

Preface

Polyolefins represent approximately 50% by weight of all commodity and commodity-plus polymers, which in turn amounts to about 90% by weight of the global polymer production. Today, literally hundreds of polyolefin grades are available commercially, with an incredible variety of properties and applications, ranging from ultra-rigid thermosets (stiffer than steel, but with the premium of a much lower density) to high-performance elastomers, via all conceivable thermoplastic and elastoplastic materials in between. Yet, if one looks at their chemical composition, polyolefins are surprisingly limited: polyethylene, polypropylene, a few copolymers of ethene with propene or another alpha-olefin, and little else. The key reason for this apparent contradiction is the unique and thorough molecular control of the polymerization process that modern transition metal-based catalysts are able to provide. With the correct choice of catalyst system and reaction conditions, it is possible to produce polyolefin materials with precisely defined and tunable chain microstructures and molecular mass distributions; this translates into a correspondingly fine control in the way such chains crystallize (when they are able to) and flow. In addition, a rich toolbox for supramolecular material design provides almost unlimited possibilities for further tailoring and diversification by means of intelligent processing, blending and additives formulations and technologies.

The result has been an unprecedented success story, as demonstrated by the exponential growth curve of the annual world consumption of polyolefins, from less than 10^5 tonnes during the mid-1950s to the present-day 10^8 tonnes. It might be worthy to add here that polyolefins should be regarded as a metastable state of the light fractions of refined oil. Rather than flaring them—as has happened in the past—they may be temporarily solidified, used for all sorts of smart applications at a nominal cost, and then burned to produce energy (the most logical way of recycling/disposing). If this point were to be understood by politicians, environmentalists and opinion-makers, polyolefins would be recognized for what they are—the greenest and most environmentally friendly materials ever invented.

For almost three decades, the industrial production of high-density polyethylene (HDPE) and isotactic polypropylene (iPP) was based exclusively on heterogeneous catalysts (of the Ziegler–Natta- or Phillips type), and characterized by many differ-

ent and ill-defined active species. However, a massive research effort resulted in major improvements of catalytic performance, although it is fair to admit that the approach was purely empirical.

It was only during the early 1980s that the serendipitous discovery of methylalumoxane as an effective activator of metallocene precatalysts made it possible to derive the first industrially appealing homogeneous ethene polymerization catalysts. Soon after that, with the implementation of stereorigid *ansa*-metallocenes with chirotopic sites, it was demonstrated that stereoregular polypropylenes could also be obtained in solution, and this opened the era of “single-site” catalysts. The strong point of a homogeneous catalyst is its well-defined structure, which translates into a single active species and a corresponding microstructural uniformity of the polymerization products. Although the active species can be designed, at least in principle, in order to achieve better/different catalytic properties, the drawback is that, for most industrial olefin polymerization process technologies, a heterogeneous catalyst is needed. Unfortunately, changing a homogeneous single-site catalyst into a heterogeneous (supported) one is a logical but by no means simple solution; in fact, the process forms the subject of this whole book.

Homogeneous “Single-site” Olefin Polymerization Catalysts: A Brief Mechanistic Introduction

In spite of the popularity of the definition, no transition metal-based olefin polymerization catalyst can be “single-site”. In fact, the reaction mechanism inherently involves two *cis* coordination sites of the metal: one for the σ -bound growing polymeryl (i.e., the active site), and one for the incoming monomer. The chain migratory insertion path ensuring the least nuclear motion results in an exchange of polymeryl and monomer coordination sites, which means that both are (or at least can be) active sites. What is important to realize is that in most cases the two sites are *not* equivalent; therefore, defining a homogeneous catalyst as “single-center” would, in our opinion, be more appropriate.

The catalytic cycle of olefin polymerization in homogeneous phase is fairly simple. The active species is usually a coordinatively unsaturated $[L_yMR]^+$ cation, generated from a $L_yM(X)(Y)$ precursor (M = transition metal; L_y = ancillary ligand(s); X and Y = monodentate anionic ligands, such as halide or amide) by alkylation and reaction with a strong Lewis acid. In the case where X and Y are alkyl groups, alkylation may be unnecessary and the coordination vacancy can also be produced by reaction with a Brønsted acid. A key point here is that the counteranion needs to be poorly coordinating, so as not to prevent/slow-down monomer access to the transition metal.

Chain propagation is believed to involve olefin π -coordination at the metal, followed by the formation of a four-center transition state and migratory insertion. A regular alternation of insertions at the two coordination sites is expected under a kinetic quench regime; at the other limit, a Curtin–Hammett regime can be

observed in case of a rapid (relative to insertion) relocation of the growing polymeryl between the two metal coordination sites (e.g., under conditions of monomer starvation).

Chain transfer can occur, for example via β -H elimination (to the monomer and/or to the metal), or by trans-alkylation with main group metal alkyl cocatalysts. Molecular hydrogen can be added deliberately to decrease the polymer molecular weight via σ -bond metathesis. In all cases, the newly formed M—H or M—R bond is an active site, and can initiate the growth of a new polymeryl.

In the homopolymerization of ethene, the above is expected to result in perfectly linear polyethylene chains, which is indeed the norm. However, with some catalysts, and under certain conditions, a vinyl-terminated polyethylene chain may be released into the reaction medium where it acts as a macromonomer and inserts into a different M—Polyethylenyl bond; this leads to the formation of a “long-chain-branched” polyethylene. A different type of branched polyethylene, on the other hand, has been obtained with a number of sterically hindered late transition metal catalysts showing a high propensity to intramolecular β -H elimination; repeated steps of β -H elimination and macro-olefin reinsertion into the M—H bond (a process often referred to as “chain walking”) can result in extensively branched polyethylenes resembling those produced by radical polymerization.

The case of alpha-olefins in general—and of propene in particular—is more complicated. A prochiral alpha-olefin molecule can insert into a M—R bond in four different ways, depending on the regiochemistry (1,2 or 2,1) and on the choice of enantioface (*re* or *si*). In most cases, a strong preference is observed for one insertion regiochemistry (usually the 1,2); compared with heterogeneous Ziegler–Natta catalysts, however, most homogeneous single-site catalysts (and particularly metallocenes) are remarkably less regioselective, and occasional regiodefects are detected in the polymer by ^{13}C NMR, typically in the form of head-to-head/tail-to-tail enchainments. For a catalyst to be stereoselective, on the other hand, a second element of chirality must combine with that arising from monomer coordination. In principle, this can be the configuration of the growing chain, and in particular of the stereogenic C in the last-inserted monomeric unit (chain end control); occasional cases of 1,3-*like* or 1,3-*unlike* asymmetric induction have indeed been reported in propene polymerizations mediated by single-site catalysts, but always at low temperatures and with modest entity. Much more important—and also industrially relevant—on the other hand, is the case of catalysts with chirotopic active sites, in which the selection of monomer enantioface results from non-bonded contacts in the active pocket shaped by the ancillary ligand(s) (site control). Notably, in practically all known cases the chiral recognition is not due to direct steric interactions between the incoming monomer and the ancillary ligand(s); rather, the latter constrains the growing polymer chain into a chiral conformation, which in turn favors monomer insertion with the enantioface pointing the alkyl substituent *anti* to the first chain C—C bond (a mechanism of stereocontrol known as “growing chain orientation”). The stereoregularity of the resulting polymer depends on the symmetry of the catalytic species: for propene polymerization, in particular, an isotactic polymer is expected out of C_2 -symmetric species with

homotopic active sites, whereas a syndiotactic polymer will form at C_2 -symmetric species with enantiotopic sites, provided that chain propagation occurs under a kinetic quench regime. Far less predictable is the case of C_1 -symmetric species with diastereotopic sites, which can yield practically all microstructures (e.g., isotactic, syndiotactic, hemi-isotactic) depending on the enantioselectivity of the individual sites and on the kinetic regime of chain propagation.

Relative to ethene, propene and higher alpha-olefins usually have a (much) lower insertion rate, which makes the concurrent processes of chain transfer and isomerizations (much) more competitive. In particular, in many cases β -H elimination to the monomer is only slightly slower than (poly-)insertion, particularly at high temperature, which is obviously undesired and must be contrasted with a proper ancillary ligand design. Intramolecular β -H elimination, in turn, can also be significant; at odds with the polyethylene case, poly(alpha-olefin) chains are too bulky to undergo chain walking, and tend to be isomerized locally (e.g., 2,1-to-3,1 isomerization, chain-end epimerization).

Immobilizing “Single-site” Olefin Polymerization Catalysts: The Basic Problems

A single-site olefin polymerization catalyst is a well-defined molecular entity which is intolerant to virtually everything; moreover, its performance is critically dependent on the precise ligand environment of the transition metal center. Therefore, immobilizing one such catalyst on a suitable solid or glassy inorganic or organic matrix is a formidably complicated task. Apart from the requirements on the support, which must be harmless to the catalyst (and also to the polymer end-user!) and also amenable to morphology control (with the related delicate issues of shape replication, fragmentation and heat/mass-transfer properties, etc.), the main difficulty is how to introduce a strong non-labile binding between the support and the active species without altering (deteriorating) the performance of the latter.

In the various chapters of this book, the possible strategies (e.g., physical or chemical adsorption, tethering, etc.) will be introduced and discussed in detail. Here, we would like to mention a few basic problems of general relevance.

- *Catalyst productivity.* For an efficient catalytic action it is mandatory that the monomer has an easy access to the active sites. Selective catalysts have an active pocket which fits tightly to the incoming monomer. We have already commented on the crucial importance of a poorly coordinating counteranion for cationic catalysts. In view of all this, it can be understood that introducing a strong link between the catalyst and the support, without limiting the accessibility of the active sites, is extremely complicated. As a matter of fact, the productivity of most immobilized catalysts is one or more orders of magnitude lower than that of the same catalysts in solution. However, there are exceptions, as we shall see. One advantage of immobilized

catalysts, on the other hand, is that intermolecular catalyst deactivation processes that can be highly detrimental in solution are usually frozen on surfaces; therefore, provided that a good productivity can be achieved, this tends to be maintained for a longer reaction time.

- *Catalyst selectivity.* The proximity to a surface inevitably represents a perturbation to the catalyst active pocket, not only in terms of accessibility, but also of symmetry. In particular, the stereoselectivity of C_5 -symmetric and C_1 -symmetric catalysts can be altered by the immobilization, because this may change the relative monomer insertion frequency at the two sites. A limiting case which has been reported is that of propene polymerization at certain C_5 -symmetric *ansa*-zirconocene catalysts, which is syndiotactic-selective in solution and can be isotactic-selective on a surface because one side of the catalyst would be obstructed by the support. C_2 -symmetric catalysts with homotopic sites are expected to be relatively insensitive to this problem; however, in case of severe decrease of insertion rate, a loss in stereoselectivity can result here due to an increased impact of growing chain epimerization (*vide infra*).
- *Competing reaction processes.* Immobilizing a single-site catalyst affects the kinetics of *all* reactions occurring at that catalyst—that is, (poly-)insertion, chain-transfer and isomerization processes. It is very unlikely that the effect is proportional for all such processes (some of which are intramolecular). Therefore, it is to be expected that some microstructural features of the polymer produced (e.g., long and/or short branches, terminal unsaturations, average molecular mass and molecular mass distribution, regiodefects, etc.) change upon catalyst immobilization. Of course, this also holds true for copolymerization statistics.

