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A Smart HTE Approach to Sustainable Polyolefin Materials

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Abstract

There is little doubt that High Throughput Experimentation (HTE) will ultimately become the gold standard of chemical R&D. On the other hand, until now the technical complexity and high Capex and Opex of HTE tools and methods have hampered a broad dissemination in several important areas of the chemical sciences. In particular, HTE approaches to organometallic catalysis began to spread in academia only recently.¹

The general aim of the present PhD project was to implement and apply 'smart' HTE protocols for tackling complex problems in olefin polymerization catalysis, with special focus on polyolefin sustainability. The main case history was Coordinative Chain Transfer Polymerization (CCTP)² and its Chain Shuttling Polymerization (CSP)³ variant: unraveling the complex kinetics governing this elusive chemistry and expanding its scope to novel monomers and materials are important open challenges. We have also addressed questions of relevance for the recycling of polyolefin wastes in the context of a circular economy.⁴

The HTE toolkit is introduced in **Chapter 2**. Despite the extensive robotic automation, a HTE platform is not a push-button setup. A complete HTE workflow can include several reaction platforms and an array of integrated analytical tools amenable to high-throughput operation and yet ensuring the precision and accuracy of conventional high-end tools.

Chapter 3 illustrates the implementation of HTE protocols for parallel olefin CSP experiments. We successfully downscaled the high-temperature

and high-pressure synthesis of statistical Olefin Block Copolymers (OBC) according to the Dow InfuseTM technology.^{5,6} A systematic exploration of the multi-dimensional variables hyperspace of ethene/1-alkene copolymerization under tandem catalysis conditions led us to elucidate unambiguously for the first time the microstructure and architecture of these advanced materials, that found commercial applications as unique thermoplastic elastomers and also as effective phase compatibilizers in immiscible polyolefin blends.

Chapter 4 illustrates a systematic and thorough search for catalyst systems amenable to CCTP/CSP other than those originally introduced by Dow Chemical. Notwithstanding the several claims in the literature,^{2,3,7} our study led us to conclude that reversible trans-alkylation in catalytic olefin polymerizations is exceedingly rare, and therefore expanding the scope of CSP via catalyst diversification is problematic.

Moving from this negative conclusion, in **Chapter 5** we explored the alternative option of OBC diversification by using unconventional comonomers. Two new classes of OBCs were prepared by CSP of ethene with 4-methyl-1-pentene or 1-hexadecene, respectively. Both comonomers are expected to provide block copolymers with unusual and interesting physical properties.^{8,9}

In **Chapter 6** we report how the HTE workflow was utilized to explore the possibility to introduce a fluorescent tag into polyethylene and polypropylene chains via copolymerization, for diagnostic purposes. The idea was to make different polyolefin grades identifiable post-mortem with a simple, cheap and fast optical measurement. Series of ethene and propene copolymerizations with 1-pyrenylheptene, a fluorescent comonomer

prepared ad hoc,^{10,11} demonstrated that the concept works very well down to incorporations of the tag at which the thermal and physico-mechanical properties of the copolymers are practically identical to those of the corresponding homopolymers.

Chapter 7 investigates catalytic depolymerization as a possible route of polymer waste recycling. It has long been known that polyolefin can be cleaved under comparatively mild conditions in the presence of certain heterogeneous transition metal catalysts.¹² Recently, this has also been shown for polydienes with a homogeneous catalyst.^{13,14} In the framework of the present thesis we explored the depolymerization of 1,4-*cis*-polybutadiene mediated by a large library of Group 4 metallocene and post-metallocene complexes. A strong dependence of molecular kinetics on catalyst structure was highlighted, and efficient catalysts were identified. This part of the project was a collaboration with Prof. Adam S. Veige at the University of Florida (Gainesville, FL).

From the conclusions of the project, which are summarized in **Chapter 8**, it is well evident that 'smart' HTE methodologies are ideally suited to rapidly identify novel and convenient routes of olefin polymerization and polyolefin/polydiene depolymerization that can improve the sustainability of these ubiquitous and important industrial processes and materials, making them ultimately better suited to a circular economy.

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List of abbreviations

1-PH	1-Pyrenylheptene
4M1P	4-Methyl-1-Pentene
AB	<i>N,N</i> -dimethylanilinium tetrakis- perfluorophenylborate
aCEF	analytical Crystallization Elution Fractionation
AF	Amorphous Fraction
BHT	4-Methyl-2,6-di-tert-butyl-phenol
Bn	Benzyl
C16	1-Hexadecene
Capex	Capital Expenditure
ССТР	Coordinative Chain Transfer Polymerization
CGC	Constrained Geometry Catalyst
CLSM	Confocal Laser Scanning Microscopy
Ср	Cyclopentadienyl
Cp*	Pentamethyl cyclopentadienyl
CRYSTAF	Crystallization Analysis Fractionation
CS	Chain Shuttling
CSA	Chain Shuttling Agent
CSP	Chain Shuttling Polymerization
СТА	Chain Transfer Agent
Da	Dalton (atomic mass unit)
DEZ	Diethyl-Zinc

DFB	1,2-Difluorobenzene
DFT	Density Functional Theory
DoE	Design of Experiment
DSC	Differential Scanning Calorimetry
E	Ethene
e.g.	Exempli gratia
EPDM	Ethylene-Propylene-Diene Terpolymer
Et	Ethyl
et al.	Et alia
etc	Et cetera
Flu	Fluorenyl
GPC	Gel Permeation Chromatography
Н	1-Hexene
HDPE	High-Density Polyethylene
HiP	High Pressure Reactor
HTE	High Throughput Experimentation
i.e.	Id est
Ind	Indenyl
iPP	Isotactic Polypropylene
<i>i</i> Pr	Isopropyl
LCB	Long Chain Branching
LDPE	Low-Density Polyethylene
LLDPE	Linear-Low-Density Polyethylene
LSP	Laboratory of Stereoselective Polymerizations

М	Metal	
m.u.	Monomeric unit	
MAO	Methylalumoxane	
Me	Methyl	
MGM	Main Group Metal	
M _n	Number Average Molecular Weight	
MW	Molecular Weight	
$M_{ m w}$	Weight Average Molecular Weight	
MWD	Molecular Weight Distribution	
<i>n</i> Bu	Normal butyl	
0	1-Octene	
OBC	Olefin Block Copolymer	
ODCB	Orthodichlorobenzene	
Opex	Operating Expense	
Р	Propene	
PB	Polybutadiene	
PDI	Polydispersity Index	
PE	Polyethylene	
PET	Polyethylene terephthalate	
РО	Polyolefin	
PP	Polypropylene	
PPR	Parallel Pressure Reactor	
PVC	Poly(vinylchloride)	
QSAR	Quantitative Structure-Activity Relations	

R&D	Research and Development	
R _p	Catalyst activity	
SAXS	Small-Angle X-ray Scattering	
SEM	Scanning Electron Microscopy	
sPP	Syndiotactic Polypropylene	
T _{el}	Elution temperature	
TEM	Transmission Electron Microscopy	
TiBAl	Tri-iso-butyl-Aluminum	
ТМ	Transition Metal	
ТМА	Trimethyl-Aluminum	
Y	Yield	
ZN	Ziegler-Natta	

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CHAPTER 1

Introduction

1.1 Progress in olefin polymerization catalysis

1.1.1 From heterogeneous Ziegler-Natta systems to molecular catalysts

The ability of polymer chemists to produce materials with useful application properties from commercially abundant and cheap monomers has revolutionized human society.¹ Polyolefins such as polyethylene (PE) and polypropylene (PP), in particular, have become the largest volume polymers on the market (Figure 1.1)², thanks to an amazing diversification of the properties envelope, resulting from the thorough control of chain microstructure and architecture ensured by a variety of coordination catalysts.



Figure 1.1. Historic growth of the global polyethylene (PE) and polypropylene (PP) market.³

The discovery of Ti-based heterogeneous Ziegler-Natta (ZN) catalysts in the mid-1950s triggered what is rightfully known as 'the plastics revolution'. These systems made it possible to produce high-density polyethylene (HDPE), isotactic polypropylene (iPP), and – some years later – linear-low-density polyethylene (LLDPE), overall an incredible success story which is highlighted in many competent books and reviews.^{4–10} It may be worthy to recall that prior to Ziegler's and Natta's breakthroughs the only commercial polyolefin available was low-density polyethylene (LDPE), a highly branched amorphous material resulting from a hightemperature, high-pressure free-radical process which was (and still is) very difficult to control.¹¹

Polyolefins experienced a second revolution after the introduction of molecular catalysts (metallocenes first, post-metallocenes later on).^{12,13} Metallocenes were actually known since the 1950s, but they were considered of no practical interest for some 20 years, until the serendipitous

discovery of methylalumoxane (MAO), used as an activator in the place of Al-trialkyls, boosted their activity by several orders of magnitude.^{14–16} The first samples of moderately stereoregular metallocene iPP were obtained using MAO-activated *rac*-Et(Ind)₂ZrCl₂, a *C*₂-symmetric *ansa*-zirconocene, by Brintzinger and Kaminsky¹⁷; few years later, syndiotactic polypropylene (sPP) was produced with the *C*_s-symmetric homolog [Me₂C(Flu)(Cp)]ZrCl₂ by Ewen and Razavi¹⁸ (Cp = Cyclopentadienyl, Ind = 1-Indenyl, Flu = 9-Fluorenyl). In the following years, several *C*₁-symmetric *ansa*-zirconocenes were disclosed yielding propene polymers with various tacticities, from atactic to isotactic through hemi-isotactic, depending on the steric demand of the alkyl substituents on the aromatic ligand framework (Figure 1.2).^{19–23}

Bercaw²⁴ and Stevens²⁵ pioneered the diversification of molecular catalysts from metallocenes to hemi-metallocenes (half-metallocenes). Their Constrained Geometry Catalysts (CGCs) clearly demonstrated that 'there is life beyond metallocenes'¹³, in particular for ethene/1-alkene copolymerizations. Moving on to 'post-metallocenes' was a logical and relatively straightforward next step.²⁶



Figure 1.2. Correlation between metallocene symmetry and tacticity of the produced polymers.

In the late 1990s, Fujita at Mitsui Chemical patented a class of octahedral bis(phenoxyimine) Group 4 complexes (Figure 1.3) featuring an amazing metal-dependent behavior. A number of Ti(IV) catalysts, in particular, polymerized ethene and propene in a 'living' (controlled) fashion, the latter with a highly syndiotactic structure.^{27–29} Almost at the same time, Busico elaborated on a class of bis(phenoxyamine) Group 4 catalysts originally

introduced by Kol^{30–32} (Figure 1.4), and reported the first living polymerizations of propene to an isotactic structure.³³



Figure 1.3. The structure of the class of bis(phenoxyimine) catalysts (TM = Ti, Zr, Hf).²⁷⁻²⁹



Figure 1.4. The structure of the class of the bis(phenoxyamine) catalysts (TM = Ti, Zr, Hf, Bn = benzyl).³⁰⁻³²

These inventions opened the door to the facile synthesis of olefin block copolymers (OBCs), including PE-*block*-sPP, PE-*block*-iPP, and PE-*block*-(ethene/1-alkene) (Figure 1.5).^{34–38}



Figure 1.5. Sequential 'living' polymerization of ethene and ethene/1-alkene mixtures to OBCs with elastoplastic properties. From Ref. 38. Reprinted with permission from AAAS.

From the scientific standpoint the new chemistry was a major breakthrough, because it gave access to materials with unprecedented properties. In particular, OBCs with the structure shown in Figure 1.5 can behave as thermoplastic elastomers breaking the paradigm of a mandatory relationship between density and melting temperature^{37,39} (we will elaborate further on this concept in a later section). On the other hand, the limitation that (at most) one polymer chain is produced per catalyst molecule severely hampers practical application.³⁸

1.1.2 The impact of High Throughput Experimentation

Until the end of the 1990s, chemical experiments were carried out sequentially in conventional batch or semi-batch reactors by human operators. In the first two decades of the new millennium, progress in electronics and robotics led to the implementation of a new approach which is comprehensively referred to as 'High-Throughput Experimentation' (HTE).⁴⁰ HTE methods are based on the parallelization of large numbers of miniaturized experiments under robotic control and with electronic data acquisition. Typical HTE reaction platforms can run 10²-10⁴ experiments per day, with reaction cell volumes of a few mL or even less.⁴¹ In olefin polymerization catalysis, HTE is typically used for the rapid screening of different catalysts under various conditions.^{42–44}

A seminal HTE workflow for catalyst discovery was implemented in the late 1990s by Symyx Technologies and Dow Chemical in the framework of a strategic alliance (Figure 1.6).^{39,44} The workflow entailed a comparatively coarse 'primary' screening of large libraries of candidate catalysts in very small scale ($\approx 10^3$ experiments per day, ≈ 1 mL working volume per experiment), the structural amplification of 'hits', and a finer 'secondary' screening for the identification of 'leads' ($\approx 10^2$ experiments per day, ≈ 5 mL working volume per experiment). Lead optimization was the only phase still relying on conventional methods.



Figure 1.6. The HTE workflow for polyolefin catalyst discovery implemented by Symyx Technologies and Dow Chemical.⁴¹

This resource-intensive strategy proved to be quite effective; indeed, Dow vastly and rapidly innovated its catalyst portfolio.^{43,45,46} A paradigmatic case is the class of (pyridylamido)Hf(IV) catalysts of Figure 1.7, which is now used for the commercial production of unique iPP homopolymers and copolymers in solution at elevated temperatures (>120 °C).^{43,46} The serendipitous ortho-metallation of the aromatic fragment linked to the pyridyl moiety turned out to be key to practically all aspects of catalytic

behavior (including stereoselectivity), because the first insertion of the monomer(s) into the strained Hf-C σ bond gives rise to a multiplicity of diversified active species.



Figure 1.7. The structure of the (pyridylamido)Hf(IV) catalysts invented by Dow.^{43,46}

That such a discovery is beyond the reach of rational design is a notable fact, but it is not the only merit that can be credited to HTE, as we shall see in the following sections.

1.1.3 New polyolefins made by Coordinative Chain Transfer Polymerization

Coordinative Chain Transfer Polymerization (CCTP)^{47,48} is a polymerization process in which a transition metal (TM) catalyst undergoes fast and reversible trans-alkylation with an excess of a main group metal (MGM) alkyl cocatalyst. The result is a pool of 'dormant' polymeryl chains on the MGM, undergoing intermittent growth when temporarily returned to the TM.

CCTP affords a controlled ('living') polymerization in the absence of termination pathways other than chain transfer to the MGM (from here on Chain Transfer Agent, CTA, or also 'Chain Shuttling' Agent, CSA); it thus belongs in the broader class of degenerative group transfer polymerizations, i.e., processes involving a dynamic equilibrium between propagating and dormant active species (Figure 1.8).



Figure 1.8. The kinetic scheme of CCTP.⁴⁹

A very important fact is that the average chain growth time on the TM catalyst in the absence of the MGM species (t_{cg}) is extended by a factor $\tau \geq$ n[MGM]/[TM], where n is the average number of polymeryls bound to each MGM center. As long as the experiment time t for a (semi)batch process, or the average catalyst residence time for a continuous process, is (well) below τ_{cg} , a linear relationship between polymer yield (Y) and average molecular weight (MW) holds. If, additionally, chain initiation is fast relative to propagation, the process mimics a living polymerization, and the molecular weight distribution (MWD) of the polymer produced in (semi)batch experiments approaches the Poisson function $(PDI = M_w/M_n = 1.0)$.^{47,48,50} At odds with a classical living polymerization, however, CCTP has the advantage that hundreds of chains can be produced per TM center (which is by far the most expensive component of the catalytic system).

The first reports of ethene and ethene/1-alkene CCTP involving metallocenes of Actinides or Hafnium and Al-alkyls are due to Samsel.^{51–53} Pioneering studies were also reported by Mortreux, who used a Samarium system, namely $[Cp_2^SmCl_2Li(OEt_2)_2]$ ($Cp^* =$ Pentamethyl cyclopentadienyl), and Mg(*n*Bu)Et as activator and CSA.^{54,55} Comprehensive reviews on olefin CCTP have been published by Kempe⁴⁷, and more recently by Zinck (who covered also styrene and conjugated dienes).⁴⁸

Apart from the scientific interest, CCTP is relevant because it can be exploited to prepare block copolymers by feeding different (co)monomers in sequence. For example, new highly stereoregular poly(myrcene-*co*-styrene), poly(myrcene-*co*-isoprene), and poly(myrcene-*co*-styrene-*co*-isoprene) copolymers (Figure 1.9) were obtained with good yields and a wide range of compositions.⁵⁶



Figure 1.9. Structures of poly(myrcene-*co*-styrene), poly(myrcene-*co*-isoprene), and poly(myrcene-*co*-styrene-*co*-isoprene).

On top of that, CCTP can give access to functional polymers: indeed, a variety of chain-end and randomly functionalized polyolefins can be prepared, and utilized as precursors for the production of block and graft copolymers, which have potential as drug delivery systems, pH- as well as stimuli-responsive materials^{57,58}, and – last but not least – phase

compatibilizers for a variety of immiscible polyolefin-containing blends, thus opening the door to mechanical recycling applications.^{59,60} As an example, Duchateau compared different routes to produce chain-end and randomly hydroxyl-functionalized PE, and concluded that CCTP is the most promising route to produce chain-end hydroxyl-functionalized PE on a large scale.⁶¹ Boisson and D'Agosto discovered that the addition of Iodine after PE CCTP on Mg-alkyls can yield end-halogenated PE (PE-I).⁶² The PE-I chains, in which the chain end is now electrophilic, are amenable to a broad range of post-polymerization reactions, including nucleophilic attacks. The same authors also investigated the possibility to employ functionalized CTAs to simplify multistep functionalization routes.⁶³ In particular, they introduced a novel Mg-dialkyl CTA containing a 2,2,5,5tetramethyl-1-aza-2,5-disilacylopentane moiety, that efficiently mediated ethene CCTP in the presence of $[(Cp^*)_2NdCl_2Li(OEt_2)_2]$. The protected amine group was tolerated by the catalyst, and allowed for the production of well-defined polymer chains that, upon protic deactivation, yielded ammonium-terminated PE chains in one step. Easy deprotonation ultimately led to amine end-functionalized PE. Recently, Lee reported the preparation of an ABA-type olefin triblock copolymer⁶⁴ by means of a CCTP process with the Pyridylamido-Hf catalyst of Figure 1.7 and a Znalkyl CSA (Figure 1.10). Zn-bound diblock copolymers, namely PE-blockpoly(ethylene-*co*-propylene)yl)₂Zn, were produced and subsequently PE-block-poly(ethylene-co-propylene)-block-PE converted to bv quenching the CCTP process with lauroyl peroxide. These materials, in which the chains were claimed to be physically crosslinked due to the crystallization of the PE blocks, exhibited thermoplastic elastomeric properties with significantly improved mechanical attributes compared with those of the diblock congener, i.e., PE-*block*-poly(ethylene-*co*-propylene) (e.g., tensile strength, \approx 2-fold; elongation at break, \approx 10-fold).



Figure 1.10. A CCTP strategy for the synthesis of ABA-type olefin triblock copolymers. Reprinted with permissions from Ref. 64. Copyright © 2018 American Chemical Society.

The definition of 'Chain Shuttling Polymerization' (CSP) is used in preference when a CCTP process is carried out using *two* different TM catalysts instead of one.^{49,50} Under proper conditions, the tandem catalytic process yields *statistical* OBCs made of chemically different blocks (Figure 1.11).



Figure 1.11. Schematic representation of Chain Shuttling Polymerization (CSP). Reprinted with permissions from Ref. 48. Copyright © 2013 American Chemical Society.

Whereas the concept of CSP is intuitive, well-documented cases are rare. Rytter reported ethene/1-hexene copolymerization in the presence of (1,2,4-Me₃Cp)₂ZrCl₂ and (Cp^{*})₂ZrCl₂, with MAO as the CSA.⁶⁵ Based on preliminary characterizations, the authors suggested that some physical properties of the copolymers differed from those of samples obtained using the individual catalysts; tentatively, that was attributed to a block(y) nature. Later Crystallization Analysis Fractionation (CRYSTAF) studies, though, led the authors to conclude that the products were rather a physical blend.⁶⁶ This early study is interesting because it is representative of many others that appeared in the subsequent years, claiming the synthesis of statistical OBCs without providing unambiguous evidence.

It is worthy to recall at this point that CCTP as well as CSP can only occur in solution, because they require the mobility of all M-polymeryl species (M = TM and MGM). For chains with crystallizable blocks, that means to operate at a temperature higher than the polymer dissolution temperature ($T > 100^{\circ}$ C, indicatively, in the specific case of PE). Yet, the vast majority of the literature studies were carried out at rather low temperature^{48,67}, likely due to the fact that controlling catalytic olefin polymerizations at high temperature is technically and kinetically demanding. In this respect, the synthesis of well-defined OBCs by 'living' polymerization is much easier, because monomer diffusion to the active sites can continue after polymer precipitation.

It was only in 2006 that a seminal study by Arriola at Dow made clarity on the question, thanks to the decisive contribution of HTE.⁶⁸ Taking advantage of a state-of-the-art HTE workflow, the team of Arriola screened

a large number of TM catalysts, individually and pairwise, in ethene/1octene (E/O) copolymerization at $T > 100^{\circ}$ C, using diethyl-Zinc (DEZ) as CSA (Figure 1.12). The main observables were (i) the drop of copolymer MW, quantifying the propensity of the catalyst(s) to undergo transalkylation with DEZ, and (ii) the MWD of the copolymers in the tandem catalysis experiments, expected to be bimodal for physical blends, monomodal instead for statistical OBCs resulting from reversible transalkylation between DEZ and the TM catalyst pair. Evidence of true OBCs was only achieved for the catalyst pair shown in Figure 1.13, 49,50,68 1^{68,69} consisting of the bis(phenoxyimine)Zr catalyst and the (pyridylamido)Hf catalyst $2^{43,68}$. In a previous section we noted that catalyst 2, in turn, was discovered by means of HTE; therefore, the impact of HTE methodologies in this breakthrough was two-fold.



Figure 1.12. The HTE discovery of olefin CSP. From Ref. 68. Reprinted with permission from AAAS.



Figure 1.13. The bis(phenoxyimine)Zr (1) and (pyridylamido)Hf (2) (pre)catalyst pair.

A fortunate circumstance was that the ability of catalyst **1** to incorporate 1octene (O) in growing PE chains is much lower than that of catalyst **2**. Therefore, at a given [E]/[O] feeding ratio, O-poor (semicrystalline, 'hard') copolymer blocks and O-rich (amorphous, 'soft') copolymer blocks are produced at the active species of **1** and **2**, respectively.⁶⁸ The relative amounts of hard and soft blocks, as well as their average numbers, lengths and compositions, can be tuned (within the constraints inherent in the nature of the catalyst pair⁷⁰) by adjusting the relative amounts of the two catalysts and of the CSA, as well as comonomer concentrations. In particular, the process can yield statistical OBCs behaving as thermoplastic elastomers, with the unique advantage of OBCs that the density (degree of crystallinity) and the melting temperature of the crystallizable blocks can be tuned independently of each other, whereas for random copolymers the two parameters are necessarily related (Figure 1.14).^{39,68}



Figure 1.14. Relationship between melting temperature and density for random and block ethene/1-alkene copolymers. From Ref. 68. Reprinted with permission from AAAS.

E/O OBCs made by CSP are now produced commercially by Dow Chemical under the InfuseTM tradename. The catalytic synthesis, solid-state structure, and physical properties of InfuseTM materials have been reported in several papers.^{70–72}

Other than as thermoplastic elastomers, OBCs can find useful applications as phase compatibilizers in immiscible polymer blends.⁷³ Chen *et al.* have shown that an iPP-PE OBC improved the interfacial interaction between PP and HDPE materials, evidenced by a reduced HDPE domain size and an increased elongation at break of the blends.⁷⁴ Moreover, compared to statistical copolymer compatibilized blends, OBC compatibilized ones featured the best combination of low brittle-to-ductile (BD) temperature and high toughness.⁷⁵

Zhang and co-workers investigated similar effects for PP/ethylenepropylene-diene terpolymer (EPDM) blends, and studied the phase morphology of the ternary system.⁷⁶ The addition of an OBC caused sufficient interfacial adhesion and enhanced mechanical properties of PP/EPDM samples, including Young's modulus, tensile strength and elongation at break.

1.2 Improving polyolefin sustainability for a circular economy

Synthetic polymers are among the most important products of the chemical industry. The overall production capacity exceeds 400 million metric tons per year, of which polyolefins represent about 50% (Figure 1.15).^{77,78}

Polyolefin materials feature an unbeatable cost/performance ratio, high versatility with respect to properties and applications, in many cases superior mechanical properties, low density (weight), excellent corrosion resistance, facile processing with short cycle times (injection molding, blow molding, fiber spinning, and extrusion), highly cost-, resource-, eco- and energy-effective mass production, flexible base of raw materials (oil, gas, coal, and biomass), high energy content (similar to oil and superior to wood), and low Carbon footprint.^{79–83}

As a real word example, one can compare a yogurt jar made of glass with another made of PP. According to most opinion-makers, the former represents the eco-friendlier option; and yet, it has much thicker walls, and can weigh as much as the yogurt itself. Moreover, its CO₂ impact is much worse; not only is more material needed to produce a jar that does not easily break, but the added weight needs to be transported to the consumer. What makes a big difference and partly justifies opinion-makers, on the other hand, is post-mortem disposal: glass wastes are easy and convenient to collect and re-use, whereas plastic wastes are not, and when a problem weighs 400 million tons yearly it is a serious one.



Figure 1.15. Historic evolution of the global plastics production from 1950 to 2015. Reprinted with permissions from Ref. 84.

From overflowing landfills to maritime litter to microplastic in the human and animal food chains, the reasons for dislike plastics have been growing more and more in recent years.^{85,86} A common emotional reaction is to ban plastics from fossil feedstocks at least for single-use applications, either outright or in favor of biodegradable plastics from renewable resources. New solutions for the market are unquestionably needed, and biodegradable plastics will provide some; however, production is energy intensive, and feedstock sourcing competes with food production.⁸⁷ Moreover, the CO₂ balance is poorer than for single-use plastics from fossil resources.⁷⁹ Currently available biodegradable polymers are only useful for certain applications, but novel materials will come on stream and the scenario may change for the better; still, longevity and resistance to degradation are indisputable superior qualities of many plastic materials, with polyolefins in the first places. For example, polypropylene drainage pipes with a 100-year-guarantee⁸⁸ or medical implants⁸⁹ will be challenging, if not impossible, to replace. High-performance plastics are the result of 80 years of continuous innovation, starting with the discovery of LDPE by Imperial Chemical Industries (ICI) in 1933.¹¹ Polyolefins are simply too good, too cheap, too stable, and too widely available to be replaced in the near-term future.

What cannot be questioned is that a sustainable future requires a circular economy, where waste is not thrown away but re-introduced into the value chain (Figure 1.16).⁹⁰



Figure 1.16. Plastics in a circular economy.

There are several strategies that can be applied for the reutilization and upcycling of polymeric materials. Mechanical recycling is an obvious possibility, and can fit in the 're-use, recycle' philosophy. However, even assuming that a thorough sorting of wastes, e.g., in mixed municipal streams can be achieved, inevitable contamination issues and degradation throughout repeated processing cycles complicate the hypothesis of reusing individual grades. Recycling by blending can represent a better option; however, most widespread polymers are thermodynamically immiscible, even when they belong in the same chemical class (e.g., PE and iPP), which results in poor mechanical properties of the mixtures.⁹¹ Utilizing phase compatibilizers can open valuable opportunities.^{92,93} For instance, it has been reported that interfacial compatibilization of phaseseparated PE and iPP with PE-block-iPP is very effective, transforming brittle into mechanically tough blends.⁵⁹ CCTP and CSP can represent practical routes to produce statistical OBCs at an affordable price for phase compatibilization purposes.94,95

A conceptually different solution is chemical recycling.^{96,97} Chemical bond scissoring of polyolefin wastes via hydrogenolysis⁹⁸⁻¹⁰² (waste-to-raw-material), for example, has a large appeal for the polyolefin industry in the context of a circular economy, because it might enable re-feeding the waste into the polymer production cycle.¹⁰³ In particular, it is conceivable that depolymerized liquid streams are fed into conventional crackers to generate olefinic monomers and ultimately convert wastes into virgin resins.

1.3 Scope and objectives

The general aim of the present PhD project was to implement and apply 'smart' HTE protocols for tackling complex problems in olefin polymerization catalysis, with special focus on polyolefin sustainability. The main subject was Chain Shuttling Polymerization (CSP):⁴⁹ unraveling the complex kinetics governing this elusive chemistry and expanding its scope to novel monomers and materials are important open challenges which bear promise for useful developments. We have also addressed questions of relevance for the recycling of polyolefin wastes in the context of a circular economy.⁸²

The HTE toolkit is introduced in **Chapter 2**. Despite the extensive robotic automation, a HTE platform is not a push-button setup. A complete HTE workflow can include several reaction platforms and an array of integrated analytical tools amenable to high-throughput operation and yet ensuring the precision and accuracy of conventional high-end tools.

Chapter 3 illustrates the implementation of HTE protocols for parallel olefin CSP experiments. We successfully downscaled the high-temperature and high-pressure synthesis of statistical Olefin Block Copolymers (OBC) according to the Dow InfuseTM technology.^{68,104} A systematic exploration of the multi-dimensional variables hyperspace of ethene/1-alkene copolymerization under tandem catalysis conditions led us to elucidate unambiguously for the first time the microstructure and architecture of these advanced materials, that found commercial applications as unique thermoplastic elastomers and also as effective phase compatibilizers in immiscible polyolefin blends.
Chapter 4 illustrates a systematic and thorough search for catalyst systems amenable to CCTP/CSP other than those originally introduced by Dow Chemical. Notwithstanding the several claims in the literature,^{48,49} our study led us to conclude that reversible trans-alkylation in catalytic olefin polymerizations is exceedingly rare, and therefore expanding the scope of CSP via catalyst diversification is problematic.

Moving from this negative conclusion, in **Chapter 5** we explored the alternative option of OBC diversification by using unconventional comonomers. Two new classes of OBCs were prepared by CSP of ethene with 4-methyl-1-pentene or 1-hexadecene, respectively. Both comonomers are expected to provide block copolymers with unusual and interesting physical properties.^{105,106}

In **Chapter 6** we report how the HTE workflow was utilized to explore the possibility to introduce a fluorescent tag into polyethylene and polypropylene chains via copolymerization, for diagnostic purposes. The idea was to make different polyolefin grades identifiable post-mortem with a simple, cheap and fast optical measurement. Series of ethene and propene copolymerizations with 1-pyrenylheptene, a fluorescent comonomer prepared ad hoc,^{107,108} demonstrated that the concept works very well down to incorporations of the tag at which the thermal and physico-mechanical properties of the copolymers are practically identical to those of the corresponding homopolymers.

Chapter 7 investigates catalytic depolymerization as a possible route of polymer waste recycling. It has long been known that polyolefin can be cleaved under comparatively mild conditions in the presence of certain heterogeneous transition metal catalysts.⁹⁸ Recently, this has also been

shown for polydienes with a homogeneous catalyst.¹⁰² In the framework of the present thesis we explored the depolymerization of 1,4-*cis*-polybutadiene mediated by a large library of Group 4 metallocene and post-metallocene complexes. A strong dependence of molecular kinetics on catalyst structure was highlighted, and efficient catalysts were identified. This part of the project was a collaboration with Prof. Adam S. Veige at the University of Florida (Gainesville, FL).

From the conclusions of the project, which are summarized in **Chapter 8**, it is well evident that 'smart' HTE methodologies are ideally suited to rapidly identify novel and convenient routes of olefin polymerization and polyolefin/polydiene depolymerization that can improve the sustainability of these ubiquitous and important industrial processes and materials, making them ultimately better suited to a circular economy.

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CHAPTER 2

The Integrated HTE Polyolefin Workflow at LSP

2.1 Introduction

The first applications of HTE in polyolefin catalysis date back to the late 1990s. As was noted in Chapter 1, the leading workflow was developed in the framework of a strategic alliance between Symyx Technologies and Dow Chemical, with the aim to accelerate catalyst discovery.¹ The strategy was to carry out a very large number of polymerization experiments in a suitably small scale and rapid sequence mode under robotic control, with the ability to assess in semi-quantitative fashion catalyst productivity and, to some extent, polymer composition and microstructure without introducing bottlenecks (Figure 1.6).

The workflow started with a primary screening phase, in which an easy-tohandle liquid olefin (e.g., 1-hexene or 1-octene) was polymerized in large arrays of small glass vials (0.25 mL working volume), and catalytic activity was estimated by spotting the released reaction heat with IR sensors. Highly active catalysts ('hits') were moved to a secondary screening phase, where gaseous monomers such as ethene or propene could be homopolymerized or copolymerized under pressure in arrays of 48 or 96 mini-reactors (5-6 mL working volume each), and the polymers characterized by means of Rapid-GPC, to determine average molecular weight (M_n and M_w) and molecular weight distribution (MWD), and IR on cast films for measuring chemical composition (e.g., ethene/1-alkene copolymers) or stereoregularity (polypropylene). Catalysts yielding polymers with interesting properties ('leads') where then moved on to a conventional optimization stage.

The research group of the Laboratory of Stereoselective Polymerization (LSP), which hosted the present PhD project, was exposed to the Symyx/Dow approach in the framework of collaborations with both companies. They soon realized that the secondary screening platform (Symyx Parallel Pressure Reactor, PPR48) was amenable to a conceptually different utilization, that is the rapid exploration of catalyst and polymer variables hyperspaces, aimed to buildup comprehensive structure-properties databases of use in HTE catalyst optimization cycles, under the guidance of an appropriate statistical model. To this end, they integrated the PPR48 setup with an array of high-end polymer characterization tools compatible with high-throughput operation, including Rapid Gel Permeation Chromatography (Rapid GPC, to measure MW and MWD), analytical Crystallization Elution Fractionation (aCEF, to measure the distribution of crystallinity), and high-temperature cryoprobe ¹H and ¹³C NMR (for a full assessment of the microstructure).

This new project had the ambition to move one more step forward, by implementing and validating 'smart' HTE protocols meant to address problems of relevance in the context of polyolefins in a circular economy, including the synthesis of novel polymers and the re-utilization of materials at the end of their life cycle. In this chapter, we briefly illustrate the technology and some representative operation protocols. In particular, Section 2.2 introduces the olefin polymerization workflow (using ethene/1-hexene CCTP as a convenient example), whereas Section 2.3 describes the polymer degradation workflow.

2.2 The olefin polymerization workflow

The main platforms and units in this workflow are listed in Table 2.1.

Part/Function	Operation	Platform/Analytical Tool		
Catalyst Screening	Toring/Waighing	Mettler-Toledo		
	ranng/weigning	Bohdan Balance Automator		
	Olefin Polymerization	Freeslate PPR48		
		Genevac EZ-2 Plus Drying Station		
	Polymer Drying	Martin Christ		
		RVC 2-33 CDplus		
Polymer Characterization	GPC Analysis	Freeslate Rapid GPC		
	Crystallization Elution	Dolumor Char of FF		
	Fractionation	Folymer Chai aCEF		
		Bruker Avance III 400		
	11/13C NMP Analysis	spectrometer with		
	n/ C INIVIK Allalysis	high-temperature cryoprobe and		
		robotic pre-heated sample changer		

Table 2.1. List of the main HTE platforms and integrated tools.

2.2.1 Freeslate Parallel Pressure Reactor (PPR48)

All olefin polymerization experiments of this project were carried out using a robotically operated Freeslate (former Symyx) Parallel Pressure Reactor (PPR) setup^{2,3} featuring 48 reaction cells (each of 5-6 mL working volume) with individual on-line control, arrayed in six 8-cell modules integrally contained in a glovebox environment (Figure 2.1). Each module can be operated between 40 and 200°C (± 0.1 °C), and 20 and 495 psi (± 1 psi), with efficient magnetically coupled mechanical stirring (up to 800 rpm). Solution or slurry polymerization reactions are run in semi-continuous (semi-batch) mode. Two Vortex stir plates (800 rpm), each fitted with a rack for 6×8 1.2 mL vials or 2×5 8.0 mL vials, accommodate the catalyst system components (namely (pre)catalyst, cocatalyst, activator, modifiers (if any), scavengers, etc) which can be pre-contacted at the glove-box temperature (25°C). The injection system consists of a dual-arm robot adopting different technologies for catalyst solutions and slurries, with specialized needles and injectors. The slurry needle, in particular, is designed so as to pierce the pressure-tight rubber gas caps of the reaction cells and dispense the catalyst slurry directly into the liquid phase (Figure 2.2); this ensures a highly accurate and precise dosing. Solvents, diluents and monomers are fed through syringe pumps (liquids) or direct lines with solenoid valves plumbed to the individual cells (gases).

The PPR software enables the operator to change the Design of Experiment (DoE) of the planned set of 48 polymerization experiments ('Library') during execution. To take full advantage of this option a rapid-sequence injection mode was adopted with a delay between consecutive catalyst injections long enough to assess the early phases of each experiment before launching the following one. A detailed illustration of the software package and commands has been reported elsewhere.⁴



Figure 2.1. Overall view of the Freeslate PPR48 setup (top), and close-up of the 6 reaction modules with the 48 reaction cells (bottom).



Figure 2.2. Close-up of the PPR slurry injection needle (left), and schematics of needle and injector port (right).

2.2.2 Olefin polymerization protocol

In this section we describe the optimized operating protocol using ethene/1hexene copolymerization under CCTP regime as a representative example. Adaptations to different cases will be highlighted in the following chapters when necessary.

Prior to the execution of a library, the PPR modules undergo 'bake-andpurge' cycles overnight (8 h at 90-140°C with intermittent dry N₂ flow), to remove any contaminants and left-overs from previous experiments. After cooling to glove-box temperature, the modules stir tops are taken off, and the 48 cells are fitted with disposable 8 mL glass inserts (pre-weighed in a Mettler-Toledo Bohdan Balance Automator) and polyether-ether-ketone (PEEK) or titanium stir paddles. The stir tops are then set back in place, and the cells are loaded with the appropriate amounts of (a) an alkane diluent, (b) the 1-hexene comonomer, and (c) a MAO scavenger solution, they are thermostated at the desired temperature, and brought to the operating pressure with ethene. At this point, the catalyst injection sequence is started; aliquots of (a) an alkane 'chaser', (b) a solution of the (pre)catalyst, (c) an alkane spacer, solutions of (d) N,N-dimethylanilinium tetrakis-perfluorophenylborate (AB) activator and (e) the DEZ CSA, and finally (f) an alkane 'buffer', are uploaded into the needle and subsequently injected into the cell of destination, thus starting the reaction. This is left to proceed under stirring (800 rpm) at constant temperature and pressure, feeding ethene continuously on demand for a desired time (usually between 1 and 30 min), and quenched by over-pressurizing the cell with 50 psi (3.4 bar) of dry air (preferred over other possible catalyst quenchers because in case of cell or quench line leakage oxygen is promptly detected by the

dedicated glove-box sensor). Once all cells have been quenched, the modules are cooled down and vented, the stir-tops are removed, and the glass inserts containing the reaction phases are taken out and transferred to a centrifugal evaporator (Genevac EZ-2 Plus or Martin Christ RVC 2-33 CDplus), where all volatiles are distilled out and the polymers are thoroughly dried overnight.

Reaction yields are double-checked against on-line monomer conversion measurements by robotically weighing the dry polymers while still in the reaction vials, subtracting the pre-recorded tare. Polymer aliquots are then sent to the characterizations.

It has been demonstrated that, despite the extensive miniaturization, a properly operated PPR platform can yield kinetic information on olefin polymerization reactions with similar precision and accuracy compared with those of conventional bench reactors, and a 48-fold throughput intensification.²⁻⁴

2.2.3 Polymer characterization tools and protocols

Accelerating polymer characterizations so as to accommodate the throughput of the PPR48 setup was all but a simple task. The typical yields of PPR cells are in the range of 0.1 to 0.3 g, whereas most standard methods for the assessment of polyolefin materials require much larger sample amounts, particularly for quality control. Moreover, all said methods take longer than what is necessary for integration with a HTE platform without generating bottlenecks.⁵ At LSP this challenge was successfully met with adaptations and customizations of commercial instruments.

GPC curves were recorded with a Freeslate Rapid GPC setup (Figure 2.3), equipped with a set of 2 mixed-bed Agilent PLgel 10 µm columns and a Polymer Char IR4 detector. The upper deck of the setup features a sample dissolution station for up to 48 samples in 8 mL magnetically stirred glass vials. With robotic operation, pre-weighed polymer amounts (typically 2 to 4 mg) were dissolved in proper volumes of orthodichlorobenzene (ODCB) mL⁻¹ of 4-methyl-2,6-di-*tert*-butyl-phenol mg containing 0.40 (butylhydroxytoluene, BHT) as a stabilizer, so as to obtain solutions at a concentration of 0.5 to 1.0 mg mL⁻¹. After 2 h at 150°C under gentle stirring to ensure complete dissolution, the sample array was transferred to a thermostated bay at 145°C, and the samples were sequentially injected into the column line at 145°C and a flow rate of 1.0 mL min⁻¹. In post-trigger delay operation mode, the analysis time was 12.5 min per sample. Calibration was carried out with the universal method, using 10 monodisperse polystyrene samples (M_n between 1.3 and 3700 kDa). Before and after each campaign, samples from a known PP batch produced with an *ansa*-zirconocene catalyst were analyzed for a consistency check.



Figure 2.3. Overall view of the Freeslate Rapid GPC setup (top), and close-up of the robotic sample preparation deck (bottom).

Analytical Crystallization Elution Fractionation (aCEF)⁶ curves were collected with a Polymer Char aCEF setup (Figure 2.4), equipped with an autosampler (42 wells), an IR5 detector and a dual capillary viscometer detector. With robotic operation, pre-weighed polymer samples (typically 8-16 mg) were dissolved in ODCB added with 0.40 mg mL⁻¹ of BHT stabilizer, so as to achieve a concentration of 2.0 mg mL⁻¹. After 90 min at 150°C under vortexing in sealed vials to ensure complete dissolution, the samples were sequentially charged into the injection loop, where they were held at 95°C for 5 min and then moved into the column. The crystallization step entailed a 2°C/min cooling ramp down to -15°C at a flow rate of 0.065

mL min⁻¹; 1 min after reaching -15°C, sample elution was started, with a 4°C min⁻¹ heating ramp up to 150°C at a flow rate of 1.0 mL min⁻¹. The analysis time was 120 min. The amount of material eluted at -15°C will be referred to as the Amorphous Fraction (AF). Elution peaks are associated with elution temperature values (T_{el}) corresponding to their maxima.



Figure 2.4. The Polymer Char aCEF setup.

Quantitative ¹H and ¹³C NMR spectra at 400 MHz and 100 MHz respectively were recorded with a Bruker Avance III 400 spectrometer (Figure 2.5) equipped with a 5 mm high-temperature cryoprobe and a robotic sample changer with pre-heated carousel (24 positions). The samples (\approx 30 mg) were dissolved at 120°C in tetrachloroethane-1,2-*d*₂ (0.7 mL) added with 0.40 mg mL⁻¹ of BHT stabilizer, and loaded in the carousel maintained at the same temperature. The spectra were taken sequentially with automated tuning, matching and shimming. Operating conditions were: [¹H NMR] 90° pulse; 2.0 s acquisition time; 10 s relaxation delay; 16-32 transients; [¹³C NMR]: 45° pulse; 2.3 s acquisition time; 5.0 s relaxation delay; 400-3K transients (depending on the polymer sample nature and on the microstructural information needed). Broad-band proton decoupling was achieved with a modified WALTZ16 sequence (BI_WALTZ16_32 by Bruker). Resonance assignment was based on the literature.⁷⁻⁹ Whenever needed, spectral simulation was carried out using the SHAPE2004 software package (M. Vacatello, Federico II University of Naples). Thanks to the superior signal-to-noise ratio (S/N) of the used high-temperature cryoprobe (approximately 10-fold larger than for a standard probe), the analysis time for quantitative ¹³C NMR measurements was in the range of 15 to 60 min. Cumulatively, the three aforementioned characterizations require roughly 50 mg of polymer.



Figure 2.5. Overall view of the Bruker Avance III 400 NMR spectrometer (top), and close-up of the pre-heated robotic sample-changer (bottom).

2.3 The polymer degradation workflow

This workflow, featuring a Freeslate Extended Core Module (XCM) platform and a Freeslate High Pressure (HiP) reactor, was configured specifically for the screening of molecular catalysts for polyolefin chain scissoring, moving from the Schwartz's catalyst archetype (Cp₂ZrHCl).¹⁰

2.3.1 Freeslate Extended Core Module (XCM) platform

This platform (Figure 2.6) is a state-of-the-art setup for parallel organic and organometallic operations. Housed in a triple high-performance MBraun LabMaster glove-box, it enables the robotic handling, weighing and dispensing of air/moisture-sensitive compounds in the solid, liquid or slurry state according to fully automated protocols. The main features are:

- Two independent robotic arms bearing a vial gripper (right arm), and dedicated needles for handling solutions (right arm) and slurries (left arm)
- Heated/cooled reaction decks (arrays of 96x1 mL, 24x4 mL, 24x8 mL, 8x20 mL vials with individual magnetic stirring)
- Internal deck-integrated analytical balance (Sartorius WZ614-CW), with ion-suppressor system
- PowderniumTM Automated Powder Dosing System
- − SavantTM SpeedvacTM SPD121P centrifugal evaporator
- Solvent purification system (MBraun SPS-800, integrated off-line)
- Two High Pressure (HiP) reactors for primary screening purposes
- Freeslate LEA[®] software package (PPR Client[®], Library Studio[®], PolyView[®], Epoch[®], Impressionist[®]);

- Renaissance Application Server
- Oracle Database Server



Figure 2.6. Overall view of the Freeslate Extended Core ModuleTM setup (top), and close-up of the reaction deck (bottom).

2.3.2 Freeslate High Pressure (HiP) reactor

This reaction setup is designed for parallel reaction screenings under pressure (Figure 2.7). It consists of a 96-well stainless steel plate accommodating 0.8-1.0 mL glass vials with individual magnetic stirring

(Figure 2.7-right), and a pressure-tight stainless steel cover with SwagelokTM fittings and an analogic manometer (Figure 2.7-left). The reaction block can be operated up to 200 $^{\circ}$ C and 25 bar.



Figure 2.7. Overall view of High Pressure (HiP) reactor.

2.3.3 Polymer degradation protocols

The main application of this workflow in the context of the present project was the investigation of polybutadiene (PB) catalytic chain scissoring.

Recently, it has been reported that the combination of Cp₂ZrCl₂ and tri*-iso*butyl-Aluminum (TiBAl) is active for catalytic hydrogenolysis.¹⁰ This process is considered to involve the *in situ*-generation of a Zr-H active species and the subsequent hydrozirconation–transmetalation steps. A HTE protocol was implemented in order to screen molecular Group 4 metal catalysts for activity in the aforementioned reaction. In a typical library of experiments, an array of up to 96 0.8 mL glass vials, pre-treated for at least 12 h at 200°C under vacuum, are fitted with ParyleneTM coated magnetic mini-stir bars, and placed into the 12x8 HiP block, which is then positioned in a XCM deck bay. To each vial are added aliquots of a toluene solution of: (a) a PB sample, (b) an organoaluminum reagent (TiBA1 or MAO), and (c) the (pre)catalyst. The reactor is closed and heated to the desired temperature, under magnetic stirring (800 rpm). Molecular H₂ at high pressure can be added. The system is left to react for a desired time, after which the stirring is stopped and the reaction is quenched with O₂. The vials are then transferred outside the XCM glovebox, and the contents characterized by means of Rapid-GPC.

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CHAPTER 3

A HTE Approach to Chain Shuttling Polymerization

3.1 Introduction

3.1.1 $Infuse^{TM}$ materials

Olefin block copolymers (OBCs) represent the latest breakthrough in polyolefin materials. Their production entails the combination of CCTP with tandem catalysis, a process commonly referred to as 'Chain Shuttling'.¹ Ethene/1-octene (E/O) OBCs, in particular, are currently commercialized by Dow Chemical under the InfuseTM tradename.² In the Introduction, we have illustrated the peculiar microstructure and architecture of these materials, and the resulting thermoplastic elastomeric properties. Yet, the details are not available; in fact, average block lengths, numbers and distributions thereof are not precisely disclosed by the producer. Moreover, it has been observed that typical InfuseTM samples can be separated into comparable amounts of a completely amorphous fraction and a semicrystalline fraction, which is not expected for a true OBC, and points to an extensive interchain dis-uniformity of unclear origin(s).^{3,4}

Figure 3.1 shows the aCEF traces of two representative InfuseTM samples (grades 9107 and 9507), recorded at the LSP. Upon elution, both separated into an amorphous fraction (AF) corresponding to about 50 wt%, and a

semicrystalline fraction featuring a broad peak.⁵ Preparative fractionation of the samples by Kumagawa extraction with boiling hexane confirmed the aCEF results (Table 3.1): for each grade, a boiling-hexane-insoluble (i-C₆) and a boiling-hexane-soluble (s-C₆) fraction were isolated. The comonomer distributions, determined by ¹³C NMR and subjected to statistical analysis^{6,7}, indicated that the amorphous s-C₆ fraction is a purely *random* E/O copolymer, whereas the semicrystalline i-C₆ fraction can be a true OBC with hard and soft blocks. This data, however, is not enough to unambiguously determine the chain architecture of the samples, nor to clarify the origin of the purely random E/O copolymer fraction.



Figure 3.1 aCEF curves of two commercial InfuseTM samples (grade 9107 (A) and 9507 (C)), and of the i-C₆ fraction of the former (B); see text. Reprinted with permissions from Ref. 5. Copyright © 2018 American Chemical Society.⁵

		¹³ C NMR		GPC		aCEF		
Fraction	(wt%)	$x_0^{(a)}$	ws ^(b) (wt%)	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$	AF ^(c) (wt%)	T _{el,max} ^(d) (°C)
Grade 9107								
Raw		0.16	0.86	63	156	2.5	41.0	94.1 107.0
s-C ₆	41.1	0.20		43	113	2.6		
i-C ₆	58.9	0.14		90	188	2.1		
			(Grade 95	07			
Raw		0.17	0.89	38	101	2.7	46.1	84.3 104.7
s-C ₆	53.0	0.20		35	89	2.5		
i-C ₆	47.0	0.14		49	117	2.4		

Table 3.1. Results of analytical and preparative fractionation for two commercial InfuseTM samples.

(a) Mole fraction of 1-octene units. (b) Weight fraction of soft blocks. (c) Amorphous fraction; material eluted at -15°C. (d) Maximum elution temperature.

3.1.2 HTE methods for molecular kinetic investigations of E/H CCTP

In order to shed some light into this ill-defined scenario, prior to the beginning of the present project, the LSP started a molecular kinetic HTE project on ethene/1-hexene (E/H) CCTP.⁵ The choice of H rather than O was only due to practical reasons.

In a first part of the study, the two catalysts used by Dow, originating from the bis(phenoxyimine)Zr precursor **1** and the (pyridylamido)Hf precursor **2** (Figure 3.2), were investigated individually in random E/H copolymerization. All experiments were carried out in alkane solution at 100°C using the PPR platform. The catalyst system formulation included the (pre)catalyst(s), *N*,*N*-dimethylanilinium tetrakis-perfluorophenylborate (AB), methylalumoxane (MAO), and diethyl-Zinc (DEZ) as the CSA. In preliminary multiple-activation studies this formulation, which includes

two activators one of which can also function as a scavenger, was identified as the one ensuring the best reaction performance in terms of catalyst productivity and reproducibility.⁵



Figure 3.2. The bis(phenoxyimine)Zr (1) and (pyridylamido)Hf (2) catalyst precursors. Bn = Benzyl.

Plots of copolymer M_n vs yield (Y) (Figure 3.3) were clearly indicative of CCTP⁸: the function was quasi-linear for **2**, whereas the asymptotic behavior observed for **1** was ascribed to the interference of slow β -H elimination. The observed trend of the PDI, which decreased slightly with increasing yield (Table 3.2), was traced to slow initiation^{9,10} entailing the buildup of the pool of 'dormant' chains on Zn starting from DEZ. Similar observations for E/O CCTP in the presence of **2** with trioctyl-Al as the CSA had been reported before.¹¹ It is also worthy to recall that both catalysts are characterized by multiple active species: **1** speciates into several non-interconverting conformational isomers ¹², whereas **2** undergoes an in-situ ligand diversification by comonomer insertion into the strained *ortho*-metalated bond of the naphthyl fragment.^{13,14}



Figure 3.3. M_n vs Y for random E/H copolymers prepared with 1 and 2 under CCTP at [Zn]/[TM] = 100 ($T = 100^{\circ}$ C, $p_E = 11$ bar, $v_H = 0.500$ mL, [E]/[H] = 0.60). Reprinted with permissions from Ref. 5. Copyright © 2018 American Chemical Society.

Catalyst	Entry	[Zn]/[TM]	Y (mg)	Mn (kDa)	Mw (kDa)	M _w /M _n	<i>х</i> н (mol%)
1	1	0	23	109	629	5.8	0.37
	2		28	6	11	1.8	0.36
	3	100	80	16	27	1.7	n.d.
	4		134	22	34	1.6	0.36
	5		141	24	37	1.5	n.d.
2	6	0	35	734	1.6×10^{3}	2.2	13
	7	100	50	13	22	1.8	13
	8		141	26	45	1.7	15
	9		164	38	63	1.6	15
	10		234	45	72	16	17

Table 3.2. Selected E/H CCTP results at 100°C with catalysts 1 and 2 (see text).

An important question is how E/H CCTP is impacted by the nature of the last-inserted unit of an active copolymer chain. It is known that the local chemical structure of the growing polymeryl affects the trans-alkylation

behavior of a given catalyst.^{9,10} In particular, **2** was shown to be far less prone to propene¹⁵ or O¹⁶ CCTP compared to ethene. Moreover, in a previous E/O CCTP study¹¹ trans-alkylation by trioctyl-Al of chains with a last-inserted O unit was reported to be negligible, likely due to the prohibitive steric demand of the hetero-dinuclear Hf- $(\mu$ -R₂)-Al adducts. For the systems investigated here, valuable information came from ¹H NMR chain-end analysis data. The reaction quench protocol with dry air (see Section 2.2) generated OH-terminated chains, due to the reaction of O_2 with all M-polymeryl species present in the system (M = Hf and MGM) followed by hydrolysis upon workup. Terminal HO-containing structures give characteristic ¹H NMR signals in the region of $\delta = 3.5$ to 4.0 ppm downfield of TMS (Figure 3.4), whose assignment was reported before.¹⁷ Differentiating and quantifying chains quenched at a last-inserted E or H unit was straightforward. With no DEZ in the catalyst system, OHterminated copolymer chains were undetectable in the products; this indicates that (irreversible) chain transfer to MAO (and/or to trimethyl-Al in equilibrium with it) was negligible. On the other hand, copolymers produced in the presence of DEZ featured clear ¹H NMR signals due to HO-CH₂-CH₂P as well as HO-CH₂-CH(Bu)P chain ends (Bu = butyl). At low Y, the mole fraction of the latter $(x_{H,OH})$ was close to that of H units $(x_{\rm H})$ in the copolymers, as measured by ¹³C NMR; with increasing Y, though, a clear tendency of $x_{H,OH}$ to increase was observed (Figure 3.5). The conclusion was that, under the used conditions, the shuttling of chains with a last-inserted H unit was slightly slower than that of chains with a lastinserted E unit, possibly due to the more open environment of Zn compared with Al centers.^{11,16}



Figure 3.4. ¹H NMR spectra of E/H copolymer samples produced with **2** in the absence (A) or in the presence of DEZ at two different yields (Y = 50 mg (B); 271 mg (C)). Signals labelled as (a) and (b) can be assigned to HO-C**H**₂-CH2(P) and HO-C**H**₂-CH(Bu)(P) chain ends, respectively.¹⁷ In the insert, a part of the HSQC-DEPT spectrum of sample B is also shown. Reprinted with permissions from Ref. 5. Copyright © 2018 American Chemical Society.



Figure 3.5. Plots of $x_{\rm H}$ (•) and $x_{\rm H,OH}$ (**I**) *vs Y* for E/H copolymers prepared with **2** under CCTP at [Zn]/[TM] = 100 ($T = 100^{\circ}$ C, $p_{\rm E} = 11$ bar, $v_{\rm H} = 0.500$ mL, [E]/[H] = 0.60). Reprinted with permissions from Ref. 5. Copyright © 2018 American Chemical Society.

3.2 Results and discussion

3.2.1 Mechanistic study of CSP and in-house replication of $Infuse^{TM}$ -type OBCs

The objective of the subsequent work was to produce OBCs reproducing Dow's InfuseTM materials. Tandem catalysis CSP experiments were carried out under conditions otherwise identical to those optimized for CCTP with single catalysts (Section 3.1.2). Running CSP in HTE semibatch mini-reactors is a very demanding exercise, and the results should be regarded as semiquantitative. This notwithstanding, we shall see that OBC samples closely mimicking InfuseTM commercial grades were indeed obtained, and a thorough exploration of the variables hyperspace provided the first complete understanding of the process and products thereof.

1 is much less reactive towards O than **2**;^{2,18} therefore, at a given [E]/[O] feeding ratio O-poor ('hard') and O-rich ('soft') copolymers are produced at **1** and **2**, respectively. Fast and reversible trans-alkylation of the growing chains with the CSA leads to statistically distributed hard-soft multiblock architectures.^{2,18} In our hands the two catalysts turned out to have very similar productivities, despite the widely different H incorporation abilities.¹⁸ As expected, **1** showed a very poor comonomer affinity: at [E]/[H] = 0.35 we measured by ¹³C NMR an incorporation of $x_{\rm H} = 0.6$ mol%. On the other hand, **2** confirmed to be a good H incorporator, since at the same feeding ratio, we measured $x_{\rm H} = 20$ mol%.

We carried out several replicates of E/H Chain Shuttling (CS) reactions at two different [1]/[2] ratios, namely 1:1 and 1:4, at [Zn]/[1+2] = 50. We decided to focus our attention on these catalysts ratios in order to obtain

OBCs with similar contents of HDPE-like hard blocks and LLDPE-like soft blocks (catalyst ratio 1:1), or with an excess of the latter (catalyst ratio 1:4) which is desirable for achieving thermoplastic-elastomeric properties.^{1,18,19} As a matter of fact, commercial InfuseTM OBCs typically feature a weight fraction of soft blocks around 80%.

In Figures 3.6 and 3.7 we report the aCEF profiles of two sets of E/H OBC samples produced in series of replicate experiments (8 each) run at the aforementioned [1]/[2] ratios: within each set, the reproducibility was truly remarkable. The sample set corresponding to [1]/[2] = 1:1 (EH9 - EH16; Figure 3.7 and Table 3.4) featured a uniform microstructure and architecture, with a single and sharp aCEF elution peak. On the other hand, the sample set obtained at [1]/[2] = 1:4 (EH1 - EH8; Figure 3.6 and Table 3.3) was separated into a semicrystalline fraction (broad elution peak around 90-110°C) and a predominantly amorphous fraction (two peaks around -15°C and 10°C), similarly to InfuseTM materials.⁵


Figure 3.6. aCEF profiles of E/H OBCs produced at [Zn]/[TM] = 50 and [1]/[2] = 1:4. The trace of a commercial InfuseTM grade is shown for comparison.



Figure 3.7. aCEF profiles of E/H OBCs produced at [Zn]/[TM] = 50 and [1]/[2] = 1:1.

This comprehensive set of data demonstrates that the molecular architecture of the OBCs produced by CSP is governed by the relative probabilities of chain shuttling (CS) between active TM species of the same (homo-CS) or different (hetero-CS) chemical identity. OBCs featuring long hard blocks and an excess of soft blocks are necessarily characterized by a pronounced interchain dis-uniformity: as a matter of fact, at the rather low [Zn]/[TM] ratio necessary for the former requirement, an excess of catalyst 2 over 1, in turn, results into the formation of a large amount of chains which underwent exclusively homo-CS events at 2, and therefore consist of soft blocks only. Under such condition, the features of commercial InfuseTM grades were well-reproduced in the PPR platform.

			GPC		¹³ C N	MR	aC	CEF
Sample	Y	Mn	Mw	<i>M/M.</i> ,	х н ^(а)	ws ^(b)	AF ^(c)	Tel,max ^(d)
ID	(mg)	(kDa)	(kDa)	17 1 W/17 1 II	(mol%)	(wt%)	(wt%)	(°C)
EH1	107	44	85	19	14 7	77 7	25.7	97.2
	107		05	1.9	11.7	,,.,	23.7	105.2
FH2	111	33	61	1.8	1/1 0	773	21.7	93.7
	111	55	01	1.0	14.9	11.5	21.7	103.8
ГЦ3	112	16	80	1.0	14.6	77 5	20.4	97.1
EIIJ	112	40	89	1.9	14.0	11.5	29.4	104.9
ГЦ/	129	52	102	1.0	15.9	017	27.0	95.4
EN4	120	55	102	1.9	13.8	01.7	57.9	104.5
ГЦ5	122	50	100	2.0	157	87 J	22.2	96.1
ЕПЭ	155	50	100	2.0	13.7	02.2	33.3	104.4
FII4	125	10	00	2.1	16.1	827	26.2	96.2
ЕПО	155	40	99	2.1	10.1	02.7	30.5	104.7
EH7	156	55	109	2.0	175	07 /	27.2	93.1
EU/	130	55	108	2.0	17.5	07.4	57.2	104.7
FIIO	175	11	80	1.0	15.0	02.2	20.4	91.7
EHS	1/3	44	00	1.8	13.8	03.3	29.4	102.6

Table 3.3. Results of the E/H CSP experiments at [1]/[2] = 1:4.

(a) 1-Hexene incorporation. (b) Weight fraction of soft blocks. (c) Amorphous fraction; material eluted at -15°C. (d) Maximum elution temperature.

			GPC			MR	aCEF		
Sample ID	Y (mg)	M _n (kDa)	M _w (kDa)	M _w /M _n	x _H ^(a) (mol%)	ws ^(b) (wt%)	AF ^(c) (wt%)	T _{el,max} ^(d) (°C)	
EH9	93	24	42	1.8	4.9	28.6	99	108.3	
EH10	93	33	61	1.9	5.2	29.0	99	107.9	
EH11	101	34	66	1.9	5.4	31.0	99	107.9	
EH12	102	27	48	1.7	6.2	33.9	100	107.2	
EH13	102	29	49	1.7	4.2	25.0	99	107.8	
EH14	105	35	65	1.9	5.9	33.5	99	107.6	
EH15	116	28	48	1.7	6.4	35.4	99	107.0	
EH16	145	36	68	1.9	5.9	33.5	99	107.5	

Table 3.4. Results of the E/H CSP experiments at [1]/[2] = 1:1.

(a) 1-Hexene incorporation. (b) Weight fraction of soft blocks. (c) Amorphous fraction; material eluted at -15°C. (d) Maximum elution temperature.

3.2.2 Chain architecture and morphology of $Infuse^{TM}$ -type OBCs

Based on the results of the previous section, we were able to estimate the average length and number of blocks for this family of OBCs with a simple molecular kinetic model.⁵

The number average length of a block of type-i (i = 1 [hard] or 2 [soft]) can be <u>BL</u>_i = $n(\underline{EL}_i)$ (n = 1, 2, 3...), where <u>EL</u>_i is the number average chain extension length at **1** or **2** (i.e., the average polymerization degree of the chain segment grown during one growth period in between two transalkylation events at said catalyst, under the given experimental conditions). Let us make the following, admittedly over-simplified assumptions:

I. For each catalyst, nominal and active catalyst concentration coincide

II. $k_{p1} = k_{p2} = k_p$

III. $k_{cs-ii} = k_{cs-ij} = k_{cs}$ (i.e., the specific rates of all chain shuttling events are the same)

The following relationships should then hold:

$$\underline{BL}_1 / \underline{BL}_2 \approx [\mathbf{1}] / [\mathbf{2}] \qquad (\text{at a given } [\text{Zn}]) \qquad (\text{Eq. 3.1})$$

$$\underline{EL}_1 = \underline{EL}_2 = \underline{EL} \tag{Eq. 3.2}$$

EL
$$\propto 1/[Zn]$$
 (at given [1] or [2]) (Eq. 3.3)

 $\underline{BL}_{i} \to \underline{EL} \text{ for } x_{CAT-i} \to 0$ (Eq. 3.4)

Of course, $\underline{BL}_1 = \underline{BL}_h$; $\underline{BL}_2 = \underline{BL}_s$; $M_{n,i} = \underline{BL}_i M_i^0$ (where M_i^0 is the reduced monomer mass of a block of type-i: in our conditions, $M_h^0 \approx 28$ Da, $M_s^0 \approx 39$ Da).

Furthermore, assuming that $T_{el,max}$ in the aCEF profile of an OBC sample is determined solely by the average length of the ethene homosequences in the hard blocks, the upper limit for $T_{el,max}$ should be dictated by the amount of H units in the hard blocks, $x_{H,h}$ (= 0.006 in the investigated case), and be reached for $L_h > 1/0.006$; otherwise, for $L_h \le 1/0.006$, the value of $T_{el,max}$ should be close to that for an E/O random copolymer with $1/x_H = L_h$ (corrected for the average length of the ethene homosequences in the soft blocks, in case L_h is not much greater than $1/x_{E,s}$).

Using an experimental $\{1/x_{\rm H}, T_{\rm el,max}\}$ correlation plot for a series of E/H random copolymers prepared with a molecular catalyst (Figure 3.8), we estimated $L_{\rm h}$ from $T_{\rm el,max}$ of the samples in Table 3.3. The length of the soft blocks, $L_{\rm s}$, was then derived considering that $L_{\rm s}/L_{\rm h}$ is directly proportional to the molar ratio of the specific catalyst pair used in the CSP experiments.



Figure 3.8. $T_{\rm el, max}$ vs $1/x_{\rm H}$ for a series of E/H random copolymers (see text). Reprinted with permissions from Ref. 5. Copyright © 2018 American Chemical Society.

Table 3.5. Estimated ranges of hard and soft block lengths (in monomeric unit numbers and kDa) and numbers for the OBC samples of Table 3.3.

Sample ID	<i>BL</i> _h (m.u.)	BL _s (m.u.)	M _{n,h} (kDa)	M _{n,s} (kDa)	$M_{\rm n}/(M_{\rm n,h}+M_{\rm n,s})$
EH1	45 - 84	112 - 209	1.3 - 2.4	4.4 - 8.2	8 - 4
EH2	37 - 74	89 - 179	1.1 - 2.1	3.5 - 7.0	7 - 4
EH3	45 - 82	110 - 200	1.3 - 2.3	4.3 - 7.8	8 - 5
EH4	40 - 79	127 - 251	1.1 - 2.2	5.0 - 9.8	9 - 4
EH5	42 - 78	138 - 257	1.2 - 2.2	5.4 - 10.1	8 - 4
EH6	42 - 80	142 - 271	1.2 - 2.3	5.6 - 10.6	7 - 4
EH7	35 - 80	172 - 393	1.0 - 2.3	6.7 - 15.4	7 - 3
EH8	33 - 66	117 - 234	0.9 - 1.9	4.6 - 9.2	8 - 4

Concerning the semicrystalline fraction, we trace the peculiar bimodal shape of the aCEF elution peak to the presence of chains with hard block length $BL_h = EL$ (eluted at $T_{el,max}$), or $BL_h = 2EL$ (eluted at a temperature

corresponding to the shoulder at the high temperature side of the peak). Indeed, the position of said shoulder is consistent with this hypothesis, based on the correlation plot of Figure 3.8. Simulation models in the literature are also in line with said interpretation.²⁰

Despite the rough approximations, and within the rather large experimental uncertainties, the values in Table 3.5 seem rather consistent, internally and with respect to Eq. 3.3. Therefore, they can be used on a semi-quantitative basis to describe sample architecture in the produced copolymers.

Notably, the results are in good agreement with those of an alternative independent approach that was recently proposed for estimating the average length of the hard blocks in the same or similar OBC samples from Small-Angle X-ray Scattering (SAXS) measurements (see Appendix, Table A3.1).²¹

Overall, we conclude that HTE tools and methods are suited to explore the complicated chemistry and physics of E/H CSP. On the other hand, some drawbacks of HTE cannot be denied. One is the low polymer yield of experiments in PPR scale, which is below what would be needed for typical structural and physico-mechanical characterizations. This limitation can be overcome by cumulating the yields of several PPR cells, provided that the reproducibility of replicate experiments is good enough. The aCEF traces in Figure 3.6 and the semi-quantitative measurements in Table 3.5 suggest that this may be the case; however, the question was investigated in more depth in the framework of a collaboration between LSP and the research group of Profs. Claudio De Rosa and Finizia Auriemma, funded by The Dutch Polymer Institute (DPI). A thorough study of the thermal (Differential Scanning Calorimetry, DSC), structural (X-ray) and

morphological (Transmission Electron Microscopy, TEM) properties of the samples of Figure 3.6 was undertaken. The structural and thermal characterizations showed that all feature melting and crystallization DSC peaks at \approx 120°C and \approx 100°C, respectively (Table A3.2). SAXS profiles and Lorentz corrected SAXS curves are reported in Figure 3.9; the SAXS analysis clearly indicated that the OBCs are structured over two hierarchical levels of organization, characterized by well distinct length scales corresponding to microphase separation of the hard and soft blocks in distinct domains. Comparison with a commercial InfuseTM OBC confirmed a close similarity (Figure 3.9). The morphology and crystallization behavior of the OBCs was also investigated by means of Transmission Electron Microscopy (TEM). As an example, in Figure 3.10 bright field TEM images of sample **EH6** are shown.



Figure 3.9. Comparison between the SAXS curves of PPR-made OBC samples and a commercial OBC grade (InfuseTM 9000). (A) SAXS desmeared profiles. (B) Lorentz corrected curves before (black) and after extrapolation at low and high q values (blue). The relevant correlation distances are indicated with dotted red lines.



Figure 3.10. Bright field TEM images of sample **EH6** (slow cooling, 10°C/min; staining RuO₄, 9h).

The image at low magnification (Figure 3.10-A) shows sheaves of lamellae splayed from center-nuclei, typical of spherulite superstructure. At higher magnification, a spotted pattern is visible (Figure 3.10-B). The bright regions correspond to the crystalline hard-block-rich domains, whereas the dark regions correspond to the amorphous soft-block-rich phase. The striped patterns in the bright regions represent PE lamellar crystals laying on-edge, tightly spaced by narrow amorphous layers. Edge-on lamellar crystals emanating from bright regions are present also in the dark regions. This indicates that the samples crystallize in a phase-separated morphology, where hard-block-rich domains are embedded in a soft-blockrich phase. In the former domains, crystallization of the orthorhombic form of PE occurs, thus producing well organized lamellar stacks.²¹ The soft blocks are, instead, rejected in separate domains. Furthermore, the edge-on lamellae crossing the soft domains reveal the occurrence of the so-called pass-through crystallization behavior. The phase-separated behavior and the occurrence of pass-through crystallization are key features in the morphology of commercial grades too.²²

All this considered, we can safely conclude that (a) OBCs produced in the PPR faithfully mimic commercial samples, and (b) PPR samples produced under the same conditions in independent reaction cells show identical behaviors, within the experimental error, and therefore can be cumulated for characterizations requiring large(r) sample amounts.

3.2.3 Improving OBC performance via reaction protocol

The average MW values of the OBC samples described in the previous section is appreciably lower than that of most commercial InfuseTM grades; this negatively affects the mechanical properties. Therefore, further E/H CSP experiments were carried out at higher comonomer concentration, so as to speed up chain propagation relative to chain transfer due to residual β -H elimination. The partial pressure of ethene was raised from 11 to 17 bar, and the amount of 1-hexene was adjusted so as to maintain the E/H feeding ratio at [E]/[H] = 0.35. Representative results are reported in Table 3.6 and Figure 3.11 (which includes data for sample **EH1** of Table 3.3 for comparative purposes). The desired increase in MW was indeed achieved, from an average M_n value of ≈45 kDa (Table 3.3) to ≈65 kDa (Table 3.6).

Notwithstanding the more demanding reaction protocol and conditions, the reproducibility of replicate experiments was good and the yields of several cells could then be cumulated for mechanical characterizations.

			GPC			MR	aCEF		
Sample ID	Y (mg)	Mn (kDa)	Mw (kDa)	M _w /M _n	x _H ^(a) (mol%)	ws ^(b) (wt%)	AF ^(c) (wt%)	T _{el, max} ^(d) (°C)	
EH17	102	57	112	2.0	13.9	77.3	16.4	98.9 106.2	
EH18	157	57	140	2.4	15.5	78.9	24.2	98.7 105.3	
EH19	191	68	151	2.2	17.6	84.0	33.9	97.0 104.9	
EH20	207	76	170	2.2	16.1	82.0	28.9	99.2 105.2	
EH21	216	73	163	2.2	16.1	79.5	28.3	99.2 105.1	

Table 3.6. Results of E/H chain shuttling experiments at 'high' monomer concentrations (see text).

(a) 1-Hexene incorporation. (b) Weight fraction of soft blocks. (c) Amorphous fraction; material eluted at -15°C. (d) Maximum elution temperature.



Figure 3.11. aCEF profiles of the OBC samples in Table 3.6 and of sample EH1 (Table 3.3), for comparison.

An OBC macro-sample obtained from merging samples **EH17-EH21** showed good ductility and remarkable strain hardening. The stress-strain curve turned out to be almost superimposable to those of two InfuseTM grades up to 500% deformation (Figure 3.12), which demonstrates that the PPR-made material matched the outstanding thermoplastic-elastomeric properties of commercial ones. On the other hand, the deformation at break (\approx 800%) was significantly lower, which we trace to technical difficulties in proper specimen preparation at very small scale.



Figure 3.12. Stress-strain curves of merged PPR samples EH17-EH21, and of commercial InfuseTM grades 9007 and 9107.

3.2.4 Improving OBC performance via catalysis

For CSP applications (pre)catalyst **1** has the drawback of an excessive propensity to β -H elimination. Therefore, new series of experiments were carried out with the homolog **3** (Figure 3.13), featuring a more hindered bis(phenoxyimine) ligand.^{12,23,24}



Figure 3.13.The chemical structure of (pre)catalyst 3 (Bn = Benzyl).

Comparative results of E/H CCTP experiments with catalysts 1 and 3 at [Zn]/[Zr] = 50 are shown in Figure 3.14 (for the raw data, see Table A3.4 in the Appendix). The improvement is evident on inspection.



Figure 3.14. M_n vs Y for E/H CCTP mediated by catalysts 1 (red dots) and 3 (blue dots); see text.

On top of a higher MW capability, the ¹H NMR spectra of the copolymers highlighted a significantly lower comonomer affinity of **3** compared with **1** (Table A3.4). This fact, which can also be traced to a more hindered active pocket, is highly desirable because it results into a higher crystallinity of the hard blocks produced at a given [E]/[H] feeding ratio.

An E/H CSP experiment was carried out with the **3**/**2** catalyst pair under conditions previously utilized for the **1**/**2** pair. In Table 3.7 and Figure 3.15, the main characterization results of the two homologous OBC samples are compared between them and with those of a commercial InfuseTM material (grade 9000). The improvements associated with the novel catalyst pair are clear.

Table 3.7. Main results of the characterization of homologous OBC samples made with catalyst pairs 1/2 (sample EH5) and 3/2 (sample EH22) at [Zr]/[Hf] = 1:4, and of InfuseTM grade 9000 for comparison.

			GPC		¹³ C N	MR	aCEF		
Sample ID	Y (mg)	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$	x _{H,s} ^(a) (mol%)	ws ^(b) (wt%)	AF ^(c) (wt%)	T _{el,max} ^(d) (°C)	
EH5	133	50	100	2.0	21.9	82.2	33	96.1 104.4	
EH22	178	76	162	2.2	24.0	76.4	15	95.7	
Infuse TM 9000	-	60	155	2.6	20.1	72.3	11	100.3	

(a) 1-Hexene content in the soft blocks. (b) Weight fraction of soft blocks. (c) Amorphous fraction; material eluted at 15°C. (d) Maximum elution temperature.



Figure 3.15. aCEF profiles for the OBC samples of Table 3.7.

A set of E/H CSP experiments with the 3/2 catalyst pair was carried out at higher comonomer concentrations ($p_E = 17$ bar, [E]/[H] = 0.175) and variable [Zr]/[Hf] ratio. The main results, reported in Table 3.8 and Figure 3.16, confirmed the higher MW value of the OBCs, and also – importantly – its stability throughout the explored range of hard/soft block compositions, at odds with the case of the 1/2 catalyst pair for which a drop of MW was associated with an increasing fraction of catalyst 1 in the catalytic pool.

			GPC			MR	aCEF		
Sample ID	[2]/[3]	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$	x _H ^(a) (mol%)	ws ^(b) (wt%)	AF ^(c) (wt%)	T _{el,max} ^(d) (°C)	
EH23	2.5	80	166	2.1	23.2	78.2	24	95.4	
EH24	2.0	72	158	2.2	18.8	67.8	7	100.3	
EH25	1.5	65	131	2.0	16.8	62.4	7	102.0	
EH26	1.0	59	121	2.1	13.4	51.8	5	102.5	

Table 3.8. Main results of the 2/3 E/H CS experiments at higher comonomer concentrations.

(a) 1-Hexene incorporation. (b) Weight fraction of soft blocks. (c) Amorphous fraction; material eluted at -15° C. (d) Maximum elution temperature.



Figure 3.16. aCEF profiles of the OBC samples in Table 3.8.

3.3 Concluding remarks

The scope and objectives of HTE as applied to polyolefin catalysis have been changing with time.²⁵ Initially aimed at catalyst discovery²⁶, at a later stage, HTE tools and methods proved to be very well-suited for rapid catalyst optimizations.^{27–30} In this chapter, we made use of HTE with yet another purpose, that is the thorough exploration of the variables hyperspace to unravel the molecular kinetics of a complex catalytic process. As a matter of fact, we managed to sort out for the first time the mechanistic details of ethene/1-alkene CSP as applied to the production of statistical OBCs (Dow InfuseTM technology).

In the following chapters, we will describe how the newly implemented HTE protocols were exploited to explore novel opportunities in olefin CSP.

3.4 Experimental part

3.4.1 Materials

All air-/moisture-sensitive chemicals were manipulated under argon or nitrogen using Schlenk techniques and/or MBraun LabMaster 130 glove boxes.

Precatalysts **1-3** were prepared in the research group of Prof. Alexander S. Voskoboynikov at Moscow State University (Russia) according to the literature.^{31,32} The specifications of all other chemicals are in Table 3.9.

Chemical	Supplier	Specifications
ISOPAR-G	Carlo Erba	>99.5%
Toluene	ROMIL	Purified by passing it in sequence through an A4-molecular-sieves and an activated-Cu fixed-bed column
1,2-Dichlorobenzene	ROMII	'Super pure solvent', >99.8%
(ODCB)	ROWIE	isomeric purity
$1,1,2,2$ -Tetrachloroetane- d_2	ARMAR Chemicals	99.5% isotopic purity
4-Methyl-2,6-di- <i>tert</i> -butyl- phenol (BHT)	Sigma-Aldrich	≥99.0 (GC)
Xylene	ROMIL	>99.5%
n-Hexane	ROMIL	>99.5%
Acetone	Carlo Erba	
Methylalumoxane (MAO)	Chemtura	$10 \% \text{ v/v in toluene}$ $[A1] = 1.64 \text{ M}$ $A1\text{Me}_3/A1_{\text{total}} \approx 20\%$
Diethyl-Zinc (DEZ)	Chemtura	>99.5%
Ethene (3.5)	Linde	Purified by passing through a
1-Hexene	Sigma Aldrich	mixed-bed activated-Cu/A4- molecular-sieves column

Table 3.9 List of used chemicals (with specifications).

3.4.2 Polymers synthesis

The synthesis of all OBC samples were performed using the HTE workflow and following the protocols described in Chapter 2. The reactions were carried out in ISOPAR-G (5.0 mL) at 100°C, $p_E = 11$ bar or 17 bar, [E]/[H] = 0.35. The (pre)catalysts (10-20 nmol) were activated with a combination of AB ([AB]/[TM] = 1.2) and MAO ($n_{AI} = 5.0-7.5 \mu$ mol), the latter also used for scavenging purposes. DEZ was the CSA ([Zn]/[TM] = 50).

3.4.3 Copolymer samples homogenization

The copolymer samples as obtained after the drying protocol can be macroscopically dis-uniform; therefore, a homogenization treatment was carried out prior to the characterizations. Each sample was dissolved in 5.0 mL of xylene containing 0.40 mg mL⁻¹ of 4-methyl-2,6-di-*tert*-butyl-phenol (BHT) as a stabilizer. After 2 h at 135 °C under gentle stirring, to ensure complete dissolution, the solutions were poured into an excess of acetone to coagulate the copolymers, which were then recovered by decantation and transferred to a centrifugal evaporator for final drying.

3.4.4 Polymer characterizations

The polymers were characterized by Rapid-GPC, aCEF and ¹³C NMR as reported in Chapter 2.

Calorimetric measurements were performed with a DSC-822 setup by Mettler Toledo, in a flowing N₂ atmosphere at a scan rate of 10°C min⁻¹, with heating-cooling-heating ramps from -70°C to 180°C.

SAXS data were collected at room temperature on isothermally crystallized samples, under vacuum, using a "SAXSess" equipment (Anton Paar KG), in the slit collimation configuration, with Cu K α radiation (wavelength λ = 1.5418 Å).

TEM micrographs were collected using a FEI TECNAI G2 200 kV TEM apparatus, operating at 120 kV and equipped with a 4K Eagle Camera. Polymer films for TEM analysis (with a thickness of 50–70 nm) were prepared via drop casting *para*-xylene solutions of 0.5 wt-% OBC on a glass slide. The obtained films were covered with carbon, floated on distilled water, and transferred to grids (300 mesh) for TEM analysis. Finally, the grids were exposed to RuO₄ vapors to stain the amorphous phase and enhance the morphological features.

The mechanical tests were performed at room temperature on melt crystallized compression-molded films with an Instron 5566 mechanical tester, following the standard test method for tensile properties of thin plastic sheeting ASTM D882.

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Appendix

Sample ID	l _c ^(a) (nm)	l _a ^(a) (nm)	$L_{hs}^{(a)}$ (nm)	M _h ^(b) (kDa)	M _{hs} ^(b) (kDa)	M _s ^(b) (kDa)	n ₁ ^(c)	n ₂ ^(c)	[hM _h -sM _s] _{n1/n2} ^(d)
EH1	8.11	1.81	37.4	1.7	7.6	5.9	5.8	11.2	[2H-6S] _{6/11}
EH2	7.62	1.68	44.9	1.5	6.4	4.9	5.1	9.5	[2H-5S] _{5/9}
EH3	8.17	1.81	35.9	1.7	7.5	5.8	6.1	11.8	[2H-6S] _{6/12}
EH4	10.23	1.81	33.2	1.7	9.2	7.6	5.7	11.0	[2H-8S] _{6/11}
EH5	8.06	1.74	34.5	1.6	8.8	7.2	5.7	11.4	[2H-7S] _{6/11}
EH6	6.67	1.81	35.9	1.7	9.8	8.1	4.9	10.1	[2H-8S] _{5/10}
EH7	9.79	2.12	32.0	2.3	18.4	16.1	2.9	5.9	[2H-16S] _{3/6}
EH8	6.54	2.11	37.4	2.3	13.8	11.5	3.2	5.8	[2H-11S] _{3/6}
Infuse TM 9000	5.70	2.10	31.0	2.3	8.2	5.9	7.3	18.8	[2H-6S] _{7/19}

Table A3.1. SAXS structural data for the OBC samples of Figure 3.6 and a commercial InfuseTM grade.

(a) lamellar parameters: long spacing (L), thickness of lamellar crystals (l_c) and of the amorphous layer (l_a), interdomain spacing (L_{hs}). (b) average MW of the hard (M_h), soft (M_s) blocks and hard-soft repeating unit (M_{hs}). (c) average number of blocks. (d) MW of blocks in a hs repeating unit and number of blocks/chain.

Sampla ID	T ^I m(a)	$\Delta H^{I}_{m}(a)$	T_{m}^{II}	$\Delta H_{m}^{II}(b)$	T _c (c)	$\Delta H_{c}^{(c)}$
Sample ID	(°C)	(J/g)	(°C)	(J/g)	(°C)	(J/g)
EH1	121.7	37.0	120.4	33.4	103.1	32.8
EH2	121.1	37.1	120.2	38.1	104.6	36.1
EH3	120.9	37.7	120.4	34.8	102.1	32.9
EH4	120.2	26.0	119.1	24.5	98.6	24.3
EH5	120.6	31.8	119.3	27.5	99.9	26.7
EH6	120.7	29.2	119.9	26.6	100.3	25.1
EH7	119.9	20.3	118.6	18.9	96.6	19.8
EH8	119.9	30.4	119.1	28.4	100.1	28.4

Table A3.2. DSC characterization data for the OBC samples of Figure 3.6.

(a) 1st melting temperature and corresponding melting enthalpy. (b) 2nd melting temperature and corresponding melting enthalpy. (c) Crystallization temperature and corresponding crystallization enthalpy.

Table A3.3. Main characterization results of E/H copolymers at higher ethene pressure ([Zn]/[TM] = 50).

				GPC			
Sample ID	Catalyst	Y (mg)	Mn (kDa)	Mw (kDa)	M _w /M _n	xH ^(a) (mol %)	
EH27	1	160	32	65	2.0	0.6	
EH28	2	272	77	162	2.1	21.6	

(a) 1-Hexene incorporation.

Catalyst	<i>n</i> Zr	[7n]/[7n]	t	Y	Mn	Mw	M /M	$x_{\mathrm{H}^{(b)}}$
Cuturyst	(nmol)	[Zn]/[Zr]	(min)	(mg)	(kDa)	(kDa)	///w/////n	(mol%)
			7	29	12	39	3.3	
			18	37	14	30	2.1	
			3	58	20	40	2.0	
			10	68	19	37	2.0	
			5	73	23	47	2.0	
			2	90	22	39	1.8	
1	20		11	102	25	52	2.1	1
1	20		2	107	22	42	1.9	1
		50	4	128	29	58	2.0	
			3	135	28	55	1.9	
			3	135	28	54	1.9	
			3	146	26	50	1.9	
			4	163	29	54	1.9	
			3	167	28	60	2.1	
			1	64	43	84	1.9	
3			4	94	50	104	2.1	
			2	94	51	99	1.9	
	10		4	104	52	105	2.0	0.6
			10	124	62	123	2.0	
			10	188	64	127	2.0	
			4	200	62	98	1.6	

Table A3.4. Raw data for the E/H OBC samples of Figure 3.14. (a)

(a) $p_{\rm E} = 17$ bar, $v_{\rm H} = 2.7$ mL. (b) 1-Hexene incorporation.

CHAPTER 4

Searching for Other CCTP/CSP Catalysts

4.1 Introduction

After unraveling the molecular kinetics of ethene/1-alkene CCTP/CSP^{1,2}, expanding its scope in catalysis and polymer science looked like a most logical next step of this project. As discussed in the previous chapter, not only are E/O OBCs commercially applied for their unique elastoplastic properties, but bear high promise as phase compatibilizers, and can be exploited to address the problem of mechanical recycling of immiscible plastic wastes.³ Well-working applications to HDPE/EPDM and HDPE/iPP blends have already been reported (Figure 4.1).⁴ Theoretical studies support the educated guess that block structures result into a higher density of interfacial bridges than random structures, and thus provide better interfacial adhesion.⁵⁻⁷

In addition to the Dow InfuseTM materials, covered extensively in Chapter 3, the only other OBC class that made it to the market until now are HDPE*block*-iPP statistical diblocks (IntuneTM), also produced by Dow through CCTP with a two-stage process.^{1,8-10} On the other hand, a variety of TM catalysts and MGM alkyls have been claimed in the literature as amenable to olefin CCTP/CSP.^{11–13} The breakthrough that started it all was achieved by Dow scientists using HTE tools and methods^{8,14,15} that are still rather uncommon in standard organometallic chemistry labs.^{16–20} In addition to the large number of reactor cells facilitating rapid parallel explorations of the relevant reaction variables, an important asset of HTE platforms for CCTP experiments is the ease to operate at high temperature ($T > 100^{\circ}$ C), a mandatory and technically demanding requirement to maintain crystallizable polymer chains in solution and thus guarantee molecular mobility.²



Figure 4.1. SEM images of an uncompatibilized HDPE/iPP blend stretched to 5% strain (a); the same blend compatibilized with different polyolefin elastomers (b-e), and with an E/O OBC (f). Reprinted with permissions from Ref. 4. Copyright © 2009 Wiley Periodicals, Inc.

Convincing evidence has been reported that 1-alkenes are less prone to CCTP than ethene, likely due to a higher conformational rigidity and/or local steric demand of poly(1-alkene) chains.²¹⁻²³ As a matter of fact, extending the application of pyridylamido Hf(IV) catalysts from ethene to propene CCTP/CSP required a delicate optimization of the reaction system and conditions, including the use of a polar solvent (1,2-difluorobenzene, DFB) instead of standard nonpolar hydrocarbon media.²⁴ Nevertheless, several papers published since the late 1990s claimed stereoblock PP materials made by CSP, including [(iPP)-block-(sPP)]_n. Surprisingly, the catalyst pairs consisted of rather trivial ansa-zirconocenes, and were used in nonpolar or weakly polar solvents (e.g., toluene) at mild or even low temperature (down to 0° C!).²⁵⁻³² C₂-symmetric *rac*-bis(η^{5} -1-Indenyl) and C_s -symmetric (η^5 -Cyclopentadienyl)(η^5 -9-Fluorenyl) ansa-zirconocenes are the most popular molecular catalysts for the production of iPP and sPP, respectively. Recently, Descour³¹ explored the feasibility of propene CCTP/CSP in toluene or chlorobenzene at 30-50°C with rac-Me₂Si(2-Me-4-Ph-1-Ind)₂ZrCl₂ and Ph₂C(Cp)(2,7-di-tert-Bu-9-Flu)ZrCl₂. The two (pre)catalysts were activated with MAO, and used individually or in equimolar mixture with or without added DEZ. The polymers were characterized with a comprehensive array of techniques including ¹³C NMR, high-temperature GPC, DSC with Successive Self-Nucleation Annealing (DSC-SSA), Crystallization Fractionation Analysis (CRYSTAF), and high-temperature HPLC with a HypercarbTM column and a linear gradient 1-decanol/trichlorobenzene eluting phase. Based on the results of all characterizations, the authors concluded that [(iPP)-block-(sPP)]n materials were indeed produced by CSP in the tandem catalysis experiments.

Although stereoregular PP samples are (much) slower to precipitate from solution compared with PE, the aforementioned findings did not look obvious to us. In our opinion, any claims of propene CSP should be supported by a solid verification of CCTP for each individual catalyst in the pair. Unfortunately, that is less trivial than one may assume. Ideally, a polymer produced in the presence of a single-center molecular catalyst under CCTP regime should feature a Poisson distribution (PDI \approx 1.0). However, at odds with a common belief, many molecular catalysts are not single-center, and therefore do not yield monodisperse polymers. A most typical case are the two catalysts used by Dow for producing InfuseTM materials (Figure 4.2). As already recalled in Chapter 3, these catalysts do give CCTP and CSP of course but, for several different reasons (i.e., a multi-site nature for both 1 and $2^{33,34}$, the propensity of 1 to β -H elimination leading to 'dead' chains¹, the accumulation of chains with a last inserted H unit slowing reversible trans-alkylation^{2,21}), even in E/H CCTP they yield products with PDI ≈ 2.0 . From this one should conclude that measurements of PDI can be misleading when assessing CCTP/CSP.



Figure 4.2. The catalyst pair originally disclosed by Dow for the synthesis of E/O OBCs.

Another popular verification is based on fractionation experiments. On paper, whenever an amorphous polymer is not separated from a semicrystalline one by means of solvent extraction or column elution, one should conclude that the two polymers are *chemically* bound. In reality, the separation can be effectively hindered by *physical* entanglements, particularly when the average MW is high. A very low MW, in turn, can hamper significant fractionation experiments whenever MW effects dominate or even overwhelm microstructure-related ones.

In our opinion, an unambiguous indication of true CCTP is a linear dependence of average polymer MW on polymerization yield. Such a verification is rather demanding, because it requires the execution of several polymerization experiments under conditions that can be harsh (i.e., high catalytic activity, high temperature), but is well-feasible with HTE tools.

In the specific case of site-controlled isotactic-selective propene polymerization with racemic catalysts, a convenient alternative is the ¹³C NMR analysis of chain microstructure. Under CCTP (CSP) conditions, the product is stereoblock iPP with unmistakable $m_x(r)m_y$ block junctures (Figure 4.3), resulting from statistical exchanges of growing polymeryls between enantiomorphous catalytic species. The method was first demonstrated by Busico²⁴ for catalyst **2** of Figure 4.2.



Figure 4.3. The stereoblock-isotactic microstructure expected for an iPP sample produced under CCTP.

In this chapter, the aforementioned methods will be applied to verify the propensity of several metallocene and post-metallocene catalysts to propene CCTP.

4.2 **Results and discussion**

4.2.1 PP chain shuttling at ansa-metallocene catalysts: legend and reality

Ref. 31 is an ideal case history to illustrate the questions at the heart of the present chapter. In principle, discriminating between a physical blend of iPP and sPP and a true [(iPP)-block-(sPP)]n sample should be straightforward, because very different and distinctive MWDs (bimodal vs monomodal) and solubility behaviors (separable vs inseparable) are expected. On the other hand, real-world cases are not necessarily clearcut, in particular when the polymers have a low stereoregularity and/or average MW. The investigated catalyst pair is shown in Figure 4.4: rac-Me₂Si(2- $Me-4-Ph-1-Ind)_2ZrCl_2$ (4) is known to yield site-controlled highly stereoregular iPP. Ph₂C(Cp)(2,7-di-tert-Bu-9-Flu)ZrCl₂ (5), in turn, produces sPP under site control with regular site epimerization, and the stereoregularity of the polymer is only modest at room temperature or above, particularly at modest propene concentration.³⁵⁻³⁸ Therefore, a physical blend of the polymers made with e.g., 4/MAO and 5/MAO is easy to recognize and separate. The story is different when an efficient CSA such as DEZ is added: as soon as polymer MW drops to the point that the chains are waxy, the idiosyncratic effects of chain microstructure on the physical properties are lost. Unfortunately, that was indeed the condition

of Ref. 31: at $M_n < 5$ kDa, polymer solubility was not informative, and the ¹³C NMR stereosequence distribution was so heavily contaminated by the resonances of the chain ends that identifying hypothetical junctures between iPP and sPP blocks was impossible. Yet, the authors did not acknowledge the limitation, and assigned a stereoblock nature to the products.



Figure 4.4. The (pre)catalyst pair used in Ref. 31 (4 was used in racemic form).

The HTE workflow introduced in Chapter 2 was used to re-investigate the behavior of catalysts 4/MAO and 5/MAO, with or without added DEZ at different [Zn]/[Zr] ratios (Table 4.1).³⁹ The polymerization protocols were adapted from the previous CCTP/CSP studies.² All experiments were carried out at 50°C (the upper temperature tested in Ref.31), using DFB as the solvent.

In line with the previous literature^{35–38}, PP samples made with 4/MAO and 5/MAO turned out to be highly isotactic and moderately syndiotactic, respectively (Tables 4.1 and 4.2, samples **PP1** and **PP2**). When the two catalysts were used in mixture, no appreciable changes in polymer properties were noted (sample **PP3** of Table 4.2).

Table 4.1. Propene polymerization experiments in DFB at 50°C with 4/MAO and 5/MAO, with or without added DEZ.

Experiment ID	Calyst(s)	[Zn]/[Zr]	<i>n</i> zr (nmol)	t (min)	Y (mg)	R _p ^(b)
PP1	4		0.5	10	78	940
PP2	5	0	20	13	110	25
PP3	4 + 5 [4]/[5] = 1:30	Ū	15	8	189	95
PP4	4		1.5	10	61	240
PP5	5	100	1.5	20	71	10
PP6	4 + 5 [4]/[5] = 1:9	100	20	9	144	50

(a) $p_{\rm P} = 6.5$ bar, 25 µmol MAO. (b) $g_{\rm PP} \cdot \text{mmol}_{Zr}^{-1} \cdot \text{h}^{-1} \cdot$

 Table 4.2. Main characterization results for the PP samples produced in the experiments of Table 4.1.

	¹³ C NMR		GPC			aCEF	
Sample ID	[<i>mmmm</i>] (%)	[<i>rrrr</i>] (%)	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$	T _{el} (°C)	Peak area (wt%)
PP1	99.75		460	1083	2.4	111.3	
PP2		79.0	92	214	2.3	52.6	
PP3	40.4	45.5	118	557	4.7	52.8 111.1	51 49
PP4	99.75		290	638	2.2	111.2	
PP5		79.2	37	72	1.9	53.4	
PP6	38.7	47.0	36	75	2.0	50.6 108.8	59 40

The addition of DEZ to the individual catalyst systems 4/MAO and 5/MAO ([Zn]/[Zr] = 100) led to a vertical drop of average PP MW (samples **PP4** and **PP5** of Table 4.2). On the other hand, for both systems HTE plots of $M_n vs Y$ (for the raw data see Appendix, Table A4.1) appear as straight lines almost parallel to the abscissa (Figure 4.5). This clearly rules out a CCTP regime, for which a straight line through the origin should be observed.^{2,40}



Figure 4.5. $M_n vs Y$ for PP samples prepared in DFB at 50°C with 4/MAO/DEZ (bottom) and 5/MAO/DEZ (top). [Zn]/[Zr] = 100.³⁹

In the polymerization runs with catalyst mixtures we adjusted the values of [4]/[5] and [Zn]/[Zr] mole ratios so as to obtain roughly 50 wt% iPP/sPP compositions, and polymer $M_n > 10$ kDa for meaningful fractionation experiments. The latter were executed by aCEF, a technique known to minimize kinetic artefacts upon elution.⁴¹

The aCEF trace of sample **PP6** (Table 4.2) is shown in Figure 4.6. The two well-separated elution peaks can be assigned to an iPP fraction ($T_{el} = 108.8$ °C, 40 wt%) and an sPP fraction ($T_{el} = 50.6$ °C, 59 wt%), which is a clear indication of a physical blend nature. Consistently with this conclusion, preparative separation of the sample by exhaustive Kumagawa extraction with boiling hexane ($T_b = 68$ °C) yielded a hexane-insoluble (i-C₆) fraction (39 wt%) and a hexane-soluble (s-C₆) fraction (61 wt%), in excellent agreement with aCEF peak integration. The aCEF traces of the two fractions (also shown in Figure 4.6) and their ¹³C NMR spectra (Figure 4.7) are fully consistent with separate iPP and sPP components.



Figure 4.6. aCEF profiles of the raw sample **PP6** (Table 4.2) and of its i-C₆ and s-C₆ fractions (see text).³⁹


Figure 4.7. Methyl region of the ¹³C NMR spectra of the raw sample **PP6** (Table 4.2) and of its $i-C_6$ and $s-C_6$ fractions (see text).³⁹

A monomodal MWD with PDI = 2.0 for the raw sample **PP6** was observed by GPC (Figure 4.8 and Table 4.2). This is intriguing, but turned out to be merely coincidental: as a matter of fact, the value of $[Zn]/[Zr_{tot}] = 100$ used in polymerization corresponded to individual [Zn]/[4] and [Zn]/[5] mole ratios at which the average M_n values of the produced iPP and sPP samples happened to be very close (Figure 4.8 and Table A4.2 in the Appendix).



Figure 4.8. GPC profiles of sample **PP6** (red trace), and of two PP samples prepared with individual catalysts **4** and **5** at [Zn]/[4] = 1000 (yellow trace) and [Zn]/[5] = 100 (green trace). See text for details.³⁹

The minor amount of sPP (\approx 10 wt%) in the i-C₆ fraction of sample **PP6** detected by aCEF (Figure 4.6) and ¹³C NMR (Figure 4.7) can be ascribed to an incomplete separation for kinetic reasons, rather than to the presence of some [(iPP)-*block*-(sPP)]_n material. As a matter of fact, in the aCEF trace this sPP contaminant is eluted separately from the iPP part, at the very same temperature of the sPP fraction in the raw sample.

One more independent confirmation that catalyst system 4/MAO/DEZ did not promote propene CCTP came from the statistical analysis of the ¹³C NMR stereosequence distribution of the polymerization products. Indeed, for all samples the experimental distribution was in excellent agreement with that calculated according to the enantiomorphic sites model, and no evidence of junctures between stereoblocks with opposite relative configurations (Figure 4.3) was noted within the (high) sensitivity of the method (Table 4.2).^{24,35,37}

4.2.2 Olefin CCTP at ansa-zirconocenes?

The negative conclusions of the previous section prompted us to move one step backward, and investigate the propensity of *ansa*-zirconocenes to *ethene* CCTP (much more facile than propene CCTP). To this end, we selected four C_2 -symmetric bis(1-Indenyl) (pre)catalysts^{35,42,43} from a vast library in the availability of the LSP team.⁴⁴ The (pre)catalyst structures are shown in Figure 4.9.



Figure 4.9. Chemical structures of the four C_2 -symmetric *ansa*-zirconocenes selected for ethene CCTP studies.

Complex **6** was chosen for a very low electrophilicity (estimated charge on the $ZrCl_2$ fragment = 0.38406 e^- , to be compared with 0.41191 e^- for complex **4** in Figure 4.4).^{44,45}

Complex 7 bears 3-Me substituents which sterically destabilize the agostic interactions in the putative four-center transition state (TS) of transalkylation with dialkyl-Zinc (Figure 4.10)^{13,46}; moreover, it has a very low comonomer affinity, as indicated by the values of E/H reactivity ratios ($r_{\rm E} = 123$, $r_{\rm H} = 0.012$, to be compared with $r_{\rm E} = 5.0$, $r_{\rm H} = 0.20$ for catalyst

 4^{47}). The 4-furyl substituents of **8** and the 4-thiophenyl substituents of **9** effect the stability of the aforementioned TS: the hard O donor⁴⁸ in **8** should establish a stabilizing Zn-O interaction, whereas the soft S donor⁴⁸ in **9** may favor TM-Zn alkyl exchange.



Figure 4.10. Schematic representation of the four-center transition state (TS) commonly assumed for trans-alkylation with dialkyl-Zn (TM = Transition Metal).

Results of Density Functional Theory (DFT) calculations (at the TPSSh-D0/TZ//TPSS/DZ level of theory; see Section 4.4.4 for more details) on models of the TS in Figure 4.10 seem in line with the above speculations. Indeed, short Zn-O and Zn-S distances were measured for DEZ/8 and DEZ/9 (Figure 4.11), and the Gibbs Free Energy values were lower by about 3 kcal/mol and 7 kcal/mol for DEZ/8 and DEZ/9, respectively, relative to DEZ/4 taken as a reference.



Figure 4.11. DFT models of the TS in Figure 4.10 for systems DEZ/4 (left), DEZ/8 (center), and DEZ/9 (right). The Zn-X (X= C, O, S) atomic distances are highlighted with colored broken lines. ΔG_{rel} values are in kcal/mol.

All four (pre)catalysts of Figure 4.9 were screened at 100°C in ethene polymerization ($p_E = 11$ bar) under the experimental conditions optimized for E/H CCTP with catalysts **1-3** (Chapter 3), namely: ISOPAR-G solvent (5.0 mL), AB ([AB]/[TM] = 1.2) + MAO ($n_{Al} = 5 \mu mol$) activation, DEZ as the CSA ([Zn]/[Zr] = 100).

The main polymerization results are summarized in the Appendix (Table A4.3). Activity in general was fairly low, and PE M_n was always independent of *Y* (Figure 4.12).





Figure 4.12. M_n vs Y for PE samples prepared with catalysts **6-9** (from top to bottom)/AB/MAO/DEZ (see text). Experimental data taken from Table A4.3.

In conclusion, notwithstanding the attempts to modulate the reactivity by means of steric and/or electronic effects, no catalyst in the set was prone to ethene CCTP, at least under the used conditions.

4.2.3 Propene CCTP at molecular catalysts: Hf vs Zr

As already recalled in previous sections, the first unambiguous evidence of propene CCTP was achieved with the pyridylamido Hf(IV) (pre)catalyst **2** (Figure 4.13) in combination with MAO and DEZ.²⁴ Due to the intrinsic chirality of the active species and an enantiomorphic-sites mechanism of stereocontrol, PP samples produced with the catalyst in racemic form featured the unmistakable stereoblock-isotactic microstructure of Figure 4.3, which was identified by means of a straightforward ¹³C NMR stereosequence analysis and traced to CSP between active sites with opposite configuration.

The catalyst library of LSP contained two pairs of Zr/Hf homologous complexes (Figure 4.13) reported to be isotactic-selective in propene polymerization due to enantiomorphic-sites control. Post-metallocenes **10-11**, patented by Symyx, are commercially applied by Dow for olefin CCTP (IntuneTM technology).^{49,50} *Ansa*-Metallocenes **12-13** were engineered at LSP.³⁵ We explored their ability to promote propene CSP by analyzing the ¹³C NMR fingerprint of the produced polymers. Catalysts **2** and **4** were included in the study for benchmarking purposes.



Figure 4.13. The catalyst set for propene CSP studies (see text).

The experimental conditions were optimized based on previous knowledge²⁴: DFB solvent, low propene pressure ($p_P = 0.7$ bar), DEZ ($n_{Zn} = 10-66 \mu mol$) or 'free' AlMe₃ (TMA) in equilibrium with MAO⁵¹ as the CSA.

The stereoblock-isotactic nature of iPP samples made with **2** is readily apparent from the ¹³C NMR spectra in Figure 4.14: the intense resonance of $m_x(r)m_y$ junctures between stereoblocks with opposite chirality, at the idiosyncratic chemical shift value indicated with a dashed red line, is revealing. In line with previous studies^{24,52}, 'free' TMA in equilibrium with MAO turned out to be a more effective CSA than DEZ for this specific catalyst.



Figure 4.14. Methyl region of the ¹³C NMR spectra of iPP samples made with **2** in combination with DEZ (bottom) and TMA/MAO (top) as the CSA. The peak arising from $m_x(r)m_y$ junctures between isotactic stereoblocks with opposite chirality is at the δ value marked with the dashed red line.

Figure 4.15 shows an overlay of ¹³C NMR spectra in the methyl region for iPP samples produced in the presence of all (pre)catalysts of Figure 4.13. Out of the two post-metallocene catalysts, a stereoblock-isotactic nature was only observed for the product of the Hf complex **10** and not, intriguingly, for that of the Zr homolog **11**. No clear evidence of $m_x(r)m_y$ junctures was detected for the iPP samples made with zirconocenes **4** (which confirms the conclusion of Section 4.2.1), and **12**. **13** turned out to be inactive under the used conditions, likely due to the formation of 'dormant' hetero-bimetallic adducts with DEZ. In no case evidence for CCTP was observed when changing the CSA from DEZ to TMA/MAO.



Figure 4.15. Methyl region of the ¹³C NMR spectra of iPP samples made with the catalysts of Figure 4.13 using DEZ as the CSA (catalyst **13** was inactive). The peak arising from $m_x(r)m_y$ junctures between stereoblocks with opposite chirality, when present, is at the δ value marked with the dashed grey line.

The propensity of **10** to undergo propene CSP was further confirmed by running experiments at variable DEZ concentration: the more DEZ was added, the shorter were the stereoblocks under otherwise identical conditions (Figure 4.16).



Figure 4.16. Methyl region of the ¹³C NMR spectra of iPP samples made with catalyst **10** at two different DEZ concentrations ($n_{Zn} = 66 \mu mol$ (bottom), 10 μmol (top)).

We are aware that the study presented in this section is still too thin to draw general conclusions. Yet, it is a fact that the only two catalysts which have been proved to be prone to propene CSP are both post-metallocenes and Hf-based species.

4.2.4 A new catalyst system for polyolefin chain shuttling?

The Hf (pre)catalyst **10** (Figure 4.13) is applied by Dow for the commercial production of statistical iPP-*block*-HDPE materials (IntuneTM) by means of CCTP in a two-stage process.⁹ Propene CCTP (CSP) in a first reactor is followed by ethene CCTP in a second reactor: a large fraction of PP chains on Zn from the first stage continues to undergo chain growth in the second stage, thus yielding the desired diblock architecture.

To conclude this part of the project, we explored the option of using catalyst **10** in the place of catalyst **2** for the synthesis of InfuseTM-type OBCs. The experimental conditions were the same used for the latter process (Chapters 2 and 3). A series of ethene CCTP experiments was carried out first. Plots of $M_n vs Y$ (Figure 4.17 and Table A4.5 in the Appendix) did confirm a CCTP regime; however, under the used conditions chain growth was very slow, and only waxes were produced.

Similar plots for E/H copolymerization experiments (Figure 4.18 and Table A4.6 in the Appendix) were not consistent with CCTP. ¹H NMR characterizations of the products (last column of Table A4.6 in the Appendix) indicated that the fraction of HO-terminated copolymer chains resulting from reaction quench with dry O_2^{53} was low and independent of copolymer yield, which suggests the presence of one or more chain transfer paths producing 'dead' chains not bound to the TM or MGM. Although the reaction protocol was not optimized and therefore definitive conclusions cannot be drawn, these preliminary observations are not encouraging for the hypothesis of E/H CSP with catalyst **10**.



Figure 4.17. M_n vs Y for PE samples produced at 100°C with catalyst system **10**/AB/MAO/DEZ. Bottom: $n_{Zn} = 15 \mu \text{mol. Top:} n_{Zn} = 30 \mu \text{mol.}$



Figure 4.18. M_n vs Y for E/H copolymer samples produced at 100°C with catalyst system **10**/AB/MAO/DEZ. $n_{Zn} = 15 \mu mol$ (green triangles), 30 μmol (red squares), 66 μmol (black diamonds).

4.3 Concluding remarks

In this chapter we reported the results of a rather comprehensive search for Group 4 metal catalysts of metallocene and post-metallocene nature applicable in propene CCTP/CSP.

Negative conclusions were reached for a library of *ansa*-zirconocenes largely differing in the electrophilicity and the steric demand of the Zr center. Surprisingly, the library included catalysts previously claimed to be amenable to PP chain shuttling in the literature.

On the other hand, evidence for propene CSP was achieved for two Hfbased post-metallocene catalysts, both discovered and commercially applied by Dow.

Although this part of the study should be considered as still preliminary, it seems clear that catalysts for propene CCTP/CSP are rare. Further studies to identify the reason(s) are certainly desirable.

4.4 Experimental part

4.4.1 Materials

All air-/moisture-sensitive chemicals were manipulated under argon or nitrogen using Schlenk techniques and/or MBraun LabMaster 130 glove boxes. DFB and propene were purchased from Sigma-Aldrich and SIAD, respectively, and purified by passing them in sequence through an A4-molecular-sieves and an activated-Cu fixed-bed column. The specifications of all other chemicals are reported in Section 3.4.1 (Table 3.9). Precatalysts **4**, **5**, **10** and **11** were kindly donated by SABIC Europe. Metallocenes **6-9**, **12** and **13** were prepared at Moscow State University (MSU) according to the literature.^{35,42,44,54}

4.4.2 Polymers synthesis

All experiments were carried out in the HTE workflow and following the protocols described in Chapter 2. Propene polymerization runs with 4 and 5 were executed in DFB at 50°C and $p_P = 6.5$ bar until a desired monomer conversion was reached (reaction time 1-25 minutes), using MAO as the scavenger/activator system and DEZ as the CSA. 25 µmol of Al(MAO) and 5.0-5.5 mL of solvent were used in each reaction cell. The Zr amount was varied in the 0.5-30 nmol range, depending on the catalyst, and the [Zn]/[Zr] ratio was fixed at 100.

Low pressure polymerizations with **2**, **4**, **5**, **10-13**, were run in DFB at 70°C and $p_P = 0.7$ bar until a desired monomer conversion was reached (reaction time 30-80 minutes), using MAO or MAO/AB as the scavenger /activator

system and DEZ or TMA as the CSA. 5 μ mol of Al(MAO) and 5.0-5.5 mL of solvent were loaded in each reaction cell; additional 20 μ mol of Al(MAO) or 1.2 equivalents of AB were added for activation purposes. Catalyst amounts ranged between 2.5 and 160 nmol, whereas the amount of CSA was set at 10 and 66 μ mol.

The ethene homopolymerization and E/H copolymerization experiments were carried out according to the general protocol illustrated in Sections 2.2 and 3.4.

4.4.3 Polymer characterizations

The polymers were characterized by Rapid-GPC, aCEF and ¹³C NMR as reported in Chapter 2. DSC curves were collected with the setup described in Section 3.4 with heating-cooling-heating ramps from 25°C to 210°C. We are grateful to Dr. Rocco De Girolamo for the DSC measurements.

4.4.4 Computational details

All geometries were fully optimized using the Gaussian 16 software package.⁵⁵ Following the protocol proposed in Ref. 56, all relevant minima were fully optimized at the TPSSTPSS⁵⁷ level of theory employing correlation-consistent polarized valence double-ζ Dunning (DZ) basis sets of cc-pVDZ(-PP) quality^{58,59} from the EMSL basis set exchange library.⁶⁰ Single point energy corrections were calculated at TPSShTPSSh level of theory, including Grimme's D0 dispersion corrections,⁶¹ employing the cc-pVTZ(-PP) basis set.^{62,63} The density fitting approximation (Resolution of

Identity, RI) was used throughout.^{64–67} All calculations were performed at the standard Gaussian 16 quality settings [Scf=Tight and Int(Grid=UltraFine)]. All structures represent true minima as indicated by the absence of imaginary frequencies.

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Appendix

Catalyst	<i>n</i> TM (nmol)	[Zn]/[Zr]	t (min)	Y (mg)	Mn (kDa)	M _w (kDa)	$M_{\rm w}/M_{\rm n}$
			5	21	393	903	2.3
			4	79	392	868	2.2
			4	146	333	722	2.2
4	1	- 100	6	162	329	758	2.3
			7	176	355	815	2.3
			7	241	360	787	2.2
			10	254	333	772	2.3
			3	13	47	95	2.0
			13	18	52	109	2.1
			7	27	54	111	2.0
5	25		13	75	57	118	2.1
			14	81	60	126	2.1
			19	129	62	128	2.1
			23	182	61	130	2.2

Table A4.1. Propene polymerization data for the experiments of Figure 4.5.^(a)

(a) $T = 50^{\circ}$ C, $p_P = 6.5$ bar, MAO activator ($n_{Al} = 25 \mu mol$)

Table A4.2. Propene polymerization data for the experiments of Figure 4.8.^(a)

Catalyst	n _{TM} (nmol)	[Zn]/[Zr]	t (min)	Y (mg)	Mn (kDa)	M _w (kDa)	M _w /M _n
4	2.5	1000	13	72	61	143	2.3
5	20	100	20	71	37	72	1.9
[4]/[5] = 1:9	20	100	10	163	36	75	2.0

(a) $T = 50^{\circ}$ C, $p_{P} = 6.5$ bar, MAO activator ($n_{Al} = 25 \mu$ mol).

Catalyst	[7 n]/[7 r]	t	Y	P (b)	Mn	$M_{ m w}$	M /M
Catalyst		(min)	(mg)	Kp,av 🖓	(kDa)	(kDa)	1 /1 W/1/1 n
		12	31		15	33	2.2
		18	43		18	35	2.0
6		21	53	2.0	19	39	2.1
		14	65		16	34	2.1
		19	91		17	37	2.1
		28	10		29	58	2.0
		39	17		28	61	2.2
7		41	18	0.6	27	59	2.2
/		34	28	0.6	29	63	2.2
		35	49		27	60	2.2
		59	73		32	68	2.1
	100	29	15	1.9	15	32	2.1
	100	20	31		16	34	2.1
		24	43		17	37	2.1
8		27	64		19	40	2.1
		34	85		19	38	2.0
		25	101		22	42	1.9
		23	117		18	38	2.2
		12	28		14	28	2.0
		12	46		14	30	2.1
0		12	54	27	15	30	2.0
y		15	67	2.7	14	30	2.2
		27	69		15	34	2.2
		24	90		15	33	2.2

Table A4.3. Ethene polymerization data for the experiments of Figure 4.12.^(a)

(a) $T = 100^{\circ}\text{C}$, $p_{\text{E}} = 11$ bar, $n_{\text{Zr}} = 80$ nmol, AB([AB]/[Zr] = 1.2) + MAO ($n_{\text{Al}} = 5 \ \mu\text{mol}$). (b) $g_{\text{P}} \cdot \text{mmol}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$.

Table A4.4. Propene polymerization data for the experiments of Figures 4.15-4.16.^(a)

Catalyst	CSA	n _{CSA} (µmol)	n _{TM} (nmol)	t (min)	Y (mg)	Mn (kDa)	M _w (kDa)	$M_{ m w}/M_{ m n}$
2	TMA ^(b)	66	119	60	126	1.1	1.5	1.3
2	DEZ ^(c)	66	24	73	73	0.7	1.0	1.5
4	DEZ ^(d)	66	30	43	114	2.0	4.6	2.3
10	DEZ ^(c)	10	30	60	82	4.5	14.3	3.2
10	DEZ ^(c)	66	40	50	95	1.4	2.5	1.8
11	DEZ ^(c)	66	40	34	82	1.3	3.6	2.7
12	DEZ ^(d)	66	160	78	100	2.5	5.7	2.2

(a) $T = 70^{\circ}$ C, $p_P = 0.7$ bar. (b) free TMA from MAO, AlMe₃/Al_{total} $\approx 20\%$. (c) MAO activator (25 µmol). (d) AB activator [AB]/[TM] = 1.2.

<i>n</i> zn (µmol)	t (min)	Y (mg)	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$
	1	50	4.1	8.2	2.0
	2	56	4.1	8.6	2.1
	7	58	5.1	11.1	2.2
15	3	64	4.8	10.4	2.2
15	6	67	5.4	11.5	2.1
	16	72	5.7	13.3	2.3
	15	79	5.5	13.1	2.4
	13	93	5.9	14.4	2.5
	2	48	2.0	3.9	2.0
	3	52	2.1	4.6	2.2
	7	60	2.6	5.5	2.1
	4	62	2.3	5.1	2.2
30	8	68	2.8	5.9	2.1
	19	72	2.8	6.3	2.3
	11	80	3.0	6.6	2.2
	12	87	3.2	6.6	2.1
	20	88	3.0	7.2	2.4

Table A4.5. Ethene polymerization data for the experiments of Figure 4.17.^(a)

(a) $T = 100^{\circ}$ C, $p_{\rm E} = 11$ bar, $n_{\rm Hf} = 5$ nmol, AB ([AB]/[Hf] = 1.2) + MAO (n_{\rm Al} = 5 \mu mol).

					GPC		¹ H NMR	
<i>п</i> тм	<i>n</i> Zn	t	Y	Mn	Mw	<i>M</i> / <i>M</i>	$x_{\mathrm{OH},\mathrm{q}^{(a)}}$	
(µmol)	(µmol)	(min)	(mg)	(kDa)	(kDa)	174 W/ 174 n	(mol%)	
		23	39	5.5	11.8	2.1		
		15	60	5.8	13.3	2.3		
		30	61	6.6	14.3	2.2		
		32	64	5.8	13.0	2.2		
	15	27	67	6.7	14.3	2.1	31	
		19	85	6.1	14.0	2.3		
		25	108	7.0	16.9	2.4		
2		20	166	8.9	20.4	2.3		
3		18	211	9.2	24.4	2.7		
		30	25	3.2	5.8	1.8		
		30	35	3.1	6.0	1.9		
		15	41	2.7	5.5	2.0		
	30	20	47	3.1	6.2	2.0	33	
		15	57	2.9	6.1	2.1		
		25	119	4.2	8.8	2.1		
		17	178	4.3	10.5	2.4		
		20	192	4.9	11.3	2.3		
		20	19	1.0	1.9	1.9		
		20	34	1.1	1.9	1.8		
		20	38	1.1	1.9	1.8		
		20	40	1.1	2.0	1.9		
		20	49	1.1	2.1	1.8		
		20	55	1.1	2.1	1.8		
		20	61	1.2	2.2	1.9		
5	((15	65	1.1	2.1	1.9	22	
3	00	5	75	1.2	2.2	1.8	33	
		18	77	1.3	2.4	1.9		
		20	82	1.3	2.4	1.8		
		8	88	1.3	2.4	1.9		
		5	103	1.3	2.5	1.9		
		9	118	1.3	2.4	1.9		
		11	138	1.5	3.1	2.0		
		18	221	1.9	4.1	2.2		

Table A4.6. E/H copolymerization data for the experiments of Figure 4.18 (see main text).

(a) Fraction of OH-terminated copolymer chains formed by O_2 quench.

CHAPTER 5

OBCs with Less Conventional Monomers

5.1 Introduction

The results of the previous section led us to conclude that molecular Group 4 olefin polymerization catalysts prone to undergo reversible transalkylation are rare. Therefore, notwithstanding the availability of state-ofthe-art HTE tools¹, we decided to discontinue the exploration of catalyst space, and move the focus of the project to other CCTP/CSP reaction variables. In particular, we speculated that monomers other than the 'classical' linear 1-alkenes would be of interest for the production of novel materials with non-conventional properties.

4-methyl-1-pentene (4M1P) is an interesting branched olefin commercially available at low price.^{2–8} E/4M1P copolymers are an interesting class of LLDPE products because the bulky comonomer disrupts PE crystallinity more effectively than linear comonomers such as e.g., 1-butene, 1-hexene and 1-octene at a given comonomer incorporation.⁹ Moreover, they have been reported to feature superior mechanical properties and processability compared with e.g., ethene/1-butene copolymers; in particular, elastomeric properties are remarkable.^{10–12} All this prompted us to consider E/4M1P OBCs as alternatives to E/O OBCs.

We did realize that the ability of catalyst pairs 1/2 and 3/2 of Chapter 3 (Figure 5.1) to copolymerize E and 4M1P under CSP regime was still undemonstrated. On the other hand, our educated guess was that the poor incorporating ability of catalyst 1^{13} would result into HDPE-like hard blocks with a lower content of 4M1P comonomeric units relative to the common O units under given reaction conditions, and correspondingly a higher melting temperature of the OBC at a given density.



Figure 5.1. The three (pre)catalysts used for this study. Bn = Benzyl

Another comonomer that raised our interest for this part of the project is 1hexadecene (C16). It has been reported that low amounts of long chain branches (LCBs) in LLDPE dramatically affect the rheological properties of the melt, while being almost immaterial with respect to density and thermodynamic properties.^{14,15} In fact, LCBs increase melt viscosity and elasticity and improve processability.¹⁴ The incorporation of C16 in PE chains/blocks mimics somehow the formation of a LCB. It has been reported that the side chains in E/C16 copolymers are long enough to form small subcrystallites¹⁶⁻²⁰ which increase the degree of crystallinity compared to E/H homologs. Therefore, the side-crystallization process can arguably provide a desirable extra 'hardness' to a hypothetical E/C16 OBC material, and also affect its phase separation and morphology.²¹

All this considered, in this part of the project we explored the possibility to prepare novel E/4M1P and E/C16 OBCs (Figure 5.2) as a convenient diversification route from commercial InfuseTM products.²² To the best of our knowledge no cases of ethene CSP in the presence of 4M1P and C16 have been reported before.



Figure 5.2. Schematic representation of the E/4M1P and E/C16 OBC structures.

5.2 **Results and discussion**

5.2.1 E/4M1P OBCs

The synthesis of E/4M1P OBCs required a prior verification that catalysts **1**, **2** and **3** (Figure 5.1) are prone to E/4M1P CCTP. To this end, the HTE protocols optimized for the production of E/H OBCs (Chapters 2 and 3) were tested with the branched comonomer.

Series of E/4M1P random copolymerization experiments in the presence of the individual catalysts **1** and **2** with DEZ as the CSA ([Zn]/[TM] = 50) were performed at $p_E = 17$ bar, with 2.00 mL of 4M1P added to the reaction cells ([E]/[4M1P] = 0.30). $M_n vs Y$ plots for the copolymers are reported in Figure 5.3 (for detailed polymerization data see Table A5.1 in the Appendix).



Figure 5.3. M_n vs Y for E/4M1P copolymers prepared with 1 (top) and 2 (bottom) in the presence of DEZ (see text).

The quasi-linear correlation observed in both cases is a clear evidence of a CCTP regime under the used conditions. This indicates that the presence of the bulky 4M1P molecule in the reaction phase did not hamper the ability of the active polymeryls to undergo fast and reversible trans-alkylation with dialkyl-Zn.

Quite surprisingly and unexpectedly, the copolymer characterization results (Table 5.2) revealed that catalyst **1** yielded copolymers with a 4M1P content $x_{4M1P} = 0.5$ mol% (see e.g., sample **E4M1P_1**), that is similar to that of H for an E/H copolymer made under the same experimental conditions (see Chapter 3, Table A3.3). The observed catalyst activity was roughly 2-fold lower than that of **2**, which in turn confirmed to be an excellent incorporator (sample **E4M1P_2**).

Table 5.1. Experimental conditions and polymer yields for selected copolymerization experiments with catalysts 1 and 2 (see text). Data for a homologous E/H copolymerization experiment were included for comparison.

Experiment ID	Catalyst ID	Comonomer ID	n _{Com} (mmol)	[Zr]/[TM]	Y (mg)
E4M1P_1	1				115
E4M1P_2	2				253
OBC1		41410	16		199
OBC2	1+2	4M1P	10	50	205
OBC3	[1] / [2] = 1:2				229
OBC4					242
EH-OBC	[1] / [2] = 1:4	Н	11		209

	GPC			¹³ C NMR			aCEF	
Sample ID	M _n (kDa)	M _w (kDa)	$M_{ m w}/M_{ m n}$	x _{Com} ^(a) (mol%)	x _{Com,s} ^(b) (mol%)	w _s (c) (wt%)	AF ^(d) (wt%)	T _{el} (°C)
E4M1P_1	26	44	1.7	0.5	-	-	-	109.6
E4M1P_2	104	241	2.3	22.3	-	-	85	13.7
OBC1	60	155	2.6	19.9	25.2	84	58	14.2 96.3 104.3
OBC2	69	153	2.2	20.6	25.8	85	56	13.4 95.4 104.1
OBC3	69	161	2.3	21.3	25.9	86	59	13.6 94.4 103.8
OBC4	58	163	2.8	21.4	27.2	84	56	13.3 95.0 103.9
ЕН-ОВС	95	226	2.4	20.0	26.0	83	37	16.3 97.2 105.2

Table 5.2. Main characterization results for the copolymer samples of Table 5.1.

(a) Comonomer incorporation in the overall sample. (b) Comonomer incorporation in the soft blocks (c) Weight fraction of soft blocks. (d) Amorphous fraction; material eluted at -15°C.

E/4M1P CSP with the 1/2 catalyst pair was then explored at a [1]/[2] ratio of 1:2 (Tables 5.1 and 5.2, samples **OBC1** to **OBC4**). The characterization data in Table 5.2 and the aCEF curves in Figure 5.4 indicate that statistical OBCs were indeed produced. As a matter of fact, all samples turned out to contain an amorphous fraction, that can be traced to homo-CS at the active species of catalyst 2, and a semicrystalline fraction with a hard/soft block architecture arising from hetero-CS between the active species of catalysts 1 and 2.²³ The reproducibility of replicate experiments was very nice (Tables 5.1-5.2 and Figure 5.5).



Figure 5.4. Overlay of the aCEF elution profiles of samples E4M1P_1 (red curve), E4M1P_2 (blue curve), and OBC1 (green trace).



Figure 5.5. Overlay of the aCEF elution profiles for the OBC samples in Table 5.2.

Compared with homologous E/H OBCs (Chapter 3), this first set of E/4M1P OBCs turned out to be characterized by a higher amount of amorphous fraction and a slightly lower T_{el} value for the semicrystalline fraction. Therefore, a second series of E/4M1P CSP experiments was carried out with the better performing **3**/**2** catalyst pair (see Section 3.2.4). The experimental conditions were adjusted so as to obtain OBCs with similar soft block composition ($x_{Com,s} = 0.20$) and chain architecture ($w_s/w_h = 80/20$) compared with the E/H OBCs of Chapter 3. The copolymerization and copolymer characterization results are summarized in Tables 5.3 and 5.4, respectively (data for an E/H OBC homolog were added for comparison). The aCEF profiles of all samples are shown in Figure 5.6.

Table 5.3. Experimental conditions and copolymer yields for selected copolymerization experiments with catalysts 2 and 3 (see text). Data for a homologous E/H copolymerization experiment (Chapter 3) were included for comparison.

Experiment ID	Catalyst ID	Comonomer ID	n _{Com} (mmol)	[Zr]/[TM]	Y (mg)			
OBC5					174			
OBC6					77			
OBC7	2+3 [2]/[3] = 4:1	4M1P	12	50	171			
OBC8					176			
OBC9					121			
OBC10					148			
EH22		Н	11		178			
		GPC			¹³ C NMR	aCEF		
--------------	-------------	-------------	---------------------	---	---	----------------------------	----------------------------	--
Sample ID	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$	x _{Com} ^(a) (mol%)	x _{Com,s} ^(b) (mol%)	ws ^(c) (wt%)	AF ^(d) (wt%)	T _{el,max} ^(e) (°C)
OBC5	60	120	2.0	15.8	23.0	75.3	15	100.3
OBC6	63	148	2.4	14.2	19.3	77.8	19	100.5
OBC7	59	153	2.6	15.2	20.2	79.6	21	99.6
OBC8	74	184	2.5	14.9	20.4	77.9	12	99.9
OBC9	53	134	2.5	14.5	19.9	77.6	17	101.8
OBC10	65	163	2.5	14.6	20.0	77.4	15	100.3
EH22	76	162	2.2	18.6	24.0	76.4	15	95.7

Table 5.4. Main characterization results for the copolymer samples of Table 5.3.

(a) Comonomer incorporation in the overall sample. (b) Comonomer content in the soft blocks. (c) Weight fraction of soft blocks. (d) Amorphous fraction; material eluted at -15°C. (e) Maximum elution temperature.



Figure 5.6. Overlay of the aCEF elution profiles for the copolymer samples of Table 5.4.

Based on the overall results, we conclude that this second set of E/4M1P OBCs is closely similar to the InfuseTM-type materials discussed in Chapter 3. The reproducibility of replicate experiments was good enough to merge the yields of different cells for thermal and mechanical characterizations. Two merged samples, namely A (OBC1-4) and B (OBC5-10) were thoroughly investigated.

Both samples crystallized in the orthorhombic form of PE, as shown in Figure 5.7: this is indicated by the presence of 110 and 200 reflections at $2\theta \approx 21^{\circ}$ and 24°. The DSC curves showed melting and crystallization peaks around 120°C and 95°C, respectively (Figure 5.8, and Table A5.2 in the Appendix). This is similar to what was observed for E/H and E/O OBCs (Chapter 3).



Figure 5.7. X-ray powder diffraction profiles of merged samples A (left) and B (right).



Figure 5.8. DSC curves (1^{st} heating in red, cooling in blue, 2^{nd} heating green) of merged samples **A** (top) and **B** (bottom).

The stress-strain curve of the two merged samples and the derived mechanical parameters are shown in Figure 5.9 and Table A5.3 (Appendix). Merged sample **A** was characterized by very low values of stress at any strain (e.g., $\sigma_y \approx 0.73$ MPa; $\sigma_b \approx 0.76$ MPa), no strain hardening, but an outstanding ductility ($\epsilon_b \approx 6000\%$). Such a high value of

ductility may be partly attributed to viscous flow of the chains occurring at high deformations. On the other hand, the low values of stress are attributable to the very low crystallinity ($\chi_c = 6\%$, see Table A5.2). Furthermore, the sample has excellent elastomeric properties, given the low value of tension set at break (t_b \approx 1100%), indicating a relevant elastic recovery.

Merged sample **B**, instead, showed lower ductility but higher mechanical resistance (Young modulus E = 9 MPa, $\sigma_b \approx 7$ MPa), and a relevant strain hardening due to the higher crystallinity ($\chi_c = 20.4\%$). This notwithstanding, the sample featured good elastomeric properties, as shown by the tension set $t_b \approx 90\%$.

The reason why merged samples **A** and **B** show significantly different mechanical behaviors while having similar thermal properties is not obvious, considering that they differ only slightly from the microstructural and architectural point of view. Further studies will be necessary to address this question.



Figure 5.9. Stress-strain curves of merged samples A (top) and B (bottom).

5.2.2 E/C16 OBCs

The ability of catalysts **3** and **2** to mediate E/C16 CCTP was verified by building M_n vs Y plots, with the same protocols already illustrated for the E/H and E/4M1P comonomer pairs. The results, shown in Figure 5.10 (for detailed polymerization data see Table A5.4 in the Appendix), do point to a CCTP regime.



Figure 5.10. $M_n vs Y$ for E/C16 copolymerization experiments with catalysts **2** (top) and **3** (bottom) in the presence of DEZ.

The next step was to attempt E/C16 CSP with the catalyst pair **2+3** and DEZ as the CSA. In Table 5.5 we report the results of a representative experiment, comparatively with those of CCTP experiments with the individual catalysts (in all cases, $p_E = 17$ bar, $v_{C16} = 2.5$ mL per reaction cell).

Table 5.5. Main characterization	n results of E/C16 copolymer	s made with catalysts 2, 3	3 and 2+3 ($[2]/[3] = 4$:	1) in the presence of
DEZ ([Zn]/[TM] = 50).				

			GPC			¹³ C NMR		aCEF	
Sample ID	Catalyst ID	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$	x _{Com} ^(a) (mol%)	x _{Com,s} ^(b) (mol%)	ws ^(c) (wt%)	AF ^(d) (wt%)	T _{el,max} ^(e) (°C)
EC16_2	2	74	233	3.2	19.7	-	-	82	2.7
EC16_3	3	40	76	1.9	1.0	-	-	-	107.5
OBC11	2+3 [2]/[3] = 4:1	91	224	2.5	15.3	23.8	81.7	47	97.6

(a) Comonomer incorporation in the overall sample. (b) Comonomer content in the soft blocks. (c) Weight fraction of soft blocks. (d) Amorphous fraction; material eluted at -15°C. (e) Maximum elution temperature.

From the overlay of the aCEF elution profiles for all three samples in Table 5.5, shown in Figure 5.11, it can be safely concluded that the CSP experiment was successful and an OBC was obtained. Similarly to the cases of E/H and E/4M1P OBCs, the material consisted of an amorphous fraction attributable to homo-CS at the active species of catalyst **2**, and a semicrystalline fraction containing hard and soft blocks formed by hetero-CS between the active species of catalysts **3** and **2**.



Figure 5.11. Overlay of the aCEF elution profiles for the samples of Table 5.5. EC16_3: red trace; EC16_2: blue trace; OBC11: green trace.

5.3 Concluding remarks

In this Chapter we highlighted the wide scope of diversifying olefin CSP by a nonconventional choice of the comonomers. In particular, novel E/4M1P and E/C16 OBCs were prepared and characterized.

We admit that the reported physical and mechanical characterization of the materials is only preliminary, due to the time limitations imposed by the COVID-19 related restrictions. On the other hand, the fact that comonomers characterized by a very high steric demand could be successfully incorporated in PE chains under a frank CCTP/CSP regime opens the door to the production of a number of innovative materials with unprecedented properties and applications.

We anticipate that the investigation can be extended to other comonomers of industrial interest (such as e.g., vinylcyclohexene, norbornene, vinyl norbornene, and α, ω -dienes).^{24,25}

5.4 Experimental part

4M1P was kindly donated by SABIC Europe (purity > 97%). C16 was purchased from TCI Chemicals (purity > 99%). Both monomers were dried over Alumina and A4-molecular sieves. The specifications of all other chemicals are reported in Section 3.4.1 (Table 3.9).

The E/4M1P and E/C16 copolymerization experiments were conducted following the general protocol illustrated in Sections 2.2 and 3.4.

The polymers were characterized by Rapid-GPC, a-CEF and ¹³C NMR as reported in Chapter 2. DSC analysis and mechanical tests were collected with the setup described in Section 3.4.

X-ray data were collected on as prepared samples using an Empyrean (PANalytical) diffractometer in the reflection geometry, with Ni-filtered CuK α radiation (wavelength $\lambda \frac{1}{4} = 0.15418$ nm).

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Appendix

Catalyst	n _{TM} (nmol)	[Zn]/[Zr]	t (min)	Y (mg)	R _{p,av} ^(b)	M _n (kDa)	M _w (kDa)	M _w /M _n
			5	51		14	27	1.9
			2	56	-	15	39	2.7
			4	62		17	29	1.7
			5	71		19	32	1.7
			2	73		15	32	2.1
1	40		4	75	29	18	31	1.8
		50	6	81		19	36	1.9
			6	91		22	41	1.9
			8	101		23	42	1.8
			3	103		18	40	2.2
			8	115		26	44	1.7
			15	35		37	78	2.1
			3	56		49	119	2.4
			5	99		84	184	2.2
2	15		8	116	57	83	187	2.2
	15		20	159	57	112	234	2.1
			9	199		115	252	2.2
			17	200		81	180	2.2
			16	227		143	296	2.1

Table A5.1. Main polymerization data for E/4M1P CCTP experiments with catalysts 1 and 2 (DEZ as the CSA).^(a)

(a) $p_{\rm E} = 17$ bar, $v_{4\rm M1P} = 2.0$ mL per reaction cell. (b) $g_{\rm P} \cdot \text{mmol}_{cat}^{-1} \cdot \text{h}^{-1} \cdot$

Table A5.2. X-ray and DSC characterization results for E/4M1P OBC merged samples A and B (see main text).

	X-ray		DSC									
Sample ID	χ ^(a) (%)	<i>T</i> ^I m ^(b) (°C)	$\frac{\Delta H^{\rm I}{\rm m}^{\rm (b)}}{\rm (J/g)}$	<i>T</i> c ^(c) (°C)	$\frac{\Delta H_{\rm c}^{\rm (c)}}{(\rm J/g)}$	<i>T</i> ^{II} m ^(d) (°C)	$\frac{\Delta H_{\rm m}^{\rm II}(d)}{(\rm J/g)}$	<i>T</i> _g ^(e) (°C)				
Merged A	6	120.6	15.4	94.6 75.7	12.8	119.9	13.1	-48.3				
Merged B	20.4	121.5	28.0	97.1	24.5	120.7	24.7	-				

(a) Degree of crystallinity. (b) 1st melting temperature and corresponding melting enthalpy. (c) Crystallization temperature and corresponding crystallization enthalpy. (d) 2nd melting temperature and corresponding melting enthalpy. (e) Glass transition temperature.

Table A5.3. Mechanical properties of E/4M1P OBC merged samples **A** and **B** (see main text).

Sample ID	E ^(a) (MPa)	σ _y ^(b) (MPa)	ε _y ^(c) (%)	σ _b ^(d) (MPa)	ε _b ^(e) (%)	t _b ^(f) (%)
Merged A	1.9±0.2	0.73±0.1	100±10	0.76 ± 0.10	6089±942	1103±255
Merged B	9.0±0.7	/	/	6.6±1.0	1050±70	87±10

(a) Young's modulus. (b) Stress at breaking. (c) Strain at breaking. (d) Stress at yield point. (e) Strain at yield point. (f) Tension set after the break.

Table A5.4. Main polymerization data for E/C16 CCTP experiments with catalysts 2 and 3 (DEZ as the CSA).^(a)

Catalyst ID	<i>n</i> тм (nmol)	[Zn]/[Zr]	t (min)	Y (mg)	Mn (kDa)	Mw (kDa)	M _w /M _n	
			1	54	52	123	2.4	
			3	81	56	167	3.0	
2	10		5	140	63	180	2.9	
2	10		2	142	74	233	3.2	
		- 50	2	156	74	214	2.9	
			13	226	96	298	3.1	
			1	63	30	62	2.0	
			1	79	32	67	2.1	
3	15		1	128	42	81	1.9	
	15		2	181	53	103	1.9	
				5	185	51	99	1.9
			12	224	54	106	2.0	

(a) $p_{\rm E} = 17$ bar; $v_{\rm C16} = 2.5$ mL per reaction cell

CHAPTER 6

Labeling Polyolefin Chains with Fluorescent Tags

6.1 Plastics production and wastes

6.1.1 Plastics market

Ever since the first pioneering discoveries of radical and transition-metalbased polymerizations in the first half of last century,^{1,2} the production and commercial application of large volume polymeric materials (comprehensively referred to as 'plastics') has grown exponentially, and is now approaching 0.5 billion tons per year.^{3,4} Polymers such as polyesters, polyamides, poly(vinylchloride) (PVC) and polyolefins have provided solutions to problems in materials science and technology that would have been unimaginable for other classes of materials like e.g., metals or inorganic glasses, thanks to a much wider application window and a superior versatility.⁵ In all such respects polyolefins, in particular, are ideally suited for applications including, but not limited to, smart packaging, automotive, construction and architectural design, textiles, rubbers, electric and thermal insulation (Figure 6.1). As a matter of fact, PE and iPP account for almost half of the global plastics market.

The low cost of virgin plastics is a most important asset, but also the indirect cause of the accumulation of plastic wastes in the environment: as a matter of fact, recycling plastic wastes is difficult and expensive, to the point that it cannot be justified in mere economic terms.



Figure 6.1. Distribution of the plastics market by sector of use.

In recent years, moreover, the market proposed ever new and often overengineered multi-material solutions which are particularly complicated to recycle (see e.g., Figure 6.2).⁶



Figure 6.2. An example of multi-material stand-up pouches. OPA = Oriented Poly(Amide); OPET = Oriented PolyEthylene Terephthalate; met = metallized.

Incinerating plastic wastes for energy production (recovery) can represent a rational and effective solution in short term, but in long term it is not sustainable: planet's resources are not endless, and it is now generally agreed that the only viable option is a transition from a linear to a circular model of economy, according to which all materials (including of course plastics) at the end of their life cycle are recovered and re-used (Figure 6.3).⁷ Therefore, implementing viable routes for recycling waste materials is a must.



Figure 6.3. The concept of Circular Economy. Credit: European Parliament.⁷

6.1.2 Used plastics recycling

Sorting the various components of typical multi-material waste streams prior to recycling is a necessary and difficult first step. Whereas separating plastics from e.g., metals and glass is relatively straightforward, the same does not hold for polymer wastes with different chemical compositions. One may imagine that blending is an option for mechanical recycling, but unfortunately most large volume polymers, including PE and iPP, are thermodynamically incompatible.^{8,9} In previous chapters we noted that block copolymers can be used as phase compatibilizers, but their cost is still rather high. Therefore, selection and sorting remain desirable.¹⁰

One can distinguish between 'manual' selection methods, in which the job is carried out by human operators, acting on a conveyor belt or on a fixed surface, and automated selection methods. The latter are generally cheaper and faster and allow for a more efficient waste stream separation; moreover, they are highly advisable for safety reasons in case of hazardous wastes. Robotic tools can be used to sort different products from the same belt, thus overcoming the limitation of human operators which can focus on one single product at a time.

Automated selection techniques can be classified into 'direct' and 'indirect'. The former exploit intrinsic materials properties to separate mixtures by means of external forces (such as e.g., magnetic fields, eddy currents, or specific gravity).^{11,12} The latter, in turn, use primarily spectrometric techniques to identify the waste components based on the specific interaction with a convenient electromagnetic radiation (such as e.g., near-IR, or X-rays in transmission or fluorescence).^{12,13} Unfortunately, all aforementioned sorting approaches have limitations, since they can be used for some polymer classes only, whereas typical plastic waste streams consist of complex mixtures of many different materials (and may also include various kinds of additives such as e.g., dyes and/or fillers).¹⁰ It should be added that most approaches fail to identify black and dark-colored polymers; this is specially problematic for the automotive and electronics sectors, which make a large use of black materials.

Lately, new techniques have been introduced to overcome this limitation. Most are based on the use of radio frequency tags, applied on individual plastic items to uniquely identify them; the main drawbacks are the concerns for possible side effects of the tag on health, and the high cost of the technology.¹⁴

Last but not least, one may consider labeling the materials with idiosyncratic fluorescent dyes.^{15,16} The great advantage is that, in order to establish an optical tracing system, only small amounts of fluorophores (at ppm level) need to be incorporated into the virgin polymers, typically during the manufacturing process (Figure 6.4).¹⁷ The low marker concentration is essentially defined by the high sensitivity of fluorescence tools, from one to three orders of magnitude higher with respect to all other spectroscopic methods used to date. This condition is extremely important because the label should not affect the visual appearance, the physical and mechanical properties, and the structural integrity of the marked polymers, nor increase appreciably their production cost.

A mandatory requirement of the approach is that different polymeric materials are labeled with different fluorescent dyes, so that selective identification is possible. Another important condition is the stability of the used dyes, which should maintain their fluorescent response as long as possible. Recent studies reported that complexes based on rare earth elements such as Europium (Eu) or Terbium (Tb) feature a long-lasting fluorescence.^{16,18}



Figure 6.4. Schematics of automated sorting of wastes labeled by fluorescent markers (here M1–M4) originally added to the virgin materials. Reprinted with permissions from Ref. 10. Copyright © 2015 Elsevier.¹⁰

In this part of the project we addressed the question by proposing a solution consisting in the labeling of PE and iPP materials with novel fluorescent dyes incorporated as comonomers in the nascent polymer chains, rather than added by physical mixing downstream of the polymerization process. This requires the design of fluorescent molecules with a dangling unsaturation amenable to insertion in catalytically active TM-C σ -bonds (TM = Transition Metal), and no heteroatom-containing functional groups in the formula that can poison the TM centers. To the best of our knowledge there is only one such example in the literature, i.e., a class of molecules featuring an anthracenyl moiety linked to an allyl bond by means of a polymethylenic tether.¹⁹ Comonomer incorporation ability was reported to increase with increasing length of the tether, which is expected, and represents a crucial structural parameter. We opted for a conceptually similar strategy using 1-pyrenylheptene (1-PH) as the prototypical fluorescent comonomer. The synthetic path of 1-PH and copolymerization experiments of **1-PH** with ethene and propene will be described in the following sections.

6.2 Results and discussion

6.2.1 Synthesis of a convenient fluorescent (co)monomer

As explained in the previous section, our strategy was to incorporate a fluorescent comonomer in PE and iPP chains via transition-metal-mediated insertion copolymerization, ending up with a permanently bound label.

Whereas the concept is simple, execution is complicated because the fluorophore must be (a) an olefin amenable to the required (poly)insertion chemistry, hence featuring a terminal C=C bond with minimal substitution and no heteroatom-containing fragments possibly poisoning the catalytic centers,²⁰ and (b) generate a strong fluorescent response down to very low concentrations, i.e., below the value at which the physical and mechanical properties of the polymers would be altered (about 0.1 mol%, indicatively).

1-Pyrenylheptene (1-PH) potentially matches all above conditions. Pyrene is the smallest *peri*-fused polycyclic aromatic hydrocarbon, characterized by a high symmetry (point group D_{2h}). Importantly, it is known to be a very strong fluorophore; its absorption and fluorescence spectra in the UV-Vis region are well-described.²¹ Connecting a pyrene moiety to an allyl bond through a pentamethylenic spacer was achieved through the synthetic path shown in Figure 6.5; all steps turned out to be high-yield, in line with the previous literature.^{20,22} The individual reaction steps, and the isolation and characterization of the intermediates and the final product are described in Section 6.4.



Figure 6.5. The synthetic path for the preparation of 1-pyrenylheptene (1-PH).

6.2.2 Copolymerizations of the novel fluorescent (co)monomer

Copolymerization experiments of **1-PH** with ethene (E) and propene (P) were carried out with the polymerization platform described in Chapter 2. *rac*-Me₂Si(2-Me-Benz-[e]-Inden-1-yl)₂ZrCl₂ (**14**, Figure 6.6) was used as the (pre)catalyst; based on the literature, this complex has a good ability to incorporate higher 1-alkenes in growing PE chains, and a fairly high isotactic selectivity in the (poly)insertion of propene.²³ Comparative experiments of E/H and P/H copolymerization were also run, in order to benchmark the reactivity of **1-PH** and the microstructural properties of its copolymers.



Figure 6.6. The *rac*-Me₂Si(2-Me-Benz-[e]-Inden-1-yl)₂ZrCl₂ (pre)catalyst (14).

Preliminary results of P/**1-PH** and P/H copolymerization (with comparative purpose) are reported in Table 6.1. The aCEF elution traces and DSC 2^{nd} melting curves of the copolymers are shown in Figures 6.7 and 6.8.

Table 6.1 Results of P/1-PH and P/H copolymerizations (at $T = 60^{\circ}$ C, $p_P = 2.4$ bar).

				GPC			¹³ C NMR	aCF	aCEF	
Sample ID	Comonomer	n _{com} (µmol)	R p ^(a)	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$	x _{com} ^(b) (mol%)	AF ^(c) (wt%)	T _{el} (°C)	$ \begin{array}{c} T^{II} \mathbf{m}^{(\mathbf{d})} \\ (^{\circ}\mathbf{C}) \end{array} $
S1	Н	230	58	57	129	2.3	1.1	1.7	88.8	132.0
S2		230	0.4	51	112	2.2	1.7	100	-	121.8
S 3	1-PH	115	1	44	96	2.2	0.85	9.4	85.6	133.7
S4		57.5	0.3	32	62	2.0	0.55	3.1	89.4	137.1

(a) Productivity, in $g_P \cdot nmol_{Zr}^{-1} \cdot h^{-1}$. (b) Comonomer incorporation. (c) Amorphous fraction; material eluted at -15°C. (d) DSC melting temperature (2nd heating).



Figure 6.7. Overlay of the aCEF elution curves for the copolymer samples of Table 6.1.



Figure 6.8. Overlay of the DSC 2nd melting curves for the copolymer samples of Table 6.1.

A first, rather surprising observation is that the incorporation of **1-PH** units in the iPP chains was higher than that of H units, despite their superior steric demand. The fraction of **1-PH** units in the copolymer increased linearly with increasing **1-PH** concentration in the feed, as expected. Copolymer crystallinity was disrupted by the **1-PH** units more than by H ones, which is consistent with the higher steric bulk of the side branch. For all samples, a PDI value of ≈ 2.0 was measured by GPC, indicating a wellcontrolled reaction at a single-center catalytic species.²⁴ One last remark concerns the rather poor solubility of the P/**1-PH** copolymers, the more so the higher the **1-PH** content; this may be traced to comparatively strong intermolecular interactions originated from π - π stackings between the pyrenyl fragments.^{25,26}

The low catalyst productivity observed in the presence of **1-PH** (Table 6.1), independently of the feeding ratio, was traced to impurities left over from the synthesis. Therefore, prior to running the set of experiments with E, the **1-PH** batch was further purified by dissolution in toluene, elution through a silica gel column, coagulation and drying. Preliminary results of E/**1-PH** and E/H copolymerization (for comparison) are reported in Table 6.2. The aCEF elution traces and DSC 2nd melting curves of the copolymers are shown in Figures 6.9 and 6.10, respectively.

Table 6.2. Results of E/1-PH and E/H copolymerizations (at $T = 60^{\circ}$ C, $p_E = 2.4$ bar).

				GPC			¹³ C NMR	MR aCEF		DSC
Sample ID	Comonomer	n _{com} (µmol)	R p ^(a)	Mn (kDa)	Mw (kDa)	M _w /M _n	x _{com} ^(b) (mol%)	AF ^(c) (wt%)	T _{el} (°C)	<i>T</i> ^{<i>II</i>} m ^(d) (°C)
S 5	Н	230	204	97	269	2.8	5.0	3.9	93.1	103.6
S6		230	47	75	287	3.8	4.0	1.4	82.8	101.5
S 7	1-PH	115	72	72	309	4.3	2.9	0.7	96.7	109.9
S8		57.5	231	101	366	3.6	1.2	0.7	101.6	119.9

(a) Productivity, in $g_P \cdot \text{nmol}_{Zr}^{-1} \cdot h^{-1}$. (b) Comonomer incorporation. (c) Amorphous fraction; material eluted at -15°C. (d) DSC melting temperature (2nd heating).



Figure 6.9. Overlay of the aCEF elution curves for the copolymer samples of Table 6.2.



Figure 6.10. Overlay of the DSC 2nd melting curves for the copolymer samples of Table 6.2.

At odds with the comparative results of P/1-PH and P/H copolymerization, those of E/1-PH and E/H (Table 6.2) indicate that the reactivity of the two substituted comonomers is rather similar. Here too, with increasing 1-PH concentration in the feed the fraction of 1-PH units in the copolymer increased linearly, as expected; on the other hand, catalyst productivity decreased only moderately with increasing 1-PH/E feeding ratio, which is normal and confirms that the strong drop observed for the P/1-PH copolymerization experiments was due to impurities in the 1-PH batch. The disruption of copolymer crystallinity by the 1-PH units confirmed to be more severe than that caused by the H units. Probably due to the high reactivity of ethene, the PDI values for the copolymers were moderately higher than those of Schulz-Flory distributions, suggesting a rather poor reaction control;²⁷ this is consistent with the rather broad aCEF and DSC peaks (Figures 6.9 and 6.10)

6.2.3 Fluorescent response of **1-PH** copolymers at 'high' **1-PH** content

The ability of **1-PH** units in the produced E/**1-PH** and P/**1-PH** copolymers to induce a fluorescent response was verified by means of Confocal Laser Scanning Microscopy (CLSM; Section 6.4).²⁸ Figures 6.11 and 6.12 show the bright field and confocal images (detected in the green channel) of samples **S2** (Table 6.1) and **S8** (Table 6.2). The very intense fluorescent response of both samples is truly remarkable, especially considering the low fluorophore contents (*x*_{1-PH} < 2 mol%) and the fact that they were used as powders.



Figure 6.11. Confocal (left) and bright field (right) CLSM image of sample S2 (Table 6.1).



Figure 6.12. Confocal (left) and bright field (right) CLSM image of sample **S8** (Table 6.2).

When switching the detection channel of the signal from green to red no fluorescent response was observed, which is consistent with the known optical properties of the pyrene moiety.²⁹ The extraordinarily intense fluorescence of the E/**1-PH** and P/**1-PH** copolymers of Tables 6.2 and 6.1 (respectively) was further confirmed by bright field observations.

6.2.4 Copolymerizations of 1-PH at 'low' concentration

Based on the results of the previous section, we anticipated an adequate fluorescent response of E/1-PH and P/1-PH copolymers for identification purposes at least down to 1-PH contents of 0.1 mol%. The thermal and physico-mechanical properties of such copolymers should not differ appreciably from those of the corresponding homopolymers. In order to confirm this educated guess, two further sets of copolymerization experiments were carried out at 'low' 1-PH/P and 1-PH/E feeding ratios. All copolymers were then characterized, with the results of Table 6.3 and Table 6.4, respectively. The aCEF and DSC curves are shown in Figures 6.13-6.16.

			GPC			¹³ C NMR	aCl	EF	DSC
Sample ID	<i>n</i> 1-рн (µmol)	R _p ^(a)	Mn (kDa)	Mw (kDa)	M _w /M _n	<i>х</i> 1-рн ^(b) (mol%)	AF ^(c) (wt%)	T _{el} (°C)	<i>T</i> ^{<i>II</i>} m ^(d) (°C)
S9	0	226	84	168	2.9	0	3.2	102.3	147.2
S10	23	18	57	119	2.1	0.225	1.3	96.8	142.1
S11	4.6	43	48	102	2.1	0.050	0.8	99.8	145.4
S12	2.3	32	45	94	2.1	0.035	0.8	99.8	146.0
S13	0.46	48	50	107	2.1	0.005	0.7	100.9	146.2

Table 6.3. Results of P/1-PH copolymerizations at 'low' 1-PH/P feeding ratios ($T=60^{\circ}$ C, $p_{P}=2.4$ bar).

(a) Productivity, in $g_P \cdot nmol_{Zr}^{-1} \cdot h^{-1}$. (b) Comonomer incorporation. (c) Amorphous fraction; material eluted at -15°C. (d) DSC melting temperature (2nd heating).



Figure 6.13. Overlay of the a-CEF profiles for the samples of Table 6.3.



Figure 6.14. Overlay of the DSC 2nd melting curves for the samples of Table 6.3.

			GPC			¹³ C NMR aCEF			DSC
Sample ID	<i>n</i> 1-рн (µmol)	$R_{p}^{(a)}$	Mn (kDa)	Mw (kDa)	$M_{\rm w}/M_{\rm n}$	<i>х</i> 1-РН ^(b) (mol%)	AF ^(c) (wt%)	T _{el} (°C)	<i>T</i> ^{<i>II</i>} m ^(d) (°C)
S14	5.8	533	142	611	4.3	0.130	0.4	110.1	130.7
S15	1.2	938	145	526	3.1	0.030	0.6	110.8	132.6
S16	0.58	999	132	545	4.1	0.015	0.3	111.3	133.9
S17	0.12	864	125	543	4.4	0.003	1.0	111.8	134.4

Table 6.4. Results of E/1-PH copolymerizations at 'low' 1-PH/E feeding ratios ($T = 60^{\circ}$ C, $p_{E} = 2.4$ bar).

(a) Productivity, in $g_p \cdot mmol_{Zr}^{-1} \cdot h^{-1}$. (b) Comonomer incorporation. (c) Amorphous fraction; material eluted at -15°C. (d) DSC melting temperature (2nd heating).



Figure 6.15. Overlay of the a-CEF profiles for the samples of Table 6.4.



Figure 6.16. Overlay of DSC 2nd melting curves for the samples of Table 6.4.

For each set of copolymers, the physical properties of the sample at the lowest **1-PH** unit content are practically coincident with those of the reference homopolymers. Importantly, a high fluorescence was observed even for such samples (Figures 6.17 and 6.18). This indicates that, at least in principle, the method can be proposed for material identification purposes on plastic wastes streams using fluorescence detectors.



Figure 6.17. Confocal CLSM images of samples S10 (left) and S13 (right) in Table 6.3.



Figure 6.18. Confocal CLSM images of samples S14 (left) and S17 (right) in Table 6.4.
6.3 Concluding remarks

Thermal or mechanical recycling of multi-material plastic wastes requires a previous identification and separation according to chemical structure. To this end we have proposed a classification method based on the introduction of fluorescent tags in the polymer chains via copolymerization, for subsequent spectrometric identification. Α convenient fluorescent comonomer, namely 1-pyrenylheptene (1-PH), was synthesized, and copolymerized with ethene and propene with a wellknown ansa-zirconocene catalyst, ending up with fluorescent PE and iPP materials with comonomer contents low enough not to diminish the thermal and mechanical properties of the commercial polymers.

For practical application, the next step will be to modify the **1-PH** structure so as to modulate the fluorescence response, making it specific to different polymer grades.

6.4 Experimental part

6.4.1 Materials

Dichloromethane was degassed by freeze-pump-thaw cycles. THF was dried by distillation over sodium and benzophenone. Chloroform-*d* was dried over Alumina. The *rac*-Me₂Si(2-Me-Benz-[e]-Inden-1-yl)₂ZrCl₂ (pre)catalyst (**14**) was kindly donated by SABIC Europe. For the specifications of all other chemicals see Section 3.4.1 (Table 3.9). All manipulations of air-sensitive compounds were carried out under Argon or Nitrogen using Schlenk techniques and/or MBraun LabMaster 130 glove-boxes.

6.4.2 NMR characterization of low-molar-mass compounds

NMR spectra were acquired at 298 K with a Bruker Avance 400 spectrometer equipped with a QNP probe. The chemical shift scale was referred to TMS ($\delta = 0$ ppm) via residual solvent signals. Operating conditions for ¹H NMR were: 90° pulse; acquisition time, 2.9 s; relaxation delay, 5 s; 8 transients. Operating conditions for ¹³C NMR were: 90° pulse; acquisition time, 1.8 s; relaxation delay, 1 s; 32 transients. Broad-band proton decoupling was achieved with a modified WALTZ16 sequence (BI_WALTZ16_32 by Bruker).

The following abbreviations are used to describe the multiplicity of the signals in the ¹H NMR spectra: s, singlet; bs, broad singlet; d, doublet; bd, broad doublet; dd, double doublet; t, triplet; dt, double triplet; m, multiplet.

6.4.3 Synthesis of pyrene-1-carbaldehyde (1)²²

In a 1 L round bottomed flask, 10.0 g of Pyrene (49.4 mmol) and 7.4 g of dichloromethyl methyl ether (64 mmol) were dissolved in 400 mL of CH₂Cl₂. At 0°C, 30 mL of a 3.0 M solution of TiCl₄ in CH₂Cl₂ were added dropwise. The reaction phase was allowed to warm slowly to room temperature and stirred for additional 3 hours. The mixture was then poured into a large amount of ice-water and extracted with CH₂Cl₂ (400 mL x 2). The organic layer was washed with water (600 mL x 2), dried over Na₂SO₄, concentrated under reduced pressure. The residue and was chromatographed over silica gel using hexane as eluent to collect the starting unreacted pyrene compound (400 mg, 4% recovery). Pyrene-1carbaldehyde was subsequently eluted with toluene. The solvent was removed under reduced pressure, and the crude product was purified by recrystallization from hexane as a yellow solid (9.6 g; 96%). The ¹H NMR spectra of pyrene-1-carbaldehyde is reported in Figure 6.19.

¹H NMR (400 MHz, CDCl₃): (ppm) 10.82 (s, 1H, CHO); 9.49 (d, J=9.38 Hz, 1H, H_{aryl}); 8.49 (d, J=8.16 Hz, 1H, H_{aryl}); 8.37 - 8.26 (m, 5H, H_{aryl}); 8.15-8.10 (m, 2H, H_{aryl}). ¹³C NMR (100 MHz, CDCl₃): (ppm) 193.1; 131.1; 131.0; 131.5; 130.89; 130.8; 130.7; 127. 5; 127.2; 127.1; 127.0; 126.9; 126.6; 124,7; 124.6; 124.1; 123.1.



Figure 6.19. ¹H NMR spectrum of pyrene-1-carbaldeyde in CDCl₃.

6.4.4 Synthesis of 1-methylpyrene $(2)^{22}$

To a stirred solution of pyrene-1-carbaldehyde (9.6 g, 42 mmol) in 29.4 mL of toluene, inside a 1 L round bottomed flask fitted with a reflux condenser, 29.4 mL of diethylene glycol and 7.6 g of hydrazine hydrate (152 mmol) were added, and the mixture was refluxed for 1 hour. After removing toluene and water by distillation, the reaction phase was cooled to room temperature and 11.8 g of potassium hydroxide (210 mmol) were added. The reaction mixture was heated at 180°C, left for 3 hours under stirring, cooled slowly at room temperature, poured into a large amount of icewater, and extracted with CH₂Cl₂. The organic layer was separated, washed with water, dried over Na₂SO₄, and concentrated. The residue was chromatographed over silica gel (250 g) with hexane to afford the compound 3 (7.5 g, 83%), as pale-yellow crystals. The ¹H NMR spectra of 1-methylpyrene is reported in Figure 6.20.

¹H NMR (400 MHz, CDCl₃): (ppm) 8.28 (d, J=9.06 Hz, 1H); 8.21 - 8.00 (m, 7H); 7.90 (d, J=7.67 Hz, 1H); 3.01 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): (ppm) 132.3; 131.5; 131.0; 129.7; 129.2; 127.9; 127.6; 127.1; 126.9; 126.6; 126.4; 125.8; 124.8; 124.7; 124.7; 123.7; 19.9.



Figure 6.20. ¹H NMR spectrum of 1-methylpyrene in CDCl₃.

6.4.5 Synthesis of 1-pyrenylheptene (1-PH, 3)²⁰

In a flame-dried flask, a stirred solution of 1-methylpyrene (7.5 g, 35 mmol) in dry THF (35 mL) was chilled to 0°C and treated with *n*-BuLi (15.3 mL/38.3 mmol, 2.5 M solution in hexanes). After stirring for 1 hour, the solution was cooled to -78°C with dry ice/acetone and added with 6-bromohexane (5.6 mL, 42 mmol). The solution was then warmed to ambient temperature. After 2 hours, excess base was neutralized by the addition of dilute aqueous ammonium chloride. The crude product was extracted with diethyl ether (50 mL x 3), washed with brine (50 mL), dried over anhydrous MgSO₄, and concentrated to a vibrant yellow solid in vacuo. Vacuum sublimation at 80 °C provided pale yellow crystals (8.5 g, 82%). The ¹H NMR spectra of 1-pyrenyleptene is reported in Figure 6.21.

¹H NMR (400 MHz, CDCl₃): (ppm) 8.31 (d, J=9.15 Hz, 1H); 8.18 (dd, J=3.39, 3.67 Hz, 2H); 8.13 (dd, J=3.11; 4.52 Hz, 2H); 8.07-7.99 (m, 3H); 7.89 (d, J=7.95 Hz, ¹H); 5.90-5.80 (m, 1H); 5.05-4.96 (m, 2H); 3.37 (t, 2H); 2.08-2.13 (m, 2H); 1.93-1.86 (m, 2H); 1.56-1.48 (m; 4H). ¹³C NMR (100 MHz, CDCl₃): (ppm) 139.0; 137.2; 137.2; 131.5; 131.07; 131.0; 129.7;

128.6; 127.6; 127.2; 126.5; 125.8; 125.1; 124.9; 124.8; 124.6; 123.5; 117.1; 114.3; 33.8; 33.6; 31.8; 29.3; 28.9.



Figure 6.21. ¹H NMR spectrum of 1-pyrenylheptene in CDCl₃.

6.4.6 Polymerization experiments

All polymerizations were run using the HTE workflow described in Chapter 2. Propene and ethene copolymerizations were carried out in toluene at 60°C and $p_{mon} = 2.4$ bar, with the monomer continuously fed on demand until a desired conversion was reached (reaction time 2-20 minutes), using MAO as the scavenger/activator ($n_{Al} = 25 \mu mol in 5 mL$ of toluene per reaction cell). The (pre)catalyst amount was varied in the 0.5-20 nmol range, depending on the **1-PH** feeding.

6.4.7 Polymer characterizations

The polymers were characterized by Rapid-GPC, a-CEF and ¹³C NMR as reported in Chapter 2. Calorimetric measurements were performed with a

DSC-822 setup by Mettler Toledo. Each sample was heated from 25°C to 210°C (1st melting), cooled from 210°C to 25°C, and finally heated again from 25°C to 210°C (2nd melting). Polymer melting temperatures (T_m) refer to the 2nd melting scan.

Fluorescence+ measurements were carried out by Confocal Laser Scanning Microscopy (CLSM), using a LSM 5 Pascal setup by Zeiss, equipped with a Helium/Neon laser (LASOS Lasertechnik GmbH, LGK SAN7460A) with emission wavelengths of 543 and 633 nm, an Argon laser emitting at three different wavelengths (458, 488, 514 nm), and combined with an inverted microscope (Axiovert 200 M by Zeiss) equipped with a high resolution digital camera (AxioCam). The 633 nm wavelength was used for excitation, and fluorescence signals from the pyrene fragment were detected in a green channel after passing through a LP560 filter and NT80/20 and NFT545 beam splitters. CLSM images were collected in bright field and in fluorescent mode with low magnification objectives (10x and 20x). The scanning module comprised a confocal pinhole with a variable diameter, and a channel equipped with high-sensitivity PhotoMultiplier Tubes (PMT) for the detection of the signal. An additional channel was used for detecting the transmitted light. The samples were previously grinded into fine powders, placed on a glass slide under a very thin top glass (125 µm), and then put under the microscope for the acquisition. The time-lapse technique was used to visualize the morphology of the structure, with several repeats to check for reproducibility.

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CHAPTER 7

Catalytic Hydrogenolysis of Hydrocarbon Polymers

7.1 Introduction

In Chapter 6 we have briefly discussed the general question of plastics recycling. Here we focus on one specific option, namely chemical upcycling. It is not always realized that plastic wastes represent a vast and untapped resource for high-value products.¹ The conversion of polymer wastes into liquid raw materials that can be fed into existing infrastructures (e.g., crackers) to produce monomers and ultimately virgin polymers may become a pillar of the emerging circular economy.^{2–4}

The principle of microscopic reversibility teaches that β -alkyl elimination is a viable pathway of chain scissoring for (waste) hydrocarbon polymers (Figure 7.1).



Figure 7.1. Energetics of metal-assisted chain scissoring for hydrocarbon polymers.

Alkene insertion into M-Polymeryl bonds (M = [Transition] Metal) is a strongly exergonic process, releasing ≈ 12 kcal/mol per monomer enchainment.⁵ Therefore, the microscopic reverse, i.e. β -alkyl elimination, is strongly endergonic. Depolymerization processes that regenerate the monomer are by virtue very energy demanding. Polymer degradation, however, becomes thermodynamically accessible in the presence of molecular hydrogen. The driving force for the chain scissoring with H₂, which can be referred to as hydrogenolysis, is the conversion of C-C bonds into stronger C-H bonds. Ultimately, short chain alkanes (diesel) can be created from polyolefin waste at much lower process temperatures.

The barrier for β -alkyl elimination is composed of a fixed term, ΔG_{rxn} , and a variable term $\Delta G^{\ddagger}_{\text{ins}}$ (insertion barrier, Figure 7.1). Only the latter can be influenced via catalyst tuning. A suitable catalyst must be thermally tolerant to overcome the expected $\Delta G_{\text{rxn}} + \Delta G^{\ddagger}_{\text{ins}}$ reverse barrier, and compatible with H_2 to drive the reaction downhill. Since the barrier to olefin insertion for many efficient catalysts is very low, the expectation is a reasonable 24-32 kcal/mol barrier for the reverse path.^{6,7}

Silica-alumina supported zirconium monohydrides, containing active $(\equiv SiO)_3Zr$ -H centers, were the first reported catalysts for the low temperature hydrogenolysis of paraffinic PE and PP oligomers. The process yielded 84% conversion of a low-MW PE (C₁₈ to C₅₀) to lower alkanes (C₁ to C₉).⁴ Infrared spectroscopy supported the proposal that Zr_{surf}-H is responsible for the initial activation of the polymer.⁸ Zr-H catalyzed hydrogenolysis of alkanes was also reported, implying that linear polymers can be broken down further.⁹⁻¹¹ Recent results by Sadow indicated that selective hydrogenolysis of polyolefins to alkanes is achievable using a solid Pt/SrTiO₃ catalysts.¹

Reports of homogenous catalysts capable of degrading polymers with pure hydrocarbon backbones are rare, but some recent results are encouraging. Schwartz's reagent¹², Cp₂ZrHCl, known to rapidly undergo olefin insertion into the Zr-H bond, was shown to mediate chain scissoring of polybutadiene (PB), polyisoprene and poly(styrene-*co*-butadiene) at room temperature. The process was catalytic in the presence of alkyl-Al compounds^{13,14} or molecular hydrogen.^{14,15}

The market of PB is close to 20 million tons/y, 70% of which are used for tire manufacturing; therefore, recycling waste PB has a significant societal and economic impact. In this last part of the PhD project, we carried out a HTE screening of diverse Group 4 metallocene and post-metallocene compounds previously applied as olefin polymerization catalysts for application in the catalytic chain scissoring of PB. We used a 'hit-or-miss'

approach to quickly identify promising catalysts/catalyst classes and suitable reaction conditions. Density Functional Theory (DFT) calculations were performed preliminarily to highlight the Free Energy landscape of the conceivable reaction paths.

The work was carried out in collaboration with Prof. Adam S. Veige at the University of Florida (Gainesville, FL).

7.2 **Results and discussion**

7.2.1 Preliminary DFT investigation of PB chain scissoring

In a recent experimental study on the controlled chain scission of PB induced by Cp₂ZrHCl, Zheng¹³ claimed a mechanism that proceeds via olefin insertion into the M-H bond followed by β -alkyl elimination (Figure 7.2, pathway a) and fast hydrozirconation of the resulting terminal double bond, which would drive the reaction. However, in this mechanism β -alkyl elimination occurs in a species with a γ -double bond, i.e., several bonds away, and essentially a chain environment similar to PE. On the other hand, degradation of PE was never observed by the authors, neither was chain scissoring of polymers with only terminal double bonds.

Our analysis of the driving force for chain scissoring using Density Functional Theory (DFT) methods (at the TPSSh-D0/TZ//TPSSh/DZ level of theory; see Section 7.4.2 for details) indicates that a lower endergonicity or even exergonicity of β -alkyl elimination can be achieved by forming the

following stabilized species: Zr-allyls (Figure 7.2, pathway b), Zr-vinyls (Figure 7.2, pathway c), and conjugated dienes (Figure 7.2, pathway d). Pathway c is consistent with the authors' observation of chain scissoring of the model compound 1,5,9-*cis*-decatriene into C₂ and C₈ fragments (only if [Zr]/[1,5,9-cis-decatriene] > 2). The degradation is slow compared to PB, and the mechanism is likely not prevalent in chains with multiple internal double bonds.



Figure 7.2. DFT driving force analysis for chain scissoring in double bond rich hydrocarbon polymers. Gibbs Free Energies of reaction at 298 K, TPSSh-D0/TZ//TPSSh/DZ level of theory. ($\mathbf{Zr} = Cp_2ZrClH$).

7.2.2 First chain scissoring experiments

Considering the work by Zheng, we selected a 98% cis-PB sample as a model substrate for chain scissoring studies under mild conditions.¹³ To the best of our knowledge, no catalysts beyond the perennial Schwartz's reagent have ever been screened for their PB degradation ability. Based on Figure 7.1, we decided to undertake a HTE screening of Group 4 metal complexes known to mediate catalytic olefin polymerization. Our starting set (Figure 7.3) included four classical metallocenes, namely Cp₂ZrCl₂ (15), Cp^{*}₂ZrCl₂ (16), rac-SiMe₂(2-Me-4-Ind)₂ZrCl₂ (4) and rac-SiMe₂(2-Me-Ind)₂ZrCl₂ (17), and two post-metallocenes, i.e., the (pyridylamido)HfMe₂ complex 2 and the Hf[OOOO]Cl₂ complex 10. The reactions were carried out in toluene solution at 30°C, in the presence of tri-iso-butyl-Aluminum (TiBAl) at [Al]/[TM] ratios of 15 and 30, both to generate the active L_nTMHCl species in situ and for catalytic turnover (Figure 7.4a and 7.4b respectively).^{13,16} The GPC results reported in Tables 7.1-7.3 and Figures 7.5-7.7 highlighted some interesting trends.



Figure 7.3. Structures of the molecular catalysts preliminarily screened for PB chain scissoring activity.



Figure 7.4. Proposed mechanism to generate Zr-H species in *situ* and subsequent PB chain scissoring (a) and regenerate the active species (b).

Unbridged metallocenes 15 and 16 were both able to significantly degrade PB (Table 7.1 and Figure 7.5). The M_n value halved after 24h, and again after 48 h (compare samples PB1 and PB2 for 15; PB5 and PB6 for 16).

Increasing the [Al]/[Zr] ratio from 15 to 30 had a detrimental effect on the performance of **15**, in line with previous observations by Zheng; a tentative explanation is that the generation of Al–Zr hetero-bimetallic adducts inactivates the hydrozirconation pathway.^{17,18} No such negative effect was observed for **16**, likely due to the greater steric bulk of the ligand framework; a broadening of product MWD was noted with this catalyst instead.

Sample ID	Catalyst	[Al]/[Zr]	<i>t</i> (h)	M _n (kDa)	M _w (kDa)	$M_{ m w}/M_{ m n}$
PB 98% cis	-	-	-	77	271	3.5
PB1	15	15	24	37	90	2.4
PB2		15	48	18	49	2.8
PB3		30	24	46	137	3.0
PB4		30	48	31	104	3.7
PB5		15	24	49	160	3.3
PB6	16	15	48	16	74	5.1
PB7		30	24	52	178	3.6
PB8		30	48	18	83	4.7

Table 7.1. Results of PB chain scissoring with 15 and 16.^(a)

(a) $n_{\text{cat}} = 342 \text{ nmol}$, $n_{\text{PB}} = 130 \text{ nmol}$ (corresponding to $\approx 185 \text{ µmol}$ of *cis* double bonds). Other experimental conditions: $T = 30^{\circ}$ C, toluene solvent.



Figure 7.5. Comparison between the GPC curves of the PB starting material and the chain scissoring products obtained with **15** (top) and **16** (bottom) at variable [Al]/[Zr] and reaction time.

 C_2 -symmetric *ansa*-zirconocenes **4** and **17** degraded the starting material with similar efficiency as the unbridged homologs (Table 7.2 and Figure 7.6). In this case, no detrimental effects of increasing [Al]/[Zr] was observed. Both catalysts performed better than **15**, at least in the first 24 h. The PDI of the products narrowed from 3.5 to around 2.

Sample ID	Catalyst	[Al]/[Zr]	<i>t</i> (h)	M _n (kDa)	Mw (kDa)	M _w /M _n
PB 98% cis	-	-	-	77	271	3.5
PB9	4	15	24	31	68	2.2
PB10		15	48	21	54	2.6
PB11		30	24	25	63	2.5
PB12		30	48	16	46	2.9
PB13		15	24	25	56	2.3
PB14	17	15	48	17	46	2.7
PB15		30	24	24	57	2.4
PB16		30	48	15	42	2.8

Table 7.2. Results of PB degradation with 4 and 17.^(a)

(a) $n_{\text{cat}} = 342 \text{ nmol}$, $n_{\text{PB}} = 130 \text{ nmol}$ (corresponding to $\approx 185 \text{ }\mu\text{mol}$ of *cis* double bonds). Other experimental conditions: $T = 30^{\circ}$ C, toluene solvent.



Figure 7.6. Comparison between the GPC curves of the PB starting material and the chain scissoring products obtained with 4 (top) and 17 (bottom) at variable [Al]/[Zr] and reaction time.

The two post-metallocenes 2 and 10, on the other hand, were unable to appreciably degrade PB in the first 24 h (Table 7.3 and Figure 7.7); only after 48 h was a modest decrease of M_n observed. One can speculate that Hf-based catalysts are less efficient than Zr ones for this chemistry, but more experiments are necessary to draw conclusions in this sense.

Sample ID	Catalyst	[Al]/[Hf]	t (h)	M _n (kDa)	M _w (kDa)	$M_{ m w}/M_{ m n}$
PB 98% cis	-	-	-	77	271	3.5
PB17	2	15	24	80	253	3.2
PB18		15	48	47	186	3.9
PB19		30	24	69	244	3.6
PB20		30	48	47	197	4.4
PB21	10	15	24	80	260	3.2
PB22		15	48	43	208	4.9
PB23	10	30	24	64	229	3.6
PB24		30	48	33	116	3.5

Table 7.3. Results of PB degradation with 2 and 10.^(a)

(a) $n_{\text{cat}} = 342 \text{ nmol}$, $n_{\text{PB}} = 130 \text{ nmol}$ (corresponding to $\approx 185 \text{ }\mu\text{mol}$ of *cis* double bonds). Other experimental conditions: $T = 30^{\circ}$ C, toluene solvent.



Figure 7.7. Comparison between the GPC curves of the PB starting material and the chain scissoring products obtained with 2 (top) and 10 (bottom) at variable [A1]/[Hf] and reaction time.

7.2.3 Tuning the reaction parameters

In view of the preliminary results of the previous section, we focused on the best performing metallocene catalysts **15** and **4**. A series of hydrozirconation experiments was run at different reaction times and [Al]/[Zr] ratios (Tables 7.4-7.5 and Figures 7.8-7.9), aiming to further highlight the effects of these reaction variables. The temperature was raised to 50°C, in order to better dissolve the starting polymer and prevent (partial) precipitation of the products throughout degradation.

Sample ID	[Al]/[Zr]	t (h)	Mn (kDa)	M _w (kDa)	$M_{ m w}/M_{ m n}$
PB 98% cis	-	-	77	271	3.5
PB25	2	2.5	10	27	2.7
PB26	2	5	9	25	2.7
PB27	2	18	12	32	2.6
PB28	8	2.5	16	45	2.7
PB29	8	5	13	36	2.7
PB30	8	18	7	22	3.1
PB31	60	2.5	46	143	3.1
PB32	60	5	41	139	3.3
PB33	60	18	24	84	3.6
PB34	120	2.5	44	154	3.5
PB35	120	5	29	145	5.1
PB36	120	18	33	125	3.8

Table 7.4. Main results of PB chain scissoring with 15 at variable reaction conditions.^(a)

(a) $n_{\text{cat}} = 684 \text{ nmol}$, $n_{\text{PB}} = 260 \text{ nmol}$ (corresponding to $\approx 370 \text{ }\mu\text{mol}$ of *cis* double bonds). Other experimental conditions: $T = 50^{\circ}$ C, toluene solvent.



Figure 7.8. M_n vs t for PB chain scissoring with 15 at different [Al]/[Zr] ratios (data from Table 7.4).

Sample ID	[Al]/[Zr]	<i>t</i> (h)	Mn (kDa)	M _w (kDa)	$M_{ m w}/M_{ m n}$
PB 98% cis	-	-	77	271	3.5
PB37	2	2.5	22	70	3.2
PB38	2	5	21	71	3.4
PB39	2	18	16	48	3.0
PB40	8	2.5	23	79	3.4
PB41	8	5	24	75	3.2
PB42	8	18	25	79	3.2
PB43	60	2.5	22	74	3.3
PB44	60	5	22	77	3.6
PB45	60	18	19	55	2.8
PB46	120	2.5	21	70	3.4
PB47	120	5	19	69	3.5
PB48	120	18	18	60	3.4

Table 7.5. Main results of PB chain scissoring with 4 at variable reaction conditions.^(a)

(a) $n_{\text{cat}} = 684$ nmol, $n_{\text{PB}} = 260$ nmol (corresponding to ≈ 370 µmol of *cis* double bonds). Other experimental conditions: $T = 50^{\circ}$ C, toluene solvent.



Figure 7.9. M_n vs t for PB chain scissoring with 4 at different [Al]/[Zr] ratios (data from Table 7.5).

The kinetic profiles in Figures 7.8 and 7.9 point to an exponential catalyst deactivation. For catalyst **15**, the reaction was slower the higher the [Al]/[Zr] ratio, as noted before.

7.2.4 Extended screening of molecular catalysts for PB degradation

Prompted by these initial results, we expanded the catalyst library, aiming to analyze the effects of varying the central metal (TM = Ti, Zr, Hf), catalyst symmetry, and some steric and electronic features. The library (Figure 7.10) included:

1) unbridged metallocenes: Cp₂ZrCl₂ (**15**), Cp^{*}₂ZrCl₂ (**16**), Cp₂HfCl₂ (**18**), Cp₂TiCl₂ (**19**).

2) *ansa*-zirconocenes: a) C_2 -symmetric metallocenes: rac-Me₂Si(2-Me-4-Ph-1-Ind)₂ZrCl₂ (**4**), rac-Me₂Si(2-Me-1-Ind)₂ZrCl₂ (**17**), rac-C₂H₄(1-Ind)₂ZrCl₂ (**20**), and rac-Me₂Si(2-*i*Pr-4-Ph-1-Ind)₂ZrCl₂ (**21**); b) C_1 -symmetric metallocenes: rac-Me₂C(3-*i*Pr-Cp)(Flu)ZrCl₂ (**22**) and rac-Me₂C(3-Adamantyl-Cp)(Flu)ZrCl₂ (**23**).

3) post-metallocenes: (pyridylamido)HfMe₂ (**2**), Hf[OOOO]Cl₂ (**10**), $Zr[OOOO]Cl_2$ (**11**), and $Cp^*(NC((o-F_2Ph)(iPr_2-N)TiCl_2$ (**24**).

All catalysts were tested in toluene solution at 50°C, at two different values of [Al]/[TM] (15, 30) and reaction time (24, 48 h). The results are summarized in Tables 7.6-7.8.



Figure 7.10. The extended catalyst library for PB degradation studies (see text).

Sample ID	Catalyst	[Al]/[TM]	<i>t</i> (h)	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$
PB 98% cis	-	-	-	77	271	3.5
PB49		15	24	15	41	2.7
PB50	15	15	48	11	34	3.2
PB51	15	30	24	19	59	3.1
PB52		30	48	15	36	2.4
PB53	16	15	24	31	160	5.2
PB54		15	48	38	159	4.1
PB55		30	24	30	145	4.9
PB56		30	48	23	74	3.3
PB57		15	24	48	167	3.5
PB58	10	15	48	23	83	3.7
PB59	10	30	24	35	157	4.5
PB60		30	48	23	84	3.7
PB61		15	24	27	129	4.8
PB62	10	15	48	16	91	5.7
PB63	19	30	24	32	148	4.7
PB64		30	48	17	58	3.5

Table 7.6. Results of PB degradation with a series of unbridged metallocenes.^(a)

(a) $n_{\text{cat}} = 684 \text{ nmol}$, $n_{\text{PB}} = 260 \text{ nmol}$ (corresponding to $\approx 370 \text{ }\mu\text{mol}$ of *cis* double bonds).

Sample ID	Catalyst	[Al]/[Zr]	<i>t</i> (h)	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$
PB 98% cis	-	-	-	77	271	3.5
PB65		15	24	21	55	2.7
PB66		15	48	18	59	3.4
PB67	4	30	24	20	62	3.1
PB68		30	48	14	37	2.6
PB69		15	24	21	67	3.2
PB70	17	15	48	18	60	3.4
PB71	1/	30	24	19	66	3.4
PB72		30	48	6	24	4.1
PB73		15	24	14	35	2.6
PB74	20	15	48	9	29	3.1
PB75	20	30	24	12	34	3.0
PB76		30	48	11	25	2.4
PB77	21	15	24	52	181	3.5
PB78		15	48	26	142	5.4
PB79		30	24	37	149	4.0
PB80		30	48	24	70	2.9
PB81		15	24	20	60	3.0
PB82	22	15	48	18	53	3.0
PB83	22	30	24	14	42	3.0
PB84		30	48	12	37	3.0
PB85		15	24	23	85	3.7
PB86	22	15	48	19	82	4.3
PB87	23	30	24	20	70	3.4
PB88		30	48	14	38	2.8

Table 7.7. Results of PB degradation with a series of *ansa*-zirconocenes.^(a)

(a) $n_{\text{cat}} = 684 \text{ nmol}$, $n_{\text{PB}} = 260 \text{ nmol}$ (corresponding to $\approx 370 \text{ }\mu\text{mol}$ of *cis* double bonds).

Sample ID	Catalyst	[Al]/[TM]	t (h)	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$
PB 98% cis	-	-	-	77	271	3.5
PB89		15	24	47	226	4.8
PB90		15	48	42	190	4.6
PB91	2	30	24	33	185	5.5
PB92		30	48	38	114	3.0
PB93		15	24	33	117	3.5
PB94	10	15	48	20	143	7.1
PB95	10	30	24	41	118	2.9
PB96		30	48	15	39	2.7
PB97		15	24	33	86	2.6
PB98	11	15	48	25	58	2.3
PB99	11	30	24	40	166	4.2
PB100		30	48	19	40	2.1
PB101		15	24	26	114	4.4
PB102	24	15	48	23	143	6.3
PB103	24	30	24	43	144	3.4
PB104		30	48	26	79	3.0

Table 7.8. Results of PB degradation with a series of post-metallocenes.^(a)

(a) $n_{\text{cat}} = 684 \text{ nmol}$, $n_{\text{PB}} = 260 \text{ nmol}$ (corresponding to $\approx 370 \text{ }\mu\text{mol}$ of *cis* double bonds).

Although most bridged and unbridged metallocenes behaved rather similarly, the two *ansa*-zirconocene complexes **17** and **20** (Table 7.7) displayed superior PB degradation performance, reaching $M_n = 6-9$ kDa after 48 h. Certain ligand substituents sorted major effects (compare e.g., 2-Me in **4** and 2-*i*Pr in **21**: the low catalytic activity of the latter is likely due to sterics, notwithstanding the fact that **21** is much more electrophilic than **4**).¹⁹ Not surprisingly, catalyst symmetry, which is key for stereoselectivity when the same catalysts are applied to olefin polymerization,²⁰ turned out to be immaterial in PB degradation: indeed, C_1 -symmetric species **22** and **23** performed similarly to C_2 -symmetric species **4**.

Regarding the post-metallocene series, the Hf complex **2** (Table 7.8) confirmed a poor degradation ability, as also observed earlier. The results

for 10, on the other hand, hint that the problem of Hf-based catalysts is not based on an inherently poor catalytic activity with this metal, but rather on their activation: as a matter of fact, the performance at 50°C was similar to the best metallocenes (i.e., a M_n of 15 kDa is reached). The fact that homologs 10 (TM = Hf) and 11 (TM = Zr) show very similar performance lends further support to this conclusion.

As far as Ti-based catalysts are concerned, the aminidate complex 24 performed less effectively than the simple titanocene 19 (compare samples **PB64** of Table 7.6 and **PB104** of Table 7.8), However, this metal is also prone to mediate PB degradation.

7.2.5 PB chain scissoring in the presence of H_2

It has been reported that H_2 can be employed to improve the chain scissoring performance of the Schwartz's reagent.¹⁴ A plausible explanation based on simple thermodynamic and kinetic considerations was anticipated in Figure 7.1. Ternary systems like Zr-H/H₂/LiH were shown to catalytically and effectively degrade hydrocarbon polymers with internal double bonds like polychloroprene, through a constant *in situ* regeneration of the Zr-H reagent.¹⁵

We screened the H_2 effect employing the same catalyst set used in the previous section under otherwise identical experimental conditions (reaction time was reduced from 24 to 15 h, though). Overall, the introduction of H_2 enhanced PB degradation activity for most catalytic species (Table A7.1); however, the effects were markedly structure-dependent.

Unbridged metallocenes performed slightly better with H₂ (Figure 7.11).



Figure 7.11. Comparison of M_n values for PB samples degraded with unbridged metallocene catalysts using TiBAl and TiBAl/H₂ (reaction time was 15 h for experiments with H₂, 24 h for experiments without H₂).

The scenario for *ansa*-metallocenes was much more complex (Figure 7.12), with some extreme cases. The performance with H_2 improved moderately for 4 and 23, by 2-fold for 22, by 4- to 5-fold for 17 and 20, and reached an absolute maximum for 21, which was nearly inactive with TiBAl alone. These findings indicate that the H_2 response is exquisitely sensitive to catalyst structure.

The M_n PB values of 2-3 kDa reached with catalysts **20** and **21** imply that roughly 40 chain scissoring events per chain took place. This exceeds the number of TiBAl equivalents in the reaction system (15-30), and indicates that catalysts regeneration involved indeed H₂.



Figure 7.12. Comparison of M_n values for PB samples degraded with *ansa*zirconocene catalysts using TiBAl and TiBAl/H₂ (reaction time was 15 h for experiments with H₂, 24 h for experiments without H₂).

 H_2 effect on post-metallocene catalysts was minor (Figure 7.13). As a matter of fact, the differences in PB degradation data with and without H_2 in the reaction system are within the uncertainty of the determinations.



Figure 7.13. Comparison of M_n values for PB samples degraded with postmetallocene catalysts using TiBAl and TiBAl/H₂ (reaction time was 15 h for experiments with H₂, 24 h for experiments without H₂).

7.2.6 PB chain scissoring catalysis: TiBAl/H₂ or MAO/H₂?

In the last part of this study, we reinvestigate all molecular catalyst in Figure 7.10 under H₂ pressure ($p_{H2} = 5$ bar) using MAO (350 equivalents) in the place of TiBAl. As a matter of fact, MAO is the preferred activator in the poly(insertion) of olefinic monomers, which can be looked at as the reverse of polymer chain scissoring. The main results are reported in Table A7.2 and Figure 7.14.





Figure 7.14. Comparison of M_n values for PB samples degraded with the unbridged metallocenes (top), *ansa*-zirconocenes (middle), and post-metallocenes (bottom) using TiBAl/H₂ and MAO/H₂ (see text).

Interestingly, whereas all screened molecular complexes turned out to be active in PB degradation using the H₂/MAO combination, the comparative performance of the three different catalyst classes in the library was reversed. As a matter of fact, the MAO/H₂ combination boosted the degradation ability of all the species that exhibited a lower degradation ability in the presence of TiBAl/H₂. A representative example is the Hf-based metallocene **18**, for which this combination proved to be the best explored until know.

Better results were also achieved with the post-metallocene catalysts, especially catalyst **24** which featured the best compromise between MW reduction ($M_n = 7$ kDa) and PDI narrowing (2.4). On the contrary, the MAO/H₂ combination did not appear to be beneficial for *ansa*-zirconocenes, especially C_1 -symmetric ones. In olefin polymerization, it is known that the activity of *ansa*-zirconocenes is highly dependent on the

[Al]/[Zr] ratio, and many catalysts require values of 10⁴ or higher.²⁰ Here we only tested one, rather low value; thus, further experiments at higher values are necessary to draw conclusions.

7.3 Concluding remarks

The propensity of several molecular Group 4 metal catalysts to mediate catalytic chain scissoring of PB was successfully demonstrated. The results are still very preliminary with respect to structure-properties relations as well as mechanistic analysis, but bear great promise for positive developments, also in terms of practical application.

We plan to further expand the catalyst library (Figure 7.15). Further efforts will include the exploration of other main group metal alkyls as chain transfer agents (e.g., ZnR₂, MgR₂, GaR₃), as well as optimization of [M]/[Polymer] ratio and H₂ pressure. An optimized catalyst system for PB degradation may offer an entry point for catalytic degradation of fully saturated polymers, with PE and PP in the first place.


Figure 7.15. Additional catalysts for PB chain scissoring investigations.

7.4 Experimental part

7.4.1 Materials and methods

PB 98% *cis*, TiBAl (purity 96.5) and H₂ (purity > 99.9%) were purchased from Sigma-Aldrich, Chemtura and Linde, respectively. The specifications of all other chemicals are reported in Section 3.4.1 (Table 3.9). Precatalysts **15-20** and **24** were kindly donated by SABIC Europe. Metallocenes **21-23** were prepared at Moscow State University according to the literature.^{21,22} All PB degradation reactions were carried out in the HiP reactor described in Section 2.3. The polymers were characterized by Rapid-GPC as reported in Chapter 2.

7.4.2 Computational details

All geometries were fully optimized using the Gaussian 16 software package.²³ Following the protocol proposed in Ref.24, all relevant minima were fully optimized at the TPSShTPSSh level²⁵ of theory employing correlation-consistent polarized valence double- ζ Dunning (DZ) basis sets of cc-pVDZ(-PP) quality^{26,27} from the EMSL basis set exchange library.²⁸ Single point energy corrections were calculated at TPSShTPSSh level of theory, including Grimme's D0 dispersion corrections,²⁹ employing the ccpVTZ(-PP) basis set.^{30,31} The density fitting approximation (Resolution of Identity, RI) was used throughout.³²⁻³⁵ All calculations were performed at the standard Gaussian 16 quality settings [Scf=Tight and Int(Grid=UltraFine)]. All structures represent true minima as indicated by the absence of imaginary frequencies.

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Appendix

Sample ID	Catalyst	[Al]/[TM]	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$	n _{chain} (µmol)
PB 98% cis	-	-	77	271	3.5	0.2
PB105	15	15	13	37	2.9	1.1
PB106	16	30	21	80	3.8	0.7
PB107	18	15	39	135	3.5	0.4
PB108	19	15	27	103	3.8	0.6
PB109	4	30	14	44	3.1	1.1
PB110	17	30	5	11	2.3	3.1
PB111	20	15	2	3	1.7	8.4
PB112	21	15	2	3	1.7	9.0
PB113	22	15	11	34	3.1	1.3
PB114	23	30	18	47	2.6	0.8
PB115	2	30	54	179	3.3	0.3
PB116	10	30	39	144	3.7	0.4
PB117	11	30	46	132	2.9	0.3
PB118	24	15	22	59	2.6	0.7

Table A7.1. Main PB degradation results with the catalysts of Figure 7.10 and TiBA1/H2. $^{(a)}$

(a) $n_{\text{cat}} = 513 \text{ nmol}$, $n_{\text{PB}} = 195 \text{ nmol}$ (corresponding to $\approx 278 \text{ µmol}$ of *cis* double bonds). Other experimental conditions: $T = 50^{\circ}$ C, toluene solvent, $p_{\text{H2}} = 5.0$ bar, t = 15h.

Sample ID	Catalyst	Mn (kDa)	Mw (kDa)	$M_{ m w}/M_{ m n}$	<i>n</i> _{chain} (µmol)
PB 98% cis	-	77	271	3.5	0.2
PB119	15	17	37	2.2	0.9
PB120	16	30	72	2.4	0.5
PB121	18	14	36	2.5	1.1
PB122	19	29	79	2.7	0.5
PB123	4	16	36	2.3	1.0
PB124	17	26	71	2.7	0.6
PB125	20	23	56	2.4	0.6
PB126	21	23	61	2.6	0.6
PB127	22	32	95	2.9	0.5
PB128	23	44	173	4.0	0.3
PB129	2	40	114	2.9	0.4
PB130	10	18	46	2.6	0.8
PB131	11	18	43	2.4	0.8
PB132	24	7	18	2.4	2.0

Table A7.2 Main PB degradation results with the catalysts of Figure 7.10 in the presence of MAO/H_2 .

(a) $n_{\text{cat}} = 513 \text{ nmol}$, $n_{\text{PB}} = 195 \text{ nmol}$ (corresponding to $\approx 278 \text{ µmol}$ of *cis* double bonds). Other experimental conditions: $T = 50^{\circ}$ C, toluene solvent, $p_{\text{H2}} = 5.0$ bar, t = 15h, [A1]/[TM] = 350.

CHAPTER 8

Conclusions

High Throughput Experimentation (HTE) will ultimately become the gold standard of chemical R&D. On the other hand, until now the technical complexity and high Capex and Opex of HTE tools and methods have hampered a broad dissemination in several important areas of the chemical sciences. In particular, HTE approaches to organometallic catalysis began to spread in academia only recently.¹

The general aim of the present PhD project was to implement and apply 'smart' HTE protocols for tackling complex problems in olefin polymerization catalysis, with special focus on polyolefin sustainability. The main case history was Coordinative Chain Transfer Polymerization (CCTP)² and its Chain Shuttling Polymerization (CSP)³ variant: unraveling the complex kinetics governing this elusive chemistry and expanding its scope to novel monomers and materials are important open challenges. We have also addressed questions of relevance for the recycling of polyolefin wastes in the context of a circular economy.⁴

The HTE toolkit was introduced in **Chapter 2**. Despite the extensive robotic automation, a HTE platform is not a push-button setup. A complete HTE workflow can include several reaction platforms and an array of integrated analytical tools amenable to high-throughput operation and yet

ensuring the precision and accuracy of conventional high-end tools. On the other hand, state-of-the-art infrastructures like the one which operates at LSP, the laboratory which hosted this project, are invaluable because they shorten the time from experiment ideation to execution, and multiply the number of experiments giving easy access to conditions that would be very difficult to achieve with conventional tools.

In **Chapter 3** we illustrated the implementation of HTE protocols for parallel olefin CSP experiments. We successfully downscaled the high-temperature and high-pressure synthesis of statistical Olefin Block Copolymers (OBC) according to the Dow InfuseTM technology.^{5,6} A systematic exploration of the multi-dimensional variables hyperspace of ethene/1-alkene copolymerization under tandem catalysis conditions led us to elucidate unambiguously, for the first time, the microstructure and architecture of these advanced materials, that found commercial applications as unique thermoplastic elastomers and also as effective phase compatibilizers in immiscible polyolefin blends.

In **Chapter 4** we highlighted a systematic and thorough search for catalyst systems amenable to CCTP/CSP other than those originally disclosed by Dow Chemical. Notwithstanding the several claims in the literature,^{2,3,7} our study led us to conclude that reversible trans-alkylation in catalytic olefin polymerizations is exceedingly rare, and therefore expanding the scope of CSP via catalyst diversification is problematic.

Moving from this negative conclusion, in **Chapter 5** we explored the alternative option of OBC diversification by using unconventional comonomers. Two new classes of OBCs were prepared by CSP of ethene with 4-methyl-1-pentene or 1-hexadecene, respectively.

Both comonomers are expected to provide block copolymers with unusual and interesting physical properties.^{8,9}

In **Chapter 6** we reported how the HTE workflow was utilized to explore the possibility to introduce a fluorescent tag into polyethylene and polypropylene chains via copolymerization, for diagnostic purposes. The idea was to make different polyolefin grades identifiable post-mortem with a simple, cheap and fast optical measurement. Series of ethene and propene copolymerizations with 1-pyrenylheptene, a fluorescent comonomer prepared ad hoc,^{10,11} demonstrated that the concept works very well down to incorporations of the tag at which the thermal and physico-mechanical properties of the copolymers are practically identical to those of the corresponding homopolymers.

Finally, in **Chapter 7** we investigated catalytic degradation as a possible route of polymer waste recycling. It has long been known that polyolefin can be cleaved under comparatively mild conditions in the presence of certain heterogeneous transition metal catalysts.¹² Recently, this has also been shown for polydienes with a homogeneous catalyst.^{13,14}

In the framework of the present thesis we explored the chain scissoring reaction of 1,4-*cis*-polybutadiene mediated by a large library of Group 4 metallocene and post-metallocene complexes. A strong dependence of molecular kinetics on catalyst structure was highlighted, and efficient catalysts were identified. This part of the project was a collaboration with Prof. Adam S. Veige at the University of Florida (Gainesville, FL).

Overall, we can conclude that 'smart' HTE methodologies are ideally suited to rapidly identify novel and convenient routes of olefin polymerization and polyolefin/polydiene degradation that can improve the sustainability of these ubiquitous and important industrial processes and materials, making them ultimately better suited to a circular economy.

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