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From Organometallic and Polymer Chemistry to Applied Materials Science: Transition Metal Catalyzed Synthesis of Polyolefins and Polyolefin-Based High-Performance Materials

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Summary: A brief history of the development of transition metal-catalyzed olefin polymerization including the present status of polyolefin chemistry is given. The entire evolution of polyolefin chemistry will be outlined, giving ample attention to the development in the catalytic systems. Starting with the first generation PP catalysts ($TiCl_3/AlClEt_2$), the success story of organometallic chemistry, which resulted in modern supported and unsupported single site systems and finally functional group-tolerant group VIII systems will be summarized. Where applicable, examples of technical application will be given. Additionally, organometallic chemistry responsible for selectivity but also for termination reactions as well as the various "living" systems and the adherent implications for materials science will be discussed. Finally, the impact of related transition metal-catalyzed metathesis chemistry on the area of specialty materials will be outlined.

Development and Present Status of α-Olefin Polymerization Catalysts

Poly(olefin) chemistry started in the 1930ies with poly(styrene) (PS), poly(vinylchloride) (PVC) and poly(methylmethacrylate) (PMMA). About 15 years later, in course of his investigations of the "Aufbaureaktion", Ziegler actually invented olefin (ethylene) polymerization [1, 2], which was extended to propylene polymerization by Natta short time later.[3, 4] Since then, polyolefins have made their way and become a multi-billion \$ business where PE (41.3% world usage share) and PP (21.9 %) are still among the most important polymers. The "first generation catalysts" based on systems such as $TiCl_4/AlR_2Cl$ were successively replaced by more and more advanced systems (*e. g.* Solvay: $TiCl_3/Et_2AlCl$; Montedison: $TiCl_4$/"activated" $MgCl_2$;etc.). Almost "hidden" by the almost revolutionary developments in poly(α-olefin) chemistry, metathesis polymerization was discovered in 1957

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by Eleuterio at DuPont[5]. Its relevance to poly(α-olefin) chemistry was not understood until the first mechanistic studies on olefin polymerization using well-defined catalysts were conducted. Already in 1975, Kaminsky and coworkes observed the effect of water on binary titanocene/AlR_3 systems[6]. These investigations lead to introduction of methylalumoxane (MAO) in 1977, a real benchmark in polyolefin chemistry. Activities of catalytic systems dramatically increased. Thus, first generation catalysts such as δ-$TiCl_3$/0.33 $AlCl_3$/Et_2AlCl allowed the synthesis of ca. 1 kg PP/g catalyst, while the metallocene/MAO system gave access to more than 10 tons of PP/g catalyst[7]. In the eighties, chiral titanocenes prepared in the groups of Kaminsky and Ewen opened the door to highly tactic PP structures[8]. In 1986 Jordan and coworkers first demonstrated that the cationic metallocene complexes were the actual polymerization-active species[9]. This finding resulted in an intense research on that topic with major contributions by Hlatky, Turner, and Marks who used perfluoro borates as non-coordinating anions[10-12] as well as by Erker who investigated “Zwitterionic” systems[13]. Nowadays, *a*-olefin polymerizations may be carried out even in a living“ manner, thus giving access to an exact yet simple control over molecular weight *via* stoichiometry[14-18].

The increasing knowledge about catalytic systems allowed the tailoring of polymers in terms of molecular weight, polydispersity, branching and in due consequence the fine-tuning of material properties. The enormous importance of such systems is underlined by the fact that they allow the controlled fabrication of polyolefin-based materials ranging from ultra-stiff construction materials to thermoplastic elastomers and speciality polymers[19]. Heterogenization on silica, Al_2O_3, $MgCl_2$, MgF_2, CaF_2 MAO, PS-DVB, etc., the use of particular supports in terms of mechanical properties as well as various polymerization technologies(*e. g.* Spheripol®, reactor granule technology, low pressure processes by Dow, DuPont, Unipol BP, Amoco Chem. or Phillips Petroleum Technology; gas phase Addipol process, etc.) significantly improved polymerization results in terms of activity and polymer properties as well as the processability of polyolefins[7]. Starting with simple homopolymers in the late fifties, a whole new family of linear and branched 1-olefin-based copolymers has been established. It is worth mentioning that reactor capacities increased from 100 and 85 kt/a for PE and PP, respectively in 1985 to 450 (PE) and 270 (PP) kt/a in the year 2000, thus participitating in the production of a total volume of more than 200 million metric tons of structural and functional polyolefins.

A drawback in conventional olefin polymerization is related to the high oxophilicity of group 4 and 5 transition metals. This high oxophilicity severely aggravates or often impedes the copolymerization of functional olefins. Despite the progress that has been made in the copolymerization of certain ethers or acrylates, the (co-)polymerization of polar or even functional monomers came into the center of interest.[20-22]

Late Transition Metal-Based α-Olefin Polymerization Catalysts

Despite the increasing consumption of commodity polyolefin-based polymers, manufacturers are facing increasing expectations by consumers in terms of materials properties. In due consequence, besides of high activity modern catalysts need to meet high standards and fulfill certain requirements such as tunable activity, the access to polymers with controlled molecular weight, controlled PDI, tunable stereoregularity, the synthesis of telechelic polymers and copolymers (block-, alternating,...), the incorporation of functional groups, etc. in order to be capable of fulfilling the expectations. In addition, it appeared be highly desirable to generate certain material properties by a simple (*i. e.* cheap) copolymerization or branching approach that would allow to partially or completely omit standard extrusion and/or blending procedures.

In the early 1990ies, Brookhardt and coworkers introduced the first late transition metal complexes, that were both highly stable and highly active in particular in ethylene homo and copolymerization (Figure 1)[23].

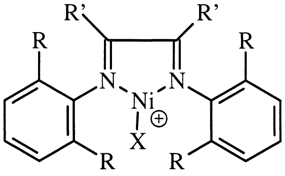
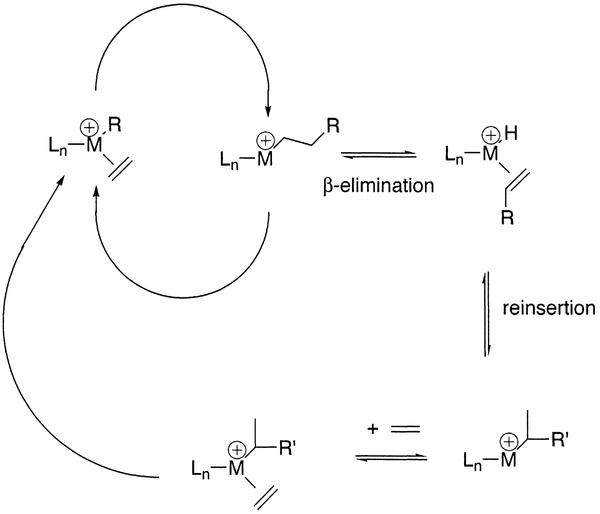


Figure 1: General formula of Brookhardt-type ethylene polymerization catalysts.

Due to the peculiar "chain walking" during polymerization (Scheme 1) highly branched PE may be obtained. The degree and nature of branching may be varied by polymerization conditions (ethylene pressure, temperature), the nature of the ligand and the transition metal itself. Thus, nickel results in a distribution of 41 Me, 6 Et, 3 Pr, 2 Bu, 1 Amyl, 5 > C_6 branches, while palladium gives more „hyperbranched“ structures. Copolymerizations of ethylene with CO or certain acrylates, vinylketone, crotonaldehyde, or 4-pentenoates have been carried out successfully, thus extending the range of functional polymers[23].

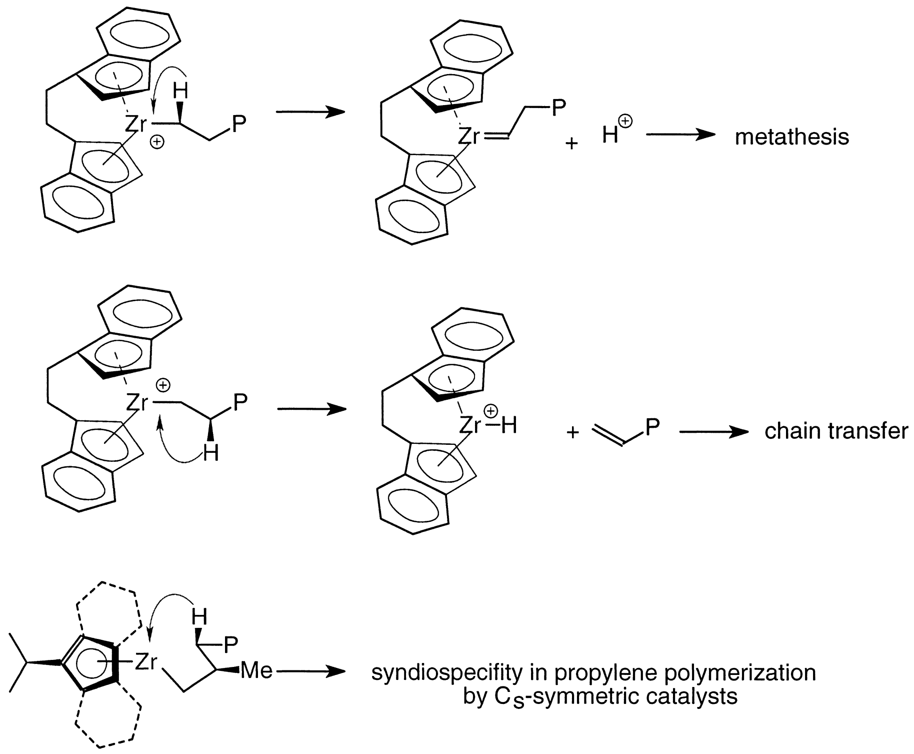


Scheme 1: „Chain walking“ mechanism in ethylene polymerization using Brookhart’s catalyst.

Since the basic properties of any polyolefin and in particular of LDPE (copolymers of ethylene and 1-octene) are governed by the short chain moieties (responsible for crystallinity, T_m, T_g) as well as by the long chain moieties, which are mainly responsible for the rheological properties of the material, such catalysts now provide an excellent approach for the regulation of materials properties.

Other Functionality Tolerant Transition Metal Catalyzed Olefin Polymerizations

Metathesis polymerization is closely related to Ziegler-Natta polymerization. In fact some Ziegler-Natta systems may switch between either of these two techniques during the (co)polymerization of cyclic olefins such as norborn-2-ene, a property which was actually responsible for its discovery. This switching is made possible *via* (reversible) α-elimination reactions (Scheme 2). Necessary requirements for such reactions are *agostic* interactions, which play an important role in many transition metal-catalyzed polymerizations and reactions. As can be seen, β-agostic interactions are responsible for chain-transfer (CT) reactions in olefin polymerization, while γ-agostic interactions determine stereoregularity in centrosymmetric catalysts[24].



Scheme 2: α–, β– and γ-agostic interactions.

Metathesis and Its Relevance to Polyolefin-Based Materials

During the last 15 years, the area of well-defined metathesis initiator systems was characterized by almost dramatic improvements in terms of initiator activity, stability, and selectivity[25]. In due consequence, control over polymer properties increased and metathesis-based polymerization techniques (in particular ring-opening metathesis polymerization, ROMP) have been adapted for materials science purposes. Well-defined systems such as the highly selective and active Schrock catalysts of the general formula $Mo(N\text{-}2,6\text{-}R_2\text{-}C_6H_3)(CHCMe_2Ph)(OCR')_2$ or the more robust first and second generation Grubbs-type initiators of the general formulae $Cl_2Ru(CHPh)(PR''_3)_2$ and $Cl_2Ru(CHPh)(PR''_3)(NHC)$, respectively, offer access to basically every polymer architecture one might think of.[25] Among metathesis-based polymerization techniques such as acyclic diene metathesis polymerization (ADMET), alkyne polymerization and ROMP, the latter one appears to be the most attractive technique for the synthesis of complex cross-linked architectures. On one hand, no volatile products as in ADMET evolve. On the other hand, a significantly broader range of monomers than in any other polymerization may be used. One additional advantage of ROMP is the possibility to use functional monomers. This and the controlled, "living"[26-30] polymerization mechanism allow a highly flexible yet reproducible polymerization setup. In course of our investigations to use ROMP[31]for the synthesis of functional high-performance materials, we already combined this polymerization technique with grafting- and precipitation techniques for the synthesis of functionalized separation media[32-43] and catalytic supports[44-48]. Nevertheless, since in particular poly(norbornene)-based materials are prone to oxidation, metathesis-based polymer technologies are not quite established in polymer science. Among the few commercially available polymers are Vestenamer® (polycyclooctene), Norsorex® (polynorbornene) as well as Telene®, a poly-(dicyclopentadiene) (poly(DCPD)) produced by reaction injection molding (RIM). Due to the fact that even complex functional groups may be polymerized, its main application lies in the area of functional polymers and speciality polymers such as LC-polymers, and organic light emitting diodes (OLEDS). For purposes of completeness it shall be mentioned that the application of metathesis is currently situated in the area of monomeric compounds. The most important processes are the Philips triolefin process, the neohexane process, olefin metathesis (*e. g.* from the "Shell Higher Olefin Process" (SHOP)), cross metathesis for olefin chemistry and finally (asymmetric) ring closing (RCM), tandem cross metathesis for fine chemical production.

Nevertheless, metathesis polymerization has found its way into the synthesis of supports for heterogeneous catalysis as well as for separation science. In the following one aspect, the synthesis of monolithic media *via* metathesis and some applications shall be outlined briefly.

Basics of Monolithic Supports Prepared by Metathesis

Generally speaking, the term "monolith" applies to any uni-body structure composed of interconnected repeating cells or channels. Such media may either be metallic or prepared from inorganic mixtures, *e. g.* by a sintering process to form ceramics, or from organic compounds, usually by crosslinking polymerization. For this particular review, the term "monolith" or "rigid rod" shall comprise crosslinked, either inorganic or organic media which are characterized by a well-defined porosity and which are used as supports for interactions/reactions between a solid and a liquid phase. Besides of advantages such as lower backpressure and enhanced diffusional mass transfer[49, 50], the ease of fabrication as well as the many possibilities in structural alteration need to be mentioned. Important enough, the enhanced diffusional mass transfer allows separation scientists to run separations at comparably high flow rates of up to 10 mm/s, resulting in fast and highly efficient separations. Similarly, one can take advantage of it to design supports for fast heterogeneous catalytic reactions.

Monolithic Media Prepared by Transition Metal Catalyzed Polymerization

Monomers and catalysts

The choice of the appropriate catalyst represents a crucial step in order to create a well-defined polymerization system in terms of initiation efficiency and control over propagation. Only in this case the entire system may be designed on a *stoichiometric base*. This is important, since for microstructure variation the composition of the entire polymerization mixture (*vide infra*) needs to be varied within extremely small increments. Thus, the catalyst needs to be carefully selected from both a chemical and a practical point of view. In principle, Schrock and Grubbs systems, both highly active in the ROMP of strained functionalized olefins, may be used. Since the preparation and in particular derivatization of ROMP-based rigid rods requires some handling that may not be performed under a strict inert atmosphere, we focused on the use of the less oxygen-sensitive ruthenium-based Grubbs-type initiators of the general formula $Cl_2(PR_3)_2Ru(=CHPh)$ (R = phenyl, Cy [Cy = cyclohexyl]) rather than on the use of the molybdenum-based Schrock-type initiators. Among the possible combinations of monomers and crosslinkers, such as norbornene (NBE), norbornadiene, dicyclopentadiene (DCPD), 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene (DMN-H6), and 1,4a,5,8,8a,9,9a,10,10a-decahydro-1,4,5,8,9,10-trimethanoanthracene (Figure 2), various Grubbs-catalysts as well as different porogenic solvents, the copolymerization of NBE with DMN-H6 in the presence of two porogenic solvents, 2-propanol and toluene, with $Cl_2(PCy_3)_2Ru(=CHPh)$ was found to work best.

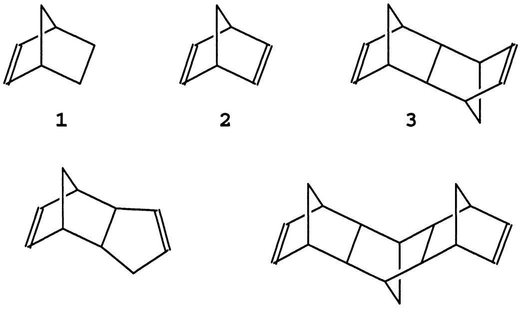


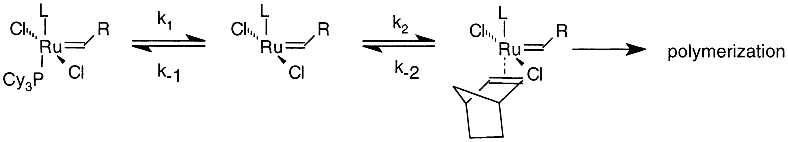
Figure 2: Structures of monomers and crosslinkers. (1) NBE, (2) norbornadiene, (3) DMNH-6, (4) DCPD, (5) 1,4a,5,8,8a,9,9a,10,10a-decahydro-1,4,5,8,9,10-trimethanoanthracene.

Initiator concentration

Initiator concentrations represent a crucial point in the preparation of monoliths. Most importantly, any uncontrolled, highly exothermic reaction must be strictly avoided. Additionally, the total amount of initiator directly determines the amount of growing nuclei that are responsible for phase separation and microglobule size. Nevertheless, in terms of a desired *in situ* derivatization (*vide infra*), higher initiator concentrations appeared favorable. In order to determine the number of active sites accessible for derivatization, the active sites were "capped" with ethyvinyl ether in order to cleave off the living termini. Surprisingly, Ru-measurement by inductively-coupled plasma optical emission spectroscopy (ICP-OES) investigations carried out with the effluent revealed that more than 98 % of the initiator (!) are located at the surface of the microglobules after the structure forming process[51]. This is in accordance with a micelle-based microglubule formation, where the catalytically active sites are located at the boundary between the solid and liquid phase. Fortunately, besides some effects on the microglobule shape, no significant influences of initiator concentration within a range of 0.1 - 1 % on the morphology in terms of pore and microglobule size of the continuous rods were observed. For experimental reasons, 0.4 % of **1** were used for rod formation and found sufficient for derivatization purposes (*vide infra*) without changing the properties of the rods in terms of microstructure. At this point, when dealing with transition metal catalyzed polymerizations, the efficiency of removing the metal from the rod after polymerization needs to be addressed. The fact that ruthenium-initiated polymerizations may conveniently be capped with ethylvinyl ether may be demonstrated by ICP-OES investigations on the Ru-content of the final rods. These investigations revealed Ru-concentrations < 10 mg/g, corresponding to a 99.8 % removal.

Monomers, monomer ratios and polymerization conditions

Based on the existing knowledge about pore-formation in monolithic materials[52-55], different mixtures of macro- and microporogens[56] were tested for their ability to form the desired, well-defined microstructures. Methanol, 2-propanol, cyclohexanol, 1-decanol, 1-dodecanol were investigated for their macropore-forming properties, dichloroethane, dichloromethane and toluene were used as microporogens. Among the many macropore-forming solvents, 2-propanol was found to possess good properties. Toluene, dichloromethane and dichloroethane were found to be capable of forming the desired microstructures in combination with 2-propanol. The choice of either toluene or methylene chloride strongly depends on the need of any subsequent derivatization. The relative ratios of all components (*i. e.* NBE, DMN-H6, the porogens and the catalyst) now allow varying the microstructure of continuous media. Due to the dissociative mechanism of the initiator (Scheme 3), the addition of phosphine offers additional access to the tuning of catalyst activtity.



Scheme 3: Dissociative mechanism of $Cl_2Ru(PCy_3)_2(CHPh)$-catalyzed metathesis polymerization.

Structural data such as microglobule diameter (d_p) may be deduced from electron microscopy (ELMI) while inverse size exclusion chromatography (ISEC) allows the determination of all porosity data (ε_z, ε_p, ε_t) as well as specific surface area (σ).[57] Alternatively, mercury intrusion (mercury porosimetry) or BET may be used, since they represent competitive alternatives for the analysis of porous systems. Particularly mercury intrusion is capable of providing data for the (here most relevant) macropores (> 1000 Å). Nevertheless, mercury intrusion turned out to be less favorable, since it requires the drying of the supports, a process that usually gives raise to significant changes in the pore size distribution, thus giving raise to ambiguous results.

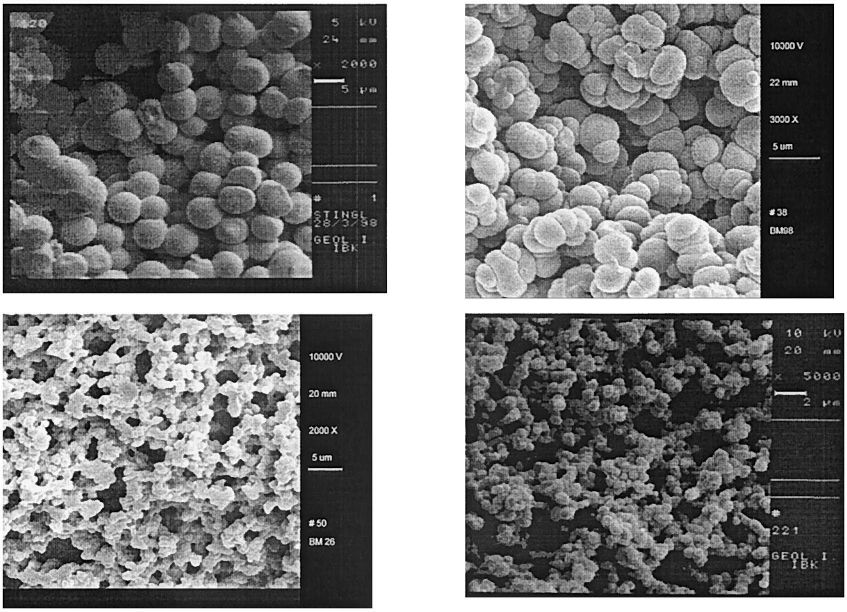


Figure 3: Variations in microstructure of various metathesis-based monoliths in terms of intermicroglubule void volume (ε_z) and volume fraction of pores (ε_p).

Since monoliths mainly consist of macropores (> 1000 Å), these are identified by this method yet may complementarily be addressed by electron microscopy (Figure 3). Nevertheless, the total porosity as obtained by this technique is in excellent agreement with the one obtained from ISEC data. Generally speaking, volume fractions of the intermicroglobule void volume (e_z) and total porosity (e_t) may be varied within arrange of 0 – 50 % and 50 – 80 %, respectively.

Applications of non-functionalized metathesis-based monoliths in separation science: structure-separation efficiency relationships

Due to the pure hydrocarbon backbone, monoliths prepared from NBE and DMN-H6 are strongly hydrophobic. The resulting materials significantly differ from PS-DVB based resins, in that the latter one contains aromatic systems that are capable of forming π-stacks with analytes possessing aromatic groups. Figure 4 shows the fast separation of eight different biologically relevant proteins by reversed phase chromatography. At flow rates of 3 mL/min, this separation may be accomplished within 90 seconds. Such separation performance at high flow rates gives an illustration of the fast mass-transfer that may be achieved[40, 42, 58]. It should be mentioned that ongoing research focuses on the synthesis of miniaturized microcolumn systems with i.d. ≤ 300 mm[59].

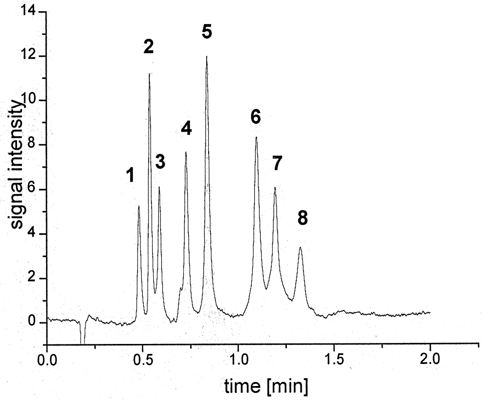


Figure 4: RP-HPLC separation of eight proteins on a metathesis-based monolith. Mobile phase: 0.1% aqueous trifluoroacetic acid; linear gradient, 14.5-37 % acetonitrile in 0.5 min, 37-46 % acetonitrile in 1 min; flow rate, 3 mL/min; T = 20 °C; detection, UV (218 nm). (1) ribonuclease A, (2) insulin, (3) cytochrome C, (4) lysocyme, (5) α-lactalbumin, (6) α-chymotrypsinogen A, (7) β-lactoglobulin B, (8) catalase. Inj. vol: 1-6: 22 µg; 7-8: 44 µg.

Functionalization

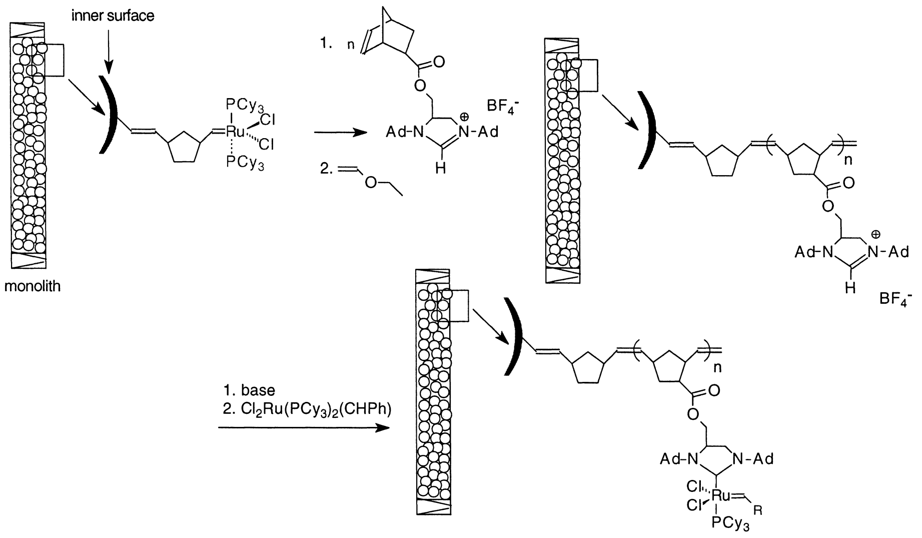
Despite the high definition in terms of microstructure (= size and form of microglobules that form the rod), specific surface area and pore volume[52-54, 60-63] as well as the impressive results that may be obtained in separation science with organic monolithic carriers prepared by radical polymerization, the preparation of *functionalized* monoliths is still somehow limited[56]. One synthetic protocol entails the copolymerization of the corresponding functional monomer during the synthesis of the rigid rod. Despite its simplicity, two problems have to be addressed. On one hand, a major part of the functional monomer is located at the interior of the rod. Since these rods are usually either non-porous or microporous, a major part of the functional groups is not available in course of the separation process. On the other hand, the presence of polar functional groups located close to the surface of the microstructure-forming polymer leads to unfavorable swelling properties. An alternative approach that avoids these problems entails the copolymerization of monomers possessing active sites for post-derivatization *e.g.* epoxide groups or azlactone groups. Those reactive groups that are located at the surface may in fact be conveniently transformed into standard functionalities such as sulfonic acids, amines[64-66] or alcohols[67, 68].

In the present ruthenium-based polymerizations [28, 29, 69, 70] one can take advantage of the "living" character and the high tolerance of the catalytic system *vs* different functionalities. While a grafting approach on 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO)-capped monoliths has been proposed recently[71], the ROMP approach appears to be even more attractive in terms of functional variety. Since any living polymerization system is not immortal[26, 72] and in view of the stability data for ruthenium-based initiators and in particular for **1**[73], optimum grafting conditions were elaborated in order to reduce loss of initiator activity to a minimum. For these purposes, the minimum time needed for the formation of the polymeric backbone (1 h) was determined[42]. Using the fraction of the initiator covalently bound to the surface (≥ 98 %, *vide supra*), the desired functional monomer is grafted onto the monolith surface by simply passing a solution thereof through the column/cartridge. Since there is no further possibility of cross-linking, tentacles attached to the surface are formed. The general degree of polymerization of any functional monomer varies within almost two orders of magnitude, depending on its general ROMP activity.

Obviously, this approach offers multiple advantages. Firstly, the structure of the continuous rod is not influenced by the functional monomer and can be optimized regardless of the functional monomer used. Secondly, other solvents than the porogens toluene and methanol such as methylene chloride, DMF may be used for the "*in situ*" derivatization of the rod. This avoids possible limitations related to the solubility of the functional monomer in the porogens (*e. g.* β-cyclodextrins are only soluble in DMF). Finally, a large variety of functional monomers may be grafted onto the continuous rod. Restrictions due to a reduced polymerization activity of the initiator *vs* any functional monomer may be avoided by a careful monomer design. The versatility of this concept is clearly underlined by the large variety of functional monomers that may be attached to the surface of monolith. For purposes of convenience, all functional monomers employed are either based on norborn-2-ene or 7-oxanorborn-2-ene. The amount of functional monomer grafted onto the monolith way be determined both in a *qualitative way* by FT-IR spectroscopy and *quantitatively* by acid-base titration and elemental analysis, respectively.[42]

Applications of functionalized metathesis-based monoliths in catalysis

As the ultimate goal in heterogeneous catalysis, one wants to combine the general advantages of homogeneous systems such as high definition, activity, etc. with the advantages of heterogeneous catalysis such as increased stability, ease of separation, recycling. Besides of a few applications in solid phase synthesis[74, 75] and enzyme immobilization[76, 77], monolithic catalytic media have basically been restricted to metal oxides, porous metals[78] and certain polysaccharides[79]. The first successful use of metathesis-based monolithic media for heterogeneous catalysis was accomplished by using these supports as carriers for Grubbs-type initiators based on N-heterocyclic carbenes (NHC-ligands)[80, 81]. In order to generate a sufficient porosity, monoliths with a suitable microporosity (40 %) and microglobule diameter (1.5 ± 0.5 mm) have been synthesized. Consecutive „*in-situ*“ derivatization was successfully accomplished using a mixture of norborn-2-ene and 1,3-di(1-adamantyl)-4-{[(bicyclo[2.2.1]hept-5-en-2-yl-carbonyl)oxy]methyl}-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate in methylene chloride (Scheme 4). The use of norborn-2-ene drastically enhances the graft yields for the functional monomer. Using this setup, tentacles of copolymer with a degree of oligomerization of 2 – 5 of the functional monomer may be generated. The free NHC necessary for recomplexation may simply be generated using 4-dimethylaminopyridine (DMAP). In a last step, excess base is removed by extensive washing and finally the catalyst is immobilized/formed by passing a solution of $Cl_2Ru(CHPh)(PCy_3)_2$ over the rigid rod. Loadings of up to 1.4 % of Grubbs-catalyst on NHC base may be achieved. Monolith-immobilized metathesis catalysts prepared by this approach show high activity in various metathesis-based reactions such as ROMP and RCM. The *cis/trans* ratio of polymers (90 %) exactly corresponds to the one found with homogeneous systems. The use of chain-transfer agents (CTAs, such as *cis*-1,4-diacetoxybut-2-ene) allows the regulation of molecular mass, in particular in the case of cyclooctene.



Scheme 4: Functionalization of metathesis-based monoliths with NHC-precursors and generation of a heterogeneous metathesis-active support.

The presence of CTAs additionally enhances the lifetime of the catalytic centers by reducing the average lifetime of the ruthenium methylidenes. This allows the repetitive use of these systems. Additionally, both the tentacle-type structure and the designed microstructure of the support reduce diffusion to a minimum. This and the enhanced stability directly translate into a high average turn-over frequency (TOF) of up to 200 s^{-1}, thus exceeding even a homogeneous analogue.[82]

These monolith-based catalytic systems may be used as pressure stable catalytic reactors as well as one-way systems for use in combinatorial chemistry. The use of NHC-ligands successfully suppresses any bleeding leading even in RCM to virtually Ru-free products with a ruthenium-content of less than 0.07 %.

Summary

Polyolefin chemistry has come a long way. The success story was made possible by contributions from many areas of chemistry including polymer chemistry, organometallic chemistry, chemical technology, etc. While activity and stereoregularity are clearly the domains of classic polyolefin chemistry, functional group-tolerant polymerization techniques such as metathesis polymerization appear – at least today - to be more attractive for the synthesis of high-tech functional polymers and polymeric supports. In contrast to Ziegler-Natta-type catalysts, the use of well-defined metathesis initiators allows the highly reproducible preparation of tailor-made materials with regards to particle size, diameter, pore volume and functionalization. Most polymerization techniques such as precipitation- graft- and even bulk polymerization (even in the presence of water) may be used for these purposes. Thus, even continuous rods are accessible *via* metathesis technology. These monolithic metathesis-based media possesses enormous potential in catalysis as well as in the synthesis of separation media including micro-applications such as CLC and CEC and catalytic supports.

Acknowledgement

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