Different Surface-Substituted Polyorganosiloxane Microgels as Support Materials for MAO-Type Cocatalysts

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ABSTRACT: Twenty-five different functionalized and nonfunctionalized polyorganosiloxane microgels were applied as support materials for methylalumoxane (MAO)-type compounds to give various heterogeneous cocatalysts which are able to activate metallocene complexes like Cp_2ZrCl_2 for ethene polymerization. The functionalization of the microgels has a strong influence on the properties of the catalysts and the produced polyethenes. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 281–285, 2001

Key words: polyorganosiloxane microgels; metallocene catalysts; support; heterogeneous polymerization; polyethene

INTRODUCTION

Metallocene complexes with group 4 metals are very attractive catalysts for olefin polymerization (refs. 1–10, and references therein). Unfortunately, one major problem for industrial application is the so-called reactor-fouling that occurs under homogeneous polymerization conditions when the formed polymer is deposited on the reactor walls. To prevent this process, heterogenization of the catalyst on a support material is necessary. Here, microgels are introduced as suitable support materials for cocatalysts on the basis of methylalumoxane (MAO).[11–13]

Microgels are strictly spherical monodisperse organosilicone micronetworks.[14] Their average molar mass weight, $\bar{M}_w$, ranges between 1×10^6 and 10×10^6 g/mol with a very low polydispersity of 1.05–1.50.

The determination of the surface after the B.E.T.* method[15] yields $300-400$ m²/g. The diameter of a particle is between 15 and 30 nm; thus, microgels are about 100 times smaller than are conventional silica particles. The synthesis of microgels with functional groups was described earlier.[14,16]

Here, the influence of differently substituted microgels as support material for cocatalysts on the basis of MAO for ethene polymerization was investigated. Zirconocene dichloride, Cp_2ZrCl_2, was chosen as a "model metallocene." The productivities of the resulting heterogeneous catalysts and the polymer properties were determined.

RESULTS AND DISCUSSION

Different Available Microgels

The surface of a support material has a decisive influence on the polymerization properties of the

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* Brunauer, Emmett, Teller.

Table I   Heterogeneous Polymerization of Ethene with Cp_2ZrCl_2 and Variously Functionalized Microgel-supported Alumoxane Cocatalysts

No.	Functionality of the Microgel[a]	Surface OH Groups[b]	Activity in $g(PE)/g(Zr)\ h^{-1}$
01	H-	Low	11,620
02	3-Chloropropyl-	None	32,740
03	ω-Hexenyl-	None	42,340
04	Phenyl-	None	22,690
05	Methyl-	None	76,200
06	n-Octyl-	None	3910
07	Dodecyl-	None	46,670
08	3-Chloropropyl-	None	28,000
09	n-Octyl-	Low	38,300
10	3-Phenylpropyl	Low	42,500
11	n-Octyl-	High	4400
12	n-Octyl-	Low	15,500
13	n-Octyl-	None	25,200
14	3-Chloropropyl-	High	1640
15	3-Chloropropyl-	None	960
16	Dodecyl-	Low	54,300
17	Octadecyl-	Low	64,400
18	3-Phenylpropyl	High	25,000
19	3-Phenylpropyl	Low	53,650
20	Phenyl-	High	8500
21	Phenyl-	Low	39,100
22	2-(p-Chlorophenyl)propyl-	High	26,500
23	2-(p-Chlorophenyl)propyl-	Low	21,500
24	1,1,1-Trifluoropropyl-	High	35,200
25	1,1,1-Trifluoropropyl-	Low	12,500

[a] Functional groups bound to silicon atoms.
[b] Relative content of OH groups; not quantified; fully endcapped: no OH groups; partly endcapped: low amount of OH groups; not endcapped: high amount of OH groups on the particle surface.

formed catalyst system.[16–20] Therefore, support materials with easily variable surface structures are desirable. Microgels represent a new support material that can be designed in a controlled manner. Unfortunately, the amount of surface hydroxyl groups can only be estimated.

Different functionalized and nonfunctionalized microgels were supplied by Wacker–Chemie GmbH (Burghausen, Germany). Methods for the surface substitution were described elsewhere.[14,16] Table I shows a selection of functionalized microgels. Depending on the used synthesis, a variable amount of surface hydroxyl groups is available. These particles were tested as support material for MAO-type cocatalysts to obtain a universal heterogeneous cocatalyst.
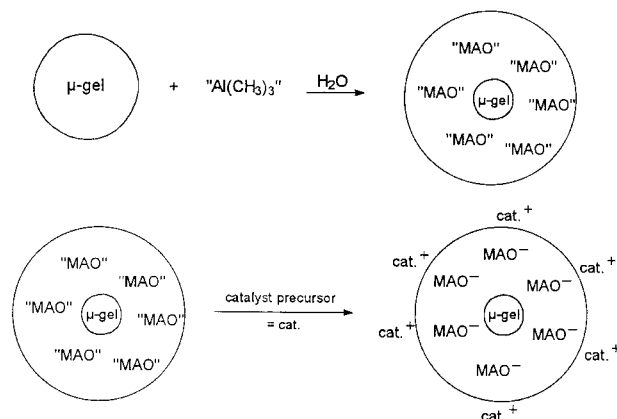
Synthesis of the Catalyst System

Microgels were redispersed in toluene and treated with trimethylaluminum (TMA). Then, a certain amount of water was added. This addition can be accomplished via different methods (see below). The cocatalyst is formed and immediately fixed on the support material. The catalyst precursor Cp_2ZrCl_2 was added and heterogenized and activated in one step (Scheme 1). After drying *in vacuo,* the heterogeneous catalyst can be used directly for olefin polymerization in a slurry polymerization process.

Hydrolysis of Trimethylaluminum

Trimethylaluminum is a highly reactive, air- and moisture-sensitive pyrophoric compound. The partial hydrolysis must be done carefully. Therefore, different methods have been developed (see Experimental part):

- Partial hydrolysis under intense cooling (method 1)
- Controlled partial hydrolysis under inverse conditions (method 2)
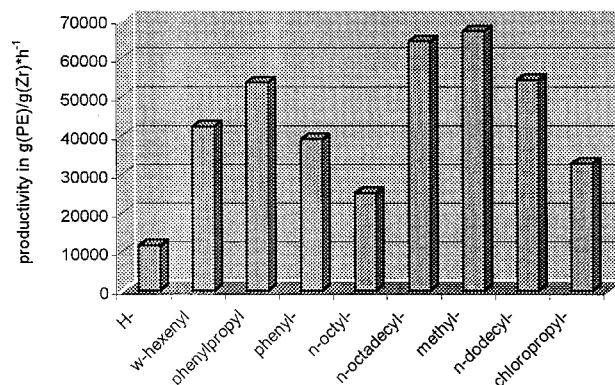
Scheme 1 Synthesis of the catalyst (model).

• Partial hydrolysis with a water-saturated argon stream (method 3).

Influence of Different Surface-Substituted Microgels on Productivity

Different surface-substituted microgels were used as a support for MAO. The catalyst was prepared according to method 1. The influence of the different functional groups becomes obvious in Figure 1. A selection of investigated microgels is shown in Table I.

Dependence of TMA-Hydrolyzation Method on Polymerization Productivity

Figure 2 shows that method 1 allows the preparation of a highly active catalyst. The disadvantage is a comparatively long reaction time. In comparison, method 2 is less time-consuming but gives a catalyst with the lowest productivity. The

best method is procedure 3, which has the advantage of a short reaction time, and it delivers a highly active catalyst.

Influence of Different Substituted Microgels on Polymer Properties

As shown before (see section Different Available Microgels), the different functionalities at the microgels influence the productivity of the catalysts and can have a strong impact on the polymer properties. The obtained polyethenes were investigated by high-temperature GPC and DSC. The data are listed in Table II.

The molecular weights, $\bar{M}_w$ (300,000–1,800,000 g/mol) and $\bar{M}_n$ (156,000–281,000 g/mol), show a monomodal distribution and comparatively low polydispersity of 2.16–9.55. The polymer samples have melting points between 131.2 and 151.2°C. The degree of crystallinity was calculated after the measured fusion enthalpies. The crystallinities range between 46.2 and 55.2%.
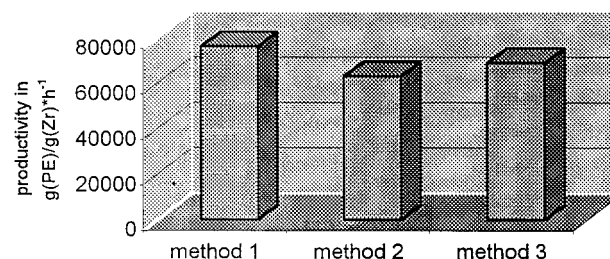
These data show that it is possible to influence polymer properties by using differently substituted microgels. It can be expected that other functional groups on the microgel surface give unprecedented results with regard to the productivity and polymer properties.

EXPERIMENTAL

All experiments were performed under an argon atmosphere using a standard Schlenk technique. A BTS catalyst and molecular sieves were used for purification. All solvents were purchased as technical grade and purified by distillation over a Na/K alloy under an argon atmosphere.

Polymerization of Ethene

Polymerization of ethene was conducted in a 1 L Büchi steel reactor equipped with a mechanical

Figure 1 Productivities of heterogeneous catalysts consisting of different surface substituted microgels, MAO, and Cp_2ZrCl_2.

Figure 2 Polymerization productivities of different methods. Methyl microgel as support material for the combination Cp_2ZrCl_2/MAO.

Table II   Polyethene Data Obtained from Differently Functionalized Microgels as Support Material for MAO and Cp$_2$ZrCl$_2$ as Catalyst Precursor

No.	Microgel Functions	$\bar{M}_w$ (g/mol)	Polydispersity	T_{melt} (°C)	$T_{cryst.}$ (°C)	$\Delta H_{cryst.}$ (J/g)	Crystallinity α (%)
1	H-	499,200	3.20	151.2	102.4	154.4	52.7
2	Chloropropyl-	621,100	3.04	137.2	108.9	138.4	47.3
3	ω-Hexenyl-	884,100	3.86	141.0	107.1	144.3	49.3
4	Phenyl-	686,400	2.95	137.3	110.4	155.0	52.9
5	Methyl-	535,200	2.53	131.2	105.2	141.2	48.2
6	Octyl-	558,900	2.81	140.0	107.6	160.2	54.7
7	Dodecyl-	1,802,000	9.55	138.3	108.7	140.7	48.0
8	Octyl-	688,000	2.82	139.8	107.0	145.0	49.5
9	Chloropropyl-	643,000	2.30	138.2	110.0	140.1	47.8
10	Phenylpropyl-	347,100	2.16	141.3	82.8	142.7	48.7
11	Octyl- high OH	560,600	2.92	142.8	101.7	148.4	50.7
12	Octyl- low OH	697,700	2.68	140.9	106.1	147.0	50.2
13	Octyl- without OH	690,300	2.95	139.1	110.1	146.2	49.9
14	Chloropropyl-	630,000	3.03	138.8	109.0	142.1	48.5
15	Chloropropyl-	655,000	3.15	140.3	109.5	142.9	48.8
16	Dodecyl-	693,900	4.09	140.3	108.3	145.4	49.6
17	Octadecyl-	706,200	2.51	142.0	102.6	135.2	46.2
18	Phenylpropyl-	299,800	1.75	138.4	111.4	166.7	56.9
19	Phenylpropyl-	631,000	2.66	138.7	108.5	149.8	51.1
20	Phenyl-	698,900	3.35	136.0	111.6	143.2	48.9
21	Phenyl-	467,300	2.52	138.2	109.7	161.7	55.2
22	p-Chlorophenylpropyl-	728,600	2.81	139.0	109.4	143.6	49.0
23	p-Chlorophenylpropyl-	655,200	2.83	137.7	92.0	145.5	49.7
24	1,1,1-Trifluoromethyl-	759,300	3.45	137.9	110.0	156.9	53.6
25	1,1,1-Trifluoromethyl-	542,400	2.87	139.4	105.3	148.3	50.6

stirrer at 60°C and 10 bar ethene pressure for 1 h in *n*-pentane. MAO was used as a 30% solution in toluene (from Witco, Bergkamen, Germany). The polymerization was stopped by venting excess ethene. The obtained polymer was washed with HCl/methanol and dried *in vacuo*.

High-temperature Gel Permeation Chromatography

Polymer data were recorded on a Waters HT-GPC 150C instrument. For the separation, four successively connected polystyrene columns were used. The pore diameters of the single columns were 500, 1000, 10,000, and 100,000 Å. For the refractometric detection, an RI Waters 401 refractometer was used. Degassed 1,2,4-trichlorobenzene with a flow rate of 1 mL/min was used as a solvent. Polymer samples were dissolved in boiling 1,2,4-trichlorobenzene. Measurements were performed at 150°C. The HT–GPC was calibrated with polystyrene.

Differential Scanning Calorimetry

The thermal properties of the polymer samples were measured on a NETZSCH DSC 200 instru-

ment. The polymer, 4–6 mg, was dried *in vacuo* and fused in standard aluminum pans (ϕ 5 mm). The following temperature program was used: (1) heating phase, 70–200°C; heating rate, 20 K min^{-1}; isothermic phase, 3 min; cooling phase, 70°C; cooling rate, -20 K min^{-1}; (2) heating phase, 70–200°C; heating rate, 20 K min^{-1}; isothermic phase, 3 min; cooling phase, 20 K min^{-1}. The temperature was linearly corrected relative to indium ($\Delta H_m = 28.45$ J g^{-1}), which was used for calibration. The degree of crystallinity (a) was calculed from the equation $a = \Delta H_m/\Delta H^0$. The parameter ΔH_m and the melting points were derived from the second course of the DSC. The fusion enthalpy $\Delta H°$ was estimated for a 100% crystalline polyethene to 292.9 J g^{-1}.[21]

General Synthesis of the Catalyst System

A microgel, 1.0 g, was dispersed in 100 mL toluene. To the solution, 30 mL of a 1.76M TMA solution in toluene was added. After stirring for 1 h, 0.75 mL of distilled water was added via the different methods as described below. After the

partial hydrolysis of the TMA, the catalyst precursor was added in the desired ratio. The mixture was stirred for additional 30 min until a color change from white to yellow indicated the activation of the catalyst precursor. The mixture was filtered over a frit (P1 filter). After filtration, the obtained solid was washed twice with *n*-pentane and dried *in vacuo* until the weight had stabilized. Yield: 80–95%.

Method 1

The dispersion was cooled to −78°C with an external dry-ice reservoir. The water was added dropwise via a 1-mL syringe. The water droplets froze immediately. The hydrolysis of TMA took place only on the surface of the ice crystals. The mixture was kept in the cooling reservoir until room temperature was reached. The slower the ice melted, the more efficiently was the cocatalyst fixed on the microgel. The catalyst precursor Cp_2ZrCl_2 was activated after the addition to the suspension.

Method 2

To the dispersion of the microgel in toluene, water was added. The mixture was treated with ultrasound until no phase separation was visible. The pretreated milky microgel dispersion was cooled to 0°C and 30 mL of the 1.76M TMA solution (in toluene) was added slowly. After completion of the reaction, Cp_2ZrCl_2 was added to give an activated heterogeneous catalyst.

Method 3

The microgel was dispersed in toluene. In a separate flask, the water was vaporized while a dry argon stream passed both flasks. The water-saturated argon bubbled through the dispersion until all water had evaporated. At a certain point, the dispersion gelated. The formed gel was diluted with toluene and the Cp_2ZrCl_2 was added for activation.

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