{-3}$ ) <sup>c</sup>	$D^c$
35	1	6	---	---	20,6	750	29,6	23,3	31	73	2,4
36	1	6	0,61	94	17,3	562	26,4	18,3	31	60	2,0
37	1	6	1,22	188	18	585	27,1	19,3	49	---	---
38	1	6	2,44	364	17,8	559	29,1	20,0	52	50	2,4

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

<sup>e</sup> $T_g$  are obtained by DSC

As expected, the effect of diethylzinc as chain transfer agent on Cat1 is mainly on the  $M_w$ : in fact  $M_w$  decreases linearly with rising the amount of diethylzinc in solution. For this catalyst also, the presence of diethylzinc decreases the activity. The effect of diethylzinc as chain transfer agent is confirmed by the values of polydispersion: D of copolymers synthesized in presence of diethylzinc are still similar to Schulz-Flory distribution (typical of a single catalyst metallocene).

The principal effect of diethylzinc on copolymerization with Cat2 (Table 11) is on molecular weight and molecular weight distribution.  $M_w$  decreases from a high value (about 470000).  $M_w$  becomes very low for Zn/Ti equal to 30 and molecular weight distribution becomes broad. Then, for higher zinc concentration, polydispersion becomes narrow and the  $M_w$  increases, but it is still lower than reference (entry 34).

**Table 11.** Effect of diethylzinc on Cat2

Entry	Cat	$\mu\text{mol}$	$\text{mmol Zn}$	$\text{Zn /Metal}$	Yield (g)	Activity <sup>b</sup>	$\text{N mol}\%$ <sup>d</sup>	Conv	$T_g^e$	$M_w$ ( $10^{-3}$ ) <sup>c</sup>	$D^c$
34	2	20	---	---	3,2	34	21,8	3,0	24	470	1,3
39	2	20	0,61	30	3,2	34	22,2	3,0	24	71	2,3
40	2	20	1,22	61	4,4	46	23,2	4,3	32	309	1,5
41	2	20	2,44	122	4,2	44	21,8	3,9	24	---	---

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

<sup>e</sup> $T_g$  are obtained by DSC

### Chain shuttling copolymerization with Cat1 and Cat2 system.

The results for Cat1/Cat2 combined copolymerization reactions are reported in Table 12. The copolymers obtained with chain shuttling mechanism have different properties compared to the references. In fact activities are intermediate to the references. Norbornene incorporation is always higher than the references and  $T_g$ s, that are strictly correlated to norbornene incorporation, are always higher than references.  $T_g$ s of the chain shuttling copolymers shows a single event.  $M_w$  becomes lower when increasing the amount of diethylzinc (entries 42, 43 and 44). Polydispersion becomes broader than references: this increase is still compatible with reversible chain transfer processes, being not too high to indicate irreversible chain transfer processes.

**Table 12.** Chain shuttling copolymers with references (Cat1 and Cat2)

Entry	Cat	mmol Zn	Zn /Metal	Yield (g)	Activity <sup>b</sup>	N mol% <sup>d</sup>	Conv	T <sub>g</sub> <sup>e</sup>	M <sub>w</sub> (10 <sup>-3</sup> ) <sup>c</sup>	D <sup>c</sup>
<b>42</b>	<b>1+2</b>	<b>0,61</b>	<b>23</b>	<b>13,5</b>	<b>109</b>	<b>32,4</b>	<b>16,1</b>	<b>65</b>	<b>67</b>	<b>2,5</b>
36	1	0,61	94	17,3	562	26,4	18,3	31	60	2,0
39	2	0,61	30	3,2	34	22,2	3,0	24	71	2,3
<b>43</b>	<b>1+2</b>	<b>1,22</b>	<b>47</b>	<b>12,8</b>	<b>103</b>	<b>28,5</b>	<b>14,2</b>	<b>42</b>	<b>50</b>	<b>2,4</b>
37	1	1,22	188	18	585	27,1	19,3	49	---	---
40	2	1,22	61	4,4	46	23,2	4,3	32	309	1,5
<b>44</b>	<b>1+2</b>	<b>2,44</b>	<b>94</b>	<b>12,5</b>	<b>101</b>	<b>30,8</b>	<b>14,5</b>	<b>55</b>	<b>64</b>	<b>3,1</b>
38	1	2,44	364	17,8	552	29,1	20,0	52	50	2,4
41	2	2,44	122	4,2	44	21,8	3,9	24	---	---

<sup>a</sup>Polymerization conditions: Temperature = 70°C; time = 15 min.

<sup>b</sup>Activity is expressed as Kg/(mol\*h\*bar).

<sup>c</sup>Molar characterization is obtained by SEC.

<sup>d</sup>Norbornene incorporation is obtained by <sup>13</sup>C-NMR.

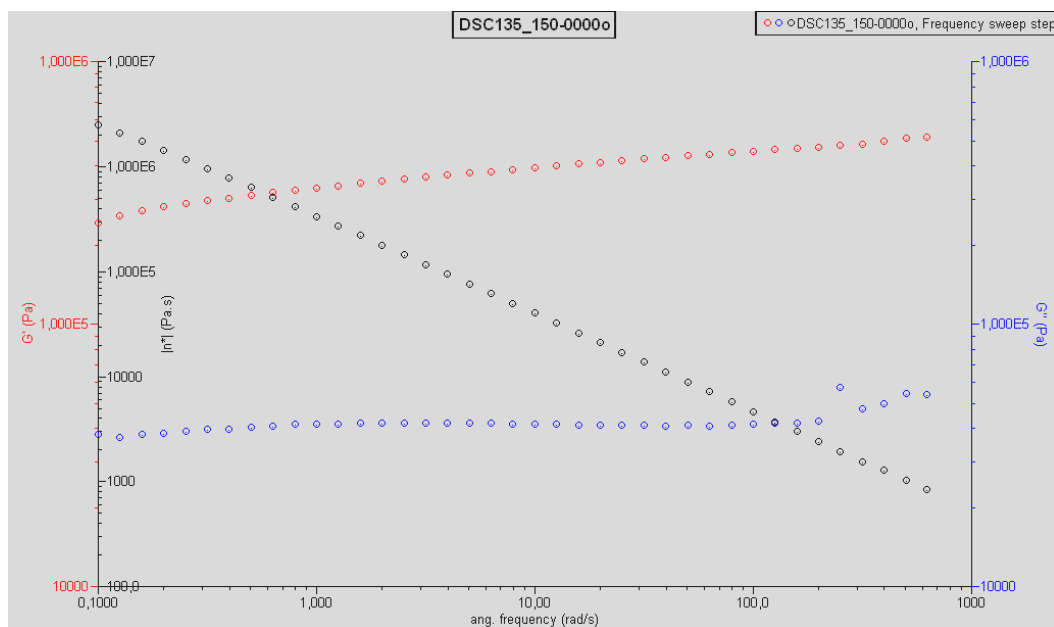
<sup>e</sup>T<sub>g</sub> are obtained by DSC

## Rheological characterization

Rheological studies have been performed to study dynamic and mechanic behaviour variation between copolymers obtained from single catalyst systems and chain shuttling synthesis procedures.

The rheology experiments were performed using a AR2000 TA Instruments rheometer. It was decided to perform the analysis using the double plate geometry and using the same  $\Delta T$  above the  $T_g$  (70°C). The standard gap was set as 500  $\mu\text{m}$  and the range of angular frequency were from 0,1 rad/s to 628 rad/s.

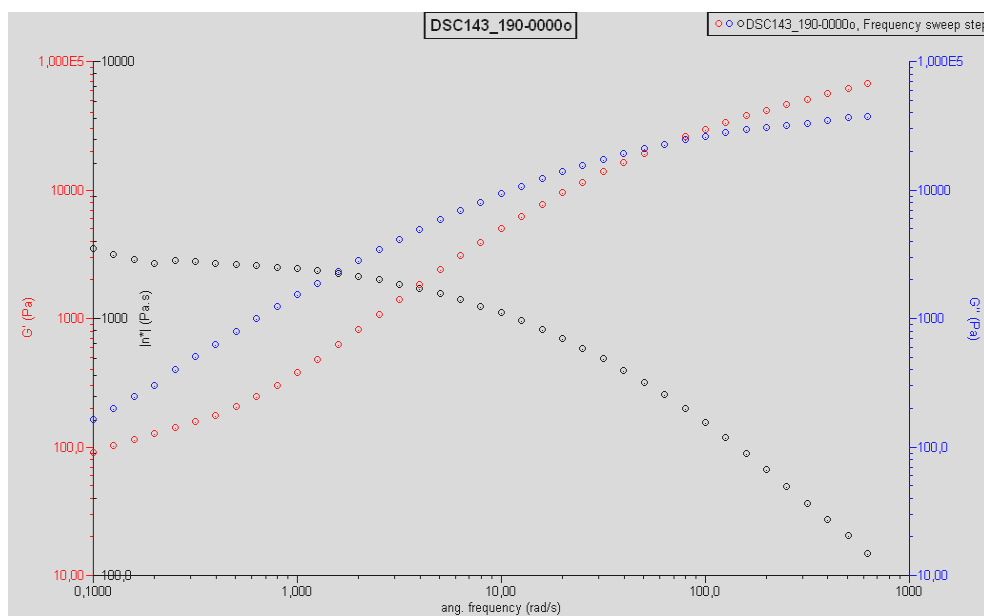
For the B1 copolymer series, the standard gap was not appropriate for the analysis because the Normal force was too high. The rheology diagrams of the three samples were similar.



**Figure 12.** Rheological diagram typical for copolymer obtained by B1 cat N/E 4.8

The  $G'$  is higher than the  $G''$  in the range explored and the complex viscosity has a value of  $10^6$  Pa\*s for low angular frequency. This behaviour can be explained by the entanglement effect due to the high  $M_w$  of the copolymer (309 kg/mol) and by its microstructure. (Catalyst B1 produces copolymers with a 37% mol of Norbornene with *meso* - alternating microstructure).

Catalyst A3 produces copolymers with random microstructure and lower  $M_w$ ; the incorporation of Norbornene is up to 45% mol. The rheological diagrams of the single-catalyst synthesis (DSC143, DSC140 and DSC142) are similar to each other. The diagram related to DSC143 is reported below.



**Figure 13.** Rheological diagram typical for copolymer obtained by A3 cat N/E 4.8

In this case the viscosity at low angular frequency has a low value, that can be explained by the random microstructure and by the low molecular

weight (61000 g/mol). The diagram shows a typical ethylene-norbornene behaviour with a viscous behaviour at low stress; increasing the oscillating stress, the  $G''$  becomes lower than the  $G'$  and this is symptomatic of elastic behaviour of the copolymer.

It was decided to obtain mixture of copolymers by solution blend instead that by thermomechanical mixing (using Brabender), because the blend obtained by solution mixing should be more intimate at a molecular level. The two single-catalyst copolymers were dissolved in toluene, mixed with a mechanical mixer and precipitated in acetone.

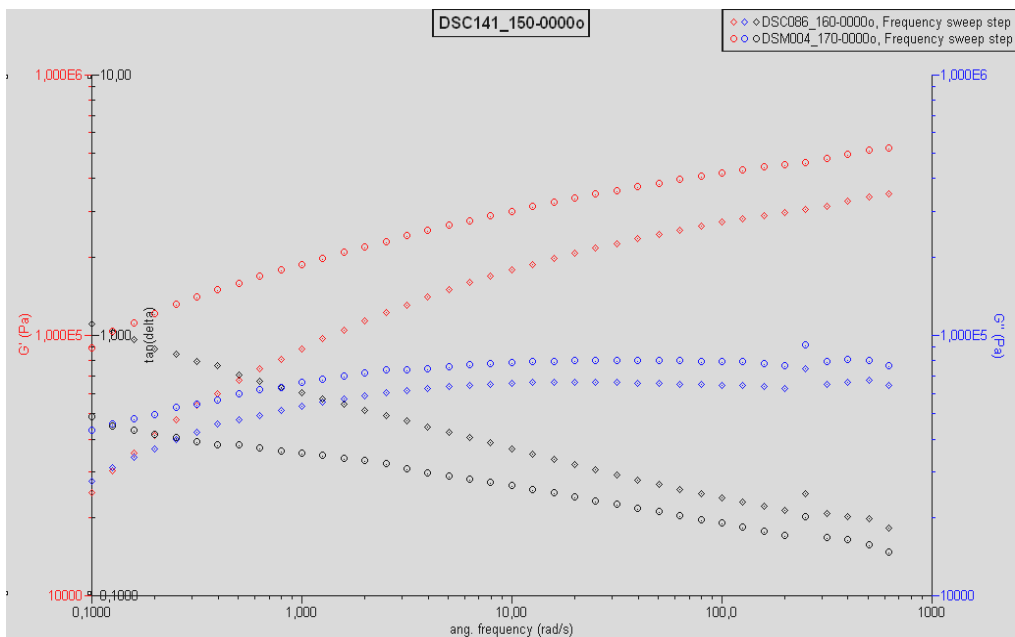
**Table 13.** Composition of physical blend for rheological comparison

	Cat	mmol Zn	%w	Weight (g)	Total weight (g)
<b>DSM004</b>	B1	1,2	78,1	2,1	2,7
	A3	1,2	21,9	0,6	
<b>DSM005</b>	B1	2,4	25,3	2,0	7,2
	A3	2,4	74,7	5,9	
<b>DSM006</b>	B1	4,8	43,7	1,5	3,2
	A3	4,8	56,3	1,9	

Rheological analysis was performed on samples obtained from chain shuttling copolymerization and on solution blends. The comparison of these results is important to understand if these copolymers have the same rheological behaviour and to understand if the rheology is a technique that can discriminate blends from pure copolymers.

First comparison of results is about samples DSC086 (B1+A3, 1,2 mmol  $ZnEt_2$ ) and DSM004.

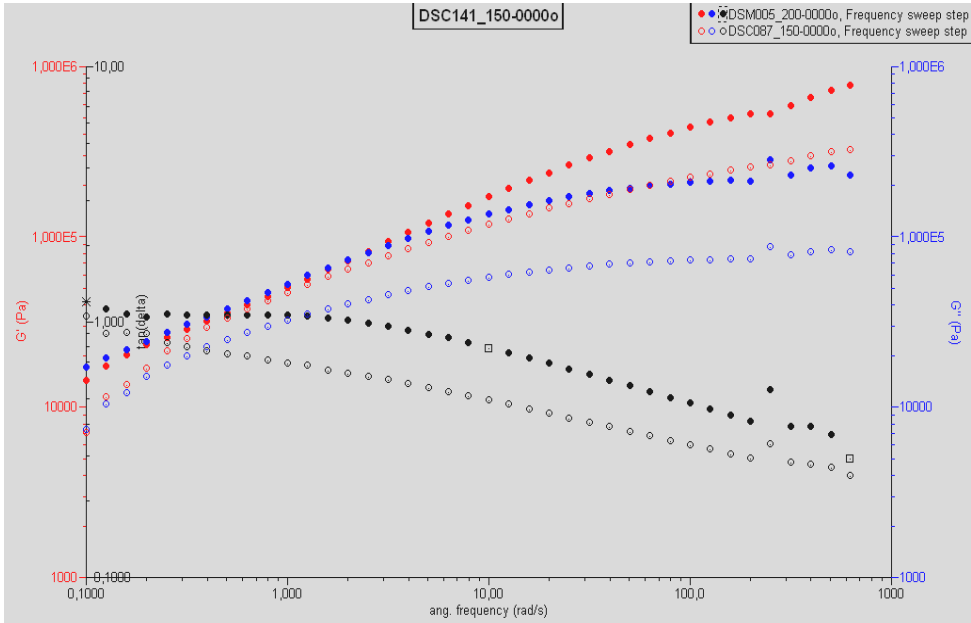




**Figure 14.** Comparison of rheological behaviour between chain shuttling copolymer (DSC086/entry 25) and physical blend (DSM004)

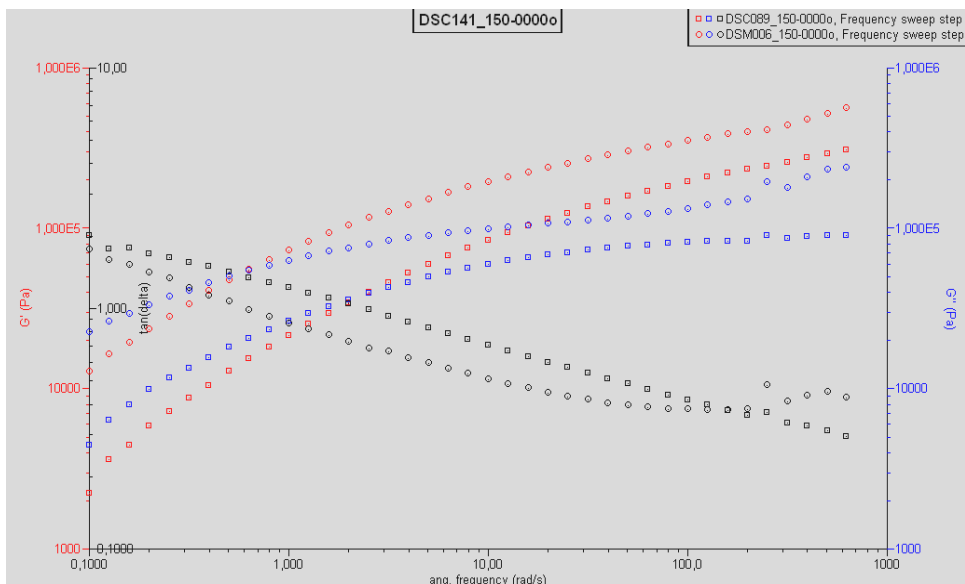
This diagram shows that at low angular frequency, solution blend has a solid behaviour that was due to the presence of copolymer B1. The two samples have the same behaviour at high angular frequency. The  $\tan\delta$  parameter has a different trend:  $\tan\delta$  in the sample DSC086 becomes lower in a linear way during the experiment in contrast to sample DSM004 that has a small area of non linear behaviour. The non-linear behaviour can suggest a two-phase system.

Another comparison is about samples DSC087 (B1+A3, 2,4 mmol  $\text{ZnEt}_2$ ) and DSM005.



**Figure 15.** Comparison of rheological behaviour between chain shuttling copolymer (DSC087/entry 26) and physical blend (DSM005)

In this diagram the samples have different behaviour at high angular frequency. In this case the non-linear behaviour of the  $\tan\delta$  parameter is more visible than in the previous diagram and it suggests a two-phase system (probably a physical blend of two copolymers obtained with separate copolymerization step).



**Figure 16.** Comparison of rheological behaviour between chain shuttling copolymer (DSC089/entry 27) and physical blend (DSM006)

The third diagram shows the comparison of a chain shuttling copolymer and a blend composed by copolymers obtained with catalysts A3 and B1. In this case also the non-linear behaviour can be observed for  $\tan\delta$  parameter.

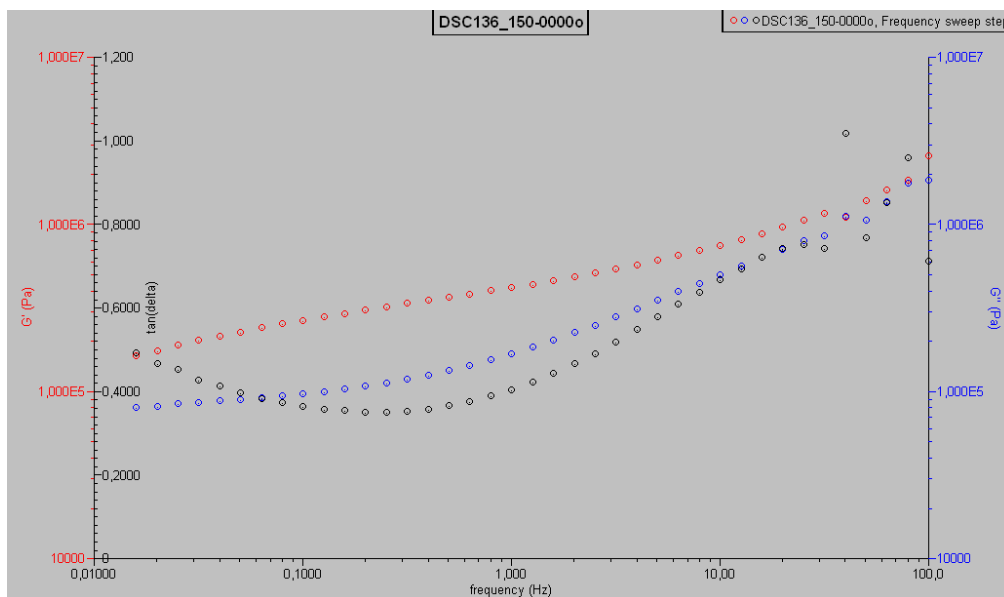
In all three cases the  $G'$  and  $G''$  of copolymers obtained by chain shuttling are lower than the value registered for blend samples.

In first comparison (DSM004 vs DSC086), blend is composed by 75% weight by copolymer B1. This leads the blend a behaviour similar to copolymer B1 ( $G'$  is always higher than  $G''$ ). This behaviour is not registered in any of chain shuttling copolymers.

The second comparison (DSM005 vs DSC087) shows that the  $G'$  and  $G''$  is higher for the blend (which is composed of 75% of A3) than DSC087 for all the range. The same behaviour is registered for the third comparison (DSM006 and DSC089).

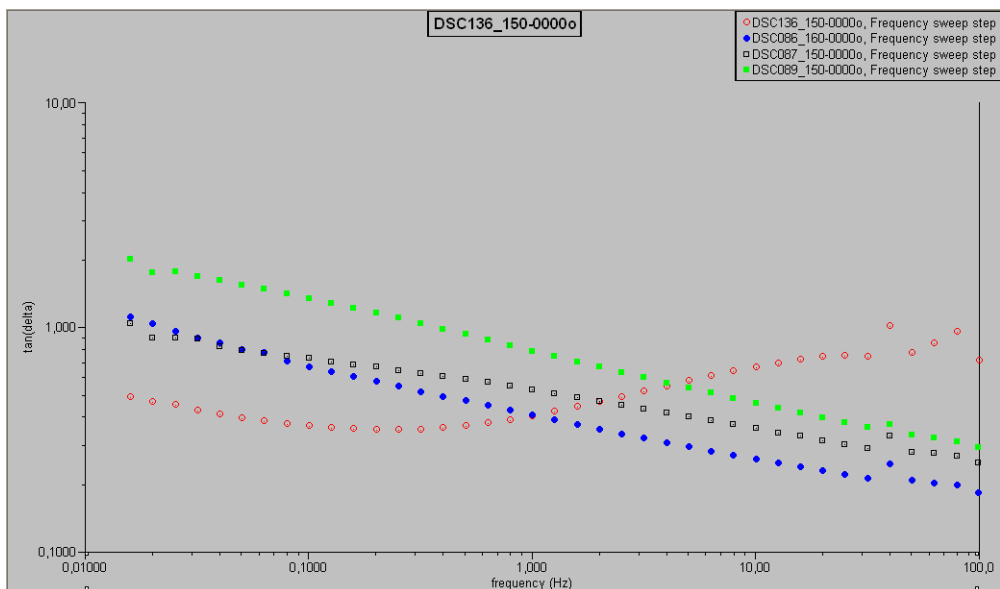
The  $\tan\delta$  can be determinant for the discrimination of mixture of copolymers and a single copolymer.

Sample DSC136 is obtained by the reaction of both catalysts without the presence of chain shuttling agent; below the rheological diagram is reported.



**Figure 17.** Rheological diagram of a copolymer synthesized without diethylzinc

The diagram shows a hard behaviour of the mixture; in fact the  $G'$  is higher than  $G''$  in all the explored range of frequency. In this case the parameter  $\tan\delta$  has a strongly non-linear behaviour may be due to the composition of the copolymer (DSC136 is a mixture of two copolymers). Plotting the behaviour of  $\tan\delta$  for samples DSC136, DSC086, DSC087 and DSC089 it is possible to evaluate the different behaviour of these samples.



**Figure 18.** Comparison of rheological behaviour between chain shuttling copolymer (DSC086/entry 25, DSC087/entry 26, DSC089/entry 27) and a mixture of copolymers DSC136.

Samples DSC086, DSC087 and DSC089 (chain shuttling reported in entries 25, 26, 27) are samples obtained by chain shuttling polymerization, they have different behaviours in the explored range of oscillation.

## Experimental section on CCTP

### Materials

All chemicals used for polymerization were manipulated under nitrogen using classical Schlenk-line and manipulation in glove box. All gaseous chemicals are purified by passage through BTS, molecular sieves and  $\text{CaCl}_2$  to remove polar impurities that poison air-sensitive compounds. Toluene used as reaction solvent was purified by distillation on Na prior use.  $\text{C}_2\text{D}_2\text{Cl}_4$  was purchased pure (99,9% of D) from Sigma Aldrich. Norbornene was purchased from Sigma Aldrich (98% pure) and purified by distillation on Na and stored in stock toluene solution at  $0^\circ\text{C}$ .

Diethylzinc solution (10% weight in toluene) was purchased from Sigma-Aldrich and manipulated in glove box. Triisobutylaluminum (TIBA) was purchased pure from Sigma-Aldrich.

Catalysts A3 and B1 and dimethylanilinium tetrakis(pentafluorophenyl)borate were supplied by TOPAS Advanced Polymers GmbH, Frankfurt, Germany. Hydrochloric acid was purchased 37% m/m from Sigma Aldrich and used as received. Ethanol was purchased as denaturated spirit from Sigma Aldrich and purified by simple distillation.

### Analytical Measurements

NMR analysis was performed on a Bruker Advance 400 instrument (400 MHz,  $^1\text{H}$  : 100,58 MHz;  $^{13}\text{C}$ : pulse angle = 12,50 ms, acquisition time = 0,94 s, delay = 16 s). Sample preparation for NMR analysis consists in weighting about 100 mg of copolymer, dissolving it in  $\text{C}_2\text{D}_2\text{Cl}_4$  in a 10 mm NMR tube and transfer to the spectrometer. The

probehead must be preequilibrated at a fixed temperature of 103°C. <sup>13</sup>C used reference was hexamethyldisiloxane (HMDS). Norbornene content is determined on the basis of peak intensity of <sup>13</sup>C NMR spectra; the calculation of norbornene content can be performed with this mathematical equation:

$$N \text{ (mol\%)} = I_N / (I_N + I_E) * 100$$

$I_N$  is the medium integral of a norbornene carbon atom. This parameter can be calculated by the equation

$$I_N = \frac{1}{3} \left[ I_{C_{7\beta}} + \frac{1}{2} (I_{C_{2\beta}} + I_{C_{3\beta}}) + \frac{1}{2} (I_{C_{4\beta}} + I_{C_{5\beta}}) \right]$$

The sum of the terms  $I_N + I_E$  can be calculated as the half of integrals of C5/C6 and CH<sub>2</sub> of ethylene units.

$$I_N + I_E = \frac{1}{2} I_{\square} (\text{from 25.00 to 30.00 ppm})$$

Chemical shifts for attribution of different carbon atom of norbornene and ethylene are reported in the literature<sup>(32)</sup>.

**Differential scanning calorimetry (DSC)** analysis were performed on a Perkin-Elmer Pyris I instrument. For copolymers with a N/E = 26,0 and 4,8 feed ratio were made a thermal cycle from 40 to 220°C using cyclic heating and cooling rates of 20°C per minute; for copolymers with a N/E = 1,3 feed ratio, the range goes from -50 to 220°C.  $T_g$  recording was performed during the second thermal cycle.

**Molar mass analysis** was performed on a GPCV2000 system from Waters equipped for high temperature analysis. The analysis of the sample consists in determination of molecular weight ( $M_w$ ) and molecular weight distribution ( $M_w/M_n$ ) at high temperature: *o*-dichlorobenzene was the solvent used during the analysis and the set

temperature was 145°C. All Size Exclusion Chromatography system was calibrated with a polystyrene standard kit.

### **Polymerization reaction.**

All synthesis were performed in a 0,6 L stainless steel Büchi Autoclave with heat jacket. Catalyst solution was prepared in a glove box using fresh distilled toluene, TIBA and precatalyst. This solution was stirred for 3 hours to guarantee the complete dissolution of precatalyst in toluene. Then the cocatalyst (dimethylanilinium tetrakis(pentafluorophenyl)borate) was introduced in the solution (B/Zr = 1,5) and the solution stirred again for 45 minutes to guarantee the complete alkylation of the precatalyst. The reactor was preliminary evacuated 3 times for 60, 45 and 30 minutes at 85°C to remove impurities. Then the reactor was cool down the polymerization temperature (70°C) and then it was filled with 150 mL of a mixture made up from toluene, triisobutylaluminum, norbornene and diethylzinc (toluene solution) in the right proportion. After thermal equilibration under mechanical stirring (about 20-30 minutes), the reactor was filled with ethylene to the desired pressure with an automatic valve system. Saturation step required almost 15 minutes. Then the catalyst solution is introduced into the autoclave using a high pressure nitrogen line. Internal pressure was kept constant during copolymerization reaction. Time was set constant to 15 minutes. To quench the reaction some mL of ethanol were introduced into the autoclave with high-pressure nitrogen line. Polymer solution was precipitated in distilled ethanol and stirred overnight. The precipitated copolymer was dissolved again in toluene and reprecipitated under



mechanical stirring in pure acetone. The copolymer was filtered and dried under vacuum at 75°C.

## **Experimental section on Chain Shuttling Polymerization (CSP)**

### **Materials.**

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with a N/E = 1,3 feed ratio, the range goes from -50 to 220°C.  $T_g$  recording was performed during the second thermal cycle.

Molar mass analysis was performed on a GPCV2000 system from Waters equipped for high temperature analysis. The analysis of the sample consists in determination of molecular weight ( $M_w$ ) and molecular weight distribution ( $M_w/M_n$  or D) at high temperature: *o*-dichlorobenzene was the solvent used during the analysis and the set temperature was 145°C. All Size Exclusion Chromatography system was calibrated with a polystyrene standard kit.

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# **CHAPTER 4**

## **CONCLUSION**

The main objective of this work was an exhaustive screening to determine the best conditions to synthesize poly(E-co-N)s by Chain Shuttling polymerization to obtain copolymers with both low and high norbornene content amorphous multiblocks in the same polymeric chain to obtain copolymers with more elastic properties.

A preliminary study has been done on the efficiency of diethylzinc as chain transfer agent with single metallocene catalysts selected in terms of Zn/metal ratio in copolymerization at various N/E feed ratios.

The molecular weight distribution of the copolymers obtained by the two catalysts A3 and B1 is typical of a Schultz-Flory distribution and gives indication of reversible chain transfers, but chain transfers are not so fast to give catalyzed chain grown on the zinc. However, by the calculation of the Zinc-Et extended, that represents the amount of diethylzinc, that participates in chain transfer mechanism, bearing a polymeryl chain, it is also possible to identify a different behaviour of the two catalysts.

In presence of catalyst B1, diethylzinc has a chain transfer rate lower than the propagation step rate (in fact zinc atom is bearing a lower amount of chains) while in presence of catalyst catalyst A3 diethylzinc has an opposite behaviour and zinc atom bears a higher amount of chains in solution. This characteristic can be correlated to the lower steric interactions between the zirconium atom and the zinc atom when zirconium atom is embedded in A3 open catalyst structure. In addition, the zirconium atom embedded in A3 catalyst structure has a higher electron density than in B1 because indenyl ligand has a higher aromaticity than fluorenyl ligand (present in B1 catalyst). So diethylzinc, which can be classified as a Lewis acid species, has a higher affinity for catalyst A3 than for B1. From analysis of the zinc-

extended studies, it is clear that for ethylene-norbornene copolymers chain transfer mechanism is more optimized when the feed is richer in ethylene content. This behaviour can be correlated to a higher steric interaction between the species when the chain transfer mechanism is interested in transalkylation between polymeryl chains bearing last inserted norbornene units.

Moreover, higher or lower norbornene content in the feed affects the mechanism of chain transfer in terms of decrease of molecular weight but does not change the reversible character of this mechanism. This information is really important because it confirms that the reversible interaction between metallocene catalysts and CTA is not affected by higher norbornene content. This characteristic is important because chain shuttling mechanism production of norbornene-based COC can be potentially applied for low- $T_g$ , medium- $T_g$  and high- $T_g$  materials. The presence of two different ligands or two different metal centers can influence the chain transfer rate against the propagation step rate, but the mechanism of chain transfer still remains reversible.

Then, the metallocene catalysts have been tested together for chain shuttling copolymerization. The copolymers obtained with A3 and B1 have been characterized by SEC and  $^{13}\text{C}$  NMR. The molecular weight and the norbornene content are intermediate to the reference ones (at the same Zn concentration). These characteristics suggest the presence of homogeneous macromolecules with intermediate characteristics between the references. The thermal analysis by DSC technique for all copolymers obtained by chain shuttling shows a single event for the glass transition temperature, that suggests the presence of homogeneous macromolecules with multiblock microstructure.

For Cat1 and Cat2, characterization could be performed only with low norbornene content because Cat2 (titanocene) is not active in presence of N/E = 4.8 molar ratio. In copolymers prepared with both catalysts at N/E = 1.3 molar ratio, the characterization of the chain shuttling copolymers brought to narrow molecular weight distribution, that indicates an optimized chain transfer process between the two catalysts. Copolymers have a single  $T_g$  even in this case and this is a clue of multiblock microstructure.

In conclusion, all chain shuttling copolymers have properties intermediate between the references in terms of norbornene content, molecular weight and  $T_g$ .values. Moreover, from rheological analysis, it was evidenced that copolymers obtained by chain shuttling have rheological behaviour different from starting materials and from a mixture of the two copolymers (blend).

From all these studies, it was confirmed the reversible chain transfer copolymerization for all these catalytic systems; copolymers obtained by chain shuttling copolymerization have all characteristics typical of homogeneous copolymers with multiblock microstructure and it can be excluded the formation of a blend of two copolymers.

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