

EP(D)M-synthesis with highly active homogeneous and heterogeneous metallocene/MAO-catalysts

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Abstract

Copolymerizations of ethene and propene were carried out either with the soluble catalyst systems dimethylsilylbis(2-methyl-4-phenylindenyl)zirconiumdichloride/methylaluminumoxane (MAO) (1), isopropylidencyclopentadienylfluorenylzirconiumdichloride/MAO (2) and isopropylidene(3-methylcyclopentadienyl)fluorenylzirconiumdichloride/MAO (3) in toluene or with the supported metallocenes (1)/SiO₂, (2)/SiO₂ and (3)/SiO₂ in the gas phase. Furthermore, terpolymerizations of ethene, propene and 5-ethylidene-2-norbornene (ENB) were performed with the homogeneous system (3) and with the heterogeneous system (3)/SiO₂ in the gas phase. The physical and chemical properties of the resulting polymers were compared in order to examine the behavior of the metallocenes when supported. In general, they work in much the same way as their soluble counterparts and the synthesis of EP(D)M co(ter)polymers with the above mentioned metallocenes can easily be transferred to gas phase processes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metallocene; Homogeneous; Heterogeneous; EP(D)M; Methylaluminumoxane

1. Introduction

Metallocene/MAO-catalysts are very efficient tools in producing polyolefins with defined microstructures and narrow molecular weight distributions [1,2]. So far, these catalyst systems have been mainly utilized in solution. For most industrial applications, however, it is more desirable to be able to employ catalysts in gas phase reactions as existing plants do not have to be modified to incorporate new catalyst systems.

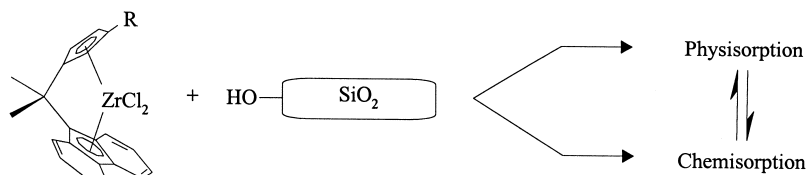
The most common method of applying metallocenes to heterogeneous polymerizations is to support the complexes on an inorganic solid, in most cases silica gel [3–6]. There are four different routes to supported catalysts (Scheme 1):

1. Direct adsorption of the metallocene on the carrier surface leading to physisorption or chemisorption of the metallocene (direct heterogenization).
2. Direct adsorption of the metallocene/MAO adduct on the support.
3. Initial adsorption of MAO to the support followed by adsorption of the metallocene (indirect heterogenization).
4. Covalent bonding of the metallocene by its ligand environment to the carrier followed by activation with external MAO.

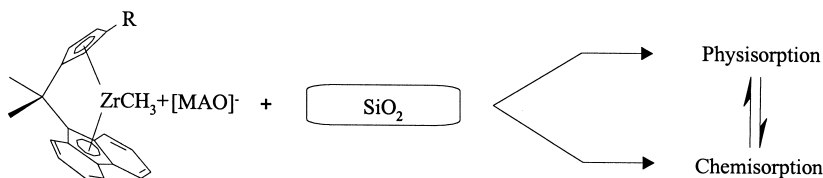
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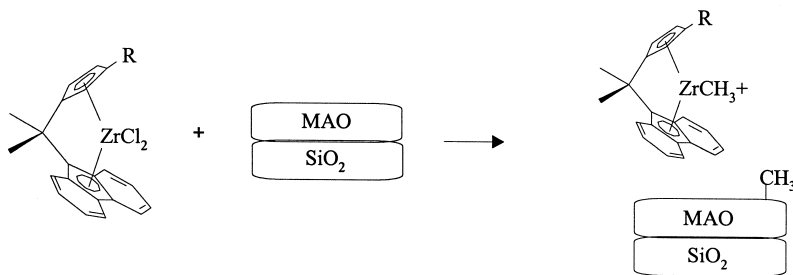
1.) Direct Heterogenization of the Metallocene



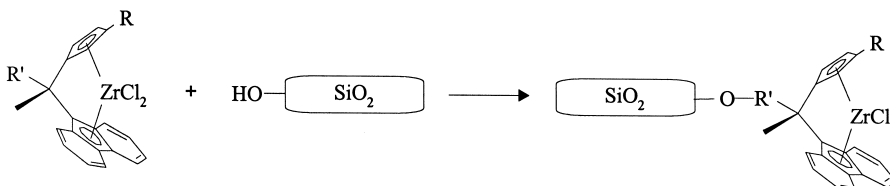
2.) Direct Heterogenization of the Metallocene/MAO-Adduct



3.) Indirect Heterogenization



4.) Covalent Bonding of the Metallocene to the Carrier



Scheme 1.

These supporting procedures can have different effects of varying severity on the polymerization characteristics of the metallocenes. Method 1, for example, can afford polymers with higher molecular weights than those produced by the corresponding homogeneous counterparts [7], but can also (and most likely method 2) change the metallocene structure and, therefore, its stereospecificity due to interaction with surface electron donor groups, such as silanol groups [8,9]. Difficulties can also arise with

method 4: a variant of this procedure is the synthesis of the covalently attached metallocene directly on the surface of the support [10]. However, the anchor groups on which the synthesis takes place are not always chemically uniform (vicinal and geminal silanol groups).

Indirect heterogenization (method 3) is the most promising procedure as the single-site character, the stereospecificity and many other polymerization characteristics of metallocenes are only slightly altered, if at all, by the support

process [3,11]. It is thought that the MAO on the carrier and the metallocene are bound by loose ionic interactions, similar to those encountered in the activation of metallocenes by MAO in solvents.

If metallocenes are to be adapted to heterogeneous polymerization, it is necessary to evaluate the degree and the nature of the changes mentioned above before employing the catalysts on a large scale.

We have investigated the copolymerization of ethene and propene with supported metallocenes and compared the results, i.e. activities (A), incorporation rates ($x_{\text{monomer, polymer}}$), molar masses (M_n), melting points (T_m) and glass transition temperatures (T_g), to those obtained with the appropriate homogeneous catalysts [12]. Furthermore, we have incorporated a third monomer, 5-ethylidene-2-norbornene (ENB), with both heterogeneous and homogeneous catalysts and examined the properties of the resulting EPDM terpolymers. ENB is an important agent in crosslinking ethene/propene copolymers; the resulting terpolymers are in current use in the rubber industry. The systems that are in current technical use today are vanadium-based (VCl_4 , $\text{VOCl}_3/\text{Et}_2\text{AlCl}$) [13]. Although vanadium may not be harmful in the concentrations found in mass polymers, the use of this metal could be of considerable concern to polymers produced for medical applications. Therefore, it is worthwhile to look for catalyst substitutes based on metals, such as zirconium, that are less problematical in a toxicological sense [14–20].

2. Experimental

All procedures were carried out under argon using Schlenk techniques.

2.1. Materials

MAO and MAO/ SiO_2 were purchased from Witco, propene from Gerling, Holz and Co. and

ethene from Linde. The gases were purified by passage through columns with Cu catalyst (BASF R3-11) and a molecular sieve of 10 Å. Toluene was refluxed over Na/K for several days and distilled prior to use. ENB (Aldrich) was dried over triisobutylaluminium (TIBA from Witco) and distilled before use.

Polyethene, kindly supplied by Bayer, and NaCl (Merck) were kept in a drying oven for several days before being used in gas phase polymerizations.

2.2. Polymerizations

2.2.1. In solution

Polymerizations were carried out in a 1 l Büchi type I autoclave equipped with an additional internal cooling system. Monomer feed of the gaseous monomers was maintained with a Peteric 3002 pressflow controller. The reaction was monitored by a Büchi Data System bds 488. For the standard experiment, the reactor was evacuated at 95°C for 1 h and charged subsequently with 400 ml toluene, 800 mg MAO and the required amount of ENB. Ethene and/or propene were added afterwards, so that the total monomer concentration was 1 mol/l. Polymerization was started by addition of toluenic metallocene solution. During the reaction, the total pressure was kept constant by supplying ethene. Polymerization was quenched by injection of 5 ml of ethanol or 5 ml of a saturated solution of 2,6-di-tert-butyl-4-methylphenol in ethanol and the polymer solution was stirred overnight with dilute hydrochloric acid followed by neutralization with NaHCO_3 , washing with water, evaporation of toluene and drying.

2.2.2. In the gas phase

Polymerizations were carried out in a 2 l Büchi type II autoclave equipped with a helical stirrer. Monomer feed of ethene and propene was maintained with a Brooks TR 5850 mass flow controller (500 ml/min) for each monomer; the reaction was controlled and monitored using a Simatic S5 from Siemens.

For the standard experiment, the reactor was filled with 300 ml of pre-dried polyethene (= 120 g) or NaCl (= 380 g) and evacuated at 95°C for 1.5 h while stirring (100 rpm). The reactor bed medium was treated with a toluenic solution of TIBA (0.6 mol/l) 30 min prior to introduction of the supported metallocene. The catalyst was prepared externally: the required amount of metallocene in toluene was injected into a toluenic suspension of MAO/SiO₂ (0.1 g/ml). The resulting suspension was allowed to stir for 10 min and was then introduced into the reactor with a syringe. After introduction of the catalyst, the reactor was evacuated for 10 min while stirring (300 rpm) in order to evaporate the surplus toluene. For terpolymerizations, the required amount of ENB was introduced at this stage via a sleuse apparatus. The reaction was started by quick pressurization (ca. 20 s) of the reactor with the monomer gases and starting the stirrer (200 rpm). During polymerization, the total pressure was kept constant by supplying ethene and propene at fixed flux ratios. The reaction was terminated by depressurization followed by short evacuation of the reactor and finally injection of 5 ml of ethanol or 5 ml of a saturated solution of 2,6-di-tert-butyl-4-methylphenol in ethanol.

The reactor content was suspended in a mixture of toluene and dilute hydrochloric acid and allowed to stir overnight. The suspension was filtered and separated from the additional PE or NaCl. The toluene fraction was washed several times with NaHCO₃ and water; after reducing the volume of the liquid in a rotary evaporator the viscose solution was poured into a large amount of ethanol (ca. 200 ml). The ethanol was separated from the precipitation and the residual polymer was dried in vacuum at 40–60°C.

2.3. Polymer analyses

Molar mass distributions were determined by gel permeation chromatography on a Waters

150-C instrument (trichlorobenzene, 135°C) using a PL-EMD-960 evaporation light scattering detector. Differential scanning calorimetry was performed on a Mettler–Toledo DSC 821e instrument at a heating rate of 20°C/min. The values obtained in the second run are reported. Incorporation rates were determined by NMR spectroscopy on a Bruker 300 MHz NMR instrument; the calculation of incorporation was performed according to methods found in the literature [21]. The NMR samples were prepared by dissolving the polymers (10 wt.%) in a mixture of perchlorobutadiene (PCB) and 1,1,2,2-tetrachloroethane (TCE-d₂); the measurements were carried out at 100°C. M_n was determined with an Ubbelohde capillary; the samples were prepared by dissolving 50 to 150 mg of polymer in 50 ml of decahydronaphthalene and measured at 135°C. The Mark–Houwink constants were taken from the literature [22,23].

3. Results and discussion

3.1. Copolymerization of ethene and propene

An important aspect of co- and terpolymerization is obviously the incorporation rate of monomers. The amount of ethene/propene in the copolymer has a strong effect on the glass transition temperature and melting point of the material, for example. The copolymerization diagrams (Figs. 1 and 2a,b) of the homogeneous catalysts (1), (2) and (3) demonstrate that, in general, the incorporation of propene (x_p) is less preferred for all mol fractions of propene in the feed (X_p). The supported metallocenes (1)/SiO₂, (2)/SiO₂ and (3)/SiO₂ behave differently for $X_p < 0.5$: the extent of the introduction of propene into the copolymer is larger than that of copolymers produced with the homogeneous catalysts and even reaches the diagonal of the diagram, indicating that in this range of X_p there seems to be no incorporation preference of one of the monomers. For $X_p > 0.5$, the copoly-

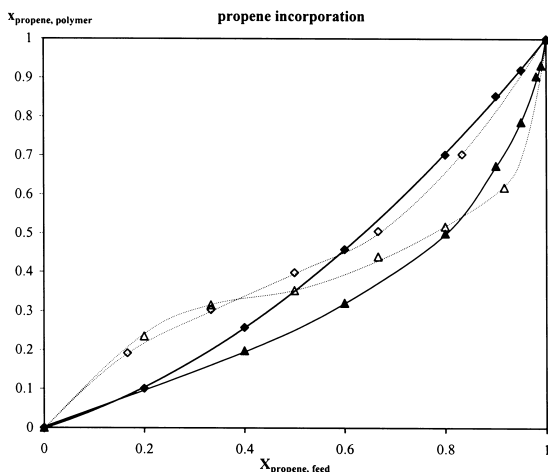


Fig. 1. Incorporation of propene dependent on the feed rate of propene using (1) = \blacklozenge , (2) = \blacktriangle , (1)/SiO₂ = \square and (2)/SiO₂ = \triangle .

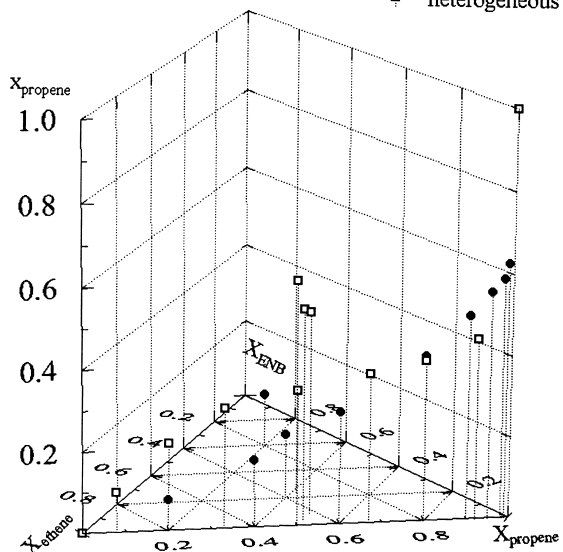
merization diagrams of both supported and soluble catalysts gradually merge.

This slight change in the copolymerization diagrams of (1)/SiO₂, (2)/SiO₂ and (3)/SiO₂ may be due to the deviation of the theoretical monomer concentration in the gas phase (calculated using the ideal gas law) and the true local monomer concentration on the support. Assuming the adsorption of propene onto the MAO/SiO₂-carrier is greater than that of ethene, then the value for X_p for the support surface would be higher than \bar{X}_p for the gas phase. This would result in a copolymer having a higher x_p value than would be expected for the corresponding X_p of the gas mixture. At higher X_p values this effect would probably not be noticeable.

As mentioned above, the incorporation rate of propene is closely connected to melting points and glass transition temperatures. Looking at the physical properties of the copolymers produced by (1), (2) and (3) (Tables 1–3), the main effect of the introduction of the comonomer is to gradually reduce the T_m of the corresponding homopolymers and, finally, to change the copolymer into an amorphous material. T_g reaches a minimum detected value of $\sim -60^\circ\text{C}$ at x_p values between 0.4 and 0.5. A similar

effect is found for the heterogeneous systems (1)/SiO₂, (2)/SiO₂ and (3)/SiO₂. A difference can be found in the x_p range of the minimum T_g . The copolymers with the lowest T_g (-60°C) have propene contents of around 25

(a) \bullet homogeneous
 \square heterogeneous



(b) \bullet homogeneous
 \square heterogeneous

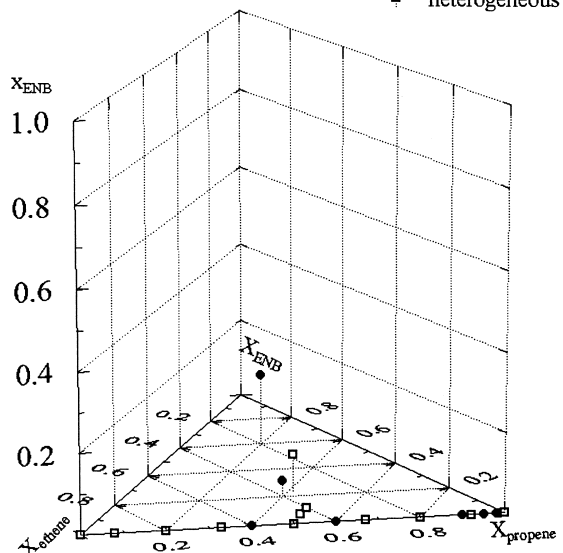


Fig. 2. (a) Incorporation of propene dependent on feed rate using (3) = \bullet and (3)/SiO₂ = \square ; (b) incorporation of ENB dependent on feed rate using (3) = \bullet and (3)/SiO₂ = \square .

Table. 1

EPM polymerizations with (1) and (1)/SiO₂

a = amorphous, n.d. = not detected, pm = polymer, mon = monomer.

Catalyst	$X_{\text{propene, feed}}$	$x_{\text{propene, polymer}}$	Activity [kg _{pm} /(mol _{Zr} h mol _{mon} /l)]	Molar mass M_{η} [g/mol]	Melting point T_m [°C]	Glass transition temperature T_g [°C]
(1)	0	0	3,220,000	600,000	138	n.d.
(1)	0.2	0.101	3,970,000	246,000	87	n.d.
(1)	0.4	0.258	3,850,000	130,000	34	-44
(1)	0.6	0.458	1,980,000	79,600	a	-49
(1)	0.8	0.702	2,136,000	86,700	a	-33
(1)	0.9	0.854	1,080,000	127,000	85	n.d.
(1)	0.95	0.921	1,096,000	200,000	118	n.d.
(1)	1	1	113,500	650,000	164	n.d.
(1)/SiO ₂	0	0	21,900	556,000	136	n.d.
(1)/SiO ₂	0.17	0.192	103,600	50,600	a	-42
(1)/SiO ₂	0.33	0.304	14,000	11,300	a	-48
(1)/SiO ₂	0.5	0.398	165,800	12,300	a	-40
(1)/SiO ₂	0.67	0.505	4000	7400	a	-46
(1)/SiO ₂	0.83	0.703	2000	16,700	a	-30
(1)/SiO ₂	1	1	4000	50,400	151	n.d.

mol%, which is slightly lower than in the case of the homogeneous catalysts.

The molar masses of the copolymers are also strongly influenced by the incorporation rate of the comonomer (Tables 1–3, Figs. 3 and 4). M_{η} of the copolymers produced by both heterogeneous and homogeneous catalysts show very

similar dependencies on x_p . Small amounts of comonomer (up to $x_p \sim 0.2$ and above $x_p \sim 0.8$) reduce the molar masses of the corresponding homopolymers drastically. M_{η} of the intermediate region of x_p generally stays at a constant level, which is slightly lower for the supported systems than for the metallocenes in solution.

Table. 2

EPM polymerizations with (2) and (2)/SiO₂

a = amorphous, n.d. = not detected, pm = polymer, mon = monomer.

Catalyst	$X_{\text{propene, feed}}$	$x_{\text{propene, polymer}}$	Activity [kg _{pm} /(mol _{Zr} h mol _{mon} /l)]	Molar mass M_{η} [g/mol]	Melting point T_m [°C]	Glass transition temperature T_g [°C]
(2)	0	0	5400	384,000	137	n.d.
(2)	0.4	0.198	22,900	45,500	43	n.d.
(2)	0.6	0.321	17,400	31,600	a	n.d.
(2)	0.8	0.5	18,100	24,400	a	-52
(2)	0.9	0.674	16,900	25,800	a	-39
(2)	0.95	0.787	13,000	35,000	a	-26
(2)	0.98	0.905	11,400	51,700	a	-15
(2)	0.99	0.933	8100	87,900	98	-10
(2)	1	1	6500	138,000	144	n.d.
(2)/SiO ₂	0	0	1800	127,200	135	n.d.
(2)/SiO ₂	0.2	0.235	900	17,400	a	-53
(2)/SiO ₂	0.33	0.316	5200	8900	a	-51
(2)/SiO ₂	0.5	0.353	3200	9100	a	-42
(2)/SiO ₂	0.67	0.439	9800	12,000	a	-30
(2)/SiO ₂	0.8	0.517	6000	13,400	a	-22
(2)/SiO ₂	1	1	2200	91,600	122	1

Table 3

EPM and EPDM polymerizations with (3) and (3)/SiO₂

a = amorphous, n.d. = not detected, pm = polymer, mon = monomer.

Catalyst	$X_{\text{propene, feed}}$	$X_{\text{ENB, feed}}$	$x_{\text{propene, polymer}}$	$x_{\text{ENB, polymer}}$	Activity [kg _{pm} / (mol _{Zr} h mol _{mon} /l)]	Molar mass M_n [g/mol]	Melting point T_m [°C]	Glass transition temperature T_g [°C]
(3)	0	0	0	0	8500	248,000	135	n.d.
(3)	0.2	0	0.076	0	30,000	52,000	95	n.d.
(3)	0.4	0	0.167	0	42,200	38,000	49	n.d.
(3)	0.6	0	0.278	0	31,400	25,000	-9	n.d.
(3)	0.8	0	0.408	0	18,700	18,000	a	-61
(3)	0.9	0	0.503	0	15,600	18,000	a	-57
(3)	0.95	0	0.559	0	12,300	18,000	a	-52
(3)	0.98	0	0.590	0	4000	17,000	a	-49
(3)	0.99	0	0.628	0	4300	18,000	a	-45
(3)	1	0	1	0	2300	28,000	a	-3
(3)/SiO ₂	0	0	0	0	1400	228,000	135	n.d.
(3)/SiO ₂	0.08	0	0.099	0	1500	44,000	70	n.d.
(3)/SiO ₂	0.2	0	0.216	0	2300	15,000	a	-49
(3)/SiO ₂	0.33	0	0.296	0	3500	7400	a	-57
(3)/SiO ₂	0.5	0	0.333	0	11,900	6400	a	-52
(3)/SiO ₂	0.67	0	0.367	0	32,800	6300	a	-47
(3)/SiO ₂	0.8	0	0.397	0	27,900	6300	a	-39
(3)/SiO ₂	0.92	0	0.444	0	15,600	5700	a	-33
(3)/SiO ₂	1	0	1	0	2700	27,200	a	-4
(3)	0.4	0.2	0.16	0.04	6600	37,000	1	-34
(3)	0.2	0.6	0.13	0.18	2600	42,500	a	20
(3)/SiO ₂	0.5	0.04	0.52	0.01	2700	6200	a	-52
(3)/SiO ₂	0.5	0.08	0.50	0.01	1800	6200	a	-50
(3)/SiO ₂	0.41	0.24	0.53	0.09	500	6000	a	-49

The latter might be due to overall lower local monomer concentrations on MAO/SiO₂. The

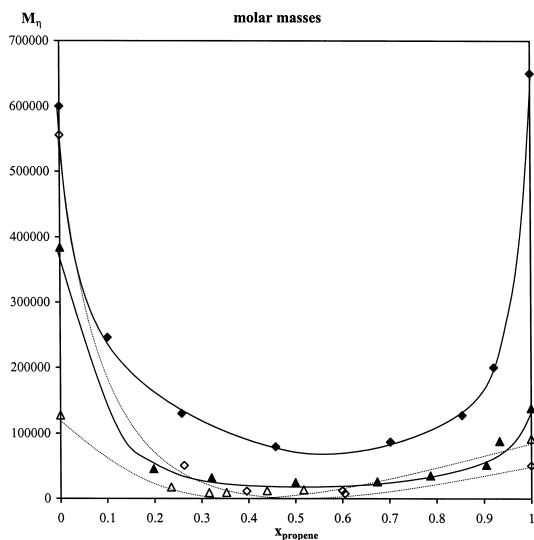


Fig. 3. Molar masses of ethene/propene copolymers dependent on the incorporation rate of propene using (1) = \blacklozenge , (2) = \blacktriangle , (1)/SiO₂ = \square and (2)/SiO₂ = \triangle .

lack of monomer molecules at the active site could lead to favoring chain termination reactions instead of the propagation reaction.

This may also be the reason for the differences in the activities of the homogeneous catalysts on the one hand and the supported metallocenes on the other (Tables 1–3, Figs. 5 and 6). Generally, the performance of supported metallocenes is considerably lower than that of their homogeneous equivalents, although the degree of this reduction can vary widely depending on the nature of the process and on the monomers and metallocenes used. Surprisingly, the activities of the gas phase reactions using polyethene as reactor bed come very close to the values achieved in solution. The reactor beds NaCl and polyethene, respectively, were used according to the expected solubility of the copolymer in toluene. At low (< 0.3) and high (~ 0.8) values of X_p , NaCl was used as reactor bed as the products were expected to become

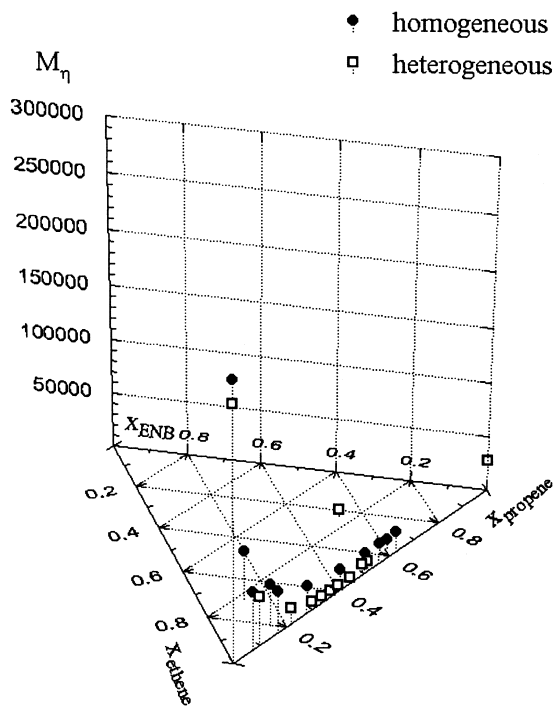


Fig. 4. Molar mass M_n dependent on the incorporation rate of propene and of ENB using (3) = ● and (3)/SiO₂ = □.

more crystalline and thus more difficult or even impossible to extract from a polyethene bed. Although the activities of (1), (2) and (3) on the

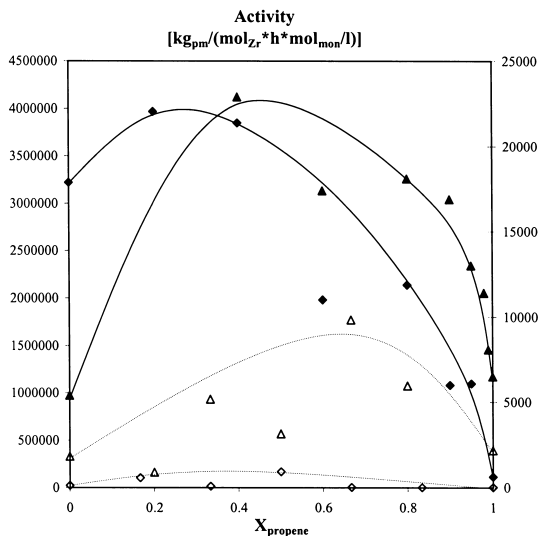


Fig. 5. Activities of ethene/propene copolymerizations dependent on the feed rate of propene, using (1) = ◆, (2) = ▲, (1)/SiO₂ = □ and (2)/SiO₂ = △; the left axis refers to (1) and (1)/SiO₂, the right axis to (2) and (2)/SiO₂.

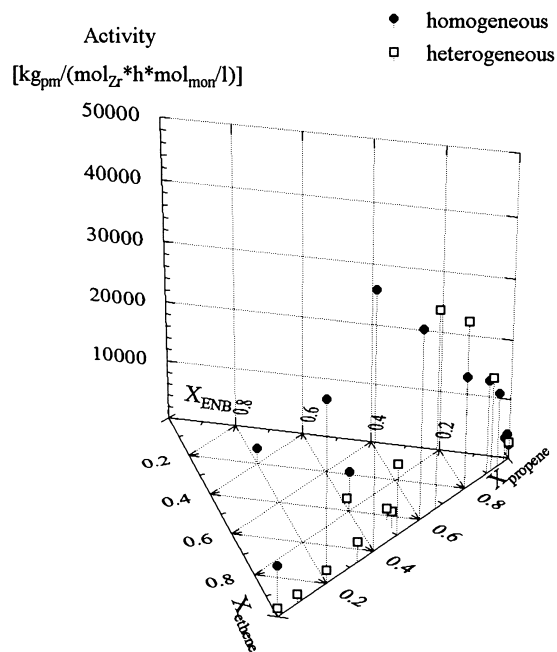


Fig. 6. Activities of ethene/propene copolymerizations and ethene/propene/ENB terpolymerizations dependent on the feed rate of propene and ENB using (3) = ● and (3)/SiO₂ = □.

one hand, and (1)/SiO₂, (2)/SiO₂ and (3)/SiO₂ on the other differ somewhat, the trends for the dependence of the activity on x_p are still comparable.

3.2. Terpolymerization of ethene, propene and ENB

The incorporation of ENB into the copolymers of ethene and propene has a strong effect on the activity of the terpolymerization (Table 3). The presence of ENB in the reaction mixture reduces the activity considerably for both the homogeneous and heterogeneous terpolymerizations. Furthermore, the incorporation of ENB in the gas phase procedure is higher than that in solution.

This is possibly caused by the coordination of ENB to the metallocene by both of its double bonds which could block the coordination sites of the catalyst at least temporarily. The reason for the difference in the decrease of the activity when comparing the homogeneous and hetero-

geneous terpolymerizations could be found in the local concentration of ENB on the catalyst particles of the supported metallocenes. Assuming that the adsorption of the diene to the metallocene/MAO/SiO₂ adduct is higher than the overall concentration of the same amount of ENB in solution, then one could expect the activity of the heterogeneous terpolymerization to drop farther than that of the terpolymerization in solution.

Apart from these difficulties, it is possible to produce ethene/propene/ENB terpolymers with ENB incorporation rates that are of technical interest using the systems (3) and (3)/SiO₂ (up to about 2 mol%).

4. Conclusions

We have shown that it is possible to utilize metallocenes in gas phase processes by supporting. We are of the opinion that the heterogenization method used, i.e. indirect supporting on a MAO/SiO₂-carrier, is of great importance if the metallocene employed is supposed to retain its specific polymerization characteristics on the support. Although minor differences were found in the physical and chemical properties of the polymers, it is conceivable that the whole range of EP(D)Ms that can be produced with metallocenes in solution can also be synthesized in the gas phase procedure outlined above.

Acknowledgements

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