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NOVEL POLYOLEFIN MATERIALS VIA CATALYSIS AND REACTIVE PROCESSING

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Abstract: Recent advances in transition metal catalyzed olefin polymerization and melt processing stimulate the production of new polymers derived from old monomers. Modern polyolefin processes do not require polymer purification and give excellent control of molecular and supermolecular polyolefin architectures. Progress in catalyst design and preparation of tailor-made homo- and copolymers is highlighted for isotactic, syndiotactic, atactic and stereoblock polypropylene (PP), novel 1-olefin copolymers, and ethylene copolymers with polar monomers, e.g., CO and acrylics. Today polyethylene short- and long-chain-branching is controlled either by uniform ethylene copolymerization with 1-olefins using „single-site" metallocene catalysts, or by migratory polyinsertion of ethylene, respectively. Stiff cycloaliphatic polymers expand the frontiers of polyolefins into engineering applications. New families of polyethylenes and EPM with pendent polypropylene chains are obtained via copolymerization of PP macromonomers or polymer-analoguous coupling of functionalized PP during melt processing.

Introduction

Both transition metal catalyzed olefin polymerization and reactive processing claim a key role in the development of novel versatile and environmentally friendly polyolefin materials, incluing diversified commodities as well as specialties. Polyolefins such as polypropylene (PP) combine low price with attractive performance, e.g., heat distortion temperature > 100 °C,

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strength, stiffness, impact resistance, low weight, corrosion resistance, and versatility in applications, ranging from automotive moldings to films, and textile fibers. Moreover, polyolefins are prime examples of environmentally friendly polymers, being produced in highly effective, solvent-free catalytic gas phase and liquid pool processes without byproduct formation, and exploiting readily available olefin resources. Upon heating above 400 °C, polyolefins are readily converted back into synthetic oil, which can be used as feed stock in petrochemistry, or as oil substitute in steel mills and incinerators, respectively. In fact, PP and other polyolefins represent a temporary solid modification of crude oil preserving oil-like energy content. The attractive PP life cycle is illustrated in Fig. 1, which reveals the hydrocarbon similarity between oil and PP. Modern PP, in contrast to PP of the 1970's, is competing very successfully with materials such as glass, wood, and metals, and is substituting other, less environmentally friendly and more expensive polymers. Soon polypropylene production in Western Europe is expected to surpass that of PVC. Polyolefins meet the demands of sustainable development and secure valuable fossile resources for future generations. At the beginning of the 21st century, forty years after its discovery, catalytic olefin polymerization in low pressure processes still represents one of the most innovative fields in chemistry and technology. Some of the opportunities and challenges of polyolefin technology are presented below.

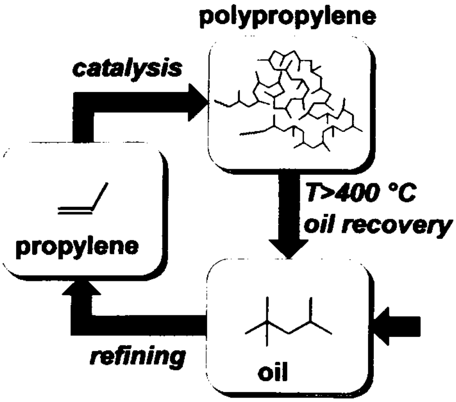

Fig. 1 The PP life cycle combines energy-saving low pressure polymerization with easy feed stocks recovery

Novel Isotactic Polypropylenes and Reactor Blends

Since the pioneering advances by Ziegler and Natta during the early 1950's remarkable progress has been made. Albizzati and coworkers gave a comprehensive view of land marks in catalyst development (Ref. 1). Highly active and stereoselective supported catalysts polymerize propylene in gas phase or liquid monomer in the absence of conventional hydrocarbon diluents, eliminate removal of corrosive catalyst residues, which are left in the polymer („leave-in" catalysts) and do not need either solvent recycle or polymer purification, e.g., separation of waxes by means of extraction with boiling solvents. As apparent in Fig. 2, Lewis bases are important components of both conventional stereoselective „Solvay"-type $TiCl_3$-based catalysts as well as modern $MgCl_2$ supported catalysts. Internal Lewis bases promote deagglomeration of primary catalyst particles during polymerization. External Lewis bases function as selective poisons to eliminate non-stereoselective sites according to the „key-lock" principle. During the 1990's 1,3 diethers were introduced as highly effective internal Lewis bases which do not require additional external donors (Ref. 1, 2).

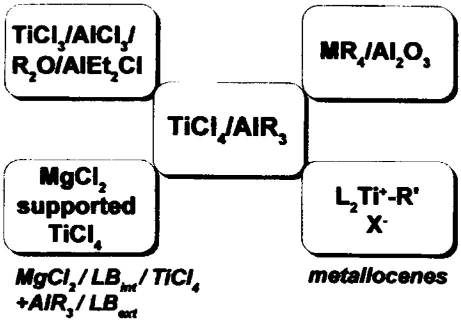

Fig. 2 Important directions in development of Ti-based catalyst systems.

Better understanding of correlations between catalyst morphology and PP morphology by Galli and coworkers (Refs. 3, 4) led to Montell's reactor granule technology. Dense or porous spherical catalyst particles act as templates producing dense or microporous PP granules, thus eliminating the need for pelletizing extrusion. Due to the uniform distribution of active catalyst primary particles throughout the PP matrix, EPM rubber can be incorporated in PP in gas phase reactor subsequent to the particle formation in liquid propylene („Catalloy" technology). Moreover, microporous spherical granules can serve as microreactors for free radical polymerization of styrene, styrene/maleic anhydride, or acrylics to produce new classes of multiphase reactor blends („Hivalloy" technology). In modern Novolen-type gas phase PP processes (Ref. 5), molecular weight distribution and PP/EPM blends can be tailored in cascade reactors to improve toughness/stiffness balance of PP. The prospects of cascade reactors, supported catalysts, and polyolefins with bimodal moecular weight distributions were described by Böhm and coworkers (Refs. 6,7,8). In future, reactor blend technology will continue to provide a very strong base for development of proprietray polyolefins with improved performance.

Among Ti-based catalyst systems, „single-site" metallocene catalysts offer several advantages with respect to traditional Ziegler-Natta catalysts: (1) they consist of essentially one type of active center which produces clean polymers with narrow molar mass distribution ($M_w/M_n=2$) and very small fraction of extractable oligomers, (2) metallocenes give exceptional control of molar mass, end groups, stereo- and regiorregularities as well as comonomer incorporation, whereas most traditional catalyst favored incorporation of comonomer in low molecular weight fractions, (3) metallocenes afford efficient copolymerization of less reactive long-chain 1-olefins, sterically hindered 1-olefins, cycloolefins and styrene, (4) metallocene give control of short-chain and long-chain branching which affects rheological behavior and processing, (5) with supported metallocenes also morphology control and reactor blend formation in gas phase polymerization is achieved. The progress in metallocene-catalyzed polymerization and correlation between metallocene structure and polymer properties was reviewed by Brintzinger (Ref. 9), Kaminsky (Ref. 10), and Hamielec (Ref. 11).

On one hand, metallocenes offer attractive potential to promote precision in stereoselective propylene polymerization. Recently Kaminsky and Soga (Ref. 12) reported the synthesis of high melting PP with $T_m=168.9$ °C when using the C_2-symmetrical zirconocene rac. $Et(2,4,7\text{-}Me_3Ind)_2/ZrCl_2/Ph_3C^+B(C_6F_5)_4^-$ and rac. $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2/\ Ph_3C^+B(C_6F_5)_4^-$ at low temperatures of -78 °C. On the other hand, Fischer found that regio- and stereoirregularities can be placed randomly along the PP chain, thus promoting formation of γ-modification with decreasing isotactic segment length between two steric irregularities. Regioirregularities due to „1,3"-type insertion account for incorporation of isolated ethylene units into PP without using ethylene comonomer. As a function of stereo- and regiorregularities PP melting temperature can be varied between 120 and 162 °C (Ref. 13). Lower melting metallocene-based PP offers several advatages, e.g., better orientation, higher spinning speed, better heat sealability, and improved optical properties (Ref. 14). In addition to obvious commercial prospects, well-defined PP serves as excellent model compounds to elucidate basic structure/property correlations and PP crystallization. Kressler and Thomann (Ref. 15) succeeded to grow crystals of pure γ- PP at low supercooling. In thin films the neat γ-modification shows networks structures which are formed by triangular entities. AFM images of etched bulk samples reveal columns with rectangular cross-sections which are densly packed. In γ-PP orthorombic unit cell is formed by bilayers composed of parallel helices with adjacent bilayers being tilted with an angle of 80°, as proposed earlier by Brückner and Meille (cf. Fig. 3) on the basis of low molecular weight samples (Ref. 16). Controlled crystallization and controlled nucleation, producing nanostructured PP, are the key to the production of novel PP with significantly improved optical clarity and very low haze, thus approaching the bench marks set by amorphous polystyrene.

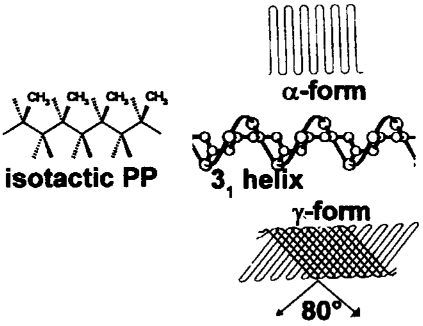

Fig. 3 Crystallization of isotactic PP

Syndiotactic Polypropylene and Stereoblock Polypropylenes

As a result of pioneering advances by Ewen and Razavi (Ref. 17) end of 1980's, syndiotactic PP is no longer the rather exotic lab chemical of previous years. In contrast to $VCl_4/AlEt_2Cl$, which gave activities of 1 g PP/ 1 g catalyst within 24 h and poor syndioselectivities even at low temperatures of -78 °C, modern $Me_2C(Cp)(Flu)ZrCl_2$ based catalysts produce syndiotactic PP in industrial processes with high molecular weight and extraordinarily high catalyst activities typical for metallocenes. Upon each insertion of propylene, the position of the growing chain changes and causes alternating changes of the chirality of the metal center. Unless the PP chain does not flip back to the other side, the next propylene approaches the metal center from the opposite side. This alternating change of chirality accounts for alternating sequence of the two configuration of the sterogenic carbon atom in adjacent propylene units.

Due to impurities of early syndiotactic PP, crystallization behavior required reexamination which showed that sPP prefers the 2_1 helical conformer, whereas iPP forms 3_1 helices. Crystallization behavior of iPP and s PP were compared and reviewed by Lotz, Wittmann and Lovinger (Ref. 18). Research by Friedrich and coworkers (Refs. 19, 20) revealed that stereoregularity influences viscoelastic properties and entanglement molecular weights, which correlate with processing and polymer properties. From the plateau moduli, derived from very high molecular weight sPP, aPP and iPP, they calculated entanglement molecular masses of approximately 7000 g/mol for both iPP and aPP, wheras the entanglement molecular mass of sPP was only 2000 g/mol. (Ref. 20). It should be noted that metallocene-based polymers are well-defined in contrast to early commercial polyolefins, which were composed of a rather complex polymer mixture. They represent excellent model systems for achieving better understanding of the influence of molecular and supermolecular architectures on processing and polyolefin properties. At present commercial sPP has comparatively stereoregularity, as reflected by <93% (rrrr) pentads, melts at temperatures < 160 °C, is much more flexible and tougher with respect to the more rigid conventional iPP, which melts at 162 °C.

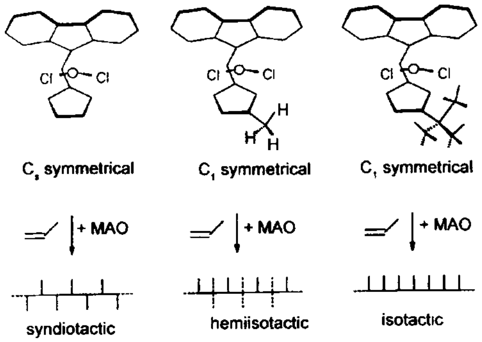

Fig. 4 Steric control as a function of metallocene structures

The substitution of syndiospecific C_s symmetrical metallocenes reveals the role of metallocene architecture on stereoselectivity (cf. Fig. 4). When bulky substituents such as tert. butyl are introduced in the 3-position at the Cp ring within the isopropylidene bridged (cyclopentadienyl)(9-fluorenyl) ligand frame work, the resulting C_1 symmetrical metallocene produces isotactic PP. Substituted metallocenes containing the sterically less hindered methyl group substituent, give hemiisotactic PP (cf. Fig. 4), which is currently of no commercial interst but served as valuable „finger print“ for polymerization mechanisms. Mechanistic features were reported in detail by Fink (Ref. 21), who proposed an intriguing alternative concept for steric control taking into account the four lowest-energy conformers of the metallocene species coordinating to propylene as well as positional changes of the polymer chain during insertion. Fink's model allows to classify and explain stereoerrors during propylene insertion.

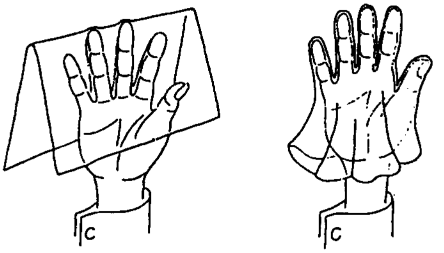

Fig. 5 Wisseroth's glove test demonstrating the usefulness of low stereoirregular, high molecular weight PP (Ref. 22)

Conventional supported catalysts produced highly isotactic polypropylene containing small amounts of low molecular weight low stereoregular polymers as impurities. Characteristic feature of low stereoregular PP are the presence of short isotactic seuqences which alternate with mainly atactic segments. Therefore, this type of PP is considered to be a stereoblock polymer although segmented polymer would be a better tehnical term in view of the absence of truly isolated block structures. Low molecular weight atactic PP was only useful as tacky component of adhesive formulations. In the early days of Ziegler catalysts such byproducts had to removed by solvent extraction. It was Wisseroth [Ref. 22] at BASF AG who discovered in 1977 that high molecular weight low stereoregular polymers exhibited interesting properties including soft elastomeric behavior. His special „glove test“ displayed in Fig. 5

demonstrated that low stereoregular polypropylene did not exhibit „peanut-butter-like consistency", as he referred to earlier reports by Natta's group, where only very tacky and viscous low molecular weight stereoisomers were obtained as byproducts. As illustrated in Fig. 5, Wisseroth's PP was soft and exhibited good mechanical properties. Later it was discovered that variation of the lengths of isotactic and atactic segments leads to elastomeric polypropylenes (ELPP). When isotactic segments crystallize, the resulting crystallites act as thermoreversible crosslinks typical for a variety of thermoplastic elastomers. Several catalyst families were reported to produce ELPP (cf. Fig. 6).

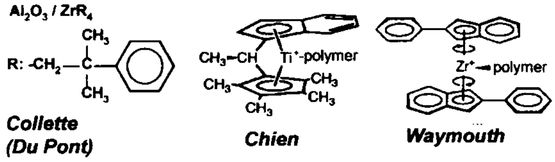

Fig. 6 Catalysts for preparation of elastomeric PP (ELPP)

End of the 1970's Collette and Setterquist at Du Pont disclosed ZrR_4/Al_2O_3 catalysts with R= $CH_2C_6H_5$ or $CH_2C(CH_3)_2C_6H_5$, which produced simultaneously highly crystalline isotactic polypropylene and very high molecular weight low stereoregular polypropylene (Refs. 23, 24). The resulting ELPP was blended together with crystalline isotactic polypropylene to tailor elastomeric properties such as tensile set, elongation at break, resilience. End of the 1980's Chien (Ref. 25) discovered special metallocene complexes which produce high molecular weight stereoblock polypropylenes consisting of alternating isotactic and atactic segments. Recent mechanistic studies by Collins (Ref. 26) and blend studies by Decandia (Refs. 27, 28, 29) indicate the presence of segmented low stereoregular PP similar to Collette's reactor blend component of segmented PP with rigid isotactic segments randomly distributed along a flexible atactic chain.

In 1996 Waymouth (Refs. 30, 31) developed a new class of oszillating metallocenes. As schematically represented in Fig. 7, during polymerization there exists a very rapid interconversion between non-stereoselective meso-like and stereoselective racemic-like rotamers where racemic-like rotamers produce rigid crystalline isotactic and meso-like conformers flexible atactic segments. The segment distribution can be influenced by the polymerization temperature. It was Resconi (Ref. 32, 33) at Montell who realized that also non-stereoselective metallocenes are able to produce elastomeric polypropylene, provided that atactic polypropylene is formed with very high molar mass to incorporate isotactic segments which are long enough to crystallize. According to Resconi $Me_2Si(Flu)_2ZrCl_2/MAO$ produces such high molecular weight atactic ELPP. Drawback of ELPP is its relatively high glass temperature in range of -5 °C. This ELPP glass transition temperature can be reduced by incorporating comonomers or by adding plasticizers. ELPP is currently being considered for industrial use as polypropylene blend component and material to produce elastomeric polypropylene fibers.

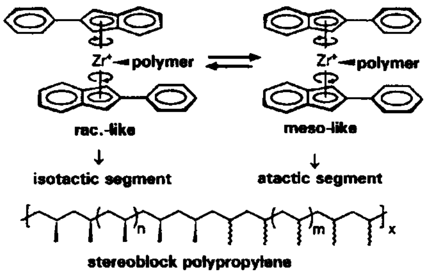

Fig. 7 Waymouth's „oszillating“ metallocene catalysts

Recently, Chien (Ref. 34) utilized chain transfer with aluminum alkyls via transmetallation to transfer the growing PP chain between different catalytically active sites with different stereoselectivity during polymerization. According to the mechanism displayed in Fig. 8, multiblock copolymers are formed, containing syndio- and isotatctic blocks alternating with atactic blocks. Such true stereoblock copolymers are new thermoplastic elastomers. This intriguing concept is likely to stimulate development of novel thermoplastic elastomers as well as block copolymers for reactor blend formation.

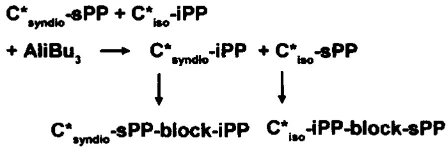

Fig. 8 Chien's stereoblock copolymers prepared by AlR_3-mediated transfer of the growing PP chain between catalytically active sites having different stereoselectivity

Copolymerization and branched polyethylenes

For many years there existed a strict separation between different groups developing ethylene copolymers for use as linear low density polyethylene (LLDPE), rubbers such as EPM and EPDM, and impact-modified polypropylene. In fact, most conventional catalysts used for manufacturing LLDPE failed to incorporate more than a few percent of higher 1-olefins into polyethylene because at high comonomer feed large fractions of wax-like byproducts, together with ethylene homo- and copolymers, were formed. For incoporation of higher 1-olefin content, e.g., for production of EPM and EPDM, special vanadium based catalysts, requiring chlorine-containing cocatalysts, have been developed. Such catalyst generations, however, were unable to produce highly isotactic polypropylene. This frontier between rubber and thermoplastics technology is fading away as a result of the development of metallocene catalyst generations.

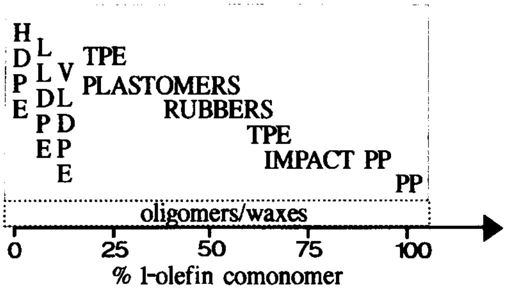

Fig. 9 Ethylene/1-olefin copolymers

As illustrated in Fig. 9, modern metallocene catalyst can produce the entire feasible range of ethylene/1-olefin copolymers with variable molecular weights: traditional linear low density polyethylene (LLDPE), medium and very low density polyethylenes (VLDPE) with densities of 0.88 - 0.92 g/cm^3, plastomers as thermoplastic elastomers with 1-olefin content >20 mol-%, elastomers and thermoplastic elastomers as well as impact-modified polypropylene containing only a few percent of ethylene copolymer. In comparison to the traditional Cp_2ZrCl_2-based catalysts, the bridged metallocenes such as halfsandwich metallocenes, referred to as „constrained geometry catalysts" (CGC) and ansa-metallocenes with specific ligand substitution pattern, e.g., MBI (cf. Fig. 10), give much better incorporation of higher 1-olefins as reflected by the copolymerization parameters. Today, molecular modeling can be applied within a specific catalyst family to predict copolymerization performance as a function of the ligand substitution pattern. (Ref. 35). In the case of ansa-metallocens it was shown that benzannelation promotes both high catalyst activity and 1-olefin incoporation, whereas the 2-methyl substitution is required to promote high molecular weight (Ref. 35, 36). At elevated temperatures, ethylene incorporation is favored with respect to 1-octene Ref. 37).

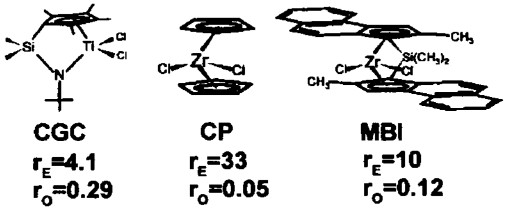

Fig. 10 Metallocenes for ethylene copolymerization

Comonomer incorporation allows to control crystallization of the ethylene as well as propylene copolymers. With less than 5 wt.-% 1-octene incoporation, crystallization via chain-folding is favored, whereas above 10 wt.-% the preferred crystallization process involves formation of „fringed-micelle" nanostructures (cf. Fig. 11), as reflected by much improved opical clarity of such nanocrystalline copolymers. This has been demonstrated for ethylene/1-octene (Ref. 38) as well as syndiospecific propylene/1-olefin copolymerization (Ref. 39). Due to the very high reactivity of higher 1-olefins, also vinyl endgroups of polyethylene chains can be copolymerized with ethylene to produce long-chain-branched polyethylene. Long-chain branching reduces melt viscosity at high shear during processing, thus facilitating processing of metallocene-based polyolefins (Ref. 40).

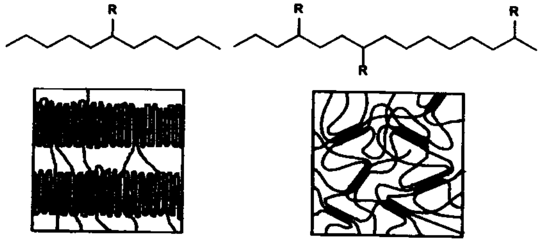

Fig. 11 Influence of polyolefin crystallization by random placement of comonomers

Novel metallocene-based ethylene/1-olefin copolymer families were introduced commercially by Dow Chemical in 1993 as part of their metallocene-based Insite Technology®. In addition to Dow's Affinity® LLDPE products, the Du Pont Dow Elastomers joint venture produces ethylene copolymers with high 1-octene content (Plastomer®) as thermoplastic elastomers. The ethylene copolymers with high butene content (Luflexen® of BASF AG) exhibit high toughness and very low content of extractables. With metallocene catalysts also EPDM, EPDM, ethylene/1-butene/(diene) and ethylene/1-octene/(diene) copolymers are available. According to Galimberti (Ref. 41) and Richter (42), metallocene catalysts give much higher molecular weight, narrow molecular weight distribution, less oligomeric byproducts, and better control on sequence distribution and regioselectivity of propylene segments with respect to state-of-the-art vanadium catalysts. Moreover, less reactive higher 1-olefins, e.g., hexadecene and others, are incorporated (Ref. 43). As displayed in Fig. 12, a wide variety of ethylene copolymers with 1-olefin, cycloolefins, and styrene is now available.

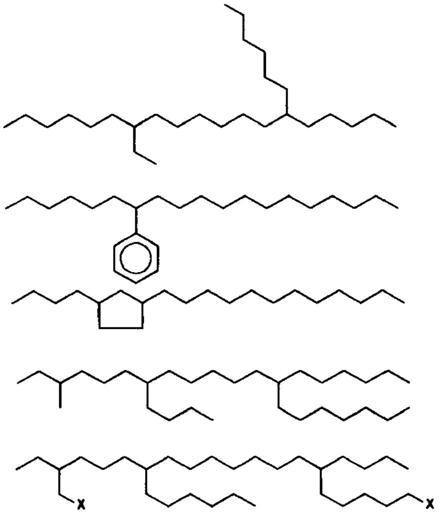

Fig. 12 Ethylene copolymers

Most traditional catalysts allowed to incoporate only traces of styrene with extensive polystyrene byproduct formation. In contrast, „constrained geometry“ metallocene catalysts, first disclosed Dow Chemical, give styrene incoporation into ethylene as well as ethylene/1-olefin copolymers where elastomer properties are controlled by styrene and 1-olefin comonomer content (Refs. 45, 46). Titanate catalysts were much less effective (Ref. 47). The presence of single sites in halfsandwich metallocene catalyzed polymerization was confirmed by temperature rising elution fractionation (TREF) (Ref. 48). Recently, Zambelli and coworkers (Ref. 49) and Longo (Ref. 50) obtained crystalline alternating ethylene/styrene copolymers with $Cp^{*}Ti(CH_2Ph)_3$/MAO. Typically glass transition temperatures increase with increasing styrene content. In order to lower glass transition temperature in ranges of -50 °C, styrene was added as termonomer to ethylene/1-octene polymerization (Ref. 51). The incorporation of aromatic side chains into rubbers and thermoplastic elastomers is expected to promote filler adhesion and compatibility with other polymer blend components and plasticizers. Cycloolefin copolymers and novel cyclocopoolymerization will be discussed in the next section.

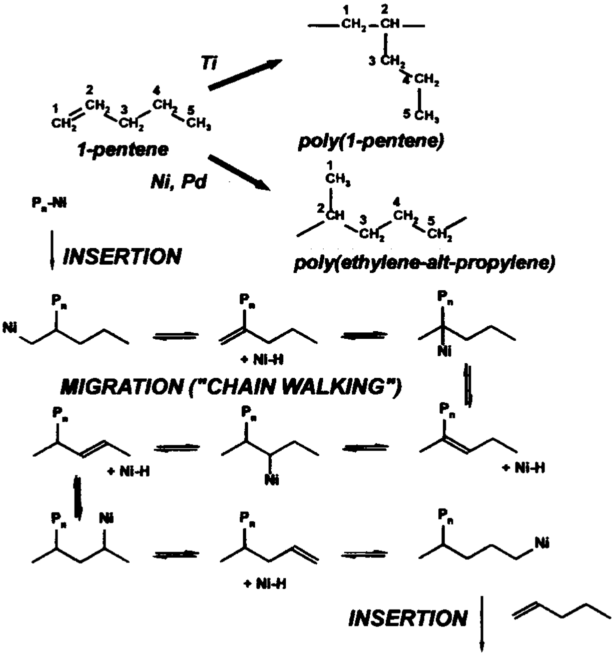

Fig. 13 Fink's 2,ω-polymerization and methyl-branching via migratory polyinsertion

Since the mid 1980's novel nickel catalysts produce short- and long-chain branched polyethylene without requiring 1-olefin comonomers. Base of this development is Fink's discovery of the 2,ω polymerization (Refs. 52, 53, 54). Polymerization of 1-olefins such as 1-pentene on nickel catalysts, displayed in Fig. 13, do not afford poly(1-olefins) as expected for titanium catalysts. Instead, 1-olefins are polymerized to form methyl-branched polyethylene, corresponding to poly(ethene-alt-propene) in the case of 1-pentene. This unexpected branching reaction was attributed to the migration of the transition metal alkyl along the polymer chain via repeated β-hydride elimination and reinsertion („migratory polyinsertion").

Similar polyethylene short- and long-chain branching were observed by Ostoja-Starzewski in ethylene polymerization (Ref. 55). Fink's „2, ω- polymerization" became also known as polymerization according to the „chain-walking" mechanism because the transition metal alkyl is walking up and down the polyethylene backbone and, especially in the case of Pd catalysts, walking up and down both polyethylene side chains and backbone. When using higher 1-olefins, it is possible to control the alkylene spacer length between two methyl branches. It should be noted that methyl- and alkyl-branches can be introduced into polyethylene without adding 1-olefin comonomers.

In 1995 Brookhart (Refs. 56. 57) disclosed that bisimine-Ni-catalyzed methyl-branching is promoted at low ethene pressure and elevated polymerization temperature, whereas bisimine-Pd-catalyzed branching, producing methyl- as well as longer alkyl-branches, appears to be much less dependent upon pressure. Fig. 14 displays a comparison of Ni- and Pd-based catalysts and branching of the resulting ethylene homopolymers by Heinemann. Brookhart's basic patent (Ref. 57), jointly filed by the University of North Carolina and Du Pont Company, discloses 562 claims! Chain migration can afford methyl- and alkyl-branched polyethylenes, which are semicrystalline LLDPE-like materials or amorphous rubbers with very low glass temperatures below -60 °C. The comparison of Ni- and Pd-based catalysts with respect to branching is displayed in Fig.14. Du Pont is developing such semicrystalline and amorphous polyethylenes under the trade name of Versipol®. Group VIII catalysts tolerate polar comonomers and can incorporate methyl-acrylate into polyethylene (Ref. 81).

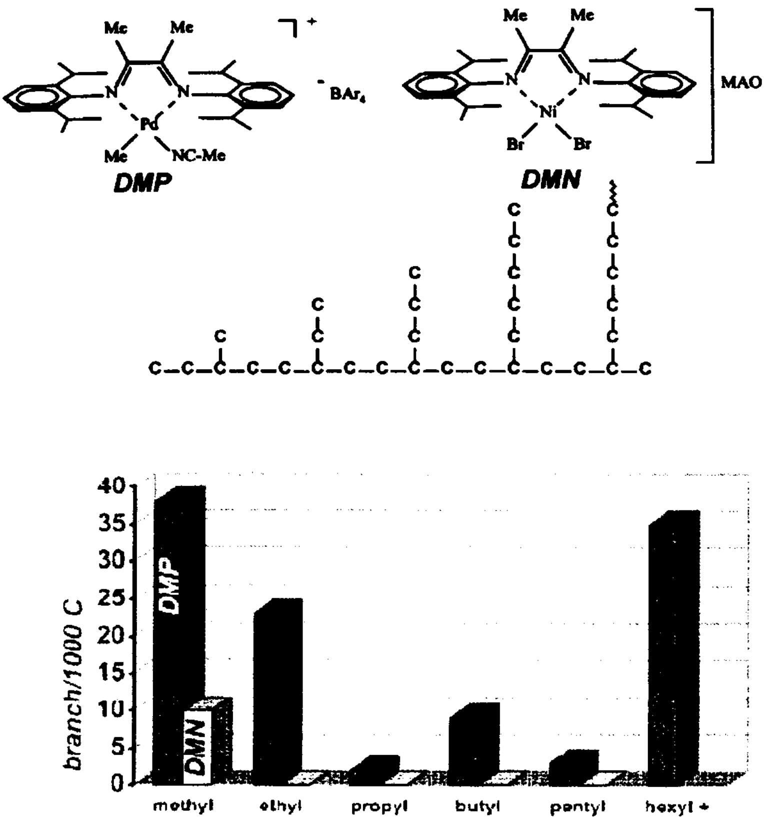

Fig. 14 Branched polyethylene via chain walking homopolymerization of ethylene using Ni- and Pd-based catalysts.

Recently, novel living catalysts systems were introduced for 1-olefin polymerization. Brookhart et al. (Ref. 58) used MAO-actiavted diimine-based catalysts such as [ArN=C(R)-C(R)=NAr]NiBr$_2$ (cf. Fig. 15) to obtain living polypropylene and living polypropylene-*block*-poly(1-hexene) as well as poly(1-octene)-*block*-poly(propene-co-1-octene)-*block*-poly(octene-1). Preferably this living 1-olefin polymerization was performed at temperatures below room temperatures. As a function of the diimine ligand type 1,2 and 2,1 insertions as well as migratory 1,ω-polymerization, equivalent to Fink's 2,ω-migratory polymerization of 1-olefins. Van der Linden et al. (Ref. 59) and Mc Conville et al. (Ref. 60) used novel diamide complexes of titanium, e.g., . $[RN(CH_2)_3NR]TiMe_2$ with R= 2,6-$^iPr_2C_6H_3$ bzw. R=2,6-$Me_2C_6H_3$, activated with equimolar amounts of $B(C_6F_5)_3$ to initiate living non-stereospecific polymerization such as 1-hexene, 1-octene, and 1-decene at room temperature in toluene or methylenechloride solution. Molar masses of living polyolefins varied between 4300 and 148100 g/mol and polydispersities M_w/M_n varied between 1.05 and 1.11. Although ethene failed to afford living homo- and copolymers, this development of novel initiators for living olefin polymerization will lead to the preparation of novel families of block and star copolymers, impact-resistant polymer blends, thermoplastic elastomers, and rubbers.

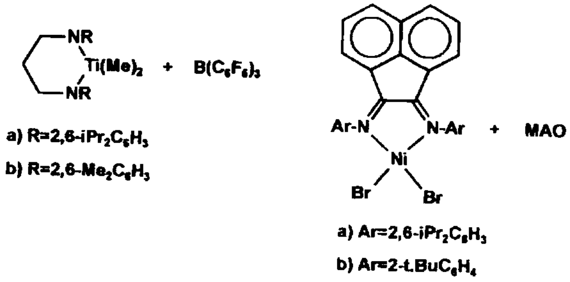

Fig. 15 Catalysts for living 1-olefin polymerization

Cycloaliphatic Polymers

New catalysts have been developed to homo- and copolymerize cycloolefins such as cyclopentene and norbornene (cf. Fig. 16). While Ti-based first generation catalysts give ring-opening metathesis polymerization („ROMP“) involving ring-opening, modern metallocene catalysts retain the ring system. According to Kaminsky (Ref. 61) and Collins (Ref. 62), cyclopentene is polymerized to afford poly(1,3-cyclopentene) due to isomerization during polymerization. Ribbon-like poly(norbornene) were obtained by Heitz via [2+2] cycloaddition polymerization of norbornadiene (Ref. 63). Most crystalline cycloolefin homopolymers melt at very high temperatures well above their decomposition temperature. Therefore, ethylene or other comonomers are incorporated to achieve melt processability (Ref. 61, 64). New families of cyclolefin copolymers („COC“) such as ethylene/norbornene were introduced by Hoechst AG using metallocene-catalyzed copolymerization (Ref. 65). They exhibit high stiffness, excellent optical properties combined with very low water-uptake and are considered for application in optical data storage media and medical packaging. New generations of nickel and palladium catalysts have been disclosed by B.F. Goodrich (Ref. 66) which give high molecular weight soluble norbornene homopolymers and very high conversions, even when using a mixture of exo- and endo-isomers of substituted and functionalized norbornenes.

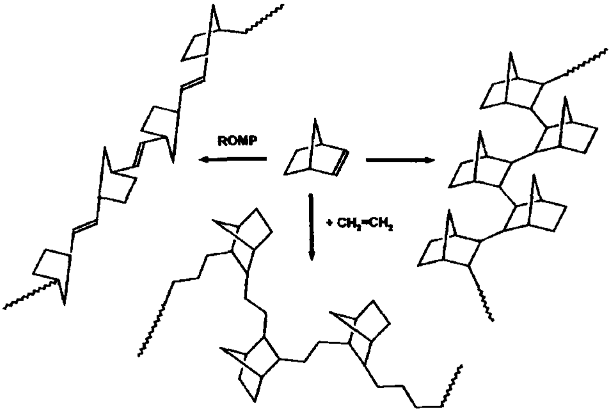

Fig. 16 Norbornene homo- and copolymers

In an alternative process, displayed in Fig. 17, Waymouth (Refs. 67, 68, 69) developed cyclopolymerization of non-conjugated dienes such as 1,5-hexadiene to produce polymers with repeat units consisting og methylene-linked cyclopentane rings of various stereochemsitry, including optically active polymers, which were obtained in the presence of chiral catalysts. When 1,5-hexadiene is copolymerized with ethylene, cycloaliphatic copolymers are obtained (Ref. 70).

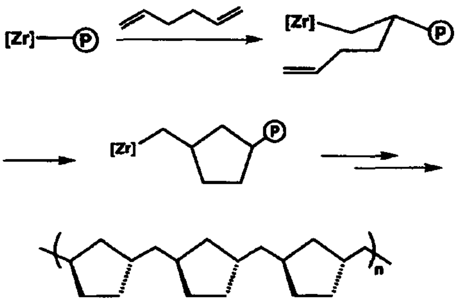

Fig. 17 Cyclopolymerization of non-conjugated dienes

Low pressure copoolymerization of olefins with polar monomers

As a result of severe catalyst poisoning of Lewis acidic group IV based catalysts due preferred complexation of Lewis bases at vacant corrdination sites, copolymerization of ethylene with acrylic monomers is performed by means of high temperature/high pressure free rdaical copolymerization. During the last decade catalyst development has been very successful to overcome this limitation. In the case of group IV metallocene catalyst systems, polar olefin comomers with reduced Lews basicity have been applied. Lofgren used undecenol, prereacted with aluminum alkyl activators, as comonomer to incoporate hydroxy groups into polyethylene (Ref. 71). Also ω-chloro-1-olefins have been incorporated by Deffieux (Ref. 72). Wilén (Refs. 73-77) has prepared polymeric antioxidants by homo- and copolymerization of 6-tert.butyl-[2-(1,1-dimethylhept-6-enyl]-4-methyl-phenol, illustrated in Fig. 18. Also the sterically hindered 5-N,N-diisopropylamino-1-pentene, 5-tert.butyl-1-dimethyl-siloxa-pentene (Ref. 77) and N,N,-bissilylated 10-aminoundecene (Ref. 78) have been copolymerized to obatin amino-functional polyolefins. Most systems, however, gave rather low catalyst activities and were severely poisoned by CO.

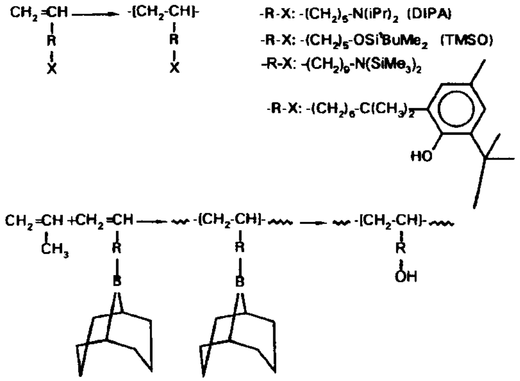

Fig. 18 Functional olefin copolymers

Recently, Chung prepared a variety of borane-functionalized polyolefins as precursors for functional polymers by means of borane conversion. This was achieved either by polymer-analoguous hydroboration of unsaturated polyolefins or by copoymerization of borane-functional 1-olefins (Ref. 79). For example, boranes were added to non-conjugated dienes to prouce borane-functional 1-olefins, which were copoymerized, followed by hydrogenperoxide conversion to afford polyolefins with pendent hydroxyalkyl groups (Ref. 80).

The development of nickel and palladium catalysts for chain walking polymerization show much improved tolerance against polar monomers. Brookhart introduced a low pressure co-polymerization process, where methylacrylate is cooligomerized together with ethylene to form new families of polar ethylene copolymers with pendent alkyl- and esteralkyl-chains (cf. Fig. 19 and Ref. 81).

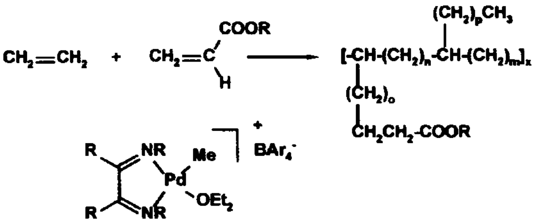

Fig. 19 Low pressure copolymerization of ethylene with alkylacrylate (Ref. 81)

Group VIII catalysts also tolerate carbon monoxide (CO), which is incorporated to form polyketones being composed of alternating olefin/CO copolymers or the corresponding poly-spiroketals, respectively (Fig. 20). Recently his remarkable developement was reviewed by Drent and Budzelaar (Ref. 82). In 1996 Shell has started commercialization of their Carilon polyketone resins which represent alternating ethylene/CO copolymers containing a few percent of propylene termonomer to lower melting temperature to 225 °C in order to facilitate melt processing. Both Shell's Carilon (Ref. 83, 84) and BP's Ketonex (Ref. 85) alternating ethylene/CO copolymers exhibit high heat distortion temperature, high toughness, excellent barrier properties with repct to hydrocarbon and oxygen permeation. Blending of Ketonex with PVC appears to improve also heat distortion temperature of PVC (Ref. 85).

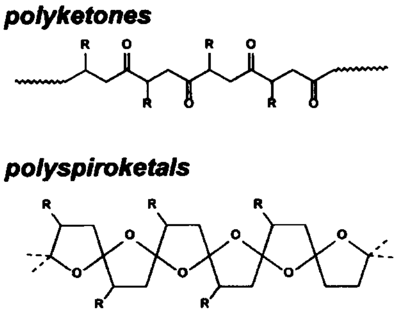

Fig. 20 Alternating olefin/CO copolymers

The transition metal catalyzed alternating copolymerization of CO with 4-t.butyl-styrene, reported by Brookhart et al. (Ref. 86), led to several families of atactic, isotactic, syndiotactic and stereoblock isomers. Ligand exchange reactions, occurring during chain propagation, accounted for fomation of stereoblock copolymers with alternating iso- and syndiotactic segments. Sen at al. (Ref. 87) performed alternating copolymerization of CO with functional alkenes such as $CH_2=CH(CH_2)_xOH$ (x=2,3,4,9) and $CH_2=CH(CH_2)_xCOOH$ (x=1,2,4,8) as well as 4-allylanisole by means of $[Pd(Me\text{-}DUPHOS)(MeCN)_2](BF_4)_2$ with Me-DUPHOS = 1,2-bis(2,5-dimethylphospholano)benzene. The resulting polymers were optically active with isotactic sequences in the backbone. With most alkenes the resulting copolymers exhibited poly(1,4-ketone) and/or polyspiroketal structures. However, with 4-penten-1-ol and 3-buten-1-ol, in situ intramolecular cyclization led to the formation of rather unusual polycyclic ketal repeat units shown in Fig. 21.

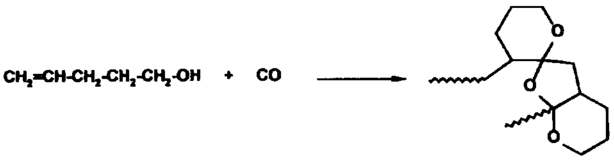

Fig. 21 Alternating copolymerization of functional olefins with CO (Sen)

According to Borkowsky and Waymouth (Ref. 88) alternating cyclocopolymerization of 1,5-hexadiene and CO with Shell-type catalyst systems produced soluble cyclocopolymers containing both 5- and 6-membered cyclic ketones (cf. Fig. 22). For example, cyclopolymerization of 1,5-hexadiene with CO in the presence of $Pd(OAc)_2$, 1,3-bis(diphenylphosphino)propane (Dppp), 1,4-naphthaquinone, and $Ni(ClO_4)_2 6H_2O$ in chlorofom/methanol gave a soluble cyclocopolymer containing both 5- and 6-membered ketones in the backbone, whereas cyclopolymerization under similar conditions in the presence of 1,3-bis(diisopropylphosphino)propane (Dipp) formed only cyclocopolymers with 6-membered cyclic ketones. The formation of cyclopentanone repeat units was attributed to 2,1 insertion, whereas cyclohexanone units result from 1,2 insertion of 1,5-hexadiene. Cycloaliphatic polyketones were also produced via copolymerization of norbornene with CO (Ref. 89).

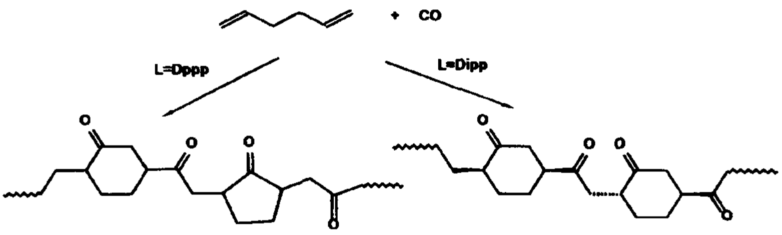

Fig. 22 Alternating cyclopolymerization of diolefins with CO (Waymouth)

Recently, Rieger et al. (Refs. 90, 91) observed that low stereoregular poly(propene-alt-CO) as well as ethene/propene/CO terpolymers afforded elastomers when molecular mass exceeded 100 000g/mol. Obviously, crystallizable segments afford physical crosslinks of the very flexible atactic polyketone chains, similar to non-polar ELPP reported above. Polyketones and polyspiroketals as well as the above reported novel alternating copolymers offer attractive potential in polymer synthesis by further exploiting the potential of cheap petrochemical resources such as CO and olefin, cyclolefin and styrene feedstocks. This is escpecially true for blend formation. According to Xu and Chien, poly(propene-alt-CO) is miscible with PMMA (Ref. 92). This indicates that there exist numerous possibilities for producing novel polymeric materials based upon such alternating copolymers.

Reactive processing

Although extraordinary progress has been made in transition metal catalyzed olefin polymerization and reactor blend technology, diversification of polymers during melt processing remains another very important route to polymeric materials with new property combinations. Diversification during melt processing allows to upgrade large volume polyolefins without modifying polymerization processes, catalysts or comonomer compositions. Several reviews describe prospects and challenges of reactive processing (Refs. 93-97), including polymer functionalization, grafting, coupling reaction, rheology control by degradation to get narrower molecular weight distribution, degradative extrusion for feedstock recycling, and compatibilization of blends by means of reactive blending technology.

The potential of reactive processing versus olefin copolymerization is illustrated for preparation of novel families of ethylene copolymers with pendent PP side chains. Soga (Ref. 98) developed special vinyl-terminated oligopropene as macromonomers which are copolymerized to incorporate PP side chains. Although novel metallocene catalysts are very efficient, new polymerization processes must be devloped to obtain macromonomers and to assure high conversion of the macromonomer, which would be left in the polymer as wax-like fraction. As is apparent from Fig. 22, melt-phase coupling reactions represent another route to diversify polymers during extrusion. Lohse (Ref. 99) used amino-functional EPM, prepared by copolymerization of amino-functional norbornene with ethylene/propylene, as functional polymer which reacts with maleic anhydride-grafted PP to produce imide-coupled graft copolymers. Schneider (Ref. 78) used amino-functional LLDPE, prepared by metallocene catalysis, which was reacted with succinic anhydride functional PP in analogy to Lohse's process. In another approach, oxazoline intermediates were used as very versatile components of reactive processing technology. Wörner and Müller (Ref. 100) prepared novel mono-oxazolin-2-yl-terminated oligopropenes, also derived from metallocene-based intermediates, which were attached to poly(ethylene-co-methacrylic acid) via oxazoline-mediated esteramide coupling (Fig. 23).

Moreover, reactive blending technology plays a key role in improving toughness/stiffness balance of PP and producing multiphase polymer blends with controlled morphology development. New percolation structures, also referred to as honeycomb- or raspberry-like structures, were produced by in-situ formation and percolation of core/shell nanopartilces with rigid PA6 core encapsulated in a thin SEBS shell, which acts as adhesive to bond together clusters of such core/shell partzicles to form cocontinuous morphologies. The shell formation resulted from interfacial coupling reaction of anhydride groups of SEBS-graft-maleic anhydride with amino end groups of PA6 (Ref. 101-104). This can be applied to filler modification in compounding. Interfacial modifications and formation of interconnected phases play a key role in the development of modern polymeric materials.

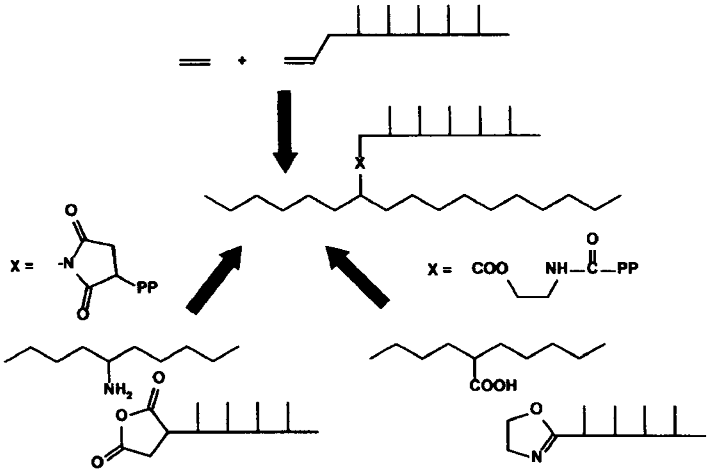

Fig. 23 Novel ethylene copolymers with PP side chains prepared by copolymerization of vinyl-terminated oligopropene macromonomers or by melt-phase coupling reaction during processing.

Outlook

In nature twenty aminoacids and glucose are the monomers polymerized by enzymes to form an extraordinary wide array of structural and functional materials. The precise control of the biopolymer sequences and molecular weights gives control on superstructure formation via self-assemblies. In industry, we are in the process of learning how to make better use of readily available and cheap petrochemical monomers and to achieve better control of superstructure formation. There is a very large potential for new self-assembly-type superstructures. During the last decades, the precision of olefin polymerization has been improved significantly and styrene and polar monomers are now being exploited as comonomers. Better control and higher purity of polymers offers attractive potential for processing and tailor-making polyolefins. In injection molding only a few percent of the theoretical modulus are being exploited,. This presents opportunities and challenges for future improvements. It is a long-standing challenge to explore new ways to improve toughness/stiffness balance. This is attempted via better control of molecular and supermolecular architectures in catalysis as well as improved processing, compounding and reactor blend formation. In view of their excellent combination of low energy consumption during polymerization and easy processability combined with low weight, versatility in applications and recycling, polyolefins will continue to grow and to compete very successfuly with other polymers in existing and new markets.

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