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Organic Nanoparticles with Polypropyleneoxide Chains as Support for Metallocene Catalysts: Ethylene Homopolymerization and Ethylene/α-olefin Copolymerization

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Summary

Novel organic nanoparticles functionalized with nucleophilic polypropyleneoxide (PPO) chains on their surfaces for supporting metallocene catalysts in heterogeneous olefin polymerization are presented. The nanoparticles (60-100 nm) were obtained by miniemulsion polymerization of styrene, divinylbenzene and PPO functionalized styrene. It is demonstrated that $Me_2Si(2MeBenzInd)_2ZrCl_2/MAO$ supported on these nanoparticles is suitable for the homopolymerization of ethylene, resulting in excellent product morphologies and high activities. It is shown that by varying the MAO/Zr ratios and Zr concentrations the activities and productivities of the catalysts as well as the qualities of the polyethylene products can be tuned. These new supported catalysts are also suitable for the copolymerization of ethylene with several comonomers (1-hexene, 1-octene, 1-decene or norbornene). As the obtained product properties like crystallinity, melting temperature or bulk density match the results of silica supported systems, these organic nanoparticles can be considered as alternative carriers in comparison to the established inorganic ones.

Introduction

Metallocene complexes have proved to be attractive catalysts for olefin polymerization, due to the possibility of influencing the catalyst activity and tailoring the properties of the polyolefins such as polymer molecular weight, comonomer incorporation, and stereospecificity by simply changing the structure of the ligands used [1]. Heterogenization of the metallocenes is necessary in order to fulfill important requirements for an industrial system, such as control of morphology of products, avoiding the use of solvents and preventing reactor fouling [2]. A number of studies have been published concerning the immobilization of metallocene catalysts on several types of inorganic carriers. Some of those supports, however, have acidic groups on their surfaces that can cause deactivation of the catalysts [3-10]. Since the middle of the 1990`s, there have been a number of reports concerning the use of polystyrene based polymers as carriers for metallocene catalysts applied in olefin polymerization [11-16]. Recently, supports based on polystyrenes containing methoxy groups or PEO chains which immobilized active methylalumoxane/metallocene complexes through non-covalent bonding with nucleophilic groups were also reported [17-19]. The catalysts using those materials as supports displayed high activities and productivities forming well-defined polymer particles with high bulk density. This concept was developed further, as polystyrene based nanoparticles, functionalized with polyethylene oxide (PEO) chains on their surfaces were used as catalyst carriers. In this way, due to the small (100 – 150 nm), uniform and well-defined carrier particles, it was proposed that during polymerization reactions, the catalyst would fragment completely and homogeneously within the final product down to the nanosized particles of the support. Such a fragmentation of the support, proven for silica based supports [20, 21], is considered being essential for the morphology control in the polyolefin polymerization. With these nanoparticles this concept was successfully transferred to organic supports [19, 22, 23]. The applicability was not only demonstrated in the homopolymerization of ethylene but also for propylene and in the copolymerization [24, 25]. To extend the concept of developing nanoparticles with ether functionalized surfaces we considered not only PEO containing systems but also polypropyleneoxide (PPO) surface functionalized particles.

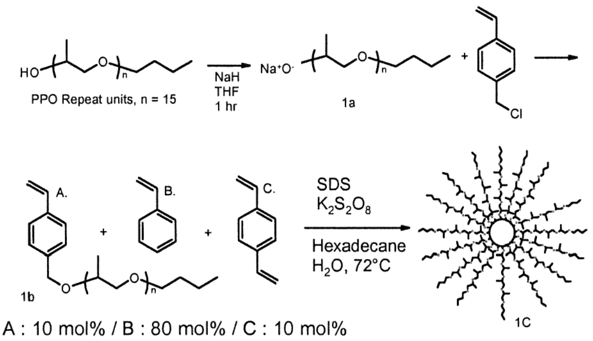
The PPO functionalized organic supports based on polystyrene nanosized latices should be obtained by miniemulsion polymerization as in such a process more defined and smaller particles are typically formed in comparison to the conventional emulsion polymerization [26]. An average diameter of the latices of below 100 nm can be expected while for the already described PEO systems prepared by emulsion polymerization a size of around 200 nm was achieved [19, 22 – 25]. It can be assumed that the catalysts prepared on these nanoparticle supports can fragment to a smaller size and result in a more uniform dispersion of the support in the polyolefin in comparison to our recently studied PEO-functionalized nanoparticles [19]. It is expected that the PPO chains on the surface of the support, due to their strong affinity towards aluminum compounds, respectively MAO, coordinate and immobilize metallocene complexes without leaching of the active metal sites during polymerization. Furthermore, the replacing of the hydrophilic and hygroscopic PEO chains by PPO should result in a less moisture sensitive system allowing good activities and productivities in heterogeneous ethylene polymerization.

Results and discussion

Preparation of the support and the supporting process of the metallocene/MAO complexes:

The first purpose of our research was to prepare novel latex particles having nano-sized core-shell structures. As surfmer in the miniemulsion process we used a PPO functionalized styrene (1b). This compound was prepared by etherification of chloromethyl styrene with the sodium salt of monohydroxy functionalized PPO (Mn = 1000) (1a) (Scheme 1). The desired latex (1c) was obtained by miniemulsion polymerization with styrene, divinylbenzene and PPO functionalized styrene (Scheme 1). In comparison to the emulsion polymerization without using a ultrasonifier, the miniemulsion polymerization is an effective method to prepare uniform nanoparticles. While the emulsion polymerization resulted in large aggregated species because the PPO functionalized styrene with the long PPO chains is difficult to be dispersed in the continuous phase, the miniemulsion polymerization showed no coagulation because the oil phase was entirely dispersed in the continuous phase by ultrasonification.

In Figure 1, the scanning electron microscopy (SEM) shows the different images of two types of latex particles obtained by emulsion and miniemusion polymerization, respectively. In case a (emulsion polymerization), the polymers appear as a flat unstructured film due to the aggregation of the latex. In case b (miniemulsion), well defined spherical nanoparticles were detected. The average diameter of the latex particles prepared from this procedure was about 50 nm.



Scheme 1. Preparation of PPO functionalized styrene and latex as support for metallocene.

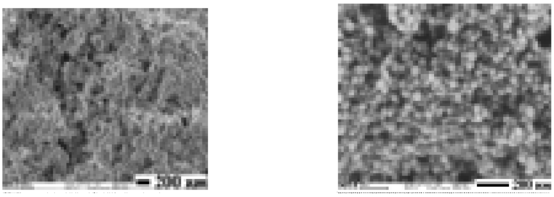
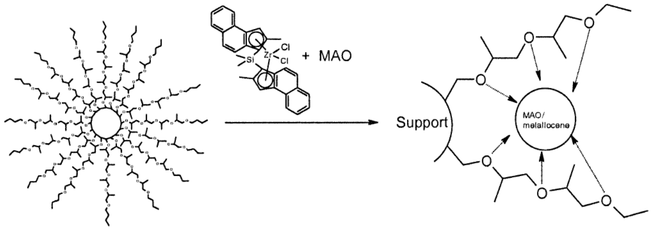

(a) (b)

Figure 1. SEM micrographs of emulsion polymers obtained by emulsion (a) and miniemulsion polymerization (b).



Scheme 2. Supporting process of PPO functionalized latex and MAO/metallocene complex.

For supporting the metallocene, the PPO-functionalized latices were mixed with a solution of MAO to remove traces of water. The amount of MAO depends on the desired activation. The solution of metallocene and MAO as co-catalyst was added to the MAO/polymer support mixture. After stirring the mixture for a few minutes, it was washed with dry hexane and the supernatant colorless hexane solution was removed via cannula. The complete immobilisation of the catalyst is indicated by the colorless supernatant solution and proven by the failing of any catalytical activity of this solution in an ethylene polymerization. After the procedure was repeated 3 times, the remaining solid was dried in vacuo. In all experiments performed, $Me_2Si(2MeBenzInd)_2$ $ZrCl_2$ (Scheme 2) was used as the metallocene. As the PPO shell of the nanoparticles consisted of very nucleophilic ether groups the immobilization via a non-covalent bonding of the MAO/metallocene complexes was almost quantitatively achieved for systems using hexane as solvent (see Table 1).

Homopolymerization of ethylene and the morphology of polyethylene particles:

Homopolymerization of ethylene was performed at 70 °C using 40 bar monomer pressure with the catalyst system of PPO functionalized support/Me_2Si (2MeBenz Ind)$_2ZrCl_2$/MAO (Scheme 2). The zirconocene concentrations as well as MAO/Zr ratios were varied in order to investigate the influence on the activities and productivities of the catalyst and the morphology of the polyethylene products obtained. The results of the homopolymerization are summarized in Table 1. The catalysts showed excellent activities and productivities in the same range or even higher than those of PEO functionalized supports [18]. The final polyethylene product was obtained as well-defined beads with high bulk density. No dust-like products or reactor fouling was observed. The activities and the productivities of these catalysts increased with increasing MAO/Zr ratio but decreased with increasing zirconocene concentration. It appears that the activities of the catalyst systems used depend more strongly on the MAO/Zr ratio than on the zirconocene concentration. According to run 6 and 8, the activity of catalyst washed by toluene was lower than that of catalyst washed by hexane. This decrease of the catalyst activity could be attributed to a limited solubility of the Zr/MAO complexes in toluene in comparison to hexane. In this way a part of the Zr/MAO complexes was washed away from the catalyst, which would cause the lower activities and productivities.

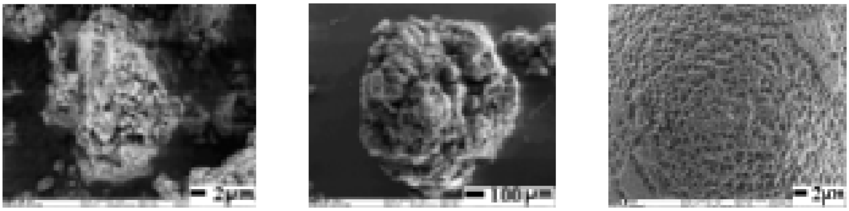
Table 1. Homopolymerization of ethylene (catalyst: $Me_2Si(2MeBenzInd)_2ZrCl_2$/MAO supported on PPO functionalized nanoparticles)[a]

Run	Zr/cat (µmol/g)	MAO/Zr	Time (min)	Activity (kg PE/mol Zr hr bar)	Productivity (g PE/g cat hr)	BD[b]
1	24	600	60	2050	1660	300
2	24	600	120	1800	1460	360
3	25	400	60	1550	1300	340
4	31	370	60	1350	1400	380
5	31	370	120	1300	1360	400
6	41	350	60	1250	1750	420
7	41	350	120	950	1300	430
8[c]	41	350	60	550	700	370
9	45	300	60	650	1000	380
10	45	300	120	750	1100	420

[a] Reaction condition: 1 L autoclave, isobutane 400 ml, ethylene pressure 40 bar, 70 °C, 1 – 2 hr, catalyst 24mg. [b] BD: bulk density(g/l). [c] catalyst washed by toluene instead of hexane.

At MAO/Zr ratios between 300 and 370 all polymers were obtained as well defined particles and bulk densities of 390 - 420 g/l were measured. When the MAO/Zr ratio was increased (400 – 600), however, the bulk density of the polyethylene products obtained decreased to the range of 300 – 360g/l. This may be explained by a faster fragmentation of the support due to the higher activity and the more exothermic reaction. By increasing the polymerization time at constant catalyst activation, the catalyst systems exhibited values of the activities and productivities similar to that of shorter time [(run 1, 2), (run 4, 5)] or (run 6, 7)] or slightly increased (run 9, 10). This indicates that the catalyst remained stable during the polymerization, as its activity was not influenced by the longer reaction time that is an important factor considering a potential technical application.

The SEM-pictures presented in Figure 2 show the morphology of catalyst (a) and of the polyethylene particles. The diameter of the catalyst particle obtained by the mixing of MAO/metallocene with the nanoparticles (Figure 2a) is typically 100 times larger than that of the latex particle (Figure 1b) due to aggregation induced by the interaction between PPO chains and the active metal sites. The catalyst (Figure 2a) forms a spherical particle but with a rough surface. The morphology of the product image (Figure 2b) was similar to that of the catalyst (Figure 2a). The product particle also appeared like an assembly of small and spherical beads and the size has increased from 10 μm to 1 mm in comparison to the initial catalyst. Such an effect of reproduction of the support is also typical for silica supports [20, 21] and considered as a proof of fragmentation of the catalyst. This conclusion was backed by investigating the surface of the polyethylene particles obtained after a polymerization time of 60 min (Figure 2c). The beads showed a cauliflower like surface also typical for polymer beads obtained from inorganic supports [2].



(a) (b) (c)

Figure 2. SEM micrographs of catalyst (a), polyethylene particles (b) and magnification of the surfaces (60min (c)): Zr/cat.: 41µ mol/g and MAO/Zr: 350.

Copolymerization of ethylene with 1-hexene, 1-octene, 1-decene or norbornene:

The tuning of properties of polyolefins like melting temperature (Tm), crystallinity or mechanical properties requires the copolymerization of different monomers. To investigate the applicability of our systems for more complex polyolefins, ethylene was copolymerized with several comonomers (1-hexene, 1-octene, 1-decene or norbornene). The copolymerization conditions were kept the same as in the ethylene homopolymerization with the catalyst system supported on PPO functionalized nanoparticles using Me$_2$Si(2MeBenzInd)$_2$ZrCl$_2$/MAO as active complex. The catalyst activation was kept constant at a Zr concentration of 41 µmol/g and a MAO/Zr ratio of 350 respectively while varying the comonomer concentration in the reactor. Table 2 shows the activities and productivities of the used catalyst which were much higher than those of ethylene homopolymerization in the case when aliphatic comonomers were used. These results can be explained by the well-known comonomer effect [23 - 25, 27 - 29]. This effect is the enhancement of the catalyst activity because of increasing copolymer solubility with the incorporation of comonomer. The activities and the productivities increased with increasing comonomer content respectively [(run 1, 2, 3, 4), (run 1, 5, 6, 7) or (run 1, 8)]. In comparison to the catalyst activities of the copolymerization of aliphatic olefin comonomers (1-hexene, 1-octene and 1-decene) those of norbornene copolymer increased upon varying the comonomer concentration between 0.13mol/l and 0.53 mol/l of norbornene but decreased when the concentration was above 1.10mol/l. The activities and productivities of norbornene were lower than those for copolymerization of aliphatic olefin comonomers due to the bulkiness of norbornene [31]. Furthermore, an influence of the comonomer concentration on the degree of crystallinity (Xc) and the melting temperature (Tm) of the product obtained was observed. As the comonomer content increased, there was a decrease for the ethylene/α -olefin copolymers. The degree of crystallinity influenced the thermal property of ethylene copolymer due to increasing amorphous regions. As all these results for polymer properties are very similar to the established silica supports [23-25, 27 - 31], one can conclude that the properties of the catalyst are not negatively affected by the PPO surface.

Table 2. Copolymerization of ethylene and 1-hexene, 1-octene, 1-decene or norbornene with the catalyst PPO functionalized organic support /$Me_2Si(2MeBenzInd)_2ZrCl_2$ /MAO[a]

Run	Comonomer	Amount of comonomer(mol/l)	Activity[b]	Productivity[c]	Tm[d] (°C)	Xc[e] (%)
1	0	0	1250	1750	134.8	48.8
2	1-hexene	0.20	2700	2950	123.3	36.7
3	1-hexene	0.40	3000	3400	111.6	29.2
4	1-hexene	1.60	6100	6800	93.6	20.7
5	1-octene	0.15	2950	3650	123.5	40.9
6	1-octene	0.34	3300	3700	115.3	32.9
7	1-octene	0.63	4400	4900	100.8	22.9
8	1-decene	1.30	3350	3700	128.8	42.8
9	norbornene	0.13	1150	1550	128.8	34.3
10	norbornene	0.28	1300	1750	122.3	30.3
11	norbornene	0.53	2000	2480	116.5	27.6
12	norbornene	1.10	500	550	-	-

[a] Reaction condition: in a 1L autoclave, isobutane 400ml, ethylene pressure 40bar, 70 °C, 1 hr, Zr/cat: 41 μ mol/g), activation 350 MAO/Zr, catalyst 24mg. [b] kg PE/mol Zr hr bar, [c] g PE/g cat hr, [d] Tm: Melting point measured by DSC. [e] Xc(%): Crystallinity = $100(\Delta H_m/\Delta H_m^*)$; $\Delta H_m^*=290$ J/g [27].

Conclusions

We have presented nano-sized organic supports (50 nm) functionalized with PPO groups obtained by miniemulsion polymerization as suitable carriers for heterogeneous metallocene catalysts. The homopolymerization of ethylene or the copolymerization of ethylene with comonomers (1-hexene, 1-octene, 1-decene and norbornene) was performed using these catalyst systems. The catalysts exhibit excellent activities and productivities in ethylene homopolymerization. The activities and the productivities of copolymerization were much higher than those of homopolymerization due to the comonomer effect. The activities and the productivities of copolymerization with norbornene were lower in comparison to the copolymerization of aliphatic olefin comonomers. This effect can be explained by the bulkiness of norbornene. In all copolymerization reactions, a decrease in the degree of crystallinity (Xc) and melting point (Tm) of the ethylene/α -olefin copolymers was obtained. The homopolymer and copolymer products with aliphatic comonomers were obtained as well-defined particles with high bulk densities.

Experimental

Materials: Ethylene (BASF AG, Ludwigshafen) was purified by passage through columns of BASF R3-15 deoxygenation catalyst and a 4 Å molecular sieve. Purification of isobutane was achieved with Oxisorb and Hydrosorb gas purification systems. The $Me_2Si(2MeBenzInd)_2ZrCl_2$ metallocene obtained from Basell GmbH, MAO (10 wt% in toluene) from Witco and triisobutylaluminium (TIBA) (1.0 M in hexane, Aldrich) were used without further purification. Monomers (styrene derivatives) were distilled under reduced pressured prior to use. THF and toluene were dried by distillation from sodium/potassium alloy under argon atmosphere to remove residural traces of moisture and oxygen. Deionized water (Millipore water) was used throughout the work for the emulsion polymerization.

Synthesis of the support (Scheme 1):
a) Synthesis of the surfmer: NaH (0.55 g, 0.023 mol) was suspended in THF (40 ml) and hydroxy terminated polypropyleneoxide-monobutylether (Mn = 1000) (19.79 ml, 0.019 mol) solution in THF (50 ml) was added dropwise. The mixture was stirred for 1hr at room temperature. p-Chloromethylstyrene (3.27 ml, 0.023 mol) in THF (10 ml) was added at 0 °C and the resultant mixture was stirred for 24 h at room temperature. The solvent was evaporated and the residue was purified by column chromatography on silica gel with dichloromethane to give a yellow oil (yield: 12.77 g, 60 %). ^1H NMR (250 MHz, $CDCl_3$): 0.85-0.91 (3H, t), 1.22- 1.76 (49H, m), 3.34- 3.55(47H, m), 4.57 (2H, s), 5.19 (1H, d), 5.69 (1H, d), 6.73 (1H, dd), 7.26-7.36 (4H, m).
b) Synthesis of the nanoparticles via miniemulsion: Styrene (0.370 g, 80 mol%), divinylbenzene (0.058 g, 10 mol%), PPO functionalized styrene (0.5 g 10 mol%) and hexadecane (250 ml) were stirred for 5 min. Sodium dodecylsulfate (72 mg) was dissolved in distilled water (24 g), mixed with oil phases and stirred at the highest power (1200 rpm) of the magnetic stirrer for 1 h to form a microemulsion. The microemulsion was ultrasonicated for 5 min with a Branson Sonifier 450W 70% power under ice cooling to form a miniemulsion. The miniemulsion was heated in an oil bath at 72 °C. 100 mg of the initiator $K_2S_2O_8$ was dissolved in a small quantity of distilled water and added to the miniemulsion reactor. The product was then filtered by a stirred Ultrafiltration "Millipore" model 8050 with polyethersulfone membrane and dried in vacuo.

Supporting of the catalyst: The PPO-functionalized support (80 mg) was mixed with a solution of MAO (2 ml) in toluene and stirred overnight to remove traces of water. The amount of MAO depended on the desired activation. After 30 min, a solution of metallocene and MAO (1.5 ml) was added to the MAO/polymer support mixture and dried hexane (20 ml) was added. Then after stirring for another 30 min, the catalyst was precipitated. The supernatant colorless hexane solution was removed, the procedure was repeated 3 times and the remaining solid was dried under vacuum. The catalyst supported metallocene complex was ready for use in polymerization.

Polyolefin polymerization, Procedure and polymer characterization: The reactor (1 L Büchi stainless steel, equipped with stirrer) was purged with argon and charged with isobutane 400 ml and TIBA (triisobutyl aluminium) 5 ml. An ethylene pressure of 40 bar was applied and the reactor heated to 70 °C. The catalyst was injected into the reactor under argon through the pressure lock without further activation with MAO.
Polymer melting points (Tm) and crystallinities (Xc) were determined on a differential scanning calorimeter (DSC) using a heating rate of 10 °C/ min in the temperature

range 20 – 200 °C. The heating cycle was performed twice, but only the results of the second scan were reported. Crystallinity (Xc) was represented as the ratio of melting enthalpy of the DSC thermogram to that of a perfect polyethylene crystal (290 J/g) [22]. Molecular weight and molecular weight distribution of the polymers were measured at 145 °C by gel permeation chromatography (GPC) using o-dichlorobenzene as solvent. The morphology of the polymer products was analyzed by SEM.

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