Modern Analytical Tools essential for Studying Olefin Polymerization

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Summary: As an alternative to inorganic supports, emulsions and organic carriers were developed for metallocene-catalyzed polyolefin synthesis in the last years. Oil-in-oil emulsions based on a perfluorinated solvent provide the possibility to synthesize polymer particles on the nanometer length scale, while the latex particles consisting of polystyrene with different surface functionalities yield particles on the micrometer range. To obtain a deeper insight to the reaction course of both techniques and to the product morphology and fragmentation behavior of the organic carriers, substantial information concerning the kinetics of these reactions is crucial. Thus, standard analytical methods were combined with real-time video microscopy and laser scanning fluorescence microscopy (LSCFM) of perylene labeled particles for improving these methods for polyolefin synthesis.

Keywords: emulsion polymerization; kinetics (polym.); morphology; polyolefins; supports

Introduction

During the last few decades, metallocenes attracted great interest as catalysts in olefin polymerization,[1–5] because they allow the synthesis of previously inaccessible polymers.[6,7] This type of catalysts allows selective control over the tacticity – in the case of prochiral monomers – and features excellent activities in polyolefin synthesis, along with high molecular weights. However, when applied for olefin polymerization under homogeneous conditions, many of these systems cause reactor fouling and allow only poor morphology control, *i.e.* product particle size and bulk density of the polymer.[8]

The most industrial applied method to overcome this drawback is the immobilization of the metallocenes on inorganic supports.[9] Thus, reactor fouling can be avoided and morphology control is gained, but as the carrier remains in the obtained polymer, inorganic species may influence the material properties negatively. Additionally, a pretreatment of the inorganic supports is crucial for the polymerization results,[10–12] which lead to the development of organic alternatives in the last years.[13,14] These polymeric particles bear metallocene catalysts covalently or non-covalently bonded, and these primary particles can be accordingly tailored by tuning parameters such as cross-linking, functional groups and the degree of surface functionalization. Another approach for metallocene-catalyzed polyolefin synthesis is the utilization of an emulsion, as it has been shown previously in our group.[15] These oil-in-oil-emulsions consist of a perfluorinated continuous phase and a hydrocarbon as the dispersed phase. It has been shown that from these systems spherical nano-sized particles of polyethylene and polypropylene with high molecular weights can be obtained from gaseous and liquid monomers with well-established metallocene catalysts.[15,16]

Since their introduction both approaches were enormously brought forward

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in terms of activity and morphology control by extensive studies with several sophisticated analytical methods. By the combination of standard techniques such as size exclusion chromatography (SEC) and ^{1}H and ^{13}C NMR spectroscopy along with kinetic studies, real-time video microscopy, scanning electron microscopy (SEM) and laser scanning confocal microscopy (LSCFM), numerous data could be obtained. The collected information have been used for further optimization of the oil-in-oil emulsions and the organic supports with focus on the polymerization activities, the morphology of the resulting polymer, etc. Herein different techniques are presented, especially with focus on their symbiotic benefits.

Results and Discussion

In recent years we have demonstrated the ability to synthesize particles from nanometer to millimeter size by using new supports and techniques.[13–15] Aside the general aspects of the question which type of the catalyst is loaded and what is the applied support, the elucidation of activation and reaction kinetics including the behavior of the support has a decisive influence on the obtained product. For both cases – organic supports as well as polymerization in emulsions – it will be demonstrated how characteristic data will be gathered to improve the understanding and to optimize a polymerization process.

Polyolefins Obtained from a Supported Process

Immobilization of the catalyst on inorganic supports is by far the most commonly industrial applied method in polyolefin synthesis, but in the last years also organic carriers based on polystyrene have been developed.[9] To create an alternative to inorganic supports, the latex particle must be compatible with traditional metallocenes as well as with post-metallocenes, *e.g.* bearing phenoxy-imine ligands (FI catalysts). Besides demands as high activities and molecular weights, further aims are morphology control of the resulting polymer and the avoidance of leaching of the active sites.

After first developments of covalently cross-linked organic supports in our group which showed low activities,[13] nano-sized PS-based primary particles were developed which are solely physically cross-linked and agglomerate to larger, fragmentable secondary particles.[17] This phenomena is accomplished via nucleophilic interactions of poly(ethylene oxide) or poly(propylene oxide) surface functionalities with MAO-complexed metal centers. These primary particles are synthesized under miniemulsion conditions which reveals the necessity of appropriate emulsifiers. These surfactants, PEO/PPO-ethoxyfattyalcohols, serve both to stabilize the emulsion and, together with the pyridine groups on the surface, as an anchor for the activated catalyst. Hence, we are able to generate supports that control the fragmentation process during the polymerization depending on the degree of cross-linking, the particle size, polarity, and interaction with the co-catalyst. Final catalyst particles can be prepared via a non-covalent process resulting in a material which is storable and ready to use in standard polymerization reactors without addition of any further MAO. These catalyst supports also enhanced production of desirable polyolefin powder without any leaching of the catalyst, thus avoiding homogeneous polymerization and lacking morphology control.

Under industrial conditions in isobutane as the solvent and at 40 bar ethene pressure and 75 °C, both the metallocene catalyst [dimethylsilanediylbis(3,3′-(2-methylbenz-[e]indenyl))]-zirconium dichloride (MBI) (**1**) and a FI-zirconium catalyst showed high activities of 8,150 and 6,100 kg PE (mol $\text{cat} \cdot \text{h} \cdot \text{bar})^{-1}$, respectively, when supported on these organic carriers, while the latter one yielded UHMWPE ($M_w = 5{,}4 \cdot 10^{6}\ \text{g} \cdot \text{mol}^{-1}$), measured by high temperature SEC in 1,2,4-trichlorobenzene.[18]

In order to conduct further studies about the latex supported systems concerning the morphology of the resulting polymer particles, gas phase polymerizations with different reaction times were carried out and the resulting materials were analyzed by SEM, which is an important tool in regard to morphology analysis. SEM pictures of a latex-supported FI-titanium and MBI catalyst, respectively, after a reaction time of 30 seconds are shown in Figure 1a, b. In both pictures the supporting material, namely latex primary particles with pyridine and PEO surface functionalities, can be recognized. In the case of the FI catalyst which yields UHMWPE, the resulting polymer shows a bubble shape while growing out of the support. In contrast to that, the primary particles loaded with MBI seem to ''swim'' on the produced polymer.

Examination of the morphology after 15 minutes (Figure 1c, d) reveals that in the case of the FI-titanium catalyst the original particles are reproduced and enlarged, while the MBI catalyst leads to larger copies of the original single nano-sized particles. After 60 minutes (Figure 1e, f), filaments can be observed with both catalysts; these fibrils come from the

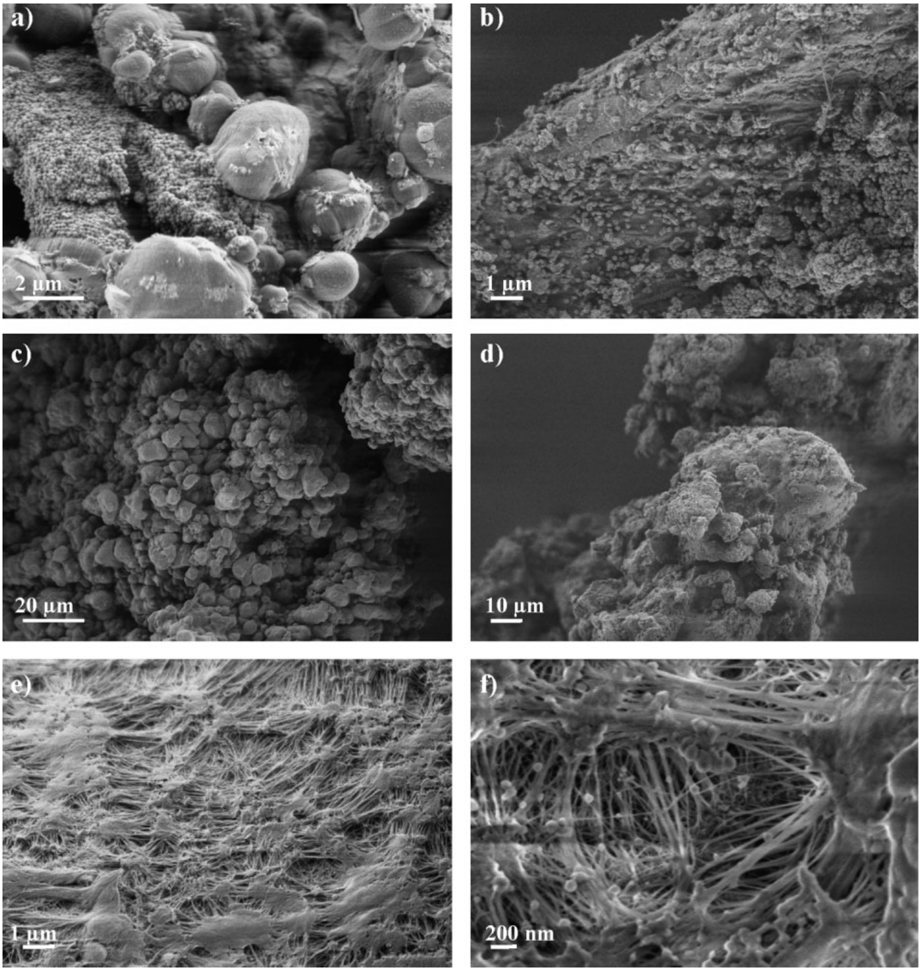

Figure 1.
Polyethylene synthesized by FI-titanium catalyst (left column) and MBI catalyst (right column) after a reaction time of 30 seconds (first row), 15 minutes (middle row) and 60 minutes (bottom row).

expansion of the polymer particles while additional polymer is formed in the inside of the particles, and the polymer chains on the surface are stretched.

Results concerning the polymerization kinetics which were observed in slurry polymerization in kinetic studies by monomer flow meters were also obtained via video microscopy, which is another important tool. Polymerizations with MBI and FI catalyst on organic supports start immediately after injection of the catalysts and reach the highest rate in few seconds after the beginning of the polymerizations. After attaining this maximum, the rate of polymerization starts to decrease slowly.

A deeper insight to the growth of individual particles was gained by "real-time video microscopy".[19] At this, the particles are placed on a silver plate into a 50 cm^3 volume reactor equipped with a borosilicate window and are treated with the gaseous monomer while the vessel is kept at the desired temperature. Particle growth can then be followed by a microscope and a camera on top of the reaction chamber. Quantitative results concerning the evolution of the particle were obtained by measuring the particle areas versus the time by taking snapshots after defined time intervals. With the assumption that all particles grow spherically and uniformly in all directions, the equivalent circle diameter (ECD) can be calculated. Comparing particles with different sizes by plotting the ECD against the time leads to different curve progressions, thus giving the impression of a non-uniform particle growth (Figure 2a). However, if all data are plotted as a relative ECD, *i.e.* the time-dependent ECD divided by the ECD_0 (ECD_0 is the ECD of the according particle at $t = 0$ s), the different particles can be compared in terms of their growth and expansion (Figure 2b). For latex particles it could be shown in an ethene polymerization that their normalized ECD develop uniformly, which leads to the conclusion that differently sized particles show all the same catalyst concentration per volume. Thus, the PS-based latex particles are homogeneously loaded with the metallocene. Hence, video microscopy as an important tool in terms of improving methods for polyolefin synthesis with supported catalysts gives a deeper insight in the particle growth behavior of each single support particle, along with information about the homogeneity of the catalyst loading and concentration.

The resulting PE particles based on these organic supports were also examined by laser scanning confocal fluorescence microscopy (LSCFM). With this versatile tool, fragmentation and inflation caused by resulting polymer of the PEO/PVP-functionalized PS particles agglomerates and morphology replication of these metallocene-loaded supports can be investigated. Stepwise fragmentation was therefore made visible by the incorporation of functionalized perylene dyes, which can be excited and, thus, detected by LSCFM.[19]

Traditional metallocenes and FI-catalysts show similar behavior with regard to the carrier fragmentation when supported on organic latex particles, whilst there are significant differences for both catalyst types in comparison to silica based systems.[20] The course of an ethene polymerization for silica supported catalysts can be divided in 4 different phases (Figure 3). At the outset a slightly increasing of the activity can be observed (pre-polymerization phase). At this time, a thin, crystalline layer of PE is built up around the silica core (Figure 4a). Hence, the diffusion of ethene to the encapsulated active centers is significantly reduced, which leads to a decrease of the activity (diffusion phase). More resulting polymer at the active centers in the inner particle areas causes hydraulic force to the carrier, which leads to fragmentation from the outside to the inside, reveling more active sites that can take part in the polymerization process. This growth of the number of active centers leads to an increase of the activity and carrier fragmentation proceeds. When fragmentation is completed, the activity reaches a maximum. This is followed by the

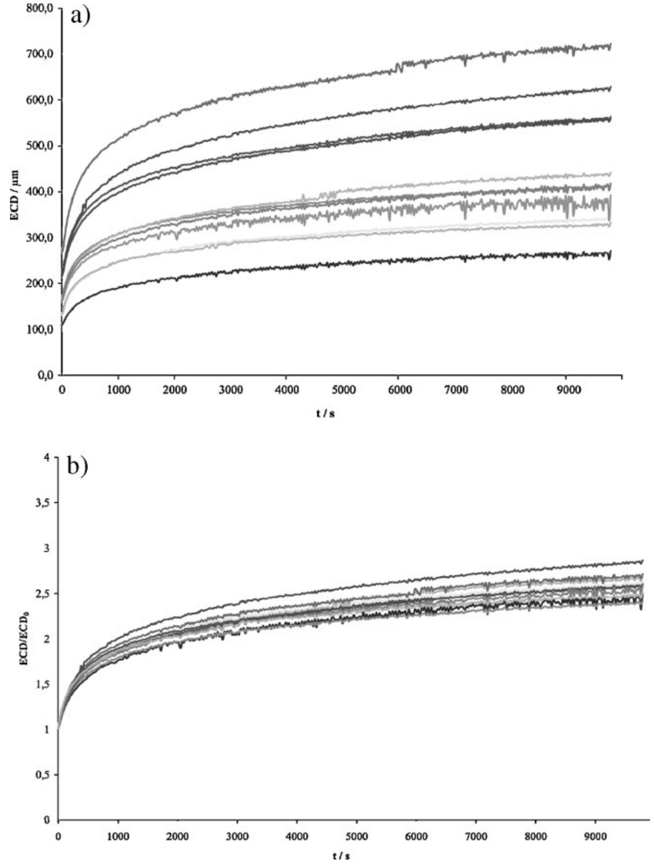

Figure 2.

a) ECD (Equivalent circle diameter) and b) relative ECD (ECD/ECD$_0$) of several PE particles (PS-PEO support) in a gas phase polymerization with MBI catalyst at 50 °C and 2 bar; particles were chosen representatively from the sample.

particle expansion phase, where a slow decrease of activity is observed due to the increasing diffusion way of the monomer through the resulting polymer to the active sites. This model of polymerization behavior of silica-supported catalyst is called ‘‘polymer-growth and particle-expansion-model’’.

In contrast to that, investigations by LSCFM of labeled latex-supported systems of metallocene and FI-catalysts show a totally different behavior than in the case of silica (Figures 2, 3 and 4b). While latter fragment step by step from outside to the inner parts of the particle, in the case of the organic counterpart chain growth starts both on the outside and inside of the particle. The summit of the activity is observed a few seconds after the reaction has been started. The absence of a significant drop of the activity indicates that no surrounding crystalline layer of polymer is formed, which could block the monomer from reaching the active sites. Going along with this ubiquitous fragmentation, activity decreases slowly in the case of organic supports due to diffusion control of the monomer through the resulting polymer particle.

The different observed behaviors of silica- and latex-supported catalysts could be due to the different consistence and morphology of the carrier materials. Non-covalently cross-linked primary latex particles, which are attached to each other only by nucleophilic interaction between the

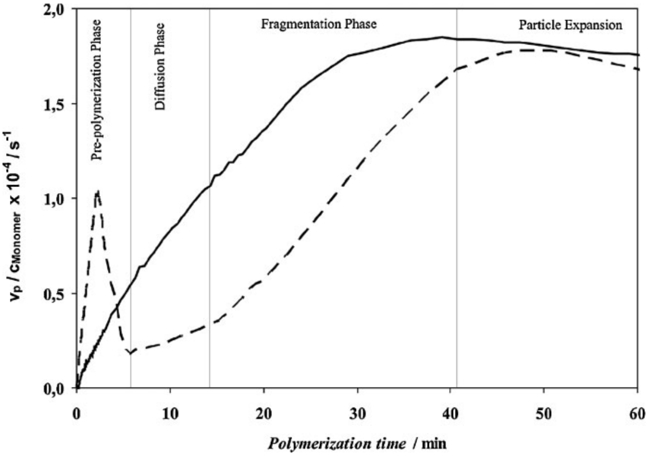

Figure 3.
Metallocene-catalyzed polymerization: Polymerization rate vs. Polymerization time for a latex support (drawn) and silica support (dashed), and different phases of silica particle fragmentation.

anchor groups and the MAO-catalyst complex, can absorb monomer in the carrier itself and swell during the reaction, in which the active sites can be fed directly from the carrier material. However, silica is a hard material which can absorb the gaseous monomer only in its pores and therefore the monomer has to diffuse trough the formed crystalline PE into the particle towards the active centers.

Polymerization of Olefins in Emulsion

While organic supports eliminate several of the drawbacks when using inorganic supports like silica, such as extensive chemical pre-treatment of the carrier and potential scattering effects due to incomplete fragmentation, olefin polymerization in an emulsion reveals the opportunity to use non-supported metallocene catalysts and thus taking the advantages of homogeneous conditions (activity, selectivity), while producing spherical shaped polyolefin particles with average diameters ranging from micrometers to several nanometers. In order to apply emulsion and miniemulsion conditions for water-sensitive reactants in polyolefin synthesis, oil-in-oil-emulsions consisting of a perfluorinated solvent as the continuous phase and a hydrocarbon as the dispersed phase were developed in our

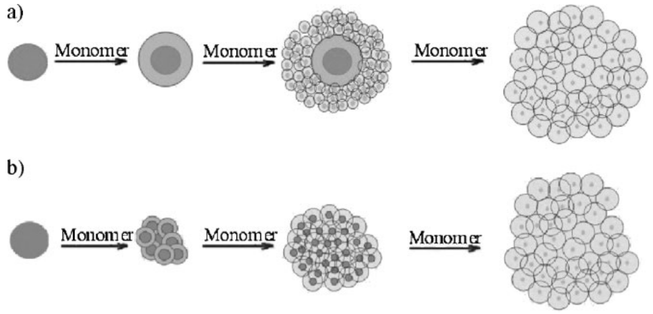

Figure 4.
Schematic description of the fragmentation behavior during olefin polymerization with supported catalysts on a) silica and b) latex particles, respectively.

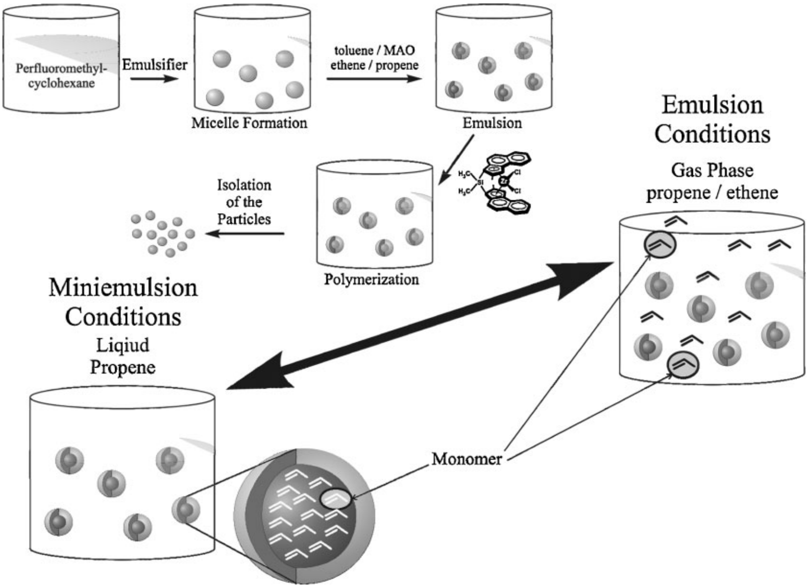

Figure 5.
Schematic description of the polymerization process: Formation of the oil-in-oil-emulsion, followed by addition of the co-catalyst MAO, toluene and saturation with the monomer; then *in situ* activation of the metallocene **1**, polymerization and isolation of the obtained particles. Additionally, schematic description of the contrast miniemulsion conditions vs. emulsion conditions.

group (Figure 5).[15,16] These systems are stabilized by block copolymers consisting of a poly(styrene) (PS) and a poly(pentafluorostyrene) (PFS), while the fluorophilicity is increased by attaching a perfluorinated C8-tail in *p*-position of the perfluorinated moieties. In these systems the metallocene **1** and the co-catalyst are exclusively soluble in the dispersed phase, and also the monomer is hardly soluble in the continuous phase. In consequence, the reaction takes place in the dispersed phase and, therefore, the hydrocarbon droplets can be considered as ‘‘nano-vessels’’. Besides controlling the size and morphology of the obtained product by the confined geometry of the micelles, the emulsions provide high heat capacity. Furthermore, these systems allow the use of well-established metallocenes and no new catalysts are necessary.

High molecular weight nanoparticles of PE ($M_w = 1{,}200{,}000\,g \cdot mol^{-1}$, PDI = 3.1) and PP ($M_w$ up to $90{,}000\,g \cdot mol^{-1}$, PDI = 5.6) were synthesized without supporting the catalyst and without reactor fouling.[15] The polymerization in these emulsions yields polyolefin particles with a spherical shape (*vide infra*) and the diameters can be controlled by parameters like polymerization time as well as pressure. Decreasing both parameters, leads also to a decrease of the particle diameters which is typical for a classic emulsion and also consistent with a diffusion controlled polymerization process. This indicates that the transport from the gas phase through the perfluorocarbon into the droplets is one of the limiting factors of the polymerization process.

To overcome this kinetic or – more precise – diffusion problem, the process has to be conducted in a different way. In colloid chemistry typically diffusion problems are solved by switching from emulsion to a miniemulsion process. In such a process the monomer is present in the micelles already from the beginning on. Thus, we succeeded by modifying the process guiding to replace the dispersed hydrocarbon solvent by propene (Figure 5).

Table 1.

Polymerization conditions and results of liquid propene with MBI catalyst in perfluorinated emulsion (250 cm^3 total volume, 60 min reaction time, 60 °C, 250 mg emulsifier PS_{180}-*b*-PFS_{150}); for further details see ref. [16].

Propene/ g	Pressure/ bar	Catalyst[a)]/ mg	Molecular Weight[b)]/M_n (PDI)	Al/Zr Ratio	Activity/kg PP · (mol Zr · hr)$^{-1}$	Yield/ g (%)
25	10	2.0	8,000 (2.2)	2,000	1,000	3 (13)
25	18	2.0	12,500 (7.5)	2,000	3,500	9 (36)
25	25	1.5	168,000 (3.6)	3,000	3,500	14 (56)
25[c)]	30	2.0	95,000 (2.4)	2,000	1,450	5 (20)
250[d)]	10	2.0	4,900 (2.1)	2,000	300	2 (0.6)
-[e)]	2	2.0	16,000 (3.5)	2,000	400	7 (-)

[a)] [Dimethylsilanediylbis(3,3′-(2-methylbenz[e]indenyl))]-zirconium dichloride;

[b)] By SEC in 1,2,4-trichlorobenzene at 135 °C vs. PS reference;

[c)] ^{13}C NMR spectrum in tetrachloroethane is given in Figure 6;

[d)] Homogeneous conditions;

[e)] Gas phase polymerization.

With this new method, monomer diffusion through the continuous phase is avoided whilst the monomer concentration is much higher in the micelles (mini-emulsion conditions) and additional organic solvents can be omitted, too. Metallocene-catalyzed polymerization of liquid propene is highly exothermic and, therefore, reactor fouling is mostly observed due to molten polymer under homogeneous conditions. In contrast to that, the perfluorinated emulsions lead to a change in the reaction characteristics and reveal the opportunity to polymerize pure liquid propene under "bulk conditions" in order to achieve activities with one order of magnitude higher than in the case of gaseous monomers (Table 1). Good heat transfer due to the surrounding solvent is guaranteed and the weight-averaged molecular weights are in the same range as reported for supported systems. Isotacticities for resulting polypropylene were determined by standard ^{13}C NMR spectroscopy to be higher than 90% when a MBI catalyst was used (Figure 6). The melting temperatures for PE and PP from oil-in-oil emulsions were determined by differential scanning calorimetry, showing endotherms of 138 °C and 144 °C, respectively.

The resulting polymers from the oil-in-oil emulsions and latex supports were subjected to morphology investigations by SEM in order to analyze the particle size, shape and reproducibility of the primary support particles. Polymer produced in emulsion from gaseous monomers like ethene and propene, consisting of particles between 0.5 and 20 μm, and showing perfect spherical shapes (Figure 7a, b). On the other hand, decreasing of the pressure and/or reaction time leads to particles with diameters of a few ten nanometers. Also the utilization of liquid propene yields PP particles in the low micrometer size range (Figure 7c, d) as it can be observed by SEM.

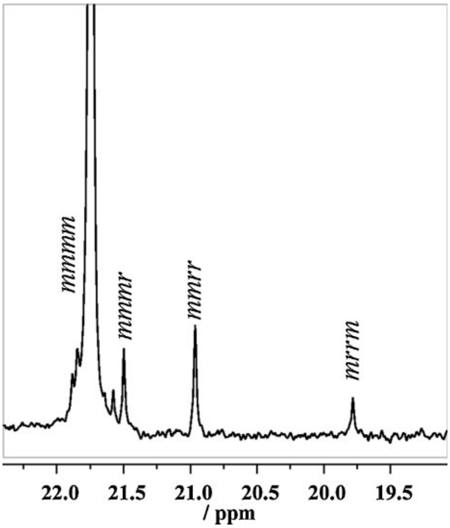

Figure 6.

^{13}C NMR spectrum of PP obtained from a fluorous emulsion – 96% isotactic (labeled with "c" in Table 1; 175 MHz in tetrachloroethane at 398 K).[21]

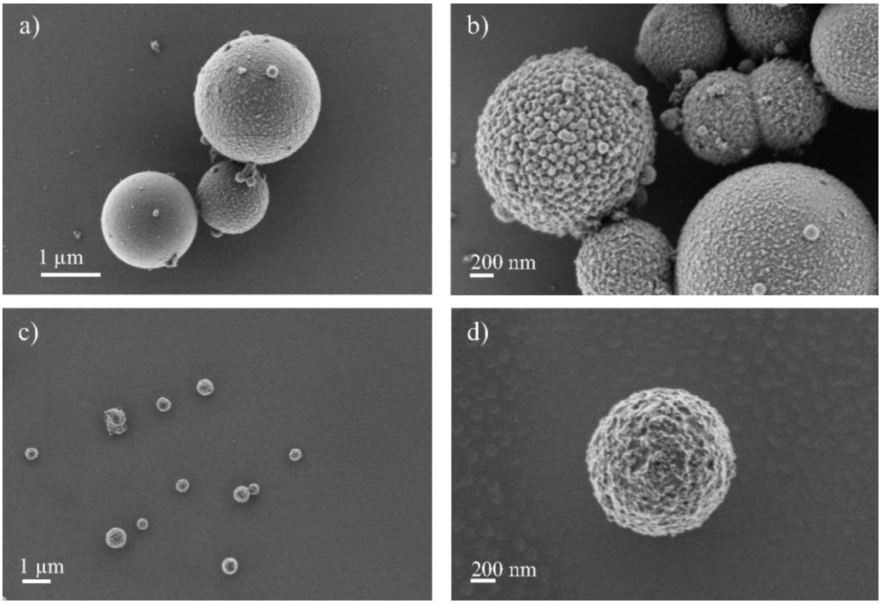

Figure 7.
SEM-photographs of PE- (a, b) and PP-particles (c, d) synthesized in perfluorinated emulsions with MBI catalyst 1 (a, b: ethene, 30 min, 60 °C, 40 bar; c, d: liquid propene, 60 min, 60 °C, 30 bar).

Conclusions

As an alternative to inorganic supports for metallocene-catalyzed olefin polymerization under heterogeneous conditions, organic latex carriers and non-aqueous emulsions based on a perfluorinated solvent were developed. Both techniques represent versatile tools for polyolefin synthesis, whereby the supported systems yield particles in the micrometer range and the emulsions lead to particles on the nanometer length scale.

In order to gain insight to the reaction course in both cases, intensive studies concerning the morphology and kinetics were carried out, and the different tools for that were presented herein. Standard techniques as SEC and ^{13}C NMR spectroscopy to measure molecular weights and tacticities were combined with LSCFM with dye labeled carriers, in order to follow the fragmentation behavior of the supports. Additionally, a deeper real-time insight into the particle growth during polymerization and morphology replication was given by polymerization in a video microscopy reactor. Furthermore, SEM was applied both to analyze particle diameters and shape of particles obtained from oil-in-oil emulsions and to follow the morphological development of latex particles loaded with MBI and a FI-titanium catalyst, respectively.

Thus, the broad variety of analytical methods applied in our group allows a comprehensive understanding of the reaction course in polyolefin synthesis with organic supports and oil-in-oil-emulsions and therefore symbiotic benefits are gained by joining all pieces of the puzzle from the different methods together. Only when all aspects of a polymerization process are well understood an optimization of the polymerization process can be expected.

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