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Organic Nanoparticles with Polypropyleneoxide Chains as Support for Metallocene Catalysts: Influence of the Concentration of PPO Chains on the Surface of Nanoparticles on the Catalyst Activity in Ethylene Polymerization

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Summary

In this paper the influence of the surface of organic nanoparticles used as supports in metallocene catalysed olefin polymerization is investigated. Several latex particles with different amounts of polypropylene oxide (PPO) chains on the surface were synthesized by miniemulsion polymerization and used as supports for the $Me_2Si(2MeBenzInd)_2ZrCl_2$ / MAO complex. These catalysts were applied in heterogeneous ethylene polymerization. It was observed that longer PPO chains on the supports coordinated more metal sites than shorter ones to give catalysts with higher activities. An increased amount of PPO chains on the supports, however, led to catalysts with lower activities. It is suggested that a higher amount of PPO chains on the support could result in a stronger network between the different nanoparticles due to the enhanced interaction of the PPO with the methylaluminoxanes so that the diffusion of the ethylene monomer to the active metal sites is hindered.

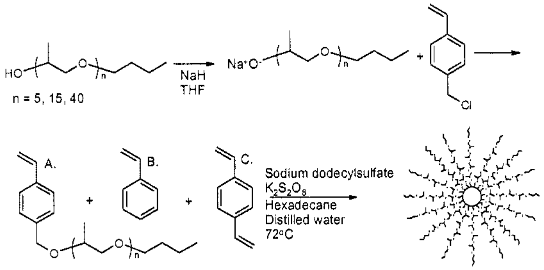
Introduction

In the recent years metallocene catalysts have shown very high activity in homogeneous olefin polymerization [1]. However, homogeneous polymerization has the disadvantage that the bulk density of the final olefin product is very low as it consists of only sponge-like material. By contrast in heterogeneous olefin polymerization, the activity and the productivity of the polymerization are lower than in homogeneous catalyzed olefin polymerization due to hindered monomer diffusion into the supported catalysts, but this process results in a good product morphology, high bulk density of the powder, and low reactor fouling [2]. Additionally, heterogenization of metallocenes is necessary to allow the industrially applied gas-phase polymerization [3]. Industrially, only inorganic supports such as SiO_2, $MgCl_2$, and Al_2O_3 for metallocene catalyst have been used [4-11] and, only a few examples of organic supports mainly based on polystyrene resins are known [12, 13]. In the recent years our group has reported several new organic supports, focussing on a non-covalent loading of the catalysts on PEO functionalized nanoparticles. This support could immobilize the active metal sites through non-covalent bonding and exhibited high catalyst activity with high bulk density [14, 15]. In a previous work we have

extended our concept of ether functionalized nanoparticles as supports for metallocenes to polypropyleneoxide (PPO) functionalized systems. Using these supports we have reported the homopolymerization of ethylene and copolymerization of ethylene/ 1-hexene, 1-octene, 1-decene or norbornene with the catalyst system of PPO functionalized support / $Me_2Si(2MeBenzInd)_2ZrCl_2$ / MAO. Excellent catalyst activities and product morphologies (Bulk densities: 400 g/l) were obtained [16].
As the role of the support and especially of the PPO chains on the surface of the supports in the polymerization is still quite unclear, we synthesized several similar supports prepared by miniemulsion polymerization. They were modified in the amount and chain length of the PPO on the surface of the latex particles to study the influence of the amount of nucleophilic groups in the PPO chains on the catalyst activities and polymer properties.

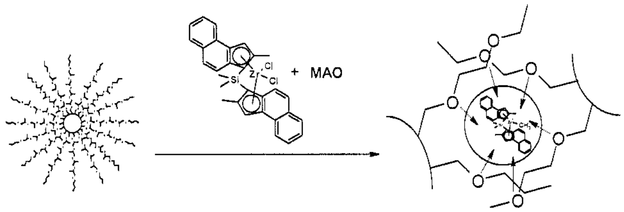
Results and discussion

The purpose of our research was first to prepare several organic latices, varying the PPO chain length (repeat units: 5, 15, 40), then to test the activities of these supported catalysts in olefin polymerization and to investigate the resulting polymers. Several organic supports were prepared; Supports containing different amount of PPO chains on their surface were prepared by varying the amount of surfmer (0.5 mol% to 20 mol%)(Scheme 1; support 2, 4-7).; In the case of a support containing 10 mol% PPO chains, the lengths of the chains were varied from 5 repeat units to 40 repeat units (Scheme 1; support 1-3).



supports	repeat units(n)	A(mol%)	B(mol%)	C(mol%)
1	5	10	80	10
2	15	10	80	10
3	40	10	80	10
4	15	0.5	89.5	10
5	15	1	89	10
6	15	5	85	10
7	15	20	70	10

Scheme 1. Preparation of supports 1-7 functionalized with PPO chains



Scheme 2. Supporting of the metallocene catalyst forming network.

Polymerization of ethylene

In an initial series of experiments we investigated the dependence of the activity and productivity on the concentration of the styryl functionalized PPO (Sty-PPO) emulsifier used in the miniemulsion process. We increased the amount of Sty-PPO from 0.5 to 20%, but keeping the PPO chain length constant (n=15). These supports (2, 4-7 see scheme 1) were loaded with a constant amount of $Me_2Si(2MeBenzInd)_2ZrCl_2$ activated with methylalumoxane (MAO) (table 1) and applied in the ethylene polymerization. According to GPC analysis, these catalysts were found to produce polyethylene with a very high molecular weight (M_w) of about 1,200,000 and a polydispersity (PDI) of 2.48 – 2.98 (Table 1).

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

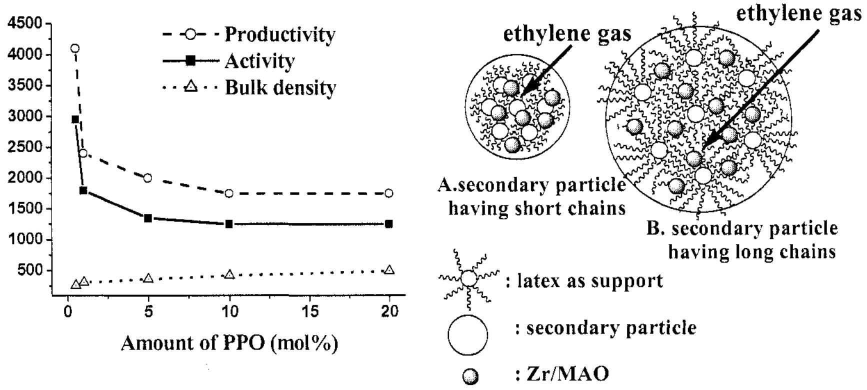
Run (support)	Length of PPO (units)	Amount of PPO(mol%)	Activity[b]	Productivity[c]	BD[d]	Mw (PDI)	Tm (°C)
1 (4)	15	0.5	2950	4100	260	905,000 (2.98)	135.8
2 (5)	15	1	1800	2400	310	1,424,000 (2.74)	134.5
3 (6)	15	5	1350	2000	360	1,271,000 (2.48)	134.3
4 (2)	15	10	1250	1750	420	1,244,000 (2.64)	134.8
5 (7)	15	20	1200	1700	490	1,399,000 (2.62)	134.2

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

As the amount of PPO chains on the support increased, the activity and the productivity of the catalyst in ethylene polymerization decreased (Figure 1a) but the bulk density increased markedly.

To explain these results several effects have to be considered. On the one hand at low PPO concentration the interaction between PPO and the MAO/metallocene complex is weak and the immobilization might be limited. This would result in a more homogeneous polymerization and therefore in higher activities and, also as is observed in our case, lower bulk densities. Furthermore, one has not only to consider the interaction between metallocene and support but also the interaction of different latex particles which are reversibility crosslinked via the MAO/PPO interaction. This interaction should be strengthened drastically by increasing the amount of PPO on the particles resulting in a more stable network. Such a denser network could limit on the one hand the diffusion of the monomer into the active sites of the catalyst (Figure 1b) and on the other hand the fragmentation of the catalyst. The slow fragmentation of catalyst, however, permits access only to the outer active centers, at the beginning the inner centers are not able to contribute to the polymerization process. This would correspond to the classical fragmentation model developed for silica supported metallocenes [17, 18].

Finally, one can conclude, there is an optimum surface functionalization for obtaining good bulk density, activity and productivity. If the surface functionalization is too low, as demonstrated in a previous work [14] only fluffy materials with a low bulk density are isolated, but the activity is high. On the other hand to get high bulk density, essential for an industrial application, a decreased activity and productivity have to be accepted as drawbacks.



(a) (b)

Figure 1. a) Influence of the amount of PPO chains on the catalyst activity and productivities in ethylene polymerization and bulk density of product, b) diffusion of the monomer into the supported catalyst [length of PPO (repeat units): 15].

In a second series of experiments we investigated the influence of the chain length of the PPO units on activity, productivity and bulk density. Again the particles were prepared by miniemulsion polymerization, the concentration of the PPO-Sty compounds was kept constant, but PPO chains with a polymerization degree of 5, 15 and 40 were applied. The molecular weight, molecular weight distribution and melting point of the isolated polyethylene prepared with these supports showed results similar to the previous ones (table 1).

Table 2. Polymerization of ethylene with the heterogeneous catalyst PPO functionalized organic support /$Me_2Si(2MeBenzInd)_2ZrCl_2$ /MAO[a].

Run (Support)	Length of PPO (units)	Amount of PPO (mol %)	Activity[b]	Productivity[c]	BD[d]	Mw (PDI)	Tm (°C)
6 (1)	5	10	1200	1650	400	1,386,000 (2.59)	134.7
7 (2)	15	10	1250	1750	420	1,244,000 (2.64)	134.8
8 (3)	40	10	1500	2050	430	1,395,000 (2.55)	134.8

[a] Reaction condition: 1L autoclave, isobutane 400 ml, ethylene pressure 40 bar, 70 °C, 1 hr. 41 Zr/cat (μ mol/g) & 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).

Table 2 presents the results of the polymerization of ethylene carried out with $Me_2Si(2MeBenzInd)_2ZrCl_2$ activated with methylalumoxane (MAO) as co-catalyst. As the length of PPO chains on the surface of support increased, the activity and productivity of the catalyst in ethylene polymerization increased as well (Figure 2). This effect is quite surprising as one would expect that with longer PPO chains the interaction between the different particles is enhanced, the fragmentation of the supported catalyst slowed down and as discussed above the activity and productivity decreased. On the other hand one can suggest that the very flexible, liquid-like PPO chains surrounding the stiff compact polystyrene cores allow for a faster diffusion of the monomer to the reactive catalyst centers, therefore, the activity and productivity of catalyst will be increased. This model would fit to the model developed for the polymerization and fragmentation process of the Ziegler-type catalysts wherein all catalyst centers more or less simultaneously become active at the beginning.

Even if the mechanism of the fragmentation of the supported catalyst and polymerization is not really clear one can conclude that the shell of the latex particles strongly influences the polymerization behaviour of these supported catalysts. A model for describing the diffusion processes and the fragmentation of catalyst seems to be essential to fully understand the effect on the polymerization of these new types of supports. Therefore, at the moment a more detailed kinetic study with our organic supports are being performed in cooperation with Prof. G. Fink at the Max-Planck Institute für Kohlenforschung in Mülheim.

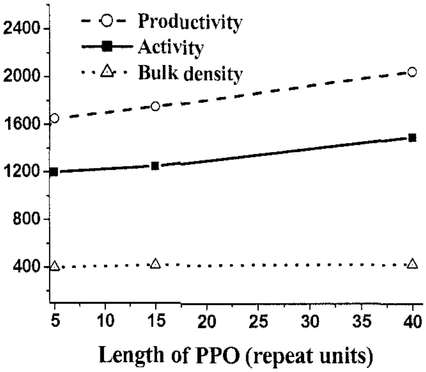
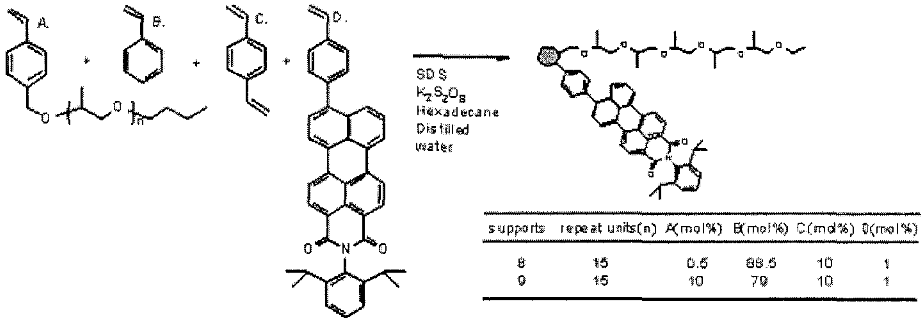


Figure 2. Influence of the length of PPO chains on the catalyst activity and productivities in ethylene polymerization and bulk density of product (concentration of PPO: 10 mol%).



supports	repeat units(n)	A(mol%)	B(mol%)	C(mol%)	D(mol%)
8	15	0.5	88.5	10	1
9	15	10	79	10	1

Scheme 3. The preparation of supports tagged with a covalently incorporated fluorescent perylenemonoimide dye.

In a previous work we used fluorescent dye labeled nanoparticles to prove the fragmentation of the polymer-supported catalyst [20]. Similarly, we incorporated a styrylperylene-monoimide (D) as a fluorescent dye [19] into the PPO functionalized nanoparticles (Scheme 3). The supports were produced by the same procedure published in our previous work [16] and applied in the polymerization of ethylene. The result is being investigated.

Conclusion

PPO functionalized organic nanoparticles for supporting metallocene catalysts in heterogeneous olefin polymerization were prepared by miniemulsion polymerization. The supports were prepared with varying lengths of PPO chains from 5 repeat units to 40 repeat units or the amount of PPO chains from 0.5 mol% to 20 mol% on the surface to study the influence of the chain parameters such as the length and concentration of PPO chains on the activity and the productivity of metallocene catalysts in ethylene polymerization. Depending on the length of PPO chains or the amount of PPO chains on the support, the activity and the productivity of the catalysts varied considerably. The catalyst prepared by the support with longer PPO chains showed higher activities than the catalyst prepared by the support with shorter PPO chains. It is suggested that the longer PPO chains on the support can immobilize more active metal sites than the shorter ones do. Additionally, the longer PPO chains on the support could create wider spaces between the chains allowing faster catalyst fragmentation. An increasing concentration of PPO chains on the supports, however, led to catalysts with lower activities. It is suggested that a higher concentration of PPO chains on the support creates denser networks between nucleophilic groups and active metal sites. This influenced the fragmentation of the supported catalyst so that the catalyst shows lower activities. A complete model of fragmentation for those type of polymeric catalyst systems including the kinetic investigation of the polymerization is being currently developed. Polyethylene products exhibited a very high molecular weight and narrow polydispersity. All melting temperatures of polyethylene obtained were similar, despite the different activities of the catalysts. All polyethylene products were obtained as well-defined particles with high bulk densities. It should be noted that in the case of an inorganic support for adjusting the concentration of nucleophilic centers on silica surfaces and for a tuning of the activity of a catalyst a controlled thermal treatment (calcination) is necessary [21]. However, for our system, we expect to control the activity by varying the concentration and the chain length of the nucleophilic PPO chains on the support.

Experimental

Materials:

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

Preparation of supports (scheme 1 and scheme 3):

Preparation of support 2:

a) Synthesis of the Surfmer: First, NaH (0.55 g, 0.023 mol) was suspended in THF (40 ml) and polypropyleneoxide-monobutylether (19.79 ml, 0.019 mol) solution in THF (50 ml) was added dropwise. The mixture was stirred for 1 hr 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 hr 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 %). ^{1}H 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) Latex particles 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 the oil phase and stirred at the highest power (1200 rpm) of the magnetic stirrer for 1 hour to form a microemulsion. The microemulsion was ultrasonificated for 5min 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. The initiator potassium persulfate 100 mg 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. The other supports (1 and 3-9) were prepared by the same procedure The yield of PPO functionalized styrene with repeat 5 and 40 were 17.47g (65%) and 10.47g (50%) respectively. The molecular weight distributions of these PPO functionalized styrenes are similar to that of the commercial polypropyleneoxide-monobutylether (PDI: about 1.1 – 1.2)

Supporting of catalyst (scheme 2):

The PPO-functionalized support (about 52 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 dimethylsilyl bis(2-methylbenzindenyl)zirconocene dichloride and MAO (1.5ml) was added to the MAO/ polymer support mixture. 20 ml of dried hexane 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 finally the remaining solid was dried under vacuum. Polymerization experiments with this solution failed proving that no catalyst was dissolved and the immobilization was complete.

Polymerization procedure and polymer characterization:

The reactor (1 L Büchi stainless steel, equipped with a stirrer) was purged with argon and charged with isobutane 400 ml and TIBA 5 ml. Ethylene pressure of 40 bar was applied and the reactor heated to 70 °C. The catalyst was injected with argon into the reactor through the pressure lock without further activation with MAO. Polymer melting points(Tm) were determined on a differential scanning calorimeter (DSC) using a heating rate of 10 °C/ min in the temperature range 20 – 200 °C. Molecular weight and molecular weight distribution of the polymers were measured at 145 °C by gel-permeation chromatography (GPC) using o-dichlorobenzene as solvent and polystyrene as standard. The polymerization experiments are repeated at least three times to exclude any experimental errors.

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