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Morphology Control in Metallocene Polymerization; Organic Supports vs. Non-aqueous Emulsion Polymerization

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Summary: Nano-sized latex support in metallocene polymerization is known to be able to avoid fuming or leaching and leads to a powder-like and well-processable polymer. Focus has been put on the fragmentation behaviour of the particles, a key parameter to morphology control. To study the different behaviour of the new systems as classical inorganic supported metallocenes, e.g. SiO_2, a wide range of analytical methods were applied. Fluorescence microscopy, polymerization video-microscopy, as well as kinetic studies led to a better understanding of the process. The performance of the supports was approved by several phenoxy-imine type catalysts (“FI-Catalyst”), which were combined with a tailored latex support. Ultra high molecular weight polyethylene (UHMWPE) was synthesized without any reactor fouling thereby. A different approach towards the metallocene catalyzed olefin polymerization is also presented. Based on emulsion polymerization, it enables very good control over product morphology. The completely hydrophobic system consists of perfluorinated solvent as a continuous phase and a hydrocarbon solvent as a dispersed phase. In contrast to the already existing water based emulsion polymerization of olefins, very high molecular weights are achieved.

Keywords: emulsion polymerization; fragmentation; metallocene; morphology; non-aqueous

Introduction

In the last thirty years, numerous types of metallocenes have been designed, enabling the synthesis of previously inaccessible polymers.[1] Unfortunately, the major drawbacks, such as reactor fouling, overheating, and poor morphology control, remain when applied in homogeneous catalysis. In order to avoid them, various procedures have been implemented on supporting the catalyst. Well-defined supports such as spherical silica particles and zeolites, as well as magnesium chloride and clays have been examined to maintain the advantages of homogeneous catalysis.[2] More recently, tailor-made polymers are in the spotlight to form a promising support material via self-immobilizing, covalent or non-covalent bonding on polysiloxanes, polyolefins, polystyrenes or dendrimers.[3] By tuning the parameters of the primary particles such as functionalization type and degree, cross-linking, and size, optimization of specifications such as bulk density and morphology was achieved while maintaining reasonable polymerization activities.[4,5]

An alternative for special applications is the production of polyolefins inside an emulsion.[6,7] Unfortunately, the majority of the catalyst systems are extremely water sensitive, and only a few are available which can tolerate water. Metallocenes, being able to produce high molecular weight polyolefins, are easily decomposed. A new type non-aqueous, oil-in-oil emulsion is utilized as a possibility to control the

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morphology of the polymers.[8] It consists of a perfluorinated solvent as a continuous phase and hydrocarbon solvent as a dispersed phase. It enables the metallocene catalyzed polymerization, leading to high molecular weight polyolefins with excellent morphology and in the same time prevents reactor fouling and overheating.

Results and Discussion

Two different approaches for morphology control are presented, both aimed to gain better control over the size of the product particles and bulk density of the polymer, while still benefiting from the advantages of the metallocene catalyst systems. In the first one, by supporting the catalyst covalently or non-covalently on aggregated nanoparticles, micrometer to milimeter sized particles with good morphology (spherical particles, high density) were generated. In the second approach, by implying the metallocene in a non-aqueous emulsion polymerization, the size of the particles was decreased to the nanometer scale. Considering both approaches, we are able to cover the whole range of possible applications.

Polymerization with Metallocene Catalyst, Supported on Organic Nanoparticles

In recent years we have developed numerous metallocene support systems based on styrene.[9-11] As fragmentation plays a crucial role for morphology control in supported polymerization, we aim to create a support which is able to provide both shape to the growing polymer grain and fragment completely into very small entities, thus enabling morphology replication. In the first approach we tested the influence of the surface modification of nano-sized primary particles via covalent agglomeration to the final secondary particles, using moieties able to undergo either chemical cross-linking via the Diels-Alder reaction or physical cross-linking via poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) interactions between the particles.[12-15] In the same study we combined laser scanning confocal fluorescence microscopy (LSCFM) with in-situ videopolymerization in a parallel setup to directly compare the morphology replication of these metallocene-loaded supports. The results indicated that covalent bonding of the particles had a negative impact on the activity, underlining the strong influence of fast and homogeneous expansion of the particles in connection with the fragmentation; therefore, we focused more on the non-covalent catalyst support systems. Binding of the MAO-metallocene complex on styrene-based latex particles leading to non-covalent aggregation turned out to meet both the criteria of homogeneous (activity, selectivity) and heterogeneous (morphology control, processability) catalysis in polyolefin polymerization. These systems consist of nano-sized primary particles (<100 nm), but have only functional surfaces used to immobilize the MAO/catalyst complex, such as PEO chains, without any cross-linking agent. Thus the particles, in conjunction with the MAO/catalyst complex, undergo an agglomeration process leading to a non-covalent, micrometer sized particle (secondary particle) which represents the final support, corresponding to a classical inorganic support such as a MAO-silica grain (Figure 1).

We examined the stepwise fragmentation of the agglomerates using dyes which were covalently incorporated into the primary particles and measurable by LSCFM within the polymer product after various polymerization times.[16] Even at early polymerization stages, fragmentation into primary particles also occurs in the centre of the secondary particles, indicating that no diffusion barrier is existent. This is in contrast to onion-like shell by shell fragmentation of silica particles as it has been observed for the MAO-SiO_2 case[17] and corresponds more to a multi-grain model established for $MgCl_2$ systems.[18]

To verify the first hints of this multi-grain-like behaviour, a more detailed and comparative study of the influence of the fragmentation behaviour between silica

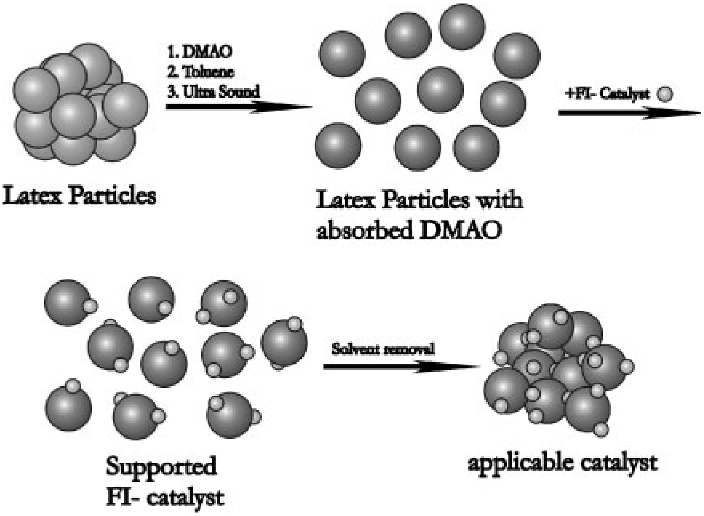

Figure 1.
Basic concept for synthesis of catalyst particles via agglomeration of surface functionalized nanostyrene particles.

and two organic supports was performed.[19] Polystyrene resin and silica was stained with (N,N′-bis(2,6-diisopropylphenyl)-1,6,7,12-tetra[4-sulfophenoxy]perylene-3,4:9, 10-tetracarboxdiimide via a swelling and shrinking process, whereas the polystyrene latex particles were stained by a sulfonic acid-free styrene derivate of the perylene. This class of dye has already proven to be stable under polymerization conditions applied in this study.[20] Both covalent and non-covalent methods of staining led to a perfectly homogeneous distributed dye within the respective particle, proven by LSCFM.

The particles, after supporting the catalyst/MAO, were ready for polymerization without any further activation. Whereas catalyst systems A and C do not change their morphology while contacting with MAO, B represents an agglomerate of 50 nm-sized nanoparticles, agglutinated by the surface-MAO-interaction (Figure 2).After a short polymerization period, one can clearly observe a considerable difference in the polymerization behaviour of the systems. Fragmentation from the shell to the centre takes part in the silica and the microsized polystyrene case. In contrast, the nanosized particle agglomerate seems to expand more homogeneously, forming from the beginning on multiple fragments. Examinations of polymerization stopped after 30 min showed that complete fragmentation is finally achieved for the silica case as well. Polymerizations for 1 h under the same conditions were performed to examine the consequence of the observed shift on the time-frame of the fragmentation process. The polydispersity and the molecular weight of the final product remained equal, while a drastic increase in the activity from 700 to 1500 kg PE/mol Zr hr bar and an increase of the bulk density from 300 to 380 g/L were observed.

Therefore, the ratio of the polar, surface-active moieties, which are responsible in forming secondary particles such as styryl-PPO, was varied. Although the bulk density of the final product could be raised to 430 g/l by a catalyst containing 10% of styryl-PPO compared to 280 for 0,5% styryl-PPO, the activity drops from 2970 to 1250 kg PE/mol Zr hr bar. It should be noted that the bulk density is strongly depending on the applied pressure. Typically all experiments are performed close to industrial conditions (40 bar). While in most cases polymerization at lower pressure results in high bulk

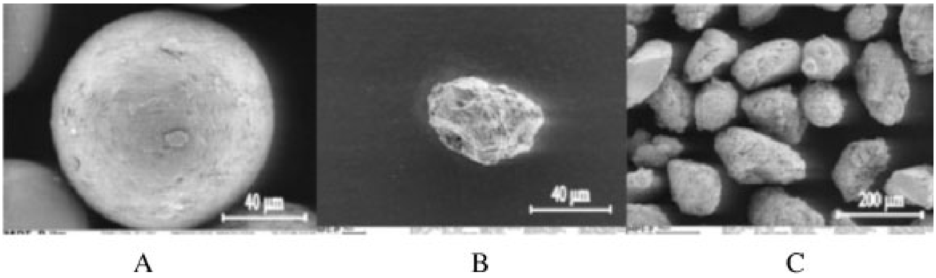

Figure 2.
SEM images of different catalyst systems. (A) microsized polystyrene (scale bar: 200 mm), (B) nanosized polystyrene (scale bar: 200 nm) and (C) silica gel (scale bar: 200 mm).

densities, at higher pressure, due to the high activities sometimes fragmentation is too fast and only fluffy polymers are obtained.[10] The styryl-PPO moiety can also be replaced by an emulsifier consisting of a PEO-chain which is utilized as the anchor for both non-covalent aggregation and the catalyst.[4,12,13] The length of the PEO-chain plays a crucial role in the fragmentation process, as short chains lead to fragmentation too quickly and a loss of morphology control. In a recent study we further modified the surface functionalities of our latex systems to other than PEO- or alcohol-functionalized primary particles by adding polyvinyl pyridine as an additional anchor for the metallocene/MAO complex. We combined this support with rather fragile FI-Catalysts such as bis[N-(3-t-butylsalicylidene) cycloheptylaminato] titanium(IV) dichloride able to produce UHMWPE.

Using conventional PEO-containing, pyridine-free systems only low activities (130 kg PE/mol Ti hr bar after 90 min) and fast deactivation was observed. Introduction of the polyvinylpyridine moiety led to much higher activities (Table 1), which is contrary to what one may expect, bearing in mind that vinylpyridine groups potentially may coordinate to the titanium centre.

It is suggested that this may result from a beneficial trapping effect of trimethyl alumina (TMA) by the vinyl group as depicted in Figure 1.

As MAO is prepared by partial hydrolysis of TMA, this is one of the inherent species always present in it. It is known that FI-catalysts are TMA-sensitive.[12,21] With a high polyvinylpyridine content ($\geq$30 mol-%) we were able to obtain extremely long-term-stable catalysts, which after 4 hours of polymerization showed almost no decrease in activity and led to a

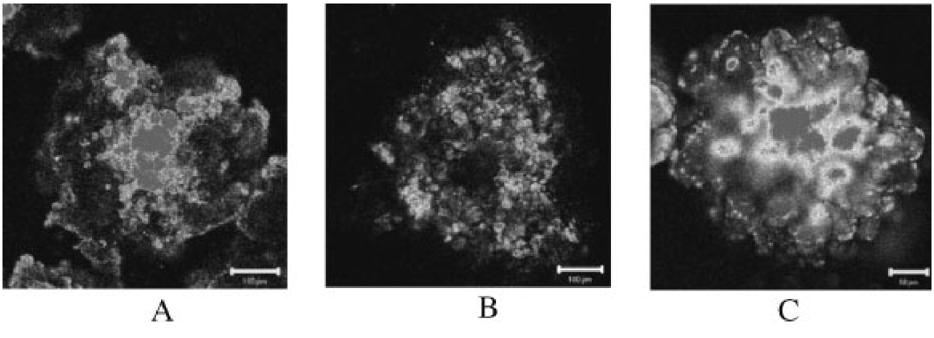

Figure 3.
LSCFM middle slice images of single PE particles corresponding to the supports in Figure 2 after polymerization. Identical conditions were applied for 10 min for (A) and (B) and 15 min for (C). The scale bar is 100 µm for (A) and (B) and 50 µm for (C).

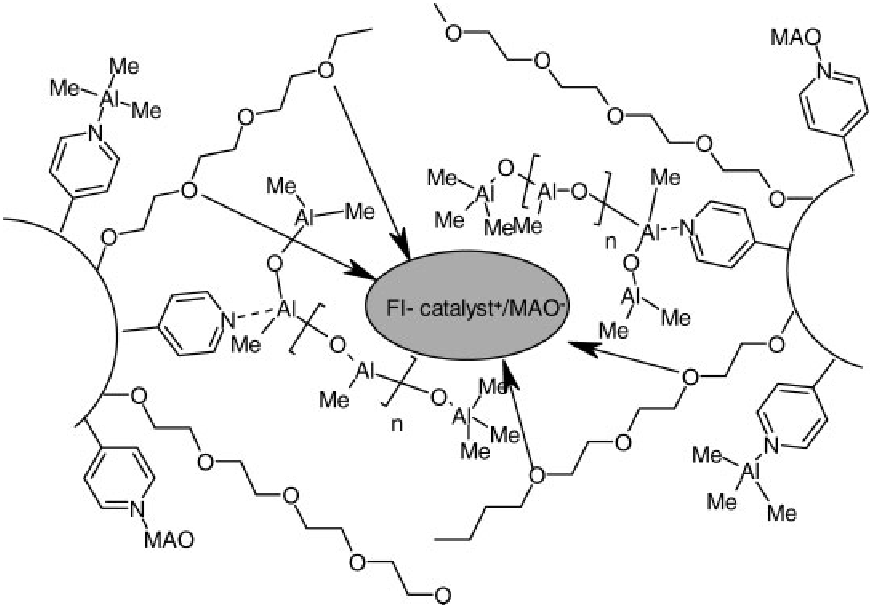

Figure 4.
Immobilization of the MAO/catalyst-complex together with trapping of TMA.

product with excellent morphology (Figure 5).

Polymerization with Metallocene Catalyst in Non-aqueous Emulsion

Olefin polymerization inside an emulsion provides another possibility to control not only the process itself, but also the product morphology, as it offers the access to spherical particles in the nanometer range. Additionally the emulsion provides high heat capacity, leading to an effective transfer of the heat of polymerization. A non- aqueous organic-in-fluorous emulsion applicable for polymerization using water sensitive catalysts is presented.[8] With statistical biphasic copolymers based on poly(4-hydroxystyrene) containing fluorinated and non-fluorinated alkyl side chains, emulsions of hydrocarbons dispersed in perfluorocarbons were stabilized. The addition of metallocenes, activated by methylalumoxane, enabled the polymerization of olefins inside this highly hydrophobic system. High molecular weight polyolefin nanoparticles of polyethylene (M_w up to 1 200 000) and polypropylene (M_w up to 90 000) were synthesized without supporting the catalyst and without reactor fouling. In this diffusion controlled process, the sizes of the particles were controlled by the reaction time, pressure, and the ratio between the emulsifier and solvents.

Stabilization of the emulsion was achieved with specially designed fluorous biphasic poly(alkoxystyrene) statistical copolymers. Statistical copolymers were chosen since their stabilizing properties in

Table 1.
Activity Dependence on the Concentration of Nucleophilic Groups in the Support.

Run	Support	Pyridine [mol %]	Time	Activity [kg PE/mol Ti h bar]	Productivity [g PE/g cat]	Mw
8	PEO-4	60	360	1350	14700	2.520.000
9	PEO-1	45	360	1250	13300	2.540.000
10	PEO-5	30	360	1500	15900	2.600.000
11	PEO-6	15	360	830	8900	2.650.000
12	PEO-7	0	90	130	350	–

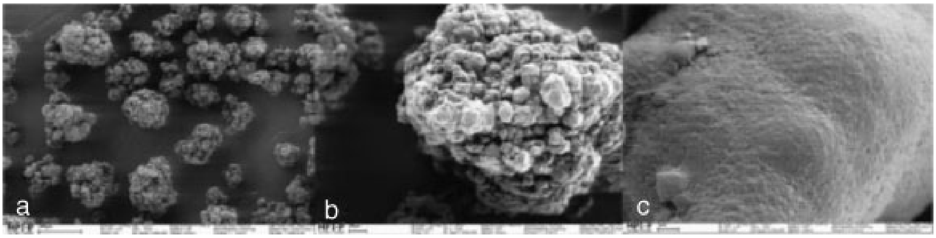

Figure 5.
SEM Pictures of UHMWPE: (a) well defined polymer particles, (b) cauliflower-like PE particles, and (c) surface of the PE particles.

inverse aqueous emulsions have been demonstrated.[5] The obtained fluorous emulsions enabled the metallocene catalyzed polymerization of olefins to high molecular weight in the droplets. It results in particles with very good morphology without using a support (Figure 7), and their sizes might be decreased to the nanometer region.

The non-polar emulsion was applied as the reaction medium for α-olefin polymerization. The emulsifier quantity was chosen to be between 0.5 and 1.5 wt.-% with respect to the amount of hydrocarbon. The metallocene, [dimethylsilanediylbis(3,3′-(2-methylbenz[e]indenyl))]-zirconium dichloride (MBI)[22,23], used for the polymerization was activated by adding MAO in situ to the reactor containing the emulsion (10 wt.-% in toluene). The polymerization was started by the addition of the catalyst to the monomer-saturated emulsion. As none of the reactants used are highly soluble in the continuous phase, but are in the droplets, it is presumed that each step of the process takes place inside the dispersed phase (Figure 6).

The polymer produced in the emulsion consisted of particles between 0.5 and 20 μm with a broad size distribution, as observed with SEM(Figure 7). By decreasing the polymerization time (from 1 h to 12 min), as well as the pressure, both polyethylene and polypropylene particle

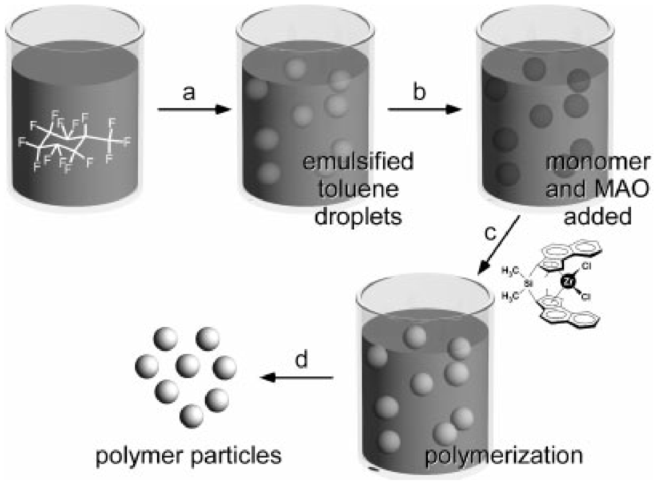

Figure 6.
The polymerization process: a) addition of emulsifier and toluene, b) addition of MAO and saturation with monomer, c) injection of the catalyst ([dimethylsilanediylbis(3,3′-(2-methylbenz[e]indenyl))]-zirconium dichloride) and subsequent polymerization, d) precipitation and solvent removal.

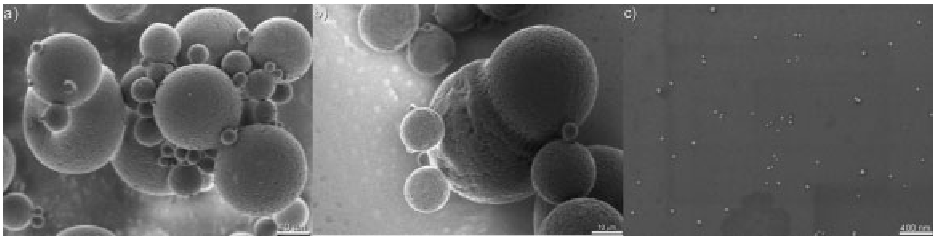

Figure 7.
Scanning electron micrographs of the resulting polyethylene particles of a) Run 1, b) Run 2, c) Run 3 (Table 2).

sizes decreased into the nanometer region (Figure 7 c, Table 2 run 3, 5). This is typical for a classic emulsion and is consistent with a diffusion controlled polymerization process indicating that the transport from the gas phase through the perfluorocarbon into the droplets is one of the limiting factors of the polymerization. In addition, an Ostwald ripening process is assumed since after longer reaction times, the product particles are magnitudes larger than the initial droplet size in the emulsion.

Conclusions

Morphology control plays a crucial role in the metallocene catalyzed olefin polymerization. Herein two different methods are demonstrated to control the product morphology, either by varying the support or by implying the metallocene in a recently developed non-aqeuous emulsion. The fragmentation behaviour of supported metallocene catalyst is important for the morphology of the final product. By LSFCM and videomicroscopy, several polymeric supports functionalized with cyclopentadiene units, poly (ethylene oxide) or poly (propylene oxide) chains and subsequently loaded with a MAO/metallocene complex were simultaneously studied. It is shown that these methods allow a direct comparison of different catalysts under identical conditions. By labelling the support with a dye, the distribution of different support fragments in the polyethylene product particles is made possible.[21] Performing the olefin polymerization inside a confined geometry is another method for morphology control. Emulsion system, consisting of fluorous/organic phase was presented. This mixture contains only aprotic solvents and is inert to highly reactive catalysts. This general strategy offers the opportunity to make well-defined nanoparticles by metallocene catalyzed polymerization. As a consequence, high molecular weight polyolefins are being produced. These two methods are also applicable to other catalysts such as the postmetallocenes based on titanium, which produce ultrahigh molecular weight polyethylene. Furthermore, the biphasic statistical copolymer emulsifier may be tuned to

Table 2.
Polymerization results inside the emulsion.

Run	Reaction Time [min]	Pressure [bar]	Emulsifier [wt.-%] (mg)	Molecular Weight M_w [g/mol]	PDI	Particle Size	Al/Zr	Activity [kg PE/mol Zr hr bar]
1	60	30	1 (80)	850 000	5.6	1–20 µm	2000	1400
2	30	25	1 (40)	1 400 000	3.1	1–10 µm	8000	650
3	12	1	1.4 (60)	700 000	3	30 nm	800	400
4*	60	2	1.4 (60)	81 000	5.6	4–16 µm	600	380
5*	5	2	1.4 (60)	80 000	5.5	120 nm	5000	200

* Propene polymerization.

balance the solubility and ultimately the stabilization characteristics of the copolymers. Using emulsion polymerization, the control of the size of polyolefin particles prepared by metallocene catalysts can now be achieved down to the nanometer scale. While latex particle-based supports generate polyolefin particles in the millimeter range, which are suitable for extrusion processing, the much smaller particles formed in an emulsion are highly attractive for cosmetics, paints, adhesives and also as precursors for coatings. Also, varieties of core-shell structures are accessible in this water-free emulsion system, broadening further the application possibilities.

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