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New Organic Supports for Metallocene Catalysts Applied in Olefin Polymerizations

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Summary: Nano-sized latex particles as organic supports for metallocenes applied in olefin polymerizations are introduced. The particles are functionalized with nucleophilic surfaces such as polyethylenoxide (PEO), polypropyleneoxide (PPO) or pyridine units allowing an immobilization of the metallocene catalysts *via* a non-covalent immobilization process. The latices are obtained by emulsion or miniemulsion polymerization with styrene, divinylbenzene as the crosslinker, and either PEO or PPO functionalized styrene or 4-vinylpyridine for surface functionalization. The supported catalysts, *e.g.* [$Me_2Si(2MeBenzInd)_2ZrCl_2$/MAO] on PPO containing latices or Cp_2ZrMe_2/([Ph_3C][$B(C_6F_5)_4$]) on pyridine functionalized materials were tested in ethylene polymerizations. Remarkably, high activities and excellent product morphologies were obtained. The influence of the degree of surface functionalization on activity and productivity was investigated. Furthermore, the fragmentation of the catalyst was studied by electron microscopy using bismuth-labeled latex particles or by fluorescence and confocal fluorescence microscopy using dye-labeled supports.
Finally, a self-immobilizing catalyst/monomer system is presented. It is demonstrated that by using PEO-functionalized olefins, the metallocenes were immobilized on the monomers. Subjecting these mixtures to an ethylene copolymerization, again high activities and productivities as well as polyolefin beads with high bulk densities are observed, indicating that an extra supporting process for controlling the product size and shape of the polyolefins is not necessary for these monomers.

Keywords: catalyst fragmentation; ethylene polymerization; latex particles; metallocene catalyst; polymeric support; self-immobilization

Introduction

Metallocenes have proven to be attractive catalysts for olefin polymerization, as they allow a tailoring of the properties of the polyolefins, such as comonomer incorporation and stereospecificity.[1] For an industrial system, heterogenization of the metallocene catalyst is

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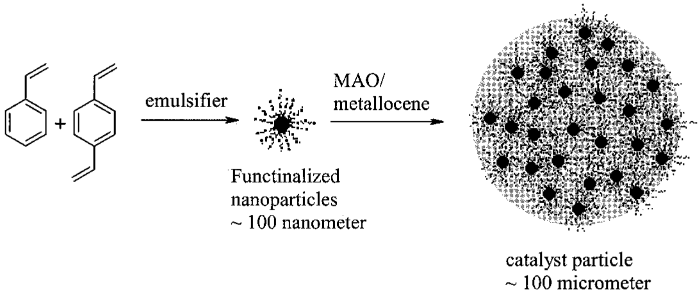
necessary in order to control the morphology of products and prevent reactor fouling.[2] Inorganic supports such as silica, magnesium chloride, zeolites, clays and polymers have been used for immobilizing the catalyst in olefin polymerization. Some of these inorganic supports, however, have acidic groups on their surfaces that can cause deactivation of the catalysts.[3]-[7]

In recent years, organic supports have also been investigated as supports for metallocenes in olefin polymerization. [8], [9] Latex-particles based on polystyrene seem to be one of the most successful examples. Supports based on polystyrenes containing methoxy groups or PEO-chains, which allow an immobilization of active methylaluminoxane/metallocene complexes through non-covalent bonding with nucleophilic groups have been reported.[10], [11] These catalysts show high activities and productivities and form distinct polymer particles with a high bulk density. This concept was developed further, applying polystyrene-based nanoparticles functionalized with polyethylene oxide (PEO) chains on the surface acting as catalyst supports. In this concept, the uniform and well-defined particles (80 – 300 nm) were reversibly aggregated by the interaction of the PEO-chains with the methylaluminoxane/zirconocene clusters (Scheme 1). It was proposed that during the polymerization, the catalysts were completely and homogeneously fragmented within the final product down to the initial nanosized particles of the support, due to the formation of the polyolefins between the latex particles. Such fragmentation, proven for silica based supports, is considered essential for the control of morphology in polyolefin polymerization.[12], [13]



Scheme 1. PEO-functionalized nanoparticles as support for metallocenes: synthesis and supporting process

Even though it has been shown that polymeric supports are applicable supports for catalysts in olefin polymerization, there are many open questions to answer in order to fully understand the role of the supports and their effects on industrial application, such as control of the size of the supports, influence of the surface functionalization and fragmentation of the support. In this paper new approaches towards organic supports for metallocenes and their application in MAO or borate activated polymerizations are presented. The fragmentation and distribution of these supports in the polymer beads is demonstrated by several microscopic techniques using metal or dye tagged supports. Finally, a self-immobilizing process of the catalysts is discussed, which permits a morphology control in the polymerization process by using polar monomers.

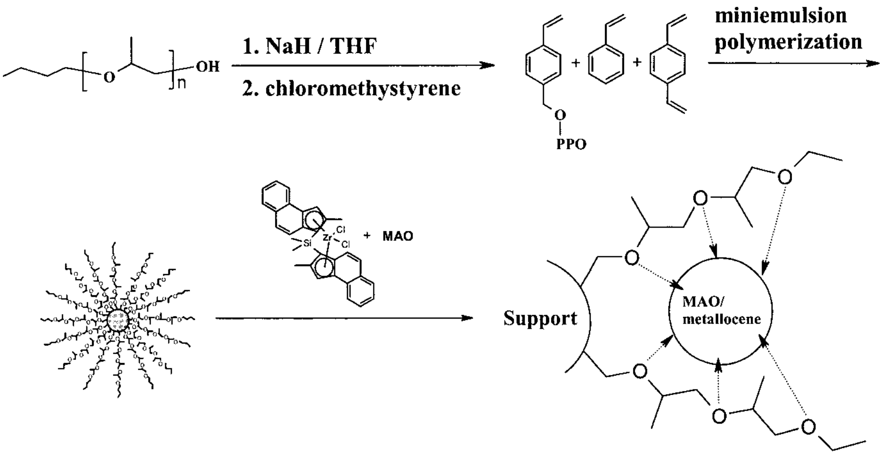
Results and Discussion

New ether-functionalized supports for metallocenes

In previous work, polyether functionalized organic latices were obtained by emulsion polymerization.[18] The obtained latex particles were, however, relatively large (80-300 nm). Therefore, we applied miniemulsion polymerization for the formation of the latex particles, typically resulting in smaller and more uniform beads of 50-100 nm.[14] It has been proposed that the catalysts prepared on these nanoparticle supports can fragment to a smaller size resulting in a more uniform dispersion of the support in the polyolefin. It is expected that the PPO chains on the surface of the support coordinate to and immobilize metallocene complexes without leaching of the active metal sites during the polymerization due to their strong affinity towards aluminum compounds, e.g. MAO. To study the influence of the concentration of nucleophilic groups in the latex particles on the catalyst activities and polymer properties, the amount of block copolymer used in the miniemulsion process was varied.

PPO functionalized nanoparticles as support for $Me_2Si(2MeBenzInd)_2ZrCl_2$*/(MAO activated)*

Nano-sized latex particles of functionalized polypropyleneoxide (PPO) were prepared and applied in ethylene polymerization (Scheme 2). To investigate the dependence of the activity and productivity on the concentration of the PPO chains the amount of PPO on the support was increased from 0.5 to 20 mol % while keeping the PPO chain length constant ($n = 15$). These supports were loaded with equal amounts of $Me_2Si(2MeBenzInd)_2ZrCl_2$, activated with methylalumoxane (MAO) and applied in polymerization of ethylene.



Scheme 2. Preparation of latexes and supporting process of latex and MAO/metallocene complex

In comparison to a homogeneous olefin polymerization, heterogeneous polymerization has always a higher hindrance of the diffusion of monomer gas to reach the active metal sites of the catalyst. In our case the diffusion and fragmentation should be drastically influenced by the interaction between the nucleophilic chains of the different latex particles which are reversibly crosslinked via the MAO/PPO interaction. The latter interaction between them could be strengthened drastically by increasing the amount of PPO on the particles resulting in a more stable network between the nucleophilic ether groups and active metal sites. Such a denser network could limit not only the diffusion of the monomer into the active sites of the catalyst but also the fragmentation of the catalyst.

This concept is supported by our experimental results. As the amount of PPO chains on the support increased, the activity and the productivity of the catalyst in ethylene polymerization decreased, but the bulk density increased drastically (Table 1). It is assumed that at low PPO concentration on the support, the interaction between PPO and the metallocene/MAO complex is weak and the immobilization is limited. This would explain the observed results of a more homogeneous polymerization and therefore, of higher activities but of a lower bulk density (Table 1).

Table 1. Polymerization of ethylene (catalyst: $Me_2Si(2MeBenzInd)_2ZrCl_2$, support PPO functionalized latex particle).[a)]

Run	Length of PPO (units)	Amount of PPO (mol%)	Activity[b]	Productivity[c]	BD[d]
1	15	0.5	2950	4100	260
2	15	1	1800	2400	310
3	15	5	1350	2000	360
4	15	10	1250	1750	420
5	15	20	1200	1700	490

[a)] Reaction conditions: 1L autoclave, isobutane 400 ml, ethylene pressure 40 bar, 70 °C, 1 hr, loading 41 μ mol/g (Zr/cat), activation: 350 MAO/Zr, catalyst 24 mg. [b)] kg PE/mol Zr hr bar. [c)] g PE/g cat hr. [d] BD: bulk density (g/l).

One can conclude, that there is an optimum degree of surface functionalization for obtaining good bulk density, activity and productivity. If the surface functionalization is too low, as demonstrated in previous work,[19] only fluffy materials with a low bulk density are isolated, although with high catalyst activity. On the other hand, to achieve a high bulk density essential for an industrial application, a decreased activity and productivity have to be accepted as drawbacks.

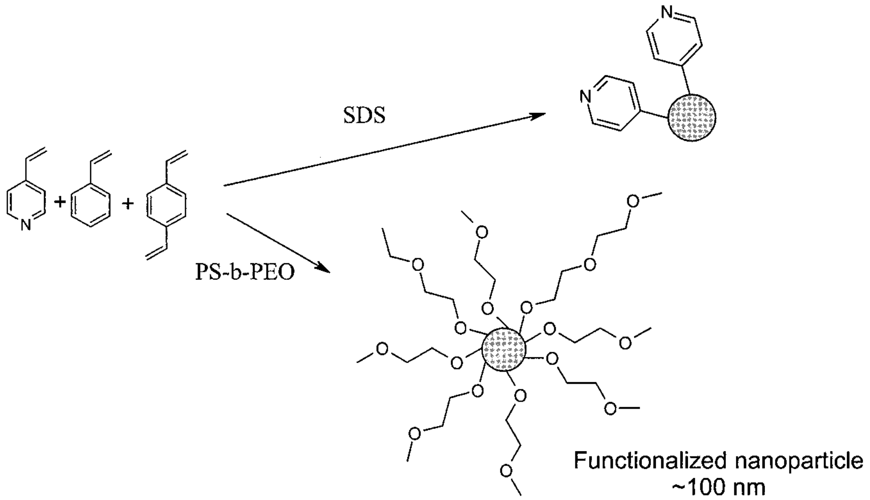
Pyridine functionalized nanoparticles as support for borate activated metallocenes

A major problem in all of the above mentioned systems is that they require high MAO-concentrations for activation in order to achieve high activities and productivities. For silica as well as for organic supports, ratios of 500 to 5000 MAO/Zr ratio are widely applied.[15]

To develop a MAO-free system which can fragment, we modified our latex particles to allow a borate activation. Bochmann *et al.* have already shown that the coordination between amines and metallocenes is strong enough to retain the cationic zirconocene without blocking the free coordinating site of the zirconocene thus not reducing the activity of the metallocene during the polymerization.[16] Fréchet *et al.* proved that amino functionalized unfragmentable polystyrene resins were able to immobilize cationic hafnocenes due to an amine hafnocene interaction and to activate the polymerisation by a borate catalyst.[17] Since pyridine moieties can easily be incorporated by radical copolymerisation and since they should be able to immobilize metallocenes we developed a synthetic approach for pyridine containing latex particles as fragmentable supports in a borate activated olefin polymerisation.

Synthesis of the supported catalysts: Pyridine (System A) or PEO/Pyridine (System B) functionalized nanoparticles / Cp_2ZrMe_2 $([Ph_3C][B(C_6F_5)_4])$

To synthesize the pyridine containing latex-particles, an emulsion polymerization technique was applied. In this process, block copolymers and/or sodium dodecylsulfate as emulsifiers, styrene and 4-vinyl pyridine as monomers and divinylbenzene as crosslinker were chosen (Scheme 4).



Scheme 3. Synthesis of nanoparticles *via* emulsion polymerization

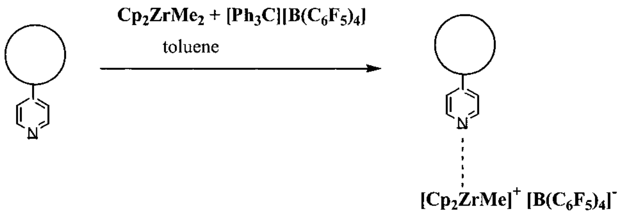
For System A, latex-particles generated by emulsion polymerization of styrene, 4-vinyl pyridine as monomer and divinylbenzene as crosslinker were applied. Sodium dodecylsulfate (SDS) was added as the emulsifier. The borate activated metallocene bis(dimethyl)zirconocene (Cp_2ZrMe_2) was weakly immobilized by the pyridine ring atoms on the surface of the latex particles. The ionic surfactant was removed by dialysis.

For System B, in addition to SDS, amphiphilic block copolymers (PS-*b*-PEO) were used as emulsifiers. In this way, the surface of the latices was functionalized additionally by PEO-chains and the nanoparticles were crosslinked by the addition of trimethylaluminium (TMA) and its interactions with PEO. The particle size, after crosslinking of these so-called secondary particles was around 100 µm. The ionic surfactant was again removed by dialysis.

It is to be expected that the pyridine functions alone are enough to allow the desired reversible crosslinking of the nanoparticles. However, we could apply vinyl pyridine only in concentrations of up to 10 % in the emulsion process, otherwise no defined nanoparticles and stable dispersion are obtained. Therefore, the pyridine concentration on the surface is relatively low and the interaction between the different latex particles is too weak, which should produce a too rapid fragmentation and fluffy product beads. To enhance the interaction between the particles, we added PS-*b*-PEO for surface functionalization to the system.

Latex-particles with pyridine surfaces as support for zirconocene catalysts (System A)

The activation of Cp_2ZrMe_2 was performed in toluene by mixing the metallocene with ($[Ph_3C][B(C_6F_5)_4]$). After stirring at room temperature for 30 minutes, this solution was added to a suspension of latex-particles) in toluene (Scheme 4).

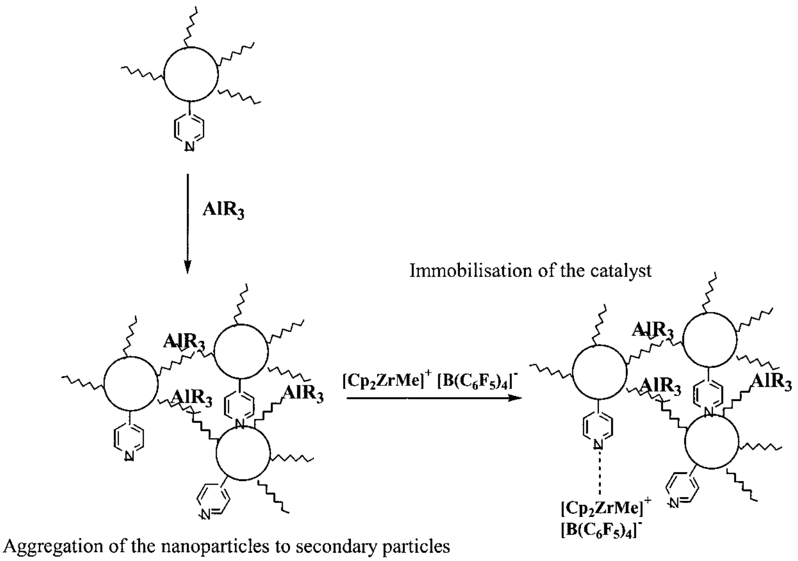


Scheme 4. Preparation of catalyst System A

After mixing this suspension for 20 minutes, the supported catalysts were dried under vacuum to achieve a free flowing powder. To obtain the catalyst particles homogeneous in size, the powder was sieved with a 50 µm and a 100 µm sieve.

Latex-particles with pyridine and PEO-functionalized surfaces as support for zirconocene catalysts (System B)

As stated above, latex-particles (primary particles) obtained by emulsion polymerization with block copolymers PS-*b*-PEO as emulsifier can form a reversible network *via* the PEO-chains on the surface. Different latex particles were generated while varying the block length and block ratio of the PS-*b*-PEO block copolymer. By adding aluminum alkyls, *e.g.* triisobutylaluminum (TIBA) or trimethylaluminium (TMA) (Al/Zr = 30), secondary particles between 50 – 100 µm were obtained in a non-covalent crosslinking process. The catalyst formation was finalized by loading the borate activated Cp_2ZrMe_2 catalyst analogous to System A (Scheme 5).



Scheme 5. Preparation of catalyst system B

After removing the solvent and sieving the particles to get a narrow size distribution of the catalyst system, the latex-particles were used in the olefin polymerization.

In Table 2 the results of some polymerization experiments using the supporting systems A and B are summarized. Even as the structure of the immobilized catalyst is not totally clear, the metallocene loaded network showed very good activities of up to 1150 kg PE/(mol Zr bar), similar to previous results for MAO-activated systems.[18] There was no adverse influence of the PEO-crosslinked system on the borate-activated metallocene. Furthermore, using trialkylaluminium compound as crosslinkers did not reduce the catalytic activity of the system.

Table 2. Results of ethylene polymerizations using latex-based supports with 4-vinyl pyridine [a)]

Run	Loading (μmol cat/ g PS)	Activity (kg PE/ mol Zr bar)	Productivity (g PE/ g cat h bar)	Bulk Density g/l
A-1	60	770	1800	140
A-2	160	860	5500	120
B-1	80	1140	3300	320
B-2	30	1150	1375	340

[a)] Reaction conditions: 1L autoclave, isobutane 400 ml, ethylene pressure 40 bar, 70 °C, 1 hr.

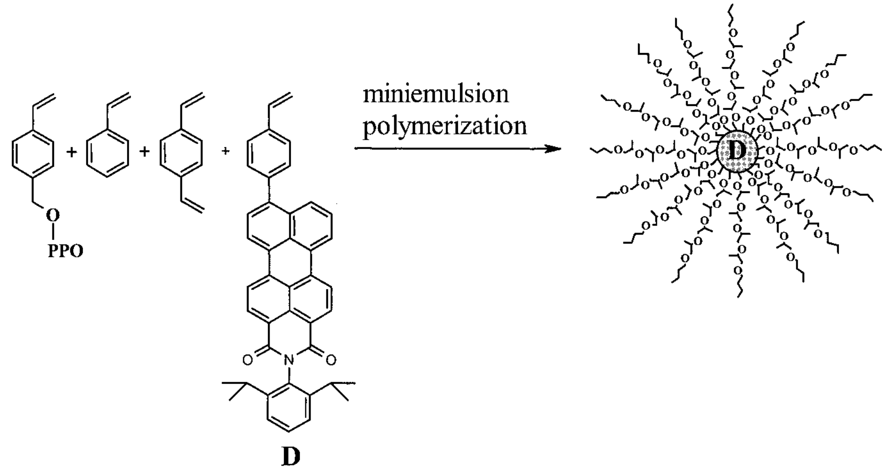
Remarkably, the bulk density of the polyolefin products obtained from PEO/pyridine surface functionalized particles (system B) were much higher in comparison to the pure vinylpyridine systems (system A) (Table 2). This indicates that due to the PEO chains the interaction between the latex particles is enhanced resulting in a slowing down of the fragmentation process. As demonstrated in previous publications this yields in higher bulk densities. [19]

Study of the Fragmentation Process

It has been shown for silica or $MgCl_2$ supported catalysts that fragmentation of the support is an essential prerequisite for a supported catalyst system. The first evidence that such a fragmentation also occurs for our polymeric supports is the excellent morphology control during the polymerization process. In all cases described herein, no reactor fouling was observed, but high bulk densities were achieved and millimeter sized spherical beads of polyolefin obtained. In order to prove such a fragmentation process, one has to investigate the catalyst (support) distribution within a product bead. In the case of a perfect fragmentation, a homogeneous distribution of the support in the particle is expected. However, to study this process, one has to consider that the concentration of the support in a polyolefin product bead, obtained as in our case from a very active catalyst system is extremely low. Therefore, for visualization, the supports have to be tagged either with strongly fluorescent dyes or stained with metals allowing the use of the very sensitive fluorescence, confocal fluorescence or electron microscopy techniques.

As similarly demonstrated for our PEO functionalized latex systems,[18] PPO functionalized supports catalysts were prepared, loaded with a fluorescent dye (9-styryl-N-(2,6-

diisopropylphenyl)perylene 3,4-dicarboxylimide) (Scheme 6) and applied in the polymerization of ethylene. [19]



Scheme 6. Preparation of latex particles tagged with a fluorescent dye

To investigate the catalyst fragmentation, the polymerization was stopped at various reaction times, the polymer was isolated and the distribution of the fluorescence dye was investigated by fluorescence microscopy. As the polymerization time increased, the fluorescence distribution in the films became more and more homogenous, indicating a progressive fragmentation during the polymerization. After 60 min, the fragmentation was almost complete.[19]

These more qualitative findings can be further strengthened by studying single product beads using confocal fluorescence microscopy.[20] With this method, the fluorescence distribution can be scanned layer by layer in a polyolefin bead. The images can be combined to a three-dimensional image indicating the positions of the support by the fluorescent spots. Figure 1 shows the distribution of the visible fluorescent spots corresponding to our dye labeled latex particles, which is very homogeneous, confirming our proposal of a nearly perfect fragmentation of the catalyst.

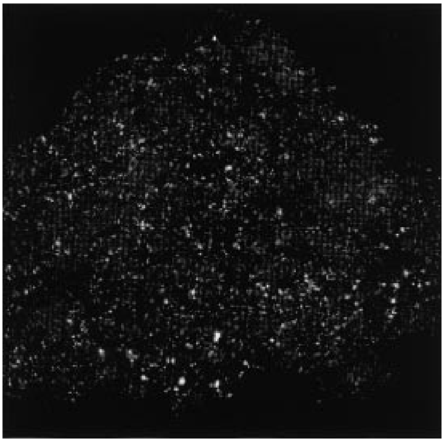
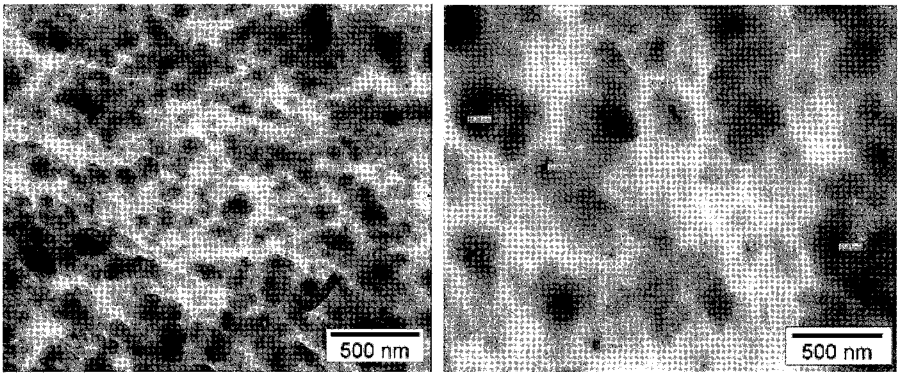


Figure 1. Fluorescence micrographs of a polyethylene particle (size 200µm) (after 60 min polymerization) obtained from a catalyst tagged with a fluorescent dye. (Laser wavelength 488 nm, emission 573 nm)

This non-invasive method does not require a slicing of the samples, therefore, the technique is very fast and easy applicable not only to organic, but also to inorganic supports such as silica. One drawback, however, is that the resolution is limited to the laser wavelength (300-600 nm). To gain a higher resolution of the structures in a polyolefin bead, electron microscopy was used. As the distinction and the selective staining of the latex particles versus polyolefin is known to be difficult, we incorporated 10 weight% of hydrophobic triphenyl bismuth into the support during the miniemulsion process[21] at the stage of the latex particle formation. Providing of the experimental procedure by K. Landfester is gratefully acknowledged.[22] This allowed us to visualize the support in the slices of the polyolefin beads in the electron microscope without any further staining.

According to Figure 2a, already after 2 minutes the bismuth containing support particles (black) were surrounded by polyethylene (white). After 7 minutes, the layer of polyolefin was relatively thick, while at longer reaction time, the support became nearly invisible due to the high dilution ,only “white images” are obtained (not shown).



a) b)

Figure 2. Electron microscopy: slice of a PE bead a) obtained after 2 min, b) obtained after 7 minutes (scale bar: 500nm)

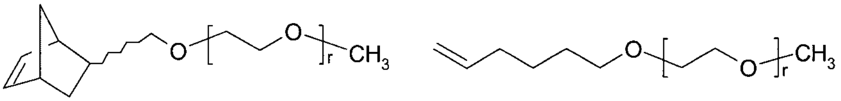
Remarkably, these preliminary results suggest that the polymerization and therefore the fragmentation starts in all latex particles at the same time. This is in contrast to the model developed by Fink for silica materials describing a fragmentation of the support starting from the outer shell proceeding slowly to the inner parts.[23,24] It does correspond, however, to the mechanism proposed for Ziegler-type catalysts supported on $MgCl_2$. A more detailed study of the fragmentation process to develop a kinetic model is presently being performed in collaboration with the group of Fink.

Polyolefins by a Self-Immobilized Catalyst

In all of the previous examples, the metallocenes were supported on latex particles to control the product morphology. However, the question arises what will happen in the case of a polar monomer allowing an interaction/immobilization of the metallocene? It had already been shown by Alt *et al.* that by using metallocenes covalently linked to monomers, the product morphology could be controlled without supporting the catalyst.[25] The major drawback was the complicated synthesis of the polymerizable catalyst.

In our concept we applied PEO-functionalized copolymerizable monomers in the olefin polymerization. Thus is similar to the experiments using latex particles as support, but the metallocene is non-covalently bound allowing for a separate synthesis of metallocene and monomer.

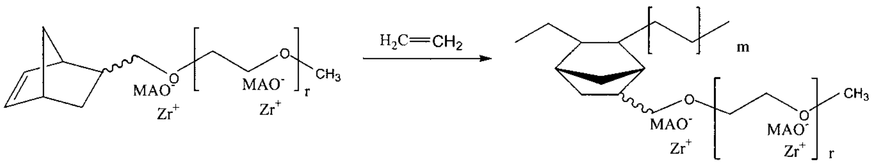
PEO–functionalized norbornene and hexene derivatives were chosen as starting materials for our self-immobilizing system. Fink and coworkers have obtained copolymers with a content of comonomer of up to 23.5 mol-% were obtained using 5-norbornene-2-methanol as comonomer in an ethylene polymerization.[26] Furthermore, Marques *et al.* have reported copolymers with a 5-hexen-1-ol (TMS protected) content of up to 10 mol-%.[27]



N - 1 **H - 1**

Scheme 7. Monomers used for the self-immobilizing approach: N-1: 5-norbornene-2-tetra ethylenglycol, H-1 1-hexene-6-polyethyleneglycol

In the copolymer the norbornene or hexene metallocene catalyst complex is directly attached to the polyolefin (Scheme 7). Thus, the system is self-immobilizing the catalyst during the polymerization. During the whole polymerization the MAO/metallocene complex remained attached to the PEO-chains since leaching of the catalyst was avoided as indicated by the absence of reactor fouling or dust formation (Scheme 8). Due to the interaction of the PEO chains with MAO the system started to aggregate and to form uniform particles.



Scheme 8. Polymerization of ethylene

Table 3 shows the activities and productivities of the self-immobilizing system. The results are

Table 3. Activity and productivity of the self-immobilizing catalyst system [a)]

Monomer (run)	Yield (g)	Activity (g PE/ mmol Zr·h)	Productivity (g PE/ g cat h bar) (g/g)
N-1 (1)	22	22000	39000
N-1 (2)	25	25000	44000
H-1 (3)	20	20000	35000
H-1 (4)	23	23000	40000

[a)] Reaction conditions: 40 bar ethene pressure, 70 °C, 5 ml TIBA (scavenger) polymerization time: 60 min. Al/Zr: 1950, metallocene: $Me_2Si(2MeBenzInd)_2ZrCl_2$ (0.001 mmol), 0,5 mmol of N-1 or H-1 in 400 ml isobutane at 70°C.

comparable to supported systems.[8], [9] Furthermore it should be noted that the use of such polar monomers does not only allow for a control of morphology without using a support but also makes a hydrophilic polyolefin accesible shown by contact angle measurements. The contact angles films of the hydrophilic copolymers containing the PEO chains resulting from the self-immobilizing system were between 66° and 80°, for a corresponding hydrophobic polyethylene film angles of above 100° were measured .

Conclusions

It has been shown that organic particles functionalized with nucleophilic surfaces are suitable supports for metallocenes. They were successfully used in MAO and Borate activated polymerizations. Due to the variety and flexibility of the synthetic procedures for obtaining surface functionalized nanoparticles, the supports can easily be modified. Controlling the size of the particles, and of the nature and concentration of the nucleophilic groups was remarkably easy. This offers many possibilities to further optimize the catalytic system, thus improving activities and productivities. Also the fragmentation process, which directly influences product morphologies (size and shape of the product beads, bulk density), can be controlled by the concentration of nucleophilic groups on the surface of the particles. Modern fluorescence techniques such as confocal fluorescence microscopy allowed us easily to prove the fragmentation of the catalyst and will be applied in the future more extensively to elucidate the fragmentation processes of various supports as they are applicable for organic as well as for inorganic supports.

Finally, even without supports, a control of product morphologies is in principle possible as some preliminary studies demonstrated using PEO functionalized monomers. Similar to the covalently attached metallocenes to monomers, we were able to immobilize our catalyst by a non-covalent interaction to the catalyst. Therefore, the concept of self-immobilization of metallocene complexes was transferred to PEO-functionalized monomers. In all cases, products with reasonable morphologies (spherical beads, high bulk densities) were obtained and the heterogeneous manner of the polymerizations was proven as no reactor fouling was observed.
One can conclude that polymeric supports are easy to synthesize and to functionalize and therefore offer many promising properties.

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