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The Polyolefin Challenges: Catalyst and Process Design, Tailor-Made Materials, High-Throughput Development and Data Mining

Dedicated to Professor Walter Kaminsky on occasion of his 60th birthday

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SUMMARY: Progress in catalytic olefin polymerization has led to the development of environmentally friendly and versatile polymeric materials which meet the demands of sustainable development and serve the needs of modern technologies. Polymer architectures and property profiles are tailored as a function of catalyst structures and process conditions. The scope of single site catalyst technology has been expanded well beyond that of metallocene-based systems to produce novel families of 1-olefin, styrene, diene and cycloolefin polymers, ranging from engineering plastics to flexible packaging and rubbers. Short- and long chain branches are introduced via copolymerization and "chain walking" in order to control polymer crystallization and polymer processing. Novel group 10 catalyst generations tolerate functional comonomers and afford aqueous polyethylene dispersions. Computer sciences, engineering and information technology are combined to exploit the potential of combinatorial chemistry and on-line monitoring in high-throughput catalyst and polymer development. Data mining tools track correlations ("fingerprints") between spectroscopic data, process parameters and catalyst as well as polyolefin properties, thus promoting high throughput development, modeling, rapid on-line analyses, as well as quality assurance. Selected recent advances are reviewed to highlight trends and opportunities in polyolefin science and technology.

1. Introduction

Since the pioneering advances of Karl Ziegler and Giulio Natta during the early 1950's , breakthroughs in catalyst and process development have revolutionized polyolefin catalyst technology. Modern highly active and stereoselective catalysts combined with gas phase and liquid pool processes have eliminated the need for solvents and removal of catalyst residues and wax-like by-products. Spherical magnesium chloride supported catalysts act as templates to produce polyolefin granules without requiring pelletizing extrusion. Such granules can be used as microreactors for catalytic and free radical

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polymerization. Materials such as polypropylene are very versatile with applications ranging from automotive bumpers to baby diapers. Fueled by innovations in catalyst, process, and product development, polypropylene production has increased significantly since the 1970's. Polypropylene competes very favorably with other materials and claims leadership in polymer in production in Western Europe [1)].

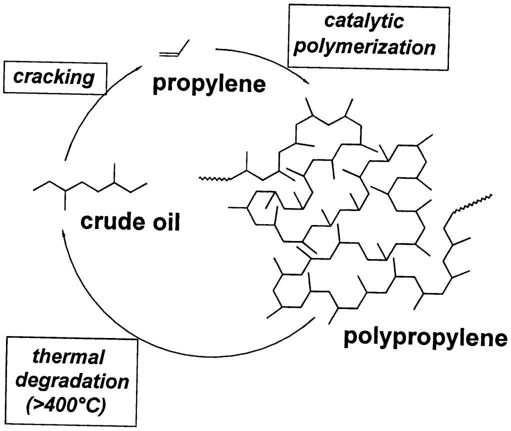

Fig. 1: Polyolefin life cycle

The attractive polyolefin life cycle is displayed in Fig. 1. Crude oil is cracked to produce olefin monomers which are converted into polyolefins by means of transition metal catalysts. Upon completing their product life, thermal degradation occurring at temperatures above 400 °C converts polyolefins quantitatively back into synthetic oil and gas, which can be used to produce new olefin monomers or serve as petrochemical feed stocks and energy source. Complete thermal degradation without residues was demonstrated in industrial scale already during the 1970's when Sinn and Kaminsky developed the Hamburg pyrolysis process[2)]. Since architectures of polyolefins and oil are very similar it is not surprising that also the energy contents of both oil and polyolefins are similar. In fact, polyolefins are environmentally friendly hydrocarbon materials, produced in energy-efficient catalytic processes without by-products. Polyolefins meet the demands of sustainable development because they save oil-like energy and are readily recycled to recover resources for future generations[3)]. In 2005 polyolefin production will exceed 80 million tons. The average size of polyethylene reactors is expected to increase significantly and to approach 600 000 tons per year[4)].

Large production growth and globalization forced well-established companies to stream-line their operations and to join forces with other companies. In future the number of polyolefin companies will continue to decline and a rather small number of very large key players will be left in a few years. In October 2000 the three companies Montell, Elenac and Targor formed the new company Basell which unifies the research cultures of Karl Ziegler and Giulio Natta. Innovation in catalyst and process technology as well as product development will continue to boost polyolefin production and new applications.

2. Single Site Catalyst Technology

Since the 1950‘s industrial slurry and gas phase processes require the development of supported catalysts in order to control polymer morphology and to prevent the formation of hazardous dust-like particles. During the late 1960‘s it was discovered that high surface area magnesium chloride and other magnesium compounds can substitute inactive bulk titanium trichloride because $MgCl_2$ and γ-$TiCl_3$ are isomorphous. Coordination of titanium alkyls on magnesium chloride surfaces increases the number of active sites significantly, thus promoting catalyst productivity. Lewis bases such as esters, silanes, and ethers were added as donors to improve stereoselectivity by selective poisoning of non-stereospecific sites. The development of magnesium-based supported catalysts has been very successful and has led to sophisticated but simplified systems. With $MgCl_2$ / 1,3-diether / $TiCl_4$ / AlR_3 catalyst systems extraordinarily high activities and stereoselectivities combined with morphology control were achieved in propylene polymerization5).

Most supported catalysts contain different types of catalytically active sites. Only in high temperature solution polymerization of ethylene at temperature exceeding 200 °C, one type of catalytically active transition metal alkyl site survives such harsh reaction conditions. In fact, high temperature polyethylene processes such as Sclair®, developed by Du Pont during the 1960’s, represent the first commercial single site catalyst technology. Characteristic feature of single site catalysts is the presence of a single type of catalytically active transition metal alkyl site producing uniform polyolefins with narrow molar mass distribution of $M_w / M_n = 2$ and low oligomer content.

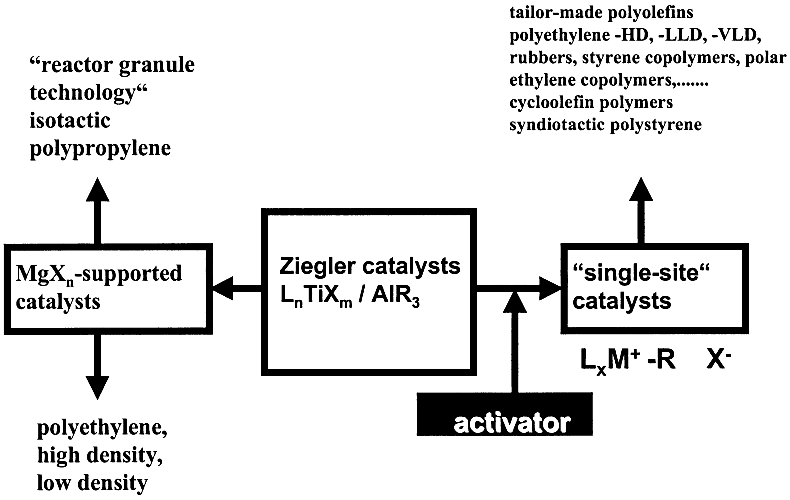

Fig. 2: Strategies of catalyst development

The development of single-site catalysts for slurry polymerization was stimulated by the discovery of highly effective activators and the evolution of metallocene-based catalyst systems. During the mid 1970's several groups discovered accidentally that traces of water accounted for improved catalyst activity in the presence of $AlMe_3$. It was Sinn and Kaminsky who first identified the potential of $AlMe_3/H_2O$ activators for metallocene-catalyzed ethylene polymerization. Their German patent DE 2608863[6)], filed jointly with BASF AG on March 4, 1976, claimed novel halogen-free catalysts comprising bis(cyclopentadienyl)titaniumdialkyl, aluminumtrialkyl and water with Ti/Al molar ratio varying between 1:1 and $1:10^5$ and Al/H_2O between 6:1 and 6: <9. Their second patent DE 2608933[7)], filed the same day, disclosed zirconocene catalysts activated with $AlMe_3$ /H_2O. The discovery of the role of the $AlMe_3/H_2O$ molar ratio ultimately led Sinn and Kaminsky to the discovery of methylalumoxanes $(\text{-AlMe-O-})_n$ (n=5-20), abbreviated as MAO, which boosted the activity of metallocene-based catalysts and produced uniform polyethylene with narrow molar mass distributions typical for single site catalysts[8,9)]. Today it is well recognized that MAO forms cationic metallocene alkyl complexes containing a weekly or non-coordinating anion which is complexed by the cage-like MAO molecule. Later MAO-free activators such as perfluoroaryl boranes and trityl and ammonium borates as well as supported activators were developed. Activator chemistry was reviewed by Chen and Marks10). In 1980, for the first time, MAO activation of metallocene by Sinn and Kaminsky afforded polymerization of propylene, producing completely atactic polypropylene11).

It should be noted that the two early patents on MAO-activated titanocenes and zirconocenes were abandoned four years later because at that time the extraordinary potential of single site catalyst technology was not recognized. In fact, many industrial managers were worried about high costs of both MAO activators and metallocenes, especially with respect to the lower costs of magnesium-based multi-site catalysts. This attitude changed during the mid 1980's when progress in metallocene chemistry offered attractive new opportunities for polyolefin technology and novel tailor-made polyolefins 12). It was Brintzinger who first proposed the use of chiral ansa-metallocenes for stereospecific 1-olefin polymerization against heavy opposition of his established German colleagues who criticized his research proposal because according to their feeling stereospecificity would remain the domain claimed exclusively by heterogeneous catalysts. Brintzinger's synthesis of chiral bridged ("ansa") metallocenes13) provided the solid scientific base for the discovery of the homogeneous stereosepecific 1-olefin polymerization and exciting progress with respect to novel stereoselective single site catalysts and the identification of correlations between catalyst structures and polymer architectures. Ewen14) and Kaminsky jointly with Brintzinger15) demonstrated that MAO-activated homogeneous catalysts were indeed able to produce stereoregular polypropylene. While meso ansa metallocenes gave atactic polypropylene, racemic ansa metallocenes produced isotactic polypropylene.

During the 1980's the performance of metallocene-based catalyst systems was improved to produce isotactic, syndiotactic, and stereoblock polypropylenes in industrial scale12). In the early 1990's supported single site metallocenes catalysts were introduced to enable gas phase polymerization16). Also ethylene/1-olefin copolymers with high 1-olefin content, cycloolefin copolymers, ethylene/styrene interpolymers, syndiotactic polystyrene, and long-chain branched ethylene copolymers became available. Metallocene-based innovations with respect to both catalyst and polymer development were reviewed in the multi-authored book entitled "Metallocene-Based

Polyolefins", edited by Scheirs and Kaminsky[17)]. The concept of single-site catalysts has been expanded successfully to bridged half-sandwich complexes[18)] and a rapidly increasing number of complexes containing chelating ligands[19)]. For many years the major focus of catalyst development was placed upon early transition metals such as Ti, Zr, Hf, V, Cr. Today also the potential of the late transition metal complexes of Ni, Pd, Co and Fe is recognized (cf. Fig. 3). A review published by Gibson and coworkers highlights catalyst design concepts of non-metallocene-based single site catalysts including mapping of catalyst activities as a function of transition metal and ligand type[19)].

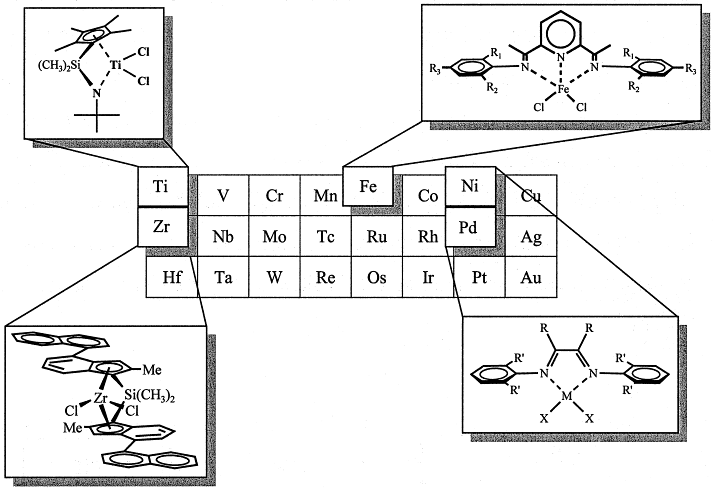

Fig. 3: Single site catalysts based upon group 4 ansa-metallocenes and bridged half-sandwich complexes as well as late transition metal complexes containing chelating ligands

3. Tailor-Made Polyolefin Materials

The development of single site catalyst technology is paralleled by achieving unprecedented control of molar mass, molar mass distribution, short and long chain branching, as well as stereochemistry. As a function of catalyst structures and process conditions it is possible to tailor polyolefin materials according to customers' demands. Today basic reaction mechanisms of stereoselective 1-olefin polymerization are well understood. Excellent reviews on metallocene-catalyzed stereoselective 1-olefin polymerization were published by Brintzinger[20], Resconi[21], Fink[22], and Coates[23]. As shown in Fig. 4, the stereoselectivity of 1-olefin polymerization can be varied from highly isotactic to syndiotactic, atactic and stereoblock polymers with application ranging from stiff engineering plastics to flexible films and rubbers.

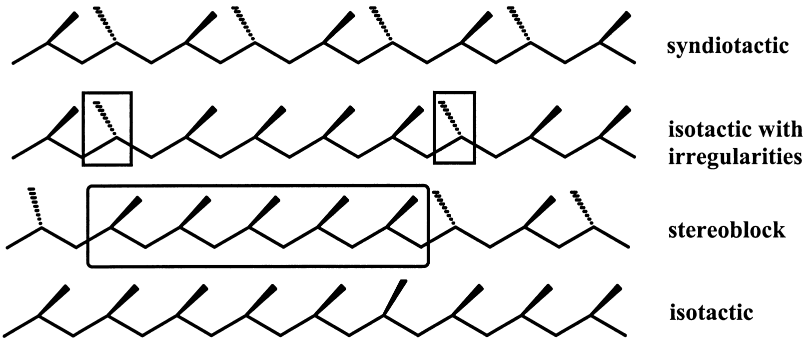

Fig. 4: Stereochemistry of metallocene-based poly(1-olefins)

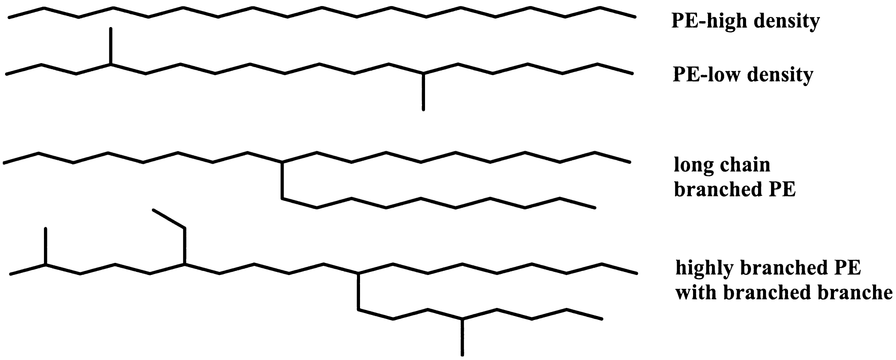

Fig. 5: Molecular architectures of polyethylenes

In contrast to conventional catalysts, stereo- and regioirregularities can be placed randomly in the polypropylene backbone. As apparent from Fig. 5, copolymerization of ethylene with 1-olefin and branching ethylene homopolymerization ("chain walking") afford polyethylene chains containing methyl and ethyl branches, complex n-alkyl branch distributions, blocks, and long chain branches. As a function of stereo- and regioirregularities as well as short chain branching it is possible to control polyolefin crystallization and superstructure formation[24)].

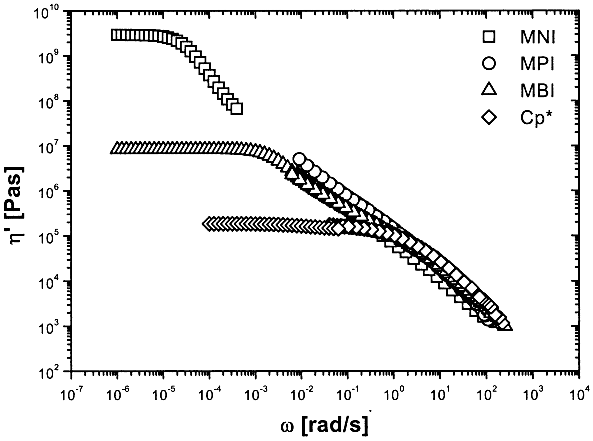

Fig. 6: Long chain branching and melt processing:

Polyethylenes prepared with MAO-activated 4-naphthyl- (MNI), 4-phenyl – (MPI), 4,5-benzo (MBI)- substituted dimethylsilylene-bridged 2-methyl-indenyl zirconocenes. Comonomer incorporation and long chain branching: MNI > MPI > MBI > Cp* (data from P. Walter)

Metallocene-based ethylene copolymerization using ansa-metallocene catalysts produces the entire feasible range of copolymer compositions without sacrificing high molar mass and molar mass independent branching. Conventional catalyst frequently produced rather complex reaction mixtures including oligomers with high comonomer content. Branched polyethylenes prepared by single site catalysts have proven to be excellent model systems which have been applied to establish correlations between degree of branching and melting temperature as well as glass temperature[25,26)]. Moreover, the control of molecular architectures affords a better insight into the basic correlations between rheological behavior and molar mass distribution as well as long chain branching. In fact, the first generation of polyolefins prepared with ansa-metallocenes were rather difficult to process due to their rather narrow molar mass distribution and shear-independent viscosity. Since the pioneering days, processing has been improved considerably but still offers opportunities for further refinement. The formation of long chain branches was attributed to copolymerization of vinyl-terminated polyethylenes[18,25,27,28)]. In Fig. 6, shear thinning, i.e., shear-induced viscosity decrease, is shown to depend upon the structure of ansa - metallocene complexes and parallels copolymerization reactivity of the complexes. Further sophistication of rheological measurements is required to examine the role of blends containing polymers with different branching distributions and the presence of branched branches (cf. Fig. 5). Since branching is dependent upon catalyst structure as well as support formation, there are many open questions in catalyst design with respect to improved processing. Rheology will continue to play a key role with respect to the commercial success of single-site catalyst technology.

Innovation in catalyst technology offers attractive opportunities for the production of cycloolefin polymers. The norbornene-based polymer family is displayed in Fig. 7. Ring-opening metathesis polymerization (ROMP) with versatile ruthenium carbene complexes ("Grubbs catalysts") affords olefinically unsaturated polymers from dicyclopentadiene and norborne[29)]. Due to the presence of olefinic groups in the backbone, melt processing and polymer stabilization of polynorbornenes obtained by ROMP are difficult. Therefore, polyinsertion of cyclopentene and norbornene has attracted more industrial attention. According to Kaminsky metallocene catalyzed polymerization of cyclic monomers such as cyclobutene, cyclopentene, norbornene and dimethanooctahydro-naphthalene gave a wide range of high molecular weight polymers with extraordinary high melting temperatures exceeding 400 °C and approaching the range of their decomposition temperatures[30,31)] Later Collins and Kaminsky reported that polycyclopentene was composed of 1,3-linked cyclopentane rings[32,33)]. Copolymerization of ethylene with norbornene was commercialized by Ticona GmbH. Topas® cycloolefin copolymers are transparent amorphous and semi-crystalline materials which are of interest in medical packaging and also engineering applications. Kaminsky and Arndt-Rosenau have examined the mechanisms of cyclolefin and olefin copolymerization[34,35)]. Novel activator-free neutral salicylaldimine nickel catalysts were reported by Grubbs and coworkers to polymerize hydroxy-functionalized norbornene without poisoning problems[36)]. This advance holds attractive potential for the preparation of novel engineering materials with high heat distortion temperature and improved compatibility with polar polymers.

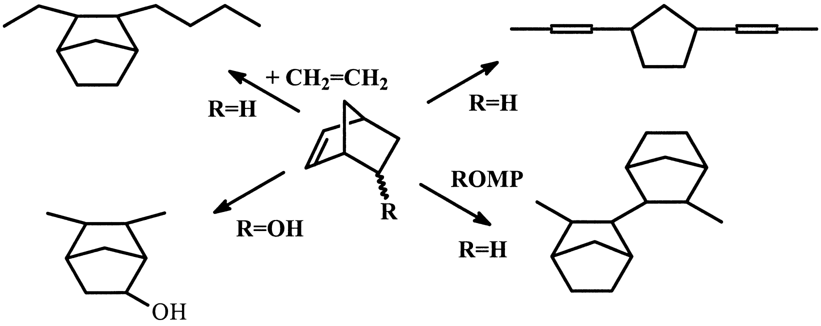

Fig. 7: Cycloolefin polymers derived from norbornene

In future the catalytic copolymerization of olefins and styrene with polar olefins such as acrylics, acrylonitrile, vinylacetate will continue to be a key challenge in catalytic polymerization because incorporation of polar monomers will help to overcome the limitation of property profiles imposed by the hydrocarbon nature of polyolefins. The state-of-the art of olefin copolymerization with polar monomers was reviewed by Novak37). Since most early transition metals compounds and main group activator alkyls are strong Lewis acids, complexation with the polar comonomers prevents coordination of olefin monomers. Therefore, large excess of activators is needed to circumvent this problem at the expense of large amounts of residual comonomer complex left in the polymer and increased demand of expensive catalyst components. In contrast, late transition metals are much less oxophilic. The opportunities of late transition metal catalysts was well recognized. Drent and coworkers used nickel catalyst in carbonylation reactions38). As shown in Fig. 8, nickel catalysts in the presence of monophosphane ligands such as triphenyl phosphine gave exclusively methylpropionate when the carbonylation of ethylene was performed in methanol. However, when chelating diphosphanes were used, alternating copolymers of ethylene and carbon monoxide were formed because the trans effect problem was circumvented. Terpolymers of ethylene and a few percent of propene with carbon monoxide were introduced by Shell under the trade name of Carilon as thermoplastic material with 225 °C melting temperature and polyamide 6 –like property profile.

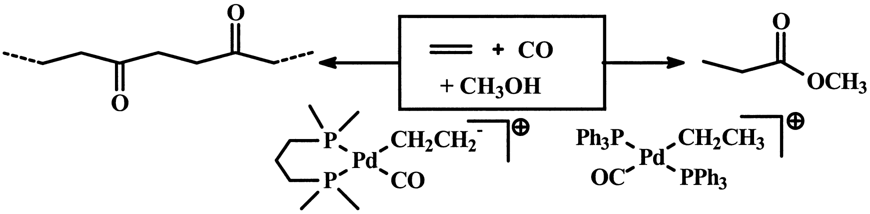

Fig. 8 Alternating ethylene / carbon monoxide copolymerization with Pd complexes containing chelating phosphane ligands[38)]

The progress in olefin polymerization catalyzed by late transition metal complexes has been reviewed by Ittel[39)] and Mecking[40,41)] . Catalysts and polymer microstructures are displayed in Fig. 9. It was Karl Ziegler who discovered the “Nickel effect”, i.e. formation of 1-butene when nickel salts were activated with aluminum alkyls. This was attributed to the very rapid β-elimination with respect to chain propagation. During the pioneering days of polyolefin research the development of Ni catalysts was aimed exclusively at industrial production of olefins such as 1-butene. Refinement of ligand frameworks by Keim and coworkers during the 1960’s and 1970’s led to the Shell higher olefin process (SHOP) based upon Ni ylide complexes[42)]. Ligand and activator variations during the SHOP development afforded accidentally high molecular weight as undesired by-product. During the 1980’s both Ostoja-Starzewski at Bayer AG[43)] and by Klabunde at Du Pont[44)] succeeded to produce high molecular weight polyethylenes and obtained ethylene copolymers with polar monomers such as undecenoate by means of tailor-made Ni ylide calatylsts. The search for electrophilic cationic nickel and palladium metal centers containing bulky chelating ligands and a weekly or noncoordinating counterion during the 1990’s led Brookhart and coworkers to the development of cationic diazadiene Ni and Pd catalysts. Such catalysts afford branching homopolymerization (“chain walking”) of ethene and 1-olefins[45)] as well as ethene copolymerization with methylacrylate, producing polyethylene containing both pendent n-alkyl and esteralkyl side chains[46)]. The migration of transition metal alkyls along the polyolefin chain followed by insertion (“chain walking”) was previously observed by Fink and coworkers for the Ni aminobis(imino)phosphorane catalyst system. This system polymerized 1-pentene to afford methyl-branched polyethylene equivalent to poly(ethene-alt-propene)[47,48)]. Brookhart’s Pd diazadiene catalysts gave liquid high molecular weight polyethylene with very high degree of short and long chain branches including branched branches. Neutral salicylaldimine catalysts reported by Grubbs and Brookhart form homo- and copolymers of functionalized norbornenes and tolerate polar reaction media36).

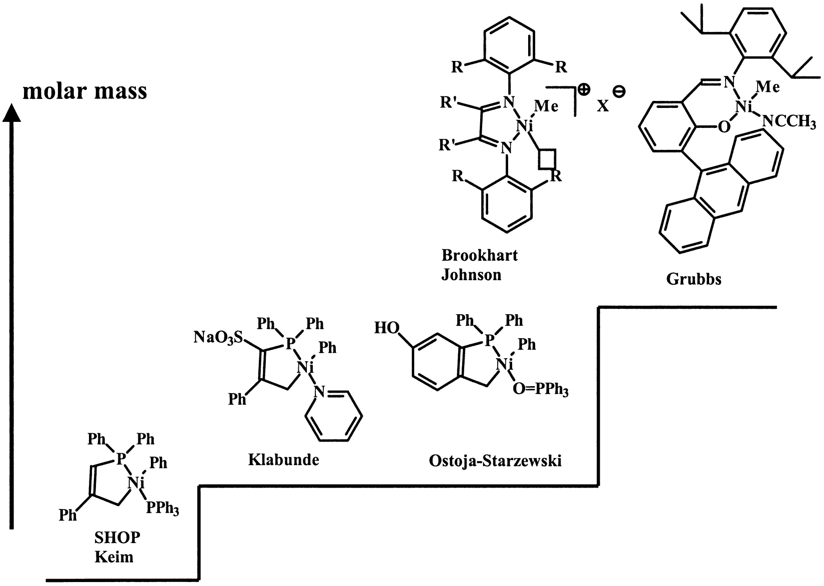

Fig. 9: Evolution of nickel-based catalyst systems

A remarkable feature of nickel catalysts is their tolerance of polar reaction media. The two groups of Claverie and Spitz49) and Mecking50,51) developed slurry and emulsion polymerization processes using either water soluble nickel complexes or miniemulsions of water-insoluble catalysts. A high molecular weight polyethylene dispersion of polyethylene is displayed in Fig. 10. Water is a non-toxic solvent which has high heat capacity and removes very effectively the heat of polymerization. Polyolefin dispersions for surface coating applications offer attractive new opportunities for polyolefin applications. Moreover, polymerization in water could turn out to be the base of a new specialty polyolefin business for non-polyolefin companies. Commercial success will require further improvement of catalyst activity, molar mass, and solid content. During the 1980's successful emulsion polymerization of 1,3-butadiene by means of cobalt catalysts was introduced by Goodyear and Japan Synthetic Rubber Coporation to produce stereoregular high molecular weight poly(1,2-butadienes) with melting temperatures around 200 °C and applications as functional filler in rubber compounding. Stereospecific 1-olefin emulsion polymerization represents a challenge for research in olefin polymerization catalyzed by late transition metal catalysts[52].

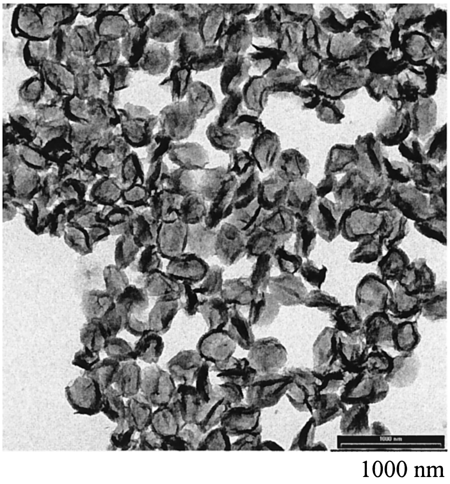

Fig. 10: TEM image of aqueous polyethylene dispersions of polyethylene with M_w=200000 g/mol and M_w/M_n = 2.2 (picture obtained by courtesy of Dr. S. Mecking, Freiburg)

4. High-Throughput Evaluation and Data Mining

The search for new or improved catalysts for olefin, styrene, and diene polymerization and copolymerization of olefins and polar monomers as well as the improvement of property profiles and processing requires tedious screening and variation of ligand substitution patterns, catalyst precursors, activators, supports, process parameters of catalyst preparation and polymerization as well as time-consuming and expensive polymer characterization and testing of materials. The search for simplified single site catalysts and polyolefin materials with new property profiles and the development of rapid analytical methods is greatly facilitated by new methods of high-throughput development, increasing the speed of development by several orders of magnitude with respect to conventional technologies. During the last ten years, applications of high-throughput screening and combinatorial chemistry has found many applications in drug discovery where large number of compounds are prepared in automated parallel synthesizers and screened for their bioactivity in fully automated biomedical test arrays. Libraries with numerous compounds and systematic variations of molecular architectures are created and coupled with modeling and computer-based evaluation to identify novel lead structures. At present high throughput development methods are also being applied in the development of new materials(53,54) including catalyst and polyolefin development(55,56) .

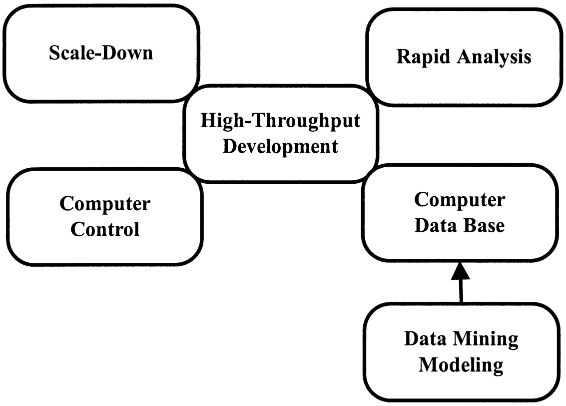

Fig. 11: Elements of high-throughput development

The key elements of modern high-throughput developments are listed in Fig. 11. Scale-down of reactions and computer-controlled rapid parallel syntheses help to save resources. Rapid analyses and on-line reaction monitoring gives immediate feedback of the experiments without delay typical for many conventional time-consuming analytical tools such as high resolution NMR spectroscopy and conventional size exclusion chromatography. High throughput produces a flood of data which must be processed and organized in computer data bases. The large number of experiments offers attractive new opportunities for data analyses. On one hand, the large number of experiments performed under standardized reaction conditions can be applied to support modeling and to propose the design of new catalyst systems. On the other hand, experimental design can be applied to identify optimum composition and optimum process conditions.

The development of single site catalysts based upon nickel and palladium has stimulated the application of high throughput processes. Performing polymerization reactions in simple arrays with on-line monitoring of the evolved reaction heat can be used to identify promising candidates for further evaluation and to establish libraries57). It was recognized that information concerning key polymer properties such as molar mass and molar mass distribution is of special value. Short column size exclusion chromatography was introduced to speed up analyses by means of size exclusion chromatography56). In another approach, Chen proposed mass spectrometry as very effective tool to acquire information on insertion reactions as a function of complex structures and to build the corresponding libraries58).It should be noted that reaction conditions and the speed of high-throughput screening should be adjusted to process conditions. In contrast to solution polymerization with hold-up times of 10-20 minutes, gas phase polymerization typically requires hold-up times of several hours and good long-term performance. Therefore the evolved reaction heat during mixing of components is not a very accurate measure for real-life catalyst performance.

At the Freiburg Materials Research Center a high-throughput method was introduced to fit the needs for polyolefin catalyst and materials development. Parallel syntheses of ligands, activators, organometallic compounds, supports and supported catalysts as well as catalyst activations are performed in a commercial automated synthesis unit ASW2000 from Chemspeed, which is shown in Fig. 12. Up to a maximum of 112 glass reactors with volumes ranging from 13 to 100 ml, and up to 80 12 bar miniautoclaves can be operated simultaneously under fully inert environment. Automated reagent addition can occur while shaking, stirring, heating and cooling. Reactions can be performed using a broad temperature range which is controlled from –70 to +150 °C. On-line evaporation (10 mbar) allows recovery of solid polymer. On-line TLC and HPLC/MS are available for characterization of ligands and organometallic compounds. Catalysts can be transferred from Chemspeed reactors into customized racks. Therefore, the catalysts produced by Chemspeed parallel syntheses can also be introduced easily into conventional fully automated reactors (50 to 1000 ml volume) equipped with autoinjection of catalysts and activators, stored in racks or carrousels, as well as with automated sampling of the produced polymers. Polymerization with fully automated minireactors can be performed in solution, slurry and gas phase. This approach can convert virtually any lab reactor into medium- to high-throughput reactors. Although the number of runs per day is reduced to approximately 100 runs per reactor, the significance of the obtained results is improved with respect to high-throughput polymerization using arrays.

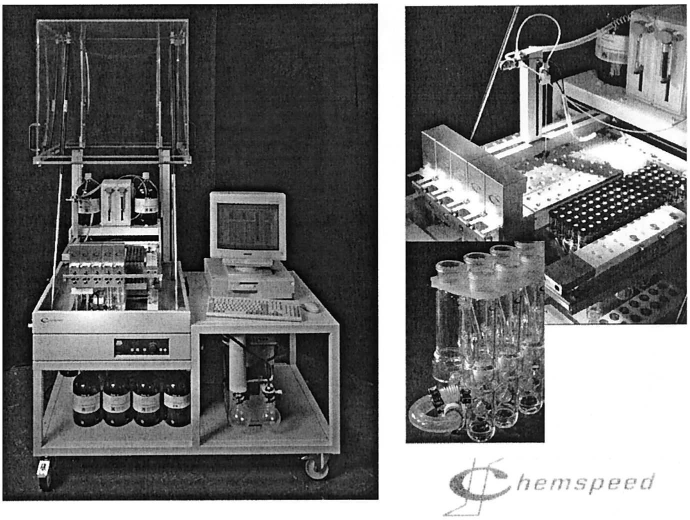

Fig. 12: High-throughput development using the Chemspeed® automated parallel synthesizer for syntheses of ligands, catalysts and supported catalysts as well as polymerization screening

In solution processes, on-line monitoring by means of AT-FTIR (“ReactIR” from Mettler AG) has proven to be very useful for measuring kinetics as well as comonomer incorporation. Since ReactIR also measures the solid content, the resulting polymer solutions with known polymer content can be injected into SEC for rapid on-line determination of molar mass and molar mass distribution. Within a few seconds, copolymerization parameters can be determined from the IR data. In olefin copolymerization it is possible to monitor the conversion of the liquid monomers and to identify by-product formation such as atactic polystyrene in styrene/olefin copolymerization or syndiospecific styrene homo- and copolymerization, respectively. Here spectroscopic methods eliminate the need for time-consuming extractions. The polymer is collected and analyzed by automated DSC, SEC, and spectroscopy. Information such as catalyst composition, process parameters, polymerization rate/time functions, maximum catalyst activity, average catalyst productivity, polymer composition, copolymerization parameters, copolymer sequence distribution, polymer properties such as melting temperature, glass temperature, mechanical properties are acquired and compiled in the data bank.

The large number of runs performed under identical conditions in reactors with excellent process control offers new opportunities for data mining. The data mining software evaluates data files for correlations. Well-defined model polymers, which are available by means of single site catalysts, can be used to calibrate correlations ("fingerprints") between polymer properties and spectroscopic data. Low resolution NMR, FT-IR and near IR can be calibrated to identify polymer properties, including short- and long-term mechanical propertes as well as molecular mass, within the model compound family by means of crossvaliditation. The software recognizes whether the prepared sample fits into the range of model polymers used for calibration. With this "fingerprint" method a large variety of polymer properties are available within seconds without using time-consuming testing or tedious sample preparation. This method is of special interest in rapid on-line analyses and in quality assurance when transferring lab products into pilot and production plants. This "fingerprint" technology can be used to identify new candidates for new catalysts and polyolefins with improved performance. There is still room for refinement of data mining tools and "fingerprint" technologies. Without any doubts the development of computer-guided high- and medium-throughput processes equipped with on-line monitoring and combined with data mining and modeling will stimulate further innovations in catalyst and polyolefin technology.

5. Outlook

Close to the 50th anniversary of the Ziegler-Natta catalysis, the transition metal catalyzed olefin, styrene, diene and cycloolefin polymerization is progressing at very rapid pace. There are several lines of important developments and new challenges. In view of the drastically increasing size of the reactors producing polyethylene and polypropylene commodities, the improvement of such processes and cost reduction will continue to play a very prominent role. Most likely, the number of grades will be reduced to enhance cost effectiveness of commodities. Continuing breakthroughs in single site catalyst technology and high-throughput development stimulate the development of simplified catalyst systems which do not require tedious and expensive multistep syntheses typical for some of the state-of-the-art stereoselective metallocene catalysts. The copolymerization of polar monomers, polymerization in aqueous media, preparation of dispersions via catalytic emulsion polymerization, stereoselective copolymerization and the exploitation of novel organometallic reactions as well as advances in post polymerization catalysis will stimulate diversification of polymers produced by means of single site transition metal catalysts. Computer-assisted molecular design of polyolefins using single-site catalysts and modern processes will continue to promote the production of environmentally friendly polyolefins with tailor-made property profiles and enhanced processability.

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