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Immobilization of Metallocenes through Noncovalent Bonding via MAO to a Reversibly Cross-Linked Polystyrene

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ABSTRACT: A novel catalyst system is presented on the basis of a reversibly cross-linked polystyrene support bearing nucleophilic functionalities such as ether bridges. The metallocene is bound noncovalently to the supporting polymer, avoiding a polymer analogous metallocene synthesis. A reversible cross-linking allows the fragmentation of the support during the polymerization process. Propene polymerization with supported $Me_2Si(2\text{-}MeBenzInd)_2ZrCl_2$ yields spherical polypropene beads with a diameter of about 1 mm, high melting points, high molecular weights, and narrow weight distributions. The properties, especially the tacticity, are similar to homogeneously polymerized propene, and the productivities of up to 8000 kg PP/(mol Zr h bar) are comparably high.

Introduction

Metallocenes have opened the way to produce polyolefins with well-defined properties. They allow one, for example, to control tacticity and to incorporate discrete ratios of comonomers. A common feature of all polymerizations catalyzed by soluble metallocenes is their homogeneous nature, which comes with some disadvantages. In particular, the production of the polymer in the form of dust or lumps makes homogeneous olefin polymerization unattractive for industrial processes. Therefore, for industrial applications, the immobilization of metallocenes on solid carriers is necessary.[1,2]

This immobilization results in product beads instead of a fine powder, making the product easier to handle. Additionally, the use of a supporting material is the only way to run a metallocene polymerization without solvent in a gas-phase reactor. Usually, zirconocene catalysts are supported on silica, but other inorganic compounds such as Al_2O_3 or $MgCl_2$ have also been used. Silica contains numerous acidic hydroxy groups on its surface. These have to be deactivated with trimethylaluminum (TMA) or methylaluminoxane (MAO) before the silica can be combined with the metallocene in order to prevent a reaction between them and the metal center, which would have a markedly negative influence on the catalyst activity as well as on the polymer properties.[3]

Investigations into the relationship between catalyst support and product morphology by Fink and co-workers on silica supported metallocenes[4,5] showed that carrier fragmentation has a major influence on the polymerization process and the activity of the catalyst. Furthermore, fragmentation of the support and a homogeneous distribution of the support fragments throughout the polyolefin are prerequisites for a uniform product.

Some organic supports have also been reported in the literature. Numerous materials have been studied,[6,7] mostly based on functionalized polystyrene/divinylbenzene resins with various content of cross-linking densities.[8−11] In contrast to the rigid surfaces of inorganic supports, hydrocarbon-based support materials provide a much closer analogue to the environment prevailing in homogeneous polymerization.[8,11,12] Drawbacks of the divinylbenzene−cross-linked resins as supports are that the synthesis occurs on a more or less insoluble support and a hindered carrier fragmentation during the polymerization process due to the irreversible cross-linking.

Recently, we reported a novel method of supporting bis(cyclopentadiene)zirconium dichloride on a reversibly cross-linked polystyrene.[13] The use of cyclopentadienyl-functionalized polystyrene as a support yielded a catalyst system for the polymerization of ethene which showed high activities. It provides a simple way to immobilize zirconocenes and obtain polyethene particles with desirable morphology. The reversible cross-linking of this catalyst system facilitates carrier fragmentation and distribution during polymerization and subsequent processing. Additionally, a polystyrene support should be more evenly incorporated into the polyolefin than inorganic particles are. This could lead to an improvement in the properties of the product, especially in its transparency. This catalyst system has shown good results in ethene polymerization, resulting in high-density polyethene. However, this method is restricted only to a few types of metallocenes which can be easily synthesized in a polymer analogous fashion.

The polymerization of propene requires more sophisticated catalyst systems. Tacticity control, for example, is provided by chiral metallocenes. The polymer analogous synthesis of such systems in high diastereomeric purity is very complicated. Some bridged systems have been reported in the literature, which have been synthesized on a polymer carrier,[8,9,14] but none of them seems to be a single site catalyst.

Here we present a novel approach based on our reversibly cross-linked resin. To coordinate metallocenes, which have been syntheszed separately, nucleophilic groups for binding them noncovalently are introduced into the polymeric support. As for the silica/metallocene catalysts, the complex is synthesized and

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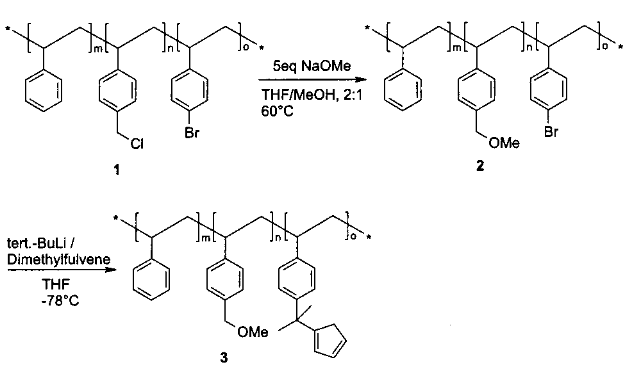

Figure 1. Synthesis of the support. All modifications are done in a homogeneous polymer solution.

purified separately and then combined with the support, allowing the use of a wide spectrum of metallocenes, with a range of stereospecifities as well as activities.

Results and Discussion

Synthesis of the Support. Polystyrene was chosen as a supporting polymer because of its low cost, good solubility, and flexibility in functionalization. Compared to our previous catalyst system, nucleophilic groups have to be introduced in addition to the cross-linking cyclopentadiene functionalities. Our experiments with non-cross-linked polymers gave only dustlike products, similar to those obtained from homogeneous polymerizations. [We synthesized the support polymer as described below but without the cross-linking groups and ran the propene polymerization. The activity was slightly higher than the activity of the cross-linked catalysts, but not as high as for the homogeneous runs. The product was obtained as a fine powder.] As coordinating groups we introduced Lewis basic methylmethoxy functions, which can coordinate to the MAO/metallocene species. They are not acidic; therefore, the pretreatment of the carrier with TMA or MAO is not necessary.

As modifying steps are easier on a soluble polymer than on an insoluble support, cross-linking should be the last step of the synthesis. Therefore, we did not use divinylbenzene, but cyclopentadiene groups. Cross-linking is achieved via a Diels–Alder reaction just before the metallocene is brought into contact with the support.

For introducing cyclopentadienyl and methoxy groups into the carrier polymer, two synthetic pathways are possible. Initially, our starting material was a styrene/4-chloromethylstyrene copolymer (70/30 mol %).[13] The functionalization could be done by partial etherification with sodium methoxide in a mixture of THF and methanol and a subsequent reaction of the remaining chloromethyl groups with sodium cyclopentadienyl.[13]

More favorable is starting with a terpolymer (**1**) of 4-bromostyrene, 4-chloromethylstyrene, and styrene. After the complete etherification of the 4-chloromethyl units the cyclopentadienyl functionalities are introduced via the 4-bromophenyl groups. Typically, 1 g of the copolymer **1** is heated in 100 mL of THF and 50 mL of methanol together with 10 equiv of sodium methoxide overnight, yielding **2** (Figure 1). After workup (precipitation and drying) polymer **2** is reacted with *tert*-butyllithium and dimethylfulvene. The reaction is complete after 1 h, providing an easier and faster access to the carrier polymer **3**. Additionally, the synthesis via dimethylfulvene has another advantage; unwanted cross-linking during the synthesis at room temperature is hindered by the more bulky substituent on the cyclopentadiene ring.

The reversibly cross-linkable polystyrene support (**3**) bearing nucleophilic groups is suitable to form noncovalent bonds with the MAO/metallocene complex. The cross-linking to a heterogeneous resin **4** is achieved by heating a 5% solution of polymer **3** in toluene to 85 °C overnight. The solution becomes viscous and can be treated directly with the metallocene solution. In this way, one obtains a homogeneous distribution of the metallocene on the support. DSC measurements before and after cross-linking showed an increase of the glass transition temperature from 95 to 110 °C.

Supporting the Zirconocene. For experiments on the catalyst supporting we used $Me_2Si(2\text{-}MeBenzInd)_2ZrCl_2$ (**5**), donated by BASF-AG. A solution of metallocene **5** ($c(Zr) = 5$ μmol/mL) in MAO solution (10 wt %) was added rapidly via a syringe to the cross-linked polymer support **4** in toluene, which immediately forms a gel. We assume that this is due to the interaction of the Lewis basic groups with the MAO present in the metallocene solution. The MAO seems to play the key role in the bonding process, with the methoxy groups coordinating to MAO which forms cagelike structures around the metallocene molecules. Supporting experiments in the absence of MAO failed. [The metallocene was dissolved in a solution of TIBA in toluene ($c(Al) =$ 1 mol/L) and added to the cross-linked supports. The polymer precipitated on the addition of hexane and was almost colorless. Polymerization attempts with this system after activation with MAO yielded no polyolefin, while the supernatant solution showed high activity. Obviously the metallocene was not bound to the carrier.]

After further stirring for 10 min, the precipitation is completed by addition of hexane. Stirring for 10 min, removal of the supernatant nearly colorless hexane solution via cannula, washing with additional hexane, and drying of the remaining solid in vacuo yields the polymer supported metallocene **6** ready for use (Figure 2). A homogeneous polymerization with the supernatant solution gave less than 10% of the polyolefin obtained from the complete metallocene solution, indicating that the metallocene is almost totally bound to the support.

Variations of the metallocene concentration in the MAO soultion showed that there is an optimum around 5 μmol/mL. At lower concentrations, which correspond to a higher metallocene/MAO ratio, more metallocene remains in solution. We assume that is this case more Lewis basic groups on the support are occupied by MAO, which is not coordinated to a metallocene molecule.

Polymerizations. Polymerizations were carried out in a 1 L stainless steel autoclave in hexane at 50 °C and at a propene pressure of 4 bar. Triisobutylaluminum (TIBA) was used to remove impurities. The catalyst was activated with MAO for 15 min before it was transferred into the reactor. Polymerizations without MAO activation showed only very low activities. The amount of MAO on the support does not seem to be high enough for a complete activation of the metallocene. Polymerization conditions and the resulting activities are given in Table 1.

The activities of the heterogeneous runs with values between 4000 and 8000 kg PP/(mol Zr h bar) are very high in comparison with other polymer supported systems.[8,9,14] They are in the range of the activities of silica supported **5** used for polymerization in hexane.[16] We have evidence that the cyclopentadiene does not

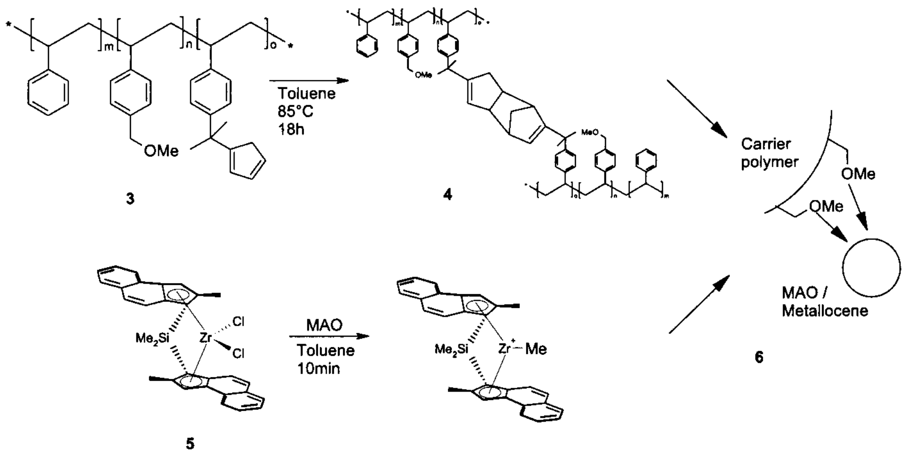

Figure 2. Supporting process. The cross-linked support polymer is combined with the metallocene in MAO solution.

Table 1. Polymerizations[a]

run	Zr/cat. [μmol/g]	catalyst [mg]	MAO/Zr	temp [°C]	yield [g]	activity [kg PP/(mol Zr h bar)]	productivity [g PP/(g cat h bar)]
1	44	60	840	50	43.7	8100	360
2	44	60	400	50	30.1	5400	240
3	44	60	300	50	18.8	3700	160
4	44	60		50	0.7	130	6
5	17	55	1800	50	13.6	7400	130
6	27	25	2400	50	5.4	4000	110
7	44	70	730	60	49.7	8200	360
8	44	36	1000	40	11.7	7900	350
9			500	50	44.0	22000	
10	44	60	400	50	14.5	2700	120

[a] 400 mL of hexane, 4 bar of propene, 30 min, run 4 without additional MAO activation, run 9 homogeneous with 1 μmol of metallocene, run 10 on a carrier containing 7% divinylbenzene, 30% methylmethoxystyrene, and 53% styrene.

interact with the metallocenes during the polymerization, as experiments with different amounts of cyclopentadiene on the support have shown no influence on the catalytic activity.

Morphology. The polypropene is produced in spherical beads of about 1 mm (Figure 3). All the product particles have a similar morphology with a bulk density around 180–200 g/L. The sizes correlate with the productivities of the catalysts as more productive catalysts produce larger particles. Products from polystyrene/divinylbenzene[11] supported metallocenes have a higher bulk density (around 250 g/L and above), but the productivities of such rigid systems are lower than for a fragmentable carrier.[8,10] Figure 3 shows visual microscopy images of the polypropene. The rough surface of the particles might be due to the higher mobility of the polymeric carrier during the polymerization.

Transparent films show inhomogenities, if they are made from polypropene containing unfragmented carrier particles. To get an idea of the distribution of our support in the product polymer, we prepared transparent films in a heated press at 160 °C and 20 kPa. About 100 mg of polypropene was heated for 10 min before the pressure was applied for 1 min. After that the sample was cooled rapidly by putting it into cold water. As one expects from a highly isotactic polypropene, the films were not totally clear due to the formation of crystallites but looked equal to those prepared from homogeneously produced polypropene. This shows that the carrier fragments are small enough not to form any scattering centers or other visible impurities in the films. For comparison, in a film made from the polypropene from run 10 (divinylbenzene cross-linked support) inhomogeneities were clearly visible. The fragmentation of the support can also be proven by confocal fluorescence microscopy and the incorporation of dyes into the carrier.[15] This is subject of a different work which will be published soon.

Microstructure. Supporting a chiral metallocene on a rigid surface has influence on the metallocene's stereo- and regioselectivity. For the polymerization of propene with a silica supported **5** in hexane at 40 °C in the presence of TIBA, melting points around 145 °C for the product have been found.[16] With these systems the product's melting points increase with increasing polymerization temperature. This trend is contrary to that seen with homogeneous polymerization.[16] Our polymer supported system produces in a temperature range between 40 and 60 °C polypropene with a melting point between 152 and 147 °C, with a higher value at lower polymerization temperatures, similar to homogeneous polymerizations (Table 2).

The tacticity was investigated by ^{13}C NMR spectroscopy according to the methods described by Ewen[17] and Hayashi.[18] We observed only resonances for [mmmm] and [mmmr] pentads, with a [mmmm] fraction of 94%, in accordance with the high melting points determined via DSC.

We assume that due to the noncovalent bond between the carrier and the MAO/metallocene, the complex is only loosely bound. Additionally, the support as well as the metallocene is relatively mobile, compared with inorganic carriers, making the polymerization more homogeneous-like. These might be reasons why the support has only minor effects on the stereocontrol of the metallocenes and why the melting points of the products decrease with increasing polymerization temperature as they do in homogeneous polymerization.

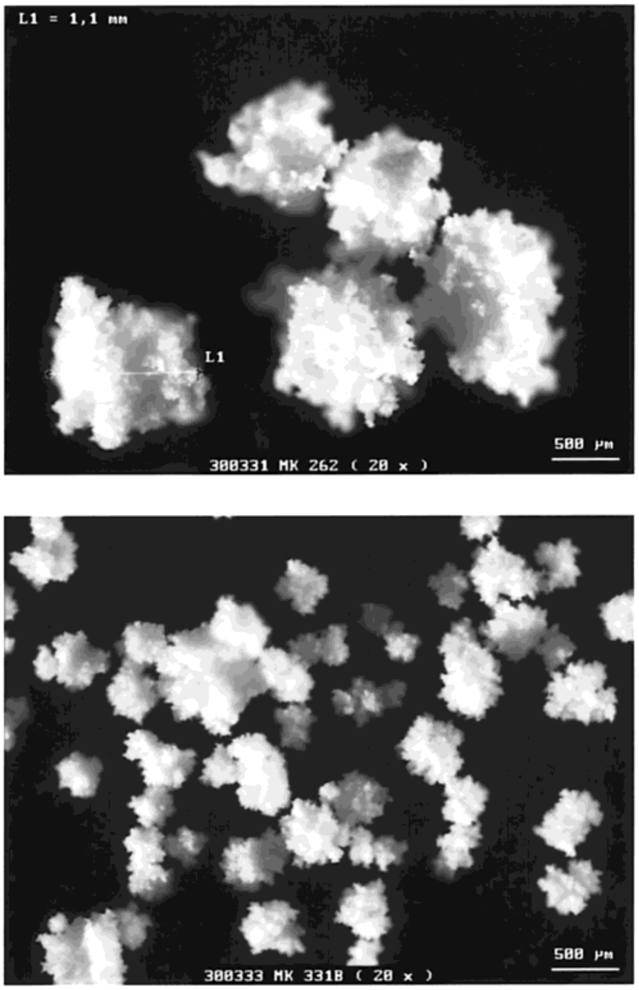

Figure 3. Visual microscopy images of product particles from run 1 (top) and 3 (bottom).

Table 2. Melting Points, Molecular Weights, and Weight Distributions of the Polypropene Products

run	T_m [°C]	M_n	M_w	PDI
1	150.4	255 000	453 000	1.77
2	151.0	273 000	464 000	1.70
3	150.9	220 000	434 000	1.98
5	150.4	255 000	453 000	1.77
6	151.0	232 000	412 000	1.77
7	148.8	201 000	342 000	1.70
8	153.4	253 000	493 000	1.94
9	150.4	284 000	469 000	1.65

The molecular weights and the polydispersities of the polypropene produced by the polymer-supported metallocene are also similar to values obtained from homogeneous polymerizations, while silica supported **5** yields polypropene with lower molecular weight and higher polydispersity.[16]

Conclusion

The metallocenes are to be attached via an interaction of MAO and oxygen-containing polymers. Advantages of this process are a separate metallocene synthesis and no need of any carrier pretratment with TMA or MAO.

The synthetic route to the polymer supported catalyst system is easy and straightforward. All reactions on the polymer are done before cross-linking and therefore on a perfectly soluble support. The cross-linking is the final step of the carrier syntheses. The support allows a fast and simple immobilization, as a deactivation is not necessary. The MAO/metallocene solution and the carrier can be joined together directly. With a methoxymethyl content of the polymer of 20% or above, MAO/**5** is bound almost completely to the support polymer in a noncovalent manner. It should be possible to use **3** for the immobilization of various metallocenes.

However, the particle morphology is typical of a heterogeneous catalyst system, and no dustlike polymer is produced; the properties of the polypropene produced, especially the high molecular weights and the narrow molecular weight distributions, are similar to those of the homogeneous run, but in a heterogeneous system. These are advantages over silica supported systems that might result from the higher carrier and metallocene mobility. Investigations on this topic as well as the fragmentation process and improvement of the product morphology will be part of our future work.

Experimental Part

The zirconocene was donated by BASF-AG. MAO (10 wt % in toluene) was obtained from Witco, Germany. All other chemicals were purchased from Aldrich Chem. Corp. Styrene and its derivatives were distilled prior to use. Hexane, THF, and toluene were dried by distillation from sodium/potassium alloy. Methanol was dried by addition of sodium and subsequent distillation. All experiments were carried out under argon using standard Schlenk techniques. NMR spectra were obtained on a Bruker DPX 250; GPC was measured on a Waters 2000 at 135 °C in 1,2-dichlorobenzene with calibration by a PS standard.

Polymeric Support. 5.2 g (50 mmol) of styrene, 3.66 g (20 mmol) of 4-bromostyrene, 4.58 g (30 mmol) of 4-chloromethylstyrene, and 75 mg of azoisobutyronitrile in 15 mL of toluene were degassed by several freeze–pump–thaw cycles and heated to 70 °C for 24 h. The solution was diluted with 200 mL of dichloromethane, and the product precipitated with 2 L of methanol. Polymer **1** was dried in vacuo at 60 °C overnight. Yield: 9.7 g (72%). ^{1}H NMR ($CDCl_3$, 250 MHz) [ppm]: $PhCH_2Cl$ 4.43, $M_w = 40\ 000$ g/mol, PDI = 1.9.

The divinylbenzene cross-linked support was prepared in the same way from 5.5 g (53 mmol) of styrene, 4.58 g (30 mmol) of 4-chloromethylstyrene, and 0.91 g (7 mmol) of divinylbenzene.

The etherification was conducted by dissolving 5 g of **1** (11 mmol of 4-chloromethylstyrene) in a mixture of 250 mL of THF and 125 mL of methanol. After the addition of 5.9 g (110 mmol, 10 equiv) of sodium methanolate the mixture was heated to 60 °C overnight. Removal of the solvents in a rotary evaporator, dissolution of the residue in 100 mL of dichloromethane, filtration, and precipitation with 1 L of methanol yielded poly(4-bromostyrene-*co*-4-methoxystyrene-*co*-styrene) (**2**) (4.2 g). ^{1}H NMR ($CDCl_3$, 250 MHz) [ppm]: $PhCH_2OMe$ 4.35, OCH_3 3.32.

The divinylbenzene cross-linked support was handled in the same way.

To introduce the cyclopentadienyl functions, 2.5 g of **2** (3.8 mmol of 4-bromostyrene) was dissolved in 250 mL of THF and cooled to −78 °C. The addition of 4.47 mL (7.6 mmol, 2 equiv) of *tert*-butyllithium (1.7 M in pentane) via a syringe precipitated the polymer. The mixture is stirred for 10 min, and 730 mg (4.56 mmol, 1.2 equiv) of dimethylfulvene was added. After stirring for an additional 10 min at −78 °C, the mixture was allowed to warm to room temperature. The solubility of the polymer increases due to the reaction of the anions with the dimethylfulvene. After 30 min the product was precipitated with 2 L of methanol, redissolved in 50 mL of dichloromethane, and precipitated again with 500 mL of methanol. Drying in high vacuum at room temperature yielded the carrier polymer **3** (1.7 g).

Catalyst Preparation. To yield a cross-linked support, a solution of 1 g of **3** in 20 mL of toluene was heated to 85 °C overnight and then allowed to cool to room temperature. 110.4 mg (0.2 mmol) of $Me_2Si(2\text{-}MeBenzInd)_2Zr_2Cl_2$ was dissolved in 40 mL of MAO solution ($c = 1.6$ mol/L), giving a metallocene concentration of 5 μmol/L and a MAO content of 87.5 mg/mL. The desired amount of this metallocene solution was added to the polymer via a syringe and stirred for 30 min. The support polymer immediately began to precipitate together with the MAO/metallocene. [For the calculation of the molar amount metallocene per gram catalyst, the mass of the support and of the MAO was taken into account.] The precipitation was completed by pouring the mixture into 250 mL of hexane. Removal of the supernatant solution via cannula, washing of the residue with an additional 100 mL of hexane, and drying in high vacuum yielded the heterogeneous catalyst.

Polymerizations. The reactor (1 L Büch stainless steel) was purged with argon and charged with 400 mL of hexane and 2 mL of TIBA. A propene pressure of 4 bar was applied, and the reactor was heated to 50 °C. The catalyst was activated with MAO solution. The addition of 1 mL of hexane prevented agglomeration of the carrier polymer. After 15 min the catalyst was injected with argon into the reactor through a pressure lock. The polymerization was terminated by releasing the pressure and adding methanol.

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