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Propene Polymerisation with *rac*-[Me₂Si(2-Me-4-(Naphthyl)-1-Ind)₂]ZrCl₂ as a Highly Active Catalyst: Influence of Monomer

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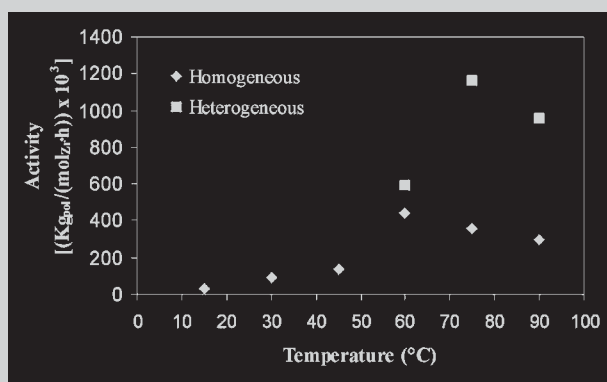
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Full Paper: Propene was polymerised at high temperatures (up to 90 °C) using *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO as the catalytic system. The increasing deactivation reaction rate of the catalyst for polymerisations above 60 °C was less for a silica supported catalyst compared with the homogeneous one. The isotacticity of polypropene decreases from 99 to 96%. Also the morphology changes with different temperatures.

Increasing of the thermal stability for the *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO/SiO₂ with respect of the *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO system.



Propene Polymerisation with *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂ as a Highly Active Catalyst: Influence of Monomer Concentration, Polymerisation Temperature and a Heterogenising Support

Dedicated to Prof. Dr. Dr. h.c. *Hans-Joachim Cantow* on the occasion of his 80th birthday

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Introduction

In the field of polyolefins group IV metallocene catalysts are a unique class allowing a perfect control on all ranges of molar masses, polymer microstructure and comonomer distribution.^[1] Furthermore, group IV metallocene complexes in presence of MAO (methylaluminoxane) constitute a single-site homogeneous system, much easier to understand than conventional Ziegler-Natta type catalysts. One of the main reasons for the enormous scientific interest raised by metallocene based catalysis originated in the discovery that stereoselectivity in propene polymerisation can be driven to an unprecedented extent.^[2] Every year more than 25 million tons of polypropene are produced using Ti/MgCl₂ type supported catalysts. Nowadays metallocenes are largely employed in industrial production of several different ethene based polymers using different processes, from solution to slurry and gas-phase

techniques.^[3,4] The resulting products normally have broad molar mass distribution^[4a] but show a high stereoregularity. As a drawback, these systems have different active sites. The use of “single site” metallocene/MAO catalysis has the big advantage of being an extremely versatile tool in the synthesis of polyolefins. For example the product can be tailored by the use of different ligand frames or metal centres,^[3a–5] showing a narrower molar mass distributions, isotacticities spanning from almost atactic to perfectly isotactic, a random distribution of regio and stereo errors in the polymer chain, and a generally lower molar mass. Therefore there is a rising desire to employ metallocene/MAO catalysts on an industrial scale.^[3c]

Since the discovery of the C₂-symmetric *rac* isomer of bridged titanium and zirconium metallocene [En(H₄-Ind)₂]ZrCl₂/MAO^[5,6] as a catalyst for α -olefin polymerisation, a lot of work has been carried out in order to optimise ligand substitution patterns and reaction conditions.^[7]

Despite the enormous importance of the ligand structure, the catalytic performance of metallocene catalysts depends strongly on polymerisation conditions. Very important for industrial processes is the stability of the catalyst at higher polymerisation temperatures. Another important parameter is the monomer concentration, which influences the polymer structure. The polymerisation temperature is mostly believed to influence the rigidity of the metallocene frame, which directly controls the stereospecificity,^[8] and the activity. As a consequence, the use of higher polymerisation temperature brings a decrease of the activity.

The concentration of propene also affects the stereoregularity because of an intramolecular reaction of the growing polymer chain.^[9] Another important role is played by the presence of a supporting material such as silica.

The catalytic system *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO was selected because of the high activity shown by aromatically substituted metallocenes in liquid propene polymerisations (up to 875.0×10^3 (kg_{pol}/(mol_{Zr} × h))^[10a] and the high rigidity of the ligand frame, useful for the “indirect steric control” of the polymer chain growth.^[10a]

The influence on the activity, stereoselectivity and molar mass of the obtained polymers in dependence of the polymerisation temperature, the monomer concentration and the supporting material was studied using this strong stereorigid zirconocene.^[10]

Experimental Part

Materials

The synthesis of zirconocene *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂ has been described previously.^[10a] All catalytic components were handled and stored under an argon atmosphere using Schlenk and drybox techniques. MAO (10 wt.-% solution in toluene) and MAO/SiO₂ (23 wt.-% Al, surface area 280 m²/g, particle size 30–90 μ m) were purchased from Witco Germany, propene from Messer Griesheim and toluene from Merck. The gaseous monomer and toluene solvent were purified by elution through columns with Cu catalyst (BASF R3-11) and molecular sieves of 10 Å. The 10 wt.-% solution of MAO in toluene was dried in vacuum at 50 °C before using. Triisobutylaluminium (TIBA) was purchased from Aldrich and employed without any further purification.

Homogeneous Reactions

Polymerisation reactions were performed in a 1l Büchi AG type steel reactor dried under vacuum at 95 °C for 1 h and flushed several times with argon before use. Toluene (200 ml) was pumped into the vessel after evacuation with argon. Afterwards, a desired quantity of MAO solution (200 mg MAO in 2 ml of toluene) was syringed into the autoclave and the system was saturated with propene. After complete saturation and thermal equilibration, the reaction was started by injection of a prepared toluenic metallocene solution. During the

reaction the total pressure was kept constant by supplying propene.

The aluminium concentration was 17.2 mmol/l corresponding to an Al/Zr ratio of 3.88×10^5 . This value was in agreement with standard polymerisation conditions. The high Al/Zr ratio was due to the low metallocene concentration. Studies on the influence of different MAO concentrations are to be performed with this catalyst. The monomer concentrations were in the range between 0.60 and 4.79 mol/l. These values were kept constant at temperatures between 0 and 90 °C by varying the partial pressure of propene. The values were taken as reported in the literature^[11] (Table 1). Monomer feed was maintained with a Peteric 3002 press-flow-controller. The reaction was monitored by a Büchi Data System bds 488.

Polymerisations were quenched after 45 minutes by injection of 1 ml of ethanol. The content of the reactor was stirred overnight with 200 ml of a solution containing hydrochloric acid (200 ml), ethanol (425 ml) and water (1450 ml) followed by filtration and neutralisation with water, washing with ethanol, 2-propanol and dried overnight at 60 °C under vacuum.

Slurry Reactions

Heterogeneous polymerisation reactions were performed in a 1l Büchi AG type steel reactor, dried under vacuum at 95 °C for 1 h and flushed several times with argon before using. Toluene (200 ml) was then pumped into the vessel and 0.01 ml of TIBA was added as a scavenger component. In a separate flask 100 mg of SiO₂/MAO was suspended in toluene and kept stirring. A prepared solution of the complex in toluene was then added to the suspension and kept stirring till a consistent change of colour was evident. After complete saturation with propene and thermal equilibration, the reaction was started by injection of the catalytic suspension into the reactor. In this case the Al/Zr ratio was 2000. The propene concentration employed was 0.60 mol/l (Table 1) and the polymerisation temperature in the range between 60 and 90 °C. During the reaction the total pressure was kept constant by supplying propene. The reaction was quenched and the obtained polymers treated as previously described.

Table 1. Pressure and concentration of propene in toluene.

Temperature °C	Propene concentration mol/l				
	0.60	1.38	2.34	3.47	4.79
	Pressure bar				
0	0.48	0.98	1.51	1.57	2.57
15	0.70	1.47	2.27	2.38	3.95
30	1.00	2.00	3.00	3.12	5.00
45	1.41	2.97	4.63	4.84	8.10
60	1.93	4.13	6.51	6.81	11.58
75	2.80	5.95	9.41	9.81	16.70
90	3.97	8.51	13.55	14.13	24.27

Polymer Analysis

Polymer microstructures were detected by NMR spectroscopy on a Bruker 400 MHz instrument. The NMR samples were prepared by dissolving the polymers (10 wt.-%) in 1,2,4-trichlorobenzene and C_6D_6 . All measurements were carried out at 100 °C. \bar{M}_n was determined with an Ubbelohde capillary. The samples were prepared by dissolving 50 mg of polymer in 50 ml of decahydronaphthalene and the viscosity measured at 135 °C. The Mark-Houwink constants were taken from the literature.^[11] Measurements of melting temperature and crystallisation behaviour were performed on a Mettler-Toledo DSC 821e instrument at a heating rate of 20 °C/min.

The sample morphologies were analysed using an Environmental Scanning Electron Microscopy-Field Emission Gun (ESEM-FEG). In this case low voltage technique was employed. The samples were looked at without treatment (i.e. they were not coated with gold or carbon). To obtain a better topographical illustration they were therefore looked at with the primary electrons having an acceleration voltage of 1 kV. In this way, sample charging was avoided and a higher topographical illustration of polymer surfaces was achieved.

Results and Discussion

Influence of Propene Concentration and Polymerisation Temperature

It is well known that isotactic propene polymerisations (i-PP) with zirconocene catalysts take place by regioselective 1,2 insertion into the zirconium-carbon bond. This kind of insertion is generally known as primary insertion. However one of the features of most isospecific metallocene catalysts is their generally lower regioselectivity compared to conventional Z-N catalysts.^[3a] Indeed, despite the fact that primary insertion is favoured by electronic factors, isolated secondary insertions are often detectable in i-PP samples and their presence is normally the signature of a metallocene catalyst. Moreover these stereodefects have a strong influence in lowering crystallinity and melting point of i-PP. Usually the number of misinsertions increases as polymerisation temperature increases.

In this work a highly isotactic polypropene was obtained at relatively high temperature (up to 90 °C, activity $3.31 \times 10^5 \text{ kg}_{\text{pol}}/(\text{mol}_{\text{Zr}} \times \text{h})$). The effect of different monomer concentration has been studied and compared at different polymerisation temperatures. First of all the polymerisation activity was analysed (Figure 1). It is easy to recognise the strict dependence, with monomer concentration showing an absolutely linear behaviour at each temperature. This behaviour allows us to presume that there is not an appearance of a diffusion control in this range of concentrations, although the growing polymer is completely insoluble in the reaction solvent. More detailed studies have to be done in order to eliminate any kind of suspects.

The maximum value of activity was found at 60 °C (up to $2.26 \times 10^6 \text{ kg}_{\text{pol}}/(\text{mol}_{\text{Zr}} \times \text{h})$) but for polymerisations at

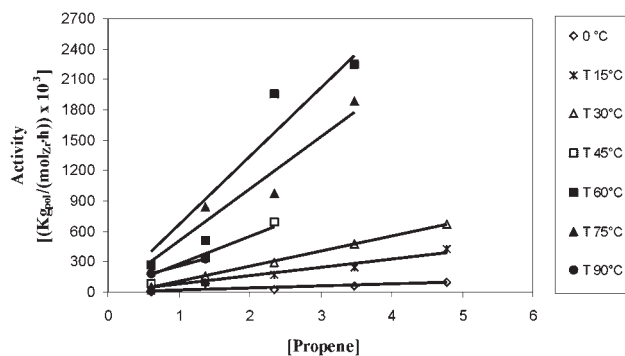


Figure 1. Comparison of activity $((\text{kg}_{\text{pol}}/(\text{mol}_{\text{Zr}} \times \text{h})) \times 10^3)$ tendency against propene concentration at different temperatures with the *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO system.

90 °C a high degree of isotacticity and a low number of regio errors were still observed ($\text{mmmm}_{\text{homo}} > 96.4\%$).

As shown in Figure 1 the tendency at 90 °C seems to be analogous to that at 45 °C. This is only an apparent behaviour as evidenced monitoring the monomer feed during the polymerisation. This method allows us to underline that deactivation processes at higher temperatures are faster. After 30 minutes at 90 °C the system seems to be mostly deactivated (Figure 2).

Influence of Silica Gel as Supporting Material

The decrease of the activity found at polymerisation temperatures above 60 °C may possibly be due to different factors such as deactivation reactions, i.e. increasing of the chain termination rate, decomposition processes of the catalyst containing a silanol group as bridge or bimetallic reactions.^[12] This effect suggested analysis of the contribution of silica as supporting material for the catalyst (*slurry reaction*).^[13,14] It was decided to employ the lower monomer concentration at higher temperatures (60–75–90 °C) in order to emphasise all possible misinsertions, most of all due to a competing intramolecular epimerisation reaction of the growing polymer chain over monomer

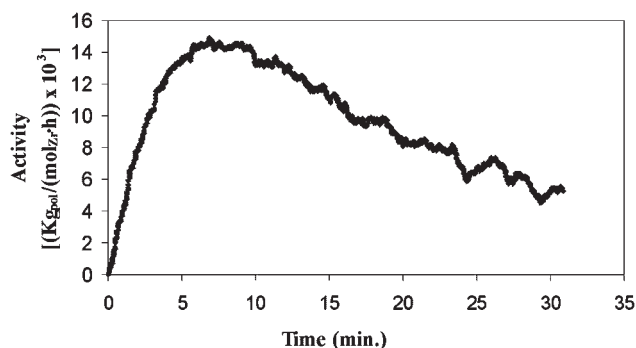


Figure 2. Monitoring of activity $((\text{kg}_{\text{pol}}/(\text{mol}_{\text{Zr}} \times \text{h})) \times 10^3)$ for the homogeneous system with respect to the time at 90 °C as polymerisation temperature.

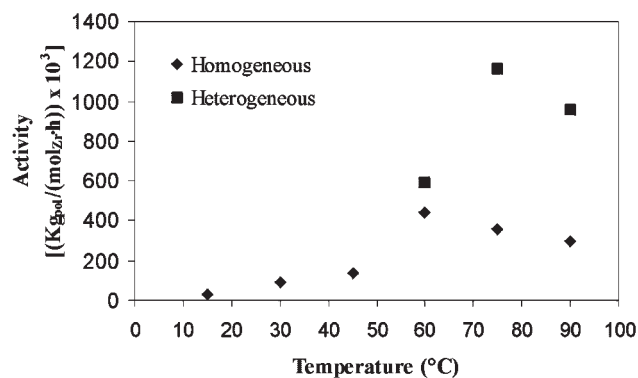


Figure 3. Comparison between polymerisations at different temperatures and 0.60 mol/l propene using the *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO/SiO₂ and the *rac*-[Me₂-Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO system.

insertion.^[15] A comparison between the activities of the homogeneous and the heterogeneous system is reported in Figure 3. The different activity found for the heterogeneous system if correlated to the homogeneous phase reaction is only due to the different polymerisation conditions required. Using this technique, the catalytic system showed a higher stability with respect to the polymerisation temperature and time. The maximum value of activity was in this case reached at 75 °C and the obtained polymer was found to still have a very high isotacticity (mmmm_{hetero} 96.9%). Monitoring the monomer feed revealed a decrease of deactivation effects due to the slurry process (Figure 4). At the end of the polymerisation time the activity was found to still be high, showing that the process is still working. This does not occur in case of the homogeneous analogue.

Isotacticity

The ¹³C NMR analysis revealed that all samples had a very high isotacticity (mmmm up to 99%). Only mmmr, mmrr and mmm + rmmr stereo errors were detectable. Regio

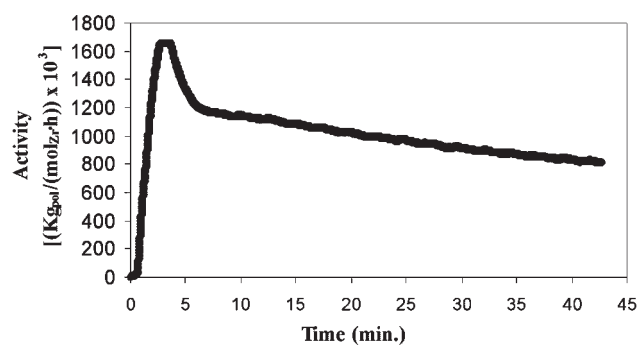


Figure 4. Monitoring of activity for the supported system with respect to the time at 90 °C as polymerisation temperature.

Table 2. Stereo and regio errors measured by pentades for polymerisations of propene (0.60 mol/l propene) with the *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO/SiO₂ system.

Temperature °C	mmmm %	mmmr %	mmrr %	2,1-rac %	2,1-meso %	1,3 %
90	95.6	2.7	0.5	–	0.8	0.2
75	96.5	2.3	0.2	–	0.4	0.2
60	96.9	2.1	0.3	–	0.7	–
90 ^{a)}	96.4	2.3	0.5	–	0.6	0.3

^{a)} With the the *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO system.

errors were observed only at polymerisation temperatures higher than 75 °C (Table 2). The high melting temperature (ca. 160 °C) and the high level of crystallinity (up to 75%) confirmed the low number of stereo and regio errors in the polymer samples.

As was easily predictable, the polypropene produced in slurry contains more misinsertion than the product obtained employing a homogeneous process. The amount of misinsertions increases if the polymerisation temperature is raised.^[16] In any case, the percentage of misinsertion always remains in a very low range, showing an isotacticity never lower than 95.6%.

Molar Mass

The molar mass was found to be strictly dependent on monomer concentration and polymerisation temperature as expected. Polymerisations carried out at low temperature and high monomer concentrations allowed us to obtain a surprisingly high molar mass and isotacticity but by changing these parameters a very wide range of different values was obtained. Hence it was possible to obtain molar masses from 100 kg/mol (at 90 °C and 0.60 mol/l propene) up to 4.3×10^3 kg/mol (at 0 °C and 4.79 mol/l propene). The samples having higher molar masses were not completely soluble in decahydronaphthalene. Only the soluble part was measured (Table 3), which allows us to presume a still higher molar mass for these samples.

Morphology

In the homogeneous polymerisation a change of morphology of the product due to the increasing reaction temperature was found. Polymerisations carried out at 30 °C resulted in a compact polymer with a high bulk density (Figure 5a). Polymerisations at higher temperature show the appearance of a filament aspect. This was recognisable in the products obtained at 45 °C using 10 000 enlargements (Figure 5b), and allows to presume the presence of

Table 3. Propene polymerisation results with the *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO system.

	Temperature	Activity	T_m	\bar{M}_n	Isotacticity [mmmm]
	°C	(kg _{pol} /(mol _{Zr} ×h))×10 ³	°C	10 ³	%
0.60 mol/l	0	6.02	158.7	1231	>99
	15	17.3	158.2	1130	>99
	30	53.3	157.4	918	>99
	45	81.3	157.8	621	>99
	60	267.0	159.2	262	98.2
	60 ^{a)}	593.1	154.1	477	96.9
	75	213.1	157.1	191	97.7
	75 ^{a)}	1176.1	154.5	222	96.5
	90	180.2	150.6	973	96.4
	90 ^{a)}	958.0	150.0	113	96.5
1.38 mol/l	0	87.2	159.2	1692	>99
	15	102.2	158.6	1591	>99
	30	157.0	159.5	1379	>99
	45	344.1	157.3	905	>99
	60	513.2	156.6	499	>98.8
	75	833.0	154.1	265	98.4
	90	331.1	152.9	180	97.2
2.34 mol/l	0	26.7	159.6	2961	>99
	15	169.1	156.8	2883	>99
	30	297.2	159.7	2108	>99
	45	691.1	159.4	188	>99
	60	1960.1	158.4	336	99
	75	976.1	158.2	123	98.6
	90	61.3	160.37	3302	>99
3.47 mol/l	15	247.1	159.8	2557	>99
	30	472.2	160.7	1469	>99
	45	1570.1	158.2	733	>99
	60	2260.1	153.1	479	>99
	75	1880.2	156.9	480877	>99
	90	93.3	157.1	4289	>99
	90 ^{a)}	427.1	156.0	1540	>99
4.79 mol/l	30	667.2	158.8	1588	>99

^{a)} With the *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO/SiO₂ system.

shear forces acting on the samples during the reaction time. The number of threads seems to be increasing as the polymerisation temperature increases and reaches a maximum at 60 °C (Figure 5c) which also represents the maximum of activity. Samples obtained at 90 °C do not show any kind of threads (Figure 5d). An analogue effect is also recognisable for the supported system (Figure 6). The presence of threads is recognisable for the sample obtained at 60 °C (Figure 6a) but not for the samples at 75 and 90 °C (Figure 6b–6c). The shape of silica was not found to be reproduced from the polymer shape as was expected, due to the low amount of silica employed with such an active catalyst, or possibly partial leaching of the catalyst from the supporting material. Using this supporting technique no catalyst leaching has been detected at lower polymerisation temperature.^[14b] Since temperature has an influence on the coordination properties of toluene, a partial leaching of the catalyst can not be excluded in these conditions.

Another interesting point is the flock aspect found at increasing polymerisation temperature (Figure 5–6). This allows us to obtain a powder as final product at high temperature instead of a thick polymer. This phenomenon was attributed to the drastic change of \bar{M}_n with respect to the temperature change.

Conclusions

The catalytic system *rac*-[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO is an excellent catalytic tool in propene polymerisation both in solution and in slurry reactions. It allows achievement of a very wide range of molar masses along with a very high isotacticity even at relatively high polymerisation temperature (up to 90 °C). This is supposed to be due to the high level of aromaticity in the ligand frame that confers a high rigidity to the metallocene complex. The temperature seems to greatly affect side

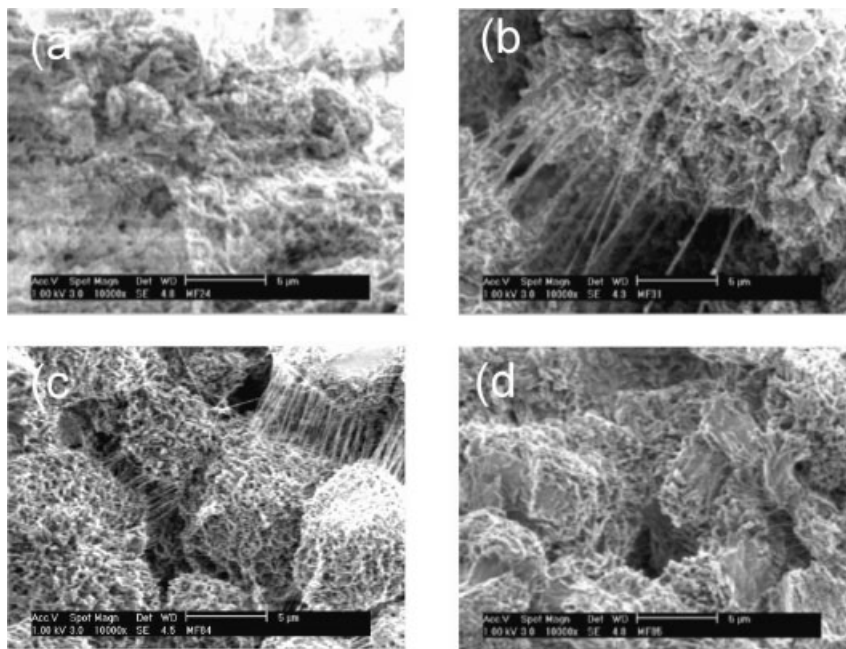


Figure 5. Electron scanning microscope enlargements 10 000 times pictures for polyolefins obtained by the rac -[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO system: a) polymer obtained at 30 °C; b) polymer obtained at 45 °C; c) polymer obtained at 75 °C; d) polymer obtained at 90 °C.

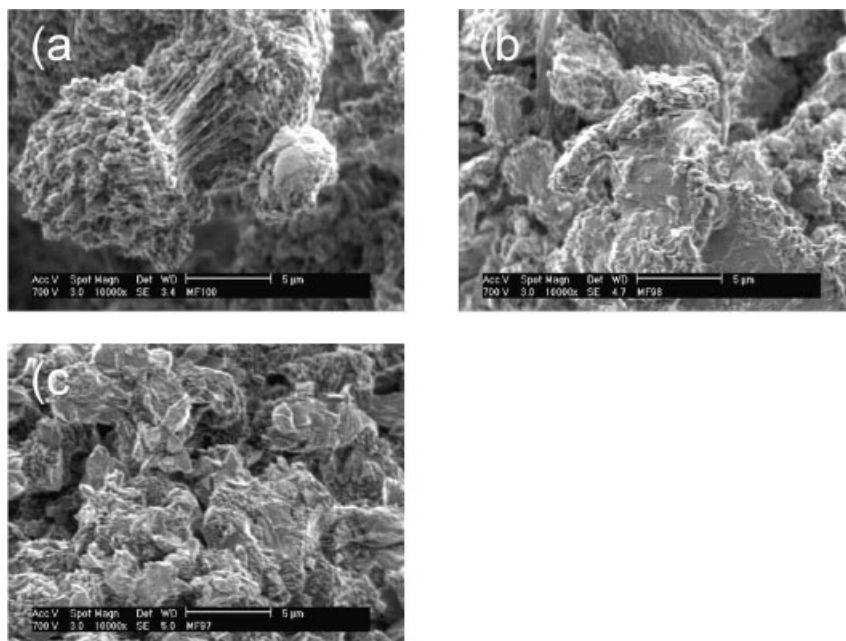


Figure 6. Electron scanning microscope enlargements 10 000 times pictures for polyolefins obtained by the rac -[Me₂Si(2-Me-4-(α -naphthyl)-1-Ind)₂]ZrCl₂/MAO/SiO₂ system: a) polymer obtained at 60 °C; b) polymer obtained at 75 °C; c) polymer obtained at 90 °C.

reactions as chain termination rate but not the molecular structure of the catalyst, as confirmed from the still high isotacticity. Furthermore, the use of a silica support guarantees a higher thermal stability along with a

decrease of deactivation effects. Hence, after a previous supporting reaction with silica, metallocene/MAO catalysts may be excellently adapted to several existing industrial processes.

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