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PEO-functionalized polystyrene as polymeric support in metallocene catalysed olefin polymerisation

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Summary

A new catalyst system based on easily accessible cross-linked (by Diels-Alder reaction) polymeric supports, functionalized with nucleophilic polyethyleneoxide-monomethylether (PEO-M) is presented. The metallocene-MAO complex is noncovalently bonded to the support, avoiding a complicated polymer analogous metallocene synthesis. The polymerisation of propene and ethene with $Me_2Si(2MeBenzInd)_2ZrCl_2$ as metallocene is performed using this support. The resulting polymers have high molecular weights and melting points and narrow molecular weight distribution. Polypropene is produced with 95% isotacticity similar to that from homogeneous catalysis. The productivities of up to 8600 for polypropene and 1300 for polyethene (kg polymer / mol Zr h bar) are comparably high. The product beads exhibit a good morphology, which can be explained by fragmentation processes of the support due to the reversibility of the network formation.

Introduction

In the last few decades there have been considerable developments in the polymerization of olefins in view of their many practical applications, and much effort has been directed to the improvement of the catalytic systems. In this way, by applying better polymerisation conditions, polymers with desired molecular characteristics (morphology, microstructure, etc) have been obtained. After the discovery of the metallocene complexes of group IV transition metals with some aluminum compounds (methylaluminoxane - MAO, trimethylaluminum – TMA) [1], [2], [3] work began on appropriate supports for immobilization of these complexes.

A suitably selected support improves the catalysts, making it possible to perform polymerization in the gas phase as well as to control the characteristics of the obtained polymer (well defined particles, higher molecular weights, higher bulk density), all of which makes this type of ionic polymerisation attractive for industrial applications.

At first inorganic compounds (magnesium chloride [4], silica [5], alumina [6]), were used as carriers, but lately more attention has been paid to the use of polymers based on functionalised polystyrene, irreversibly crosslinked with divinylbenzene, where the metallocene is synthesized directly on the support [7], [8]. Unfortunately, in this case one can use supports containing only some simple metallocenes (due to the complicated synthetic routes), and the irreversible crosslinking makes the fragmentation of the polymer difficult .

Recently, a new catalyst using reversibly crosslinked polystyrene as support based on the Diels-Alder reaction between cyclopentadienes (Cp)-groups has been reported [9]. This catalyst shows good activity and the obtained polymer exhibits the desired morphology. However the problem with the restricted number of metallocenes which can be used this way remains, and the latest direction of research in this field is into finding new ways for immobilization of the metallocenes.

The method of formation and the nature of the complexes between metallocenes and MAO or other aluminum compounds, has been established [10], [11], [12], and it has been shown that complexation, rapid alkylation, and dissociation into an ion pair take place. Because of the cationic character of these complexes, it is appropriate to immobilize them noncovalently on polymer support which carries nucleophilic groups containing oxygen. In this case, because of the non-acidic character of the centres, no treatment with MAO (prior to the metallocene immobilization) is necessary, as is done with silica supports having OH-groups which have to be deactivated.

Our first attempts were directed towards the use of supports containing MeO-groups [13]. We used such supports mainly for propene polymerisation due to the possible tacticity control, which requires more suitable sophisticated catalytic systems and metallocenes with constrained geometry. The characteristics of polypropene obtained on such supports are very close to those of polypropene prepared by homogeneous polymerisation (high molecular weight, narrow molecular weight distribution). These features however are combined with particle morphology typical for heterogeneous catalytic systems (no dust like product).

In this paper we demonstrate a new polymer carrier for metallocene-MAO complexes based on polystyrene, functionalized with short polyethyleneoxide-monomethylether (PEO-M) chains and cyclopentadiene groups. The PEO-M chains, due to their strong nucleophilic character (containing several ether bridges), lead to better coordination and immobilization of the metallocene complex on the surface of the carrier. Through Diels-Alder reaction, cyclopentadiene groups provide the reversible crosslinking of the support. This contributes to metallocene immobilization and facilitates carrier fragmentation and distribution during polymerization. With this catalytic system we performed polymerizations of ethene and propene. The polymers obtained exhibit the desired morphology and high molecular weight, while the used catalyst showed very good activity and productivity (calculated as g polymer per g catalyst per hour) .

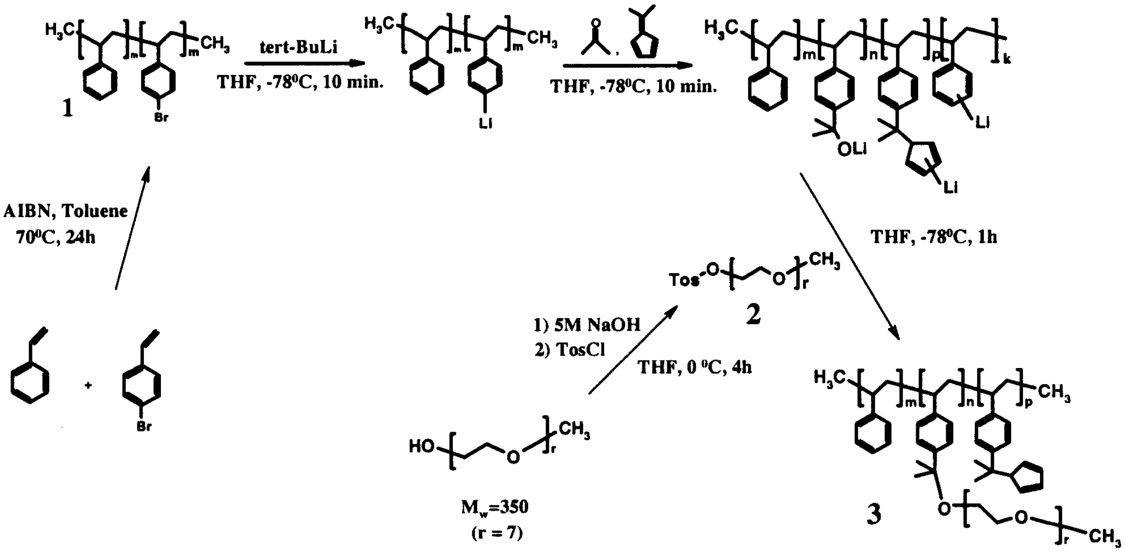
Results and Discussion

Synthesis of the support

In order to obtain the desired functionalized carrier, we considered two possible synthetic routes. First we carried out the copolymerization of 1-vinyl-4-oxy-oligoethyleneglycol-monomethylether, (previously obtained from vinylphenol and tosylated PEO-M), with styrene and bromo-styrene. As the last step the Cp-groups are introduced via bromine functionalities. However this way is not very convenient because of the several steps which have to be performed.

We found out that a much more favorable route was to use a copolymer of styrene and bromo-styrene **1** in equivalent amounts as a starting material (scheme 1). For introducing OEG-M chains to the copolymer the bromine groups were lithiated with tertiary butyllithium (tert.-BuLi) (1.5 eq per Br unit). For carrying out this procedure, 1 g of copolymer **1** was dissolved in 100 ml of dry THF and after cooling to −78 °C (dry ice-acetone bath), tert. - BuLi was added. As the base obtained this way in 4th position of the benzene rings is very strong, for the next grafting of the glycol chains, we decreased its activity using acetone for 0.2 eq of the lithiated centres. On another 0.4 eq of the lithiated centers, Cp-groups were introduced using dimethylfulvene. After stirring for 15 minutes 0.2 eq of tosylated PEO-M **2** (scheme1), were grafted selectively on the O^- anionic centers, due to the higher nucleophilicity of the alcoholate in comparison to the aromatic Cp-anion. After additional stirring for one hour the desired polymer support **3** (scheme 1), was obtained. The whole synthetic procedure to produce carrier ready for use takes only 1.5 hours. Using this route the end product is obtained by a one-pot method. This provides a fast non-complicated procedure for the preparation of desired supports.

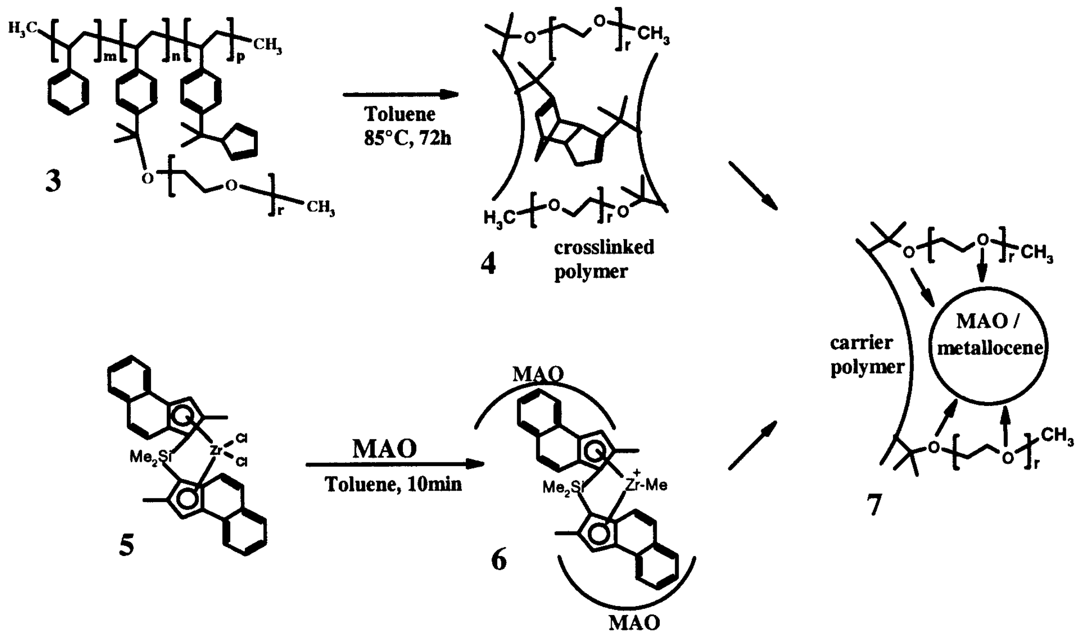
Such reversibly crosslinkable supports containing nucleophilic glycol chains are very suitable for immobilization of MAO-metallocene complexes **6** (scheme 2). The crosslinking was performed by heating a 20 weight percents solution of the support in toluene at 85 °C for 72h. The gel-like crosslinked support **4** can be subsequently treated directly with the metallocene-MAO complex **6** (scheme 2).



Scheme 1: Synthesis of the support

Supporting process

In all our experiments $Me_2Si(2MeBenzInd)_2ZrCl_2$ **5**, was used as metallocene. A solution of metallocene **5** in MAO was added rapidly via syringe to the crosslinked polymer support (gel in toluene). After stirring for 10 min, dry hexane was added and the catalyst precipitates. Stirring for another 10 min, removal of the supernatant colorless hexane solution *via cannula*, washing with additional hexane and drying the remaining solid *in vacuo*, yield the polymer supported metallocene complex **7** ready for use. A homogeneous polymerization with the supernatant hexane solution supposed to contain the non-adsorbed Zr-complex failed. That indicates that the supporting process is quantitative. To add the catalyst before performing the crosslinking is not possible as the MAO/metallocene complex is not stable under the in the Diels-Alder reaction applied reaction conditions (85°C, 72h).



Scheme 2: Supporting process

Polymerisation of ethylene and propylene.

Polymerization of propene:

Polymerizations were carried out in a 1 L stainless-steel autoclave in hexane at 50 °C and at a propene pressure of 5 bar. Triisobutylaluminum (TIBA) was used to remove impurities. The catalyst was activated with MAO for 10 min before it was transferred into the reactor. Polymerisation conditions and resulting activities are given in Tab. 1.

Table 1. Polymerisations of propene (400 ml hexane, 5 bar propene, 30 min., 50 °C)

Run	Zr/cat. (μmol/g)	Catalyst (mg)	MAO/Zr	Yield (g)	Activity (kg PP/mol Zr h bar)	Productivity (g PP/g cat h)
1	47	68	920	69	8640	2180
2	47	80	660	36	3830	900
3	47	87	540	37	2470	580
4	47	100	325	6	1000	120
5[a)]	45	80	817	8.6	955	215

a) Polymerisation temperature : 40 °C

The activity and productivity of the catalytic system used in these polymerization reactions are very high when compared with other polymer supported catalysts [7]. They are in the range of the activities and productivities observed by the polymerisation of propene with metallocene 5 supported on polystyrene containing MeO-groups (activity between 3000 and 8000) [13], as well as on silica (activity between 800 and 12 000) [14].

Polymerisation of ethene :

Polymerization of ethene was performed in a 1L stainless steel reactor (isobutane as a solvent) at 40 bar ethene pressure and 70 °C polymerization temperature. TIBA was used for removing the impurities. Because of the higher activity of ethene and its high pressure applied in the polymerisation, additional activation of the catalyst with MAO before polymerization was not necessary. Polymerisation conditions and the resulting activities are given in Table 2.

Table 2. Polymerisations of ethylene (400ml isobutane, 40 bar ethylene, 70°C)

run	Zr/cat	MAO/Zr	Cat (mg)	Time (min)	Yield (g)	activity (kg PE/mol Zr h bar)	productivity (g PE/g cat h)
1	25	400	100	60	83	830	830
2	40	300	60	60	81	915	1350
3	36	200	70	90	37	305	350
4	33	150	90	60	21	175	230

Activity and productivity observed here are high compared with other runs [8], [16], [19], having in mind the low ratio MAO/Zr as well as the low amount of Zr per g support.

Characteristics of the obtained polymers

Polypropene :

Polypropene is obtained as nearly spherical beads of about 3 mm in size having a similar shape as the support shwon by SEM. The size correlates with the ratio MAO/Zr – a higher ratio produces bigger particles and a higher productivity and activity of the catalytic system. The particles have relatively low bulk density (130-150 g/L, runs 1-4) and the reason for this may be the high ratio MAO/Zr which was needed because of the applied low pressure of propene. We assume that during the polymerization, polymer particles pack together and form bigger beads in the case of more active catalyst. Several runs performed at lower temperature (40°C) showed a drastic decrease in producitvity and activity of the catalyst but the particles obtained were about 1mm in diameter having slightly higher bulk density (180g/L). (Table 1, run 5).

Table 3. Melting points, molecular weights[a)] and weight distributions of polypropene products.

Run	T_m (°C)	M_n	M_w	PDI
1	147.1	165000	360000	2.17
2	148.6	141000	330000	2.33
3	150.0	125000	270000	2.17
4	149.0	136000	330000	2.44
5	149.8	142000	230000	1.60

a) from gel permeation chromatography

The chiral metallocene which we used is bounded strongly non-covalently to the rigid surface of the support. The polypropene obtained exhibit M_w in the range 260 000 –

360 000 and melting points (T_m) of 147 °C to 150 °C. The M_w and T_m observed are relatively high in comparison with melting points and molecular weights of polypropene obtained by homogeneous systems [14] or heterogeneous systems supported on polystyrene-co-divinylbenzene [15] and on silica [16][20]. The polydispersity of polypropene obtained by the different runs varies from 1.84 to 2.44 – low values compared to polypropene prepared with homogeneous catalysts.

The tacticity was investigated by means of ^{13}C-NMR Spectroscopy according to the methods described by Hayashi [17] and Ewen [18]. The ^{13}C NMR spectrum of the polypropene obtained by us shows resonances for [mmmm], [mmmr] and [mrrm] pentads, with a [mmmm] fraction of 95 %, typical for isotactic polypropene and in accordance with the high melting points and high molecular weights of the polymer.

Polyethene :

Polyethene was obtained as fine particles about 0.4 mm in size. They exhibit high bulk density (380-400 g/L) and high molecular weights exceeding 900 000 for M_w. The polydispersity of polyethene obtained by the different runs varied from 1.8 to 3.7. These values are relatively low compared to the dispersity of polyethene synthesized on polystyrene-co-divinylbenzene supported catalysts (polydispersity 4.4-12.3 [8]) . The melting points - 131-133 °C are not as high as those of polyethene obtained by heterogeneous runs with catalysts supported on silica [16], but the activity of these systems and the molecular weights of the produced polyethene are lower. With increasing MAO/Zr ratio the particles obtained get bigger due to the higher activation. However, the MAO/Zr ratio influences only slightly the T_m and M_w of the polymers.

Table 4. Melting points, molecular weights and weight distributions of polyethylene products

Run	T_m (°C)	$M_{n(GPC)}$	$M_{w(GPC)}$	PDI
1	132.6	283800	923300	3.25
2	132.1	444770	1041000	2.34
3	131.1	378140	1071900	2.83
4	132.0	331650	1099300	3.31

Conclusions

The synthetic route for the preparation of oligoethyleneglycol-monomethylether containing support proposed by us is performed by a one-pot method in a short time. The Cp functions allow for an easy and reversible crosslinking of the carrier. They do not interact with the metallocene during the polymerisation. Due to the strongly nucleophilic PEG- groups, the MAO-Zr complex is almost completely bound to the support and therefore negligible reactor fouling is observed.The high activities suggest that all of the metallocene catalysts are active. This supports our concept of reversibility of the network. Without reversibility the catalyst activity should be quite low as discussed in ref. 9. Although the reaction temperature for the retro Diels_Alder reaction is quite low the equilibrium between dimer and monomeric structure is totally shifted to the side of the non-crosslinked species due to the instantaneously occuring deprotonation of the in the retro reaction formed cyclopentadienyl units via MAO. The polyolefins obtained by this method exhibit high molecular weights, high T_m and the desired morphology. At the same time the catalytic system attains high activities and productivities. Improvement of the morphology of the polymers, especially increasing of polymer densities as well as the fragmentation process has to be further investigated..

Experimental part

The metallocene used was donated by BASF-AG. MAO (10 wt% in toluene) was obtained from Witco, Germany. All other chemicals were purchased from Aldrich. Styrene and bromo-styrene were distilled prior to use. Hexane, THF and toluene were dried by distillation from sodium/potassium alloy under argon. All experiments were carried out under argon using standard Schlenk techniques. NMR spectra were recorded on a Bruker DPX 250, GPC measurements were performed on a Waters 2000 apparatus at 135 °C (eluent trichlorobenzene, PS standards).

*Tosylation of PEG-monomethylether **2** :*

30ml of 5M NaOH (5.7g of NaOH in 30 ml H_2O) were added to 0.1 tool (31.9ml, 35g) PEG-monomethylether (M_n=350 , Aldrich) dissolved in 25 ml THF. The mixture was stirred and cooled down to 0 °C. 0.09 mol (17.2 g) of TosCl dissolved in 25 ml THF were added dropwise. The reaction mixture was stirred for 3 h. The two phases were separated in a separation funnel. The organic phase was extracted with ether, washed with water and dried with $MgSO_4$ overnight. After filtration ether was removed *in vacuo* Pale yellow oil was obtained - 39 g (87%). (scheme 1 **2**). ^{1}H-NMR ($CDCl_3$, 250 MHz) [ppm]: RO_3-SC(CH)$_2$ 7.77; OCH_2 3.62-3.45; OCH_3 3.34; $ArCH_3$ 2.41

*Polymeric support **3:***

As starting carrier polymer we used a copolymer of styrene and 4-bromostyrene (1:1). Mixture of 39 mmol styrene (4.1 g, 4.5 ml) , 39 mmol of 4-bromostyrene (7.2 g, 5.2 ml) , AIBN (0.05 g, 0. 3mmol) and toluene (10 ml) were degassed by several pump-thaw cycles and heated at 70 °C for 24 h. After cooling to room temperature, 20 ml dichloromethane were added and the mixture was precipitated in 1L methanol. The polymer was filtrated off, dissolved in 50 ml dichloromethane and precipitated from 500 ml methanol. After drying in vacuum oven at 60 °C overnight, the polymer was ready for use (8.78 g, 78%) (scheme 2 **3**).^{1}H-NMR ($CDCl_3$, 250 MHz) [ppm] : CHPh 7.6-6.85; 6.85-6.0 ; CH_2CH 2.3-1.55; 1.55-0.95, M_w = 50 000 g/mol, PDI = 1.8.

The copolymer- polystyrene- co- 4-bromo-styrene (2 g, 6.88 mmol Br-units) was dissolved in 200 ml dry THF and the solution was cooled to -78° . 1.5 eq of tert-BuLi (8.5 mmol, 5 ml of 1.7M solution in pentane) were added. After stirring for 10min , 0.2 eq (1.37 mmol, 0.15 ml) acetone and 0.4 eq (2.75 mmol, 0.58 ml) dimethylfulvene were added. The mixture was stirred for another 10 min and 0.2 eq (1.37 mmol, 0.91ml) Tos-PEG-monomethylether were added. After 1 h the mixture was allowed to warm to room temperature and was precipitated in 2 L hexane. The polymer was filtered, dissolved in 100 ml chloroform and precipitated in 1 L hexane. After filtering it was dried at room temperature in high vaucum for 48 h. Yield - 2.15 g. ^{1}H-NMR ($CDCl_3$, 250 MHz) [ppm] : OCH_2 3.72-3.65; OCH_3 3.36.

Catalyst preparation

For the crosslinking process, 0.5 g of the support **3** were dissolved in 3 ml of toluene and this solution was heated at 85 °C for 72 h. After cooling the solution to room temperature the appropriate amount of the solution of $Me_2Si(2MeBenzInd)_2ZrCl_2$ **5** in MAO was added. (for typical experiment - 0.15 mmol of the metallocene were dissolved in 30 ml MAO, and 4.5 ml of this solution were added giving Zr concentration of 25 µmol/g and ratio MAO/Zr 300).For the calculation of the molar amount metallocene per gram catalyst, the mass of the support and of the MAO was taken into account. After stirring for 10 min, 50 ml of dry hexane were added. Removing the supernatant solution *via canulla*, and drying in high vacuum over night, yielded the heterogeneous catalyst **7**.

a) Polymerisation of propene:

The reactor (1L Büchi stainless steel, equipped with stirrer) was purged with argon and charged with 400 ml hexane and 5 ml TIBA. A propene pressure of 5 bar was applied and the reactor heated up to 50 °C. The catalyst was set in the pressure lock and activated there with MAO solution. The addition of 1 ml hexane prevented agglomeration of the carrier polymer. After 10 min. the catalyst was injected with argon into the reactor.

b) Polymerisation of ethene

The reactor (1 L Büchi stainless steel, equipped with stirrer) was purged with argon and charged with 400 ml isobutane and 5 ml TIBA. Ethene 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.

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