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# New Polyolefin-Nanocomposites by In Situ Polymerization with Metallocene Catalysts

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**Summary:** Polypropylene-nanocomposites were prepared by in-situ polymerization with the catalysts systems rac[Et($IndH_4$)$_2$]$ZrCl_2$, $Me_2Si$(Flu)(Ind)$ZrCl_2$ and rac[$Me_2Si$(2-Me-4-(1-Naph)Ind)$_2$]$ZrCl_2$. The type and size of the nanoparticles and the concentration of the propene were varied. The activity is independent of the type and the size of the filler. It was observed that the filler contents in the polypropylene-nanocomposites depend on the catalysts system used. The morphology results using TEM revealed that the nanoparticles are uniformly distributed in the isotactic polypropylene matrix. Additionally, the melting points, glass temperatures and crystallization temperatures changed with the amount of the fillers.

**Keywords:** filler; in situ polymerisation; metallocene catalysts; nanocomposites; polypropylene

## Introduction

Within the last years, much research in academic and industrial laboratories has focused on the field of polyolefin nanocomposites because of their high potential as materials with novel properties such as improved mechanical properties, increased heat distortion temperature, reduced permeability and flammability.[1–3]

The properties of the nanocomposites are not only influenced by the kind of fillers, but also by the microstructure of the polyolefins and the preparation process. A lot of work has been carried out to use layered silica and metal oxides,[4] clay, self-assembled nanoboehmites,[5] or montmorillonite as fillers to obtain composite materials which show a lower permeability for gases such as oxygen, nitrogen and steam. In the past, most composites were commonly prepared by mechanical blending of the particles or fibers above the melting temperatures. Blending or melt compounding of polyolefins with nanoparticles is hard to achieve, especially because high filler content leads to aggregation and intercalation which decreases the mechanical properties of the nanocomposites.[6] More than 60 wt% filler content in the polymer result in highly particle aggregation. For mixing in solution, the solubility of polyethylene is too low. Another problem is the hydrophilic nature of most inorganic fillers and the hydrophobic nature of the polyolefins. The differences result in weak interfacial adhesion between filler and polymer matrix and low mechanical properties. Therefore, fillers must be modified by surface active agents. Both disadvantages can be solved by *in situ* generation where the catalyst is absorbed on the surface of the nanofillers, changing the surface to a hydrophobic one. In a second step, the activated fillers are used as catalysts for olefin polymerization. Each particle or fiber is covered by a polyolefin film. For bigger particles, heterogeneous nanosized Ziegler-Natta catalysts can be used.[7] For nanoparticles, homogeneous catalysts are preferred to cover the surface with active sites.

Metallocene/methylaluminoxane (MAO) and other single site catalysts are soluble in hydrocarbons and therefore they can cover perfectly the surface of particles or they can permeate in the layers of layered silicates

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and oxides. Aluminium flake filled polyethylene was first prepared by this procedure showing high thermal but low electrical conductivity.[7,8]

Metallocene/methylaluminoxane (MAO) catalysts are highly active for the production of precisely designed polyolefins. Especially zirconocene complexes have opened a frontier in the area of new polymer synthesis and process. The transition metal complexes can be activated by MAO but also by other bulk cocatalysts such as perfluorophenylborate. By changing the ligand structure, these catalysts allow the synthesis of polymers with a tailored microstructure tacticity and stereoregularity as well as new copolymers with superior properties such as film clarity, tensile strength and lower extractables.

With these single site catalysts and by *in situ* polymerization introduced nanofillers with a large aspect ratio, layered silicates, fibers into polyolefin matrix cause a tremendous boost of the physical and chemical properties of polymers such as a dramatically improved stiffness with a neglible loss of impact strength, high gas barrier properties, better clarity and gloss, and high crystallization rates. Even low nanoparticle contents are already sufficient to obtain new or modified material characteristics.

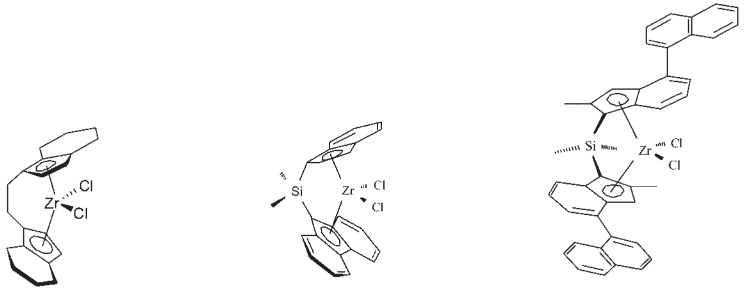
Silica spheres (200 nm) can be covered with isotactic or syndiotactic polypropylene offering a hard and stiff composite material by a filler content of up to 85 wt%.[9]

Carbon fibers and carbon nanotubes can be covered also with isotactic or syndiotactic polypropylene. Because of the hydrophobic character of the carbon surface, the polymer is drawing on the fiber. This leads to a reinforced combined polymer with special properties. The crystallization temperature is 10 °C higher and therefore the crystallization rate up to 20 times faster than that of pure syndiotactic polypropylene.[10]

## Experimental Part

As fillers were applied aluminium oxide, magnesium oxide (100 nm from Alfa Aesar), bornitride (325 Mesh from Alfa Aesar), calcium carbonate (socal P31, 70 nm from Solvay) and silica (monosphers 250 from Merck). Three different aluminium oxides were used: aluminium oxide dispersal 20, aluminium oxide dispersal 40 from Sasol and aluminium oxide from Alfa Aesar with 37.5 nm. The fillers were dried at 120 °C for 12 hours. A filler mass of 0.5 g was transferred to a buchi glass reactor which was heated at 90 °C. After fillers were evacuated one hour, 400 mg methylaluminoxane (MAO) was added and evacuated for another ten minutes. The reactor was cooled down to 60 °C and filled with 400 mL dried toluene as a solvent. The solution was saturated with propene. There were used propene pressures of 1 and 2.5 bar. The polymerizations were started by adding a toluene solution of the catalyst. For both catalyst systems $rac[Et(IndH_4)_2]ZrCl_2$ and $Me_2Si(Flu)(Ind)ZrCl_2$ $5 \times 10^{-6}$ mol of the catalyst were used for the polymerizations with a propene pressure of 1 bar. For the catalyst system $rac[Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Naph)Ind)_2]ZrCl_2$, $1.3 \times 10^{-6}$ mol was added for the polymerizations and for the catalyst $rac[Et(IndH_4)_2]ZrCl_2$ $2.5 \times 10^{-6}$ mol using 2.5 bar propene pressure. The polymerizations were quenched with 5 mL ethanol. After stirring the solution with 200 mL ethanol over night, the solvent was removed and the polymers were dried under vacuum at 60 °C for 12 hours. The polymerizations carried out with the $rac[Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Naph)Ind)_2]ZrCl_2$ catalyst were stirred over night with 200 mL ethanol and 50 mL hydrochloric acid. The polymers were filtered and dried under vacuum at 60 °C for 12 hours.

The melting temperatures and the crystallization temperatures were measured by a differential scanning calorimetry (DSC) with a DSC 821e from Mettler-Toledo. The DSC was calibrated with cyclopentane ($T_m = -93.9$ °C), mercury ($T_m = -38.8$ °C), gallium ($T_m = 29.8$ °C), indium ($T_m = 156.6$ °C) and zinc ($T_m = 419.5$ °C). Samples of 4–8 mg were used for DSC analysis. Melting temperatures were determined from the second heating



*rac*[Et(IndH$_4$)$_2$]ZrCl$_2$ Me$_2$Si(Flu)(Ind)ZrCl$_2$ *rac*[Me$_2$Si(2-Me-4-(1-Naph)Ind)$_2$]ZrCl$_2$

**Figure 1.**
used metallocene catalyst systems.

cycle at a heating rate of 20 °C per minute. Crystallization temperatures were determined by DSC from the cooling curve after complete melting at 200 °C for 5 minutes. The cooling rate was 10 °C per minute. The Electron microscopy was performed with a Philips CM 300 microscope.

## Activity

The polymerizations were carried out with three different catalysts and seven different nanofiller and by different filler contents and propene pressures. Figure 2 showed the relation between the activity of the different zirconocene catalysts and the filler contents. There was a link between the activity and the filler content. The activity decreased with the amount of the filler, because the catalysts have different activities also in relation of the kind of the filler. Activity up to 11000 kg PP/mol Zr · h · [pro-[propene] can be reached with a filler content of 0.5 wt% and the *rac*[Et(IndH$_4$)$_2$] ZrCl$_2$ as a catalyst system. The catalyst system Me$_2$Si(Flu)(Ind)ZrCl$_2$ produced nanocomposites with 20 wt% filler with

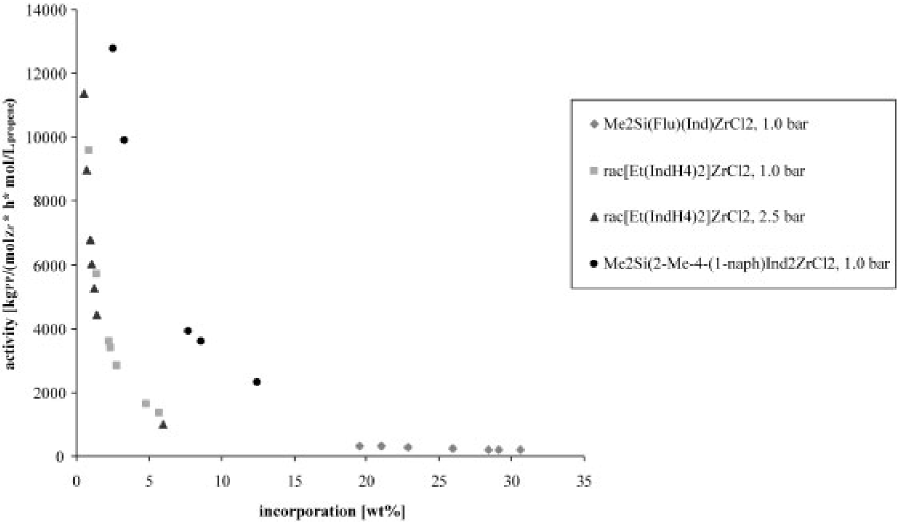


**Figure 2.**
Activity of PP-nanocomposites with different nanoparticles, catalyst and concentration in dependence of the incorporation of the filler.

low catalyst activity 300 kg PP/mol Zr · h · [propene]. The activity of the polymerisations with catalyst *rac*[$Me_2Si$(2-Me-4-(1-Naph)Ind)$_2$]$ZrCl_2$ which ligand was substituted, decreased less more rapidly with a higher amount of the filler than the other used catalysts.

Figure 3 shows the influence of the different kinds of fillers on the activity using *rac*[Et($IndH_4$)$_2$]$ZrCl_2$ by 2.5 bar propene pressure. The highest activity was reached using.

The activity of the polymerisations with catalyst *rac*[$Me_2Si$(2-Me-4-(1-Naph)Ind)$_2$]$ZrCl_2$ which ligand was substituted, decreased less more rapidly with a higher amount of the filler than the other used catalysts.

Figure 3 shows the influence of the different kinds of fillers on the activity using *rac*[Et($IndH_4$)$_2$]$ZrCl_2$ by 2.5 bar propene pressure. The highest activity was reached using boron nitride nanoparticles, the lowest by alumina ordered by Alfa Aesar. The differences depend on the adhesion of the methylaluminoxane on the filler surface.

## Morphology

In Figure 4a PP-Nanocomposite with aluminium oxide nanoparticles, produced with the *rac*[Et($IndH_4$)$_2$]$ZrCl_2$-catalyst by 2.5 bar propene pressure, were pictured. The Al2O3-nanoparticles were encased with a thin film of polypropylene. The distribution of the particles was uniformly. The main part of the polymer is located on the surface of the alumina particles, but there is also some polymer in between the particles, because there was no filtration step after the absorption of the methylaluminoxane on the alumina particles.

## Crystallization Behavior

For the characterization of the polymers the DSC was used to investigate the crystallization behaviour of the polymers. Figure 5 shows the melting points, glass temperatures and crystallization temperatures of the nanocomposites synthesised with the rac[Et($IndH_4$)$_2$]$ZrCl_2$ and $Me_2Si$(Flu)(Ind)$ZrCl_2$-catalyst-systems, which were especially influenced by the filler content. All curves presented the same characteristic. The melting points, glass temperatures and crystallization temperatures rose with a higher filler content. The increase in the area with lower filler content till 5 wt% was larger than in the area with higher filler

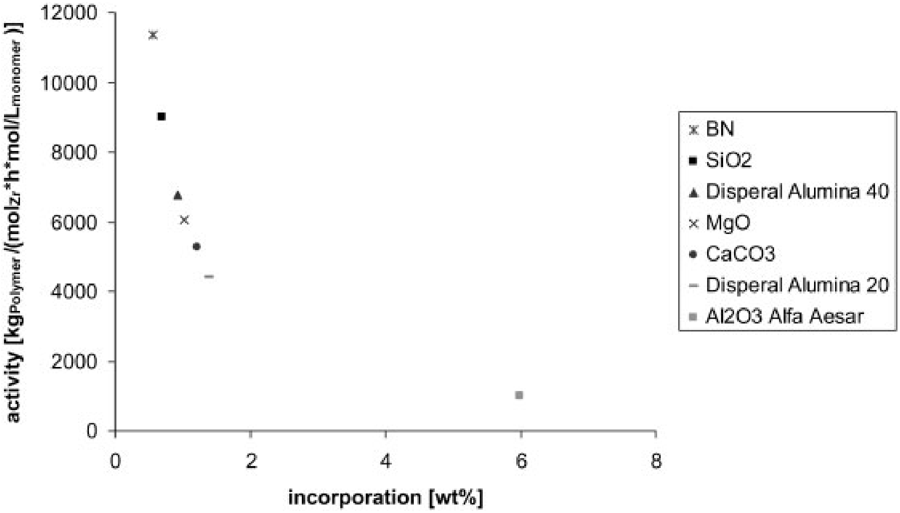


***Figure 3.***
Activity of PP-nanocomposites of the different nanoparticles with the *rac*[Et($IndH_4$)$_2$]$ZrCl_2$-catalyst by 2.5 bar propene pressure.

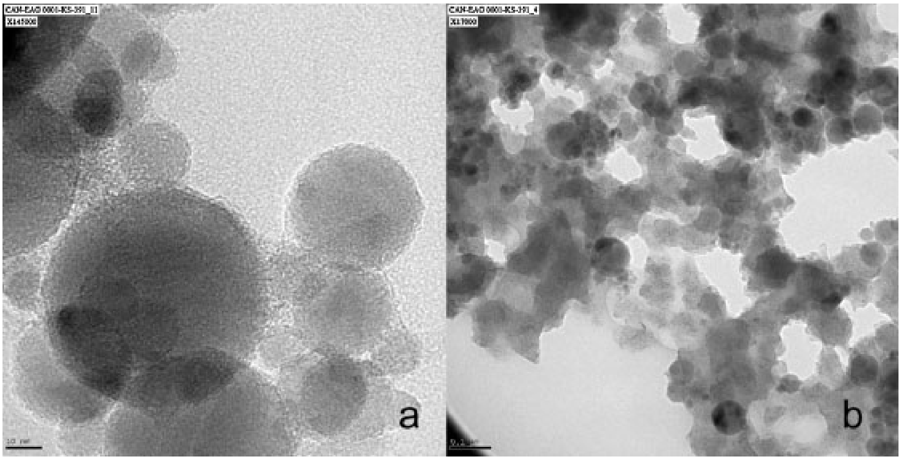


***Figure 4.***
TEM picture of PP-Nanocomposite with Al2O3 as nanofiller, a: enlargement 45000, b: 7000.

content. The melting points, glass temperatures and crystallization temperatures of the nanocomposites were similar with a filler contents higher than 20 wt %. The influence of the increasing crystallization temperature with the filler content can be explained by the nucleation effect.

The melting points of the polymers produced with the rac[$Me_2Si$(2-Me-4-(1-Naph)Ind)$_2$]$ZrCl_2$-catalyst were higher than the melting points of the other polymers synthesized with the other catalysts system, because this catalyst produces polypropenes with the highest isotacticty. The

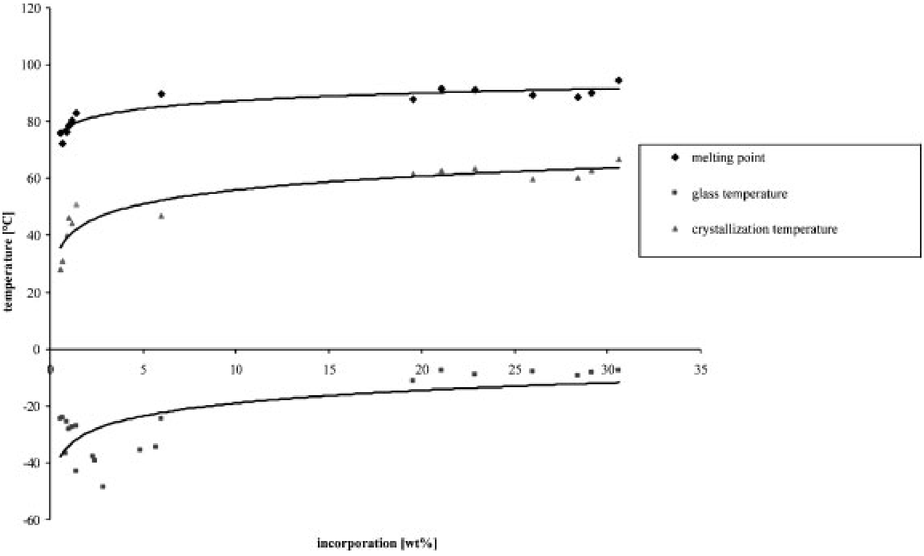


***Figure 5.***
Melting points, glass temperatures and crystallization temperatures of PP-nanocomposites synthesised with the rac[Et($IndH_4$)$_2$]$ZrCl_2$ and $Me_2Si$(Flu)(Ind)$ZrCl_2$-catalyst-systems and with different nanoparticles, catalyst and concentration in dependence of the amount of incorporation of the filler.

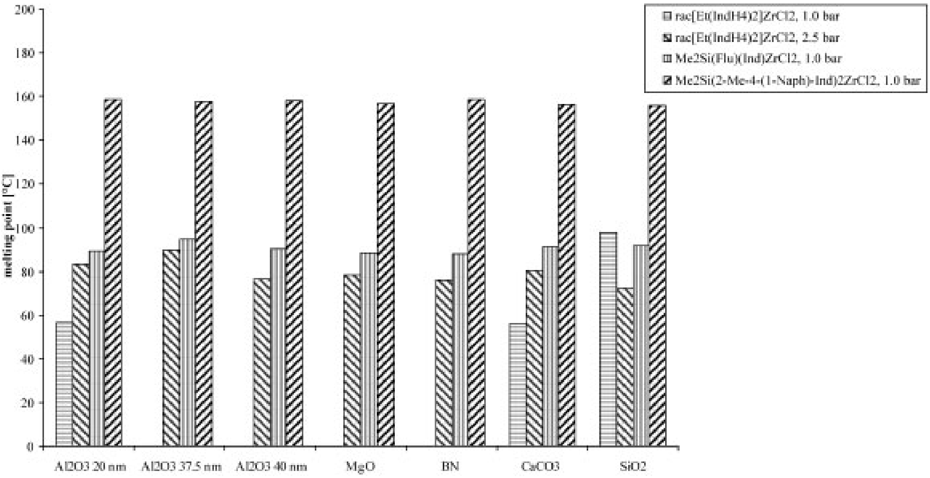


***Figure 6.***

Melting points of PP-nanocomposites with different nanoparticles by 500 mg of nanofillers in the starting reaction mixture and with different metallocene catalysts.

nanocomposites produced with rac[Et(Ind$H_4$)$_2$]Zr$Cl_2$ and 1 bar propene had low molecular weights, this was the reason for not detecting melting points for every polymer. There is no significant influence of the different kind of the fillers on the melting points.

The glass temperatures of the polymers produced with the rac[$Me_2$Si(2-Me-4-(1-Naph)Ind)$_2$]Zr$Cl_2$-catalyst were lower than the glass temperatures of the polymers synthesized with the catalysts systems rac[Et(Ind$H_4$)$_2$]Zr$Cl_2$. The nanocomposites produced with rac[Et(Ind$H_4$)$_2$]Zr$Cl_2$

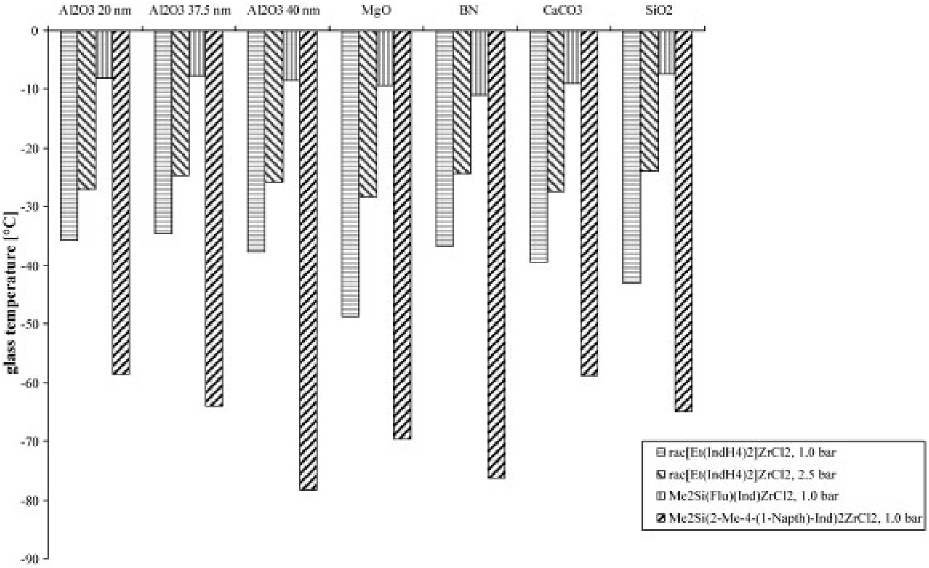


***Figure 7.***

Glass temperatures of PP-nanocomposites with different nanoparticles by 500 mg of nanofillers in the starting reaction mixture and with different metallocene catalysts.

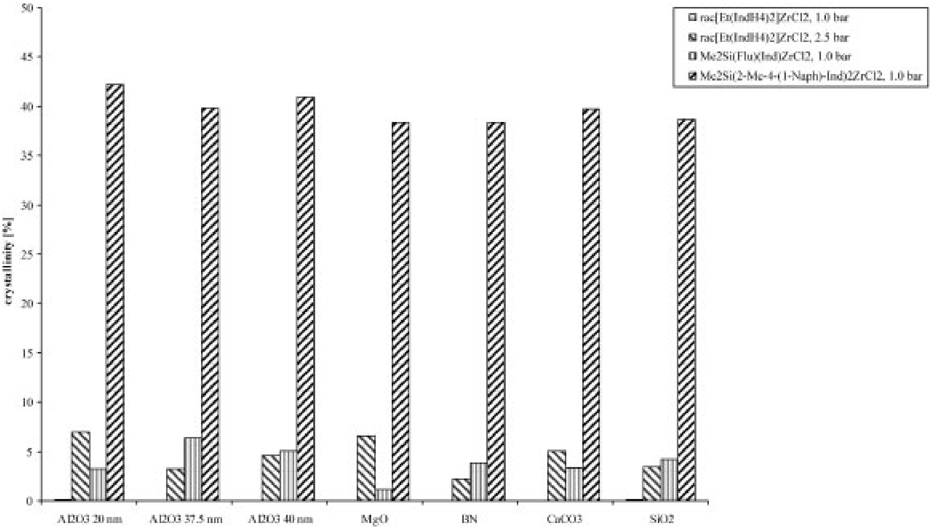


***Figure 8.***
crystallinity of PP-nanocomposites with different nanoparticles by 500 mg of nanofillers in the starting reaction mixture and with different metallocene catalysts.

and 1 bar propene had the highest glass temperatures. The kind of the fillers have nearly no influence.

The crystallinity is calculated consider to 100% crystal material (PP: 207 J/mol 12]). The crystallinities of the nanocomposites produced with the rac[Et(IndH$_4$)$_2$]ZrCl$_2$ and Me$_2$Si(Flu)(Ind)ZrCl$_2$-catalyst-systems were very low. The crystallinities of all nanocomposites produced with the rac[Et(IndH$_4$)$_2$]ZrCl$_2$ and Me$_2$Si(Flu)(Ind)ZrCl$_2$-catalyst-systems detected under 7%. Only the crystallinities of the polymers synthezised with the rac[Me$_2$Si(2-Me-4-(1-Naph)Ind)$_2$]ZrCl$_2$-catalyst were high. They varied between 38 and 43%.

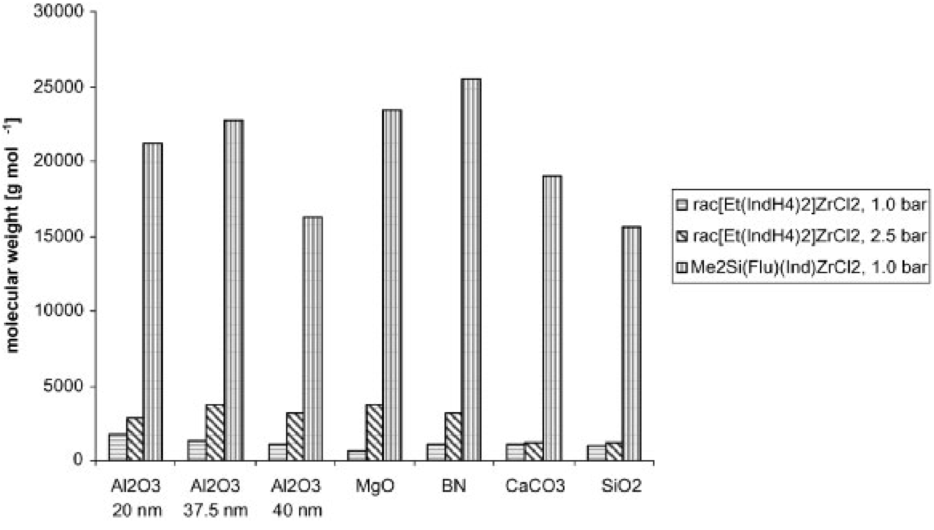


***Figure 9.***
molecular weight of the PP-nanocomposites.

## Molecular Weight and Microstructure

The molecular weight of the obtained polymers depends on the catalyst-system and the concentration of the propene. Also the size of the particles had a small influence on the molecular weight.

The molecular weights of the nanocomposites, which were produced with $Me_2Si(Flu)(Ind)ZrCl_2$ and 1 bar, were in between 6000 and 26000 g/mol. The variation of the propene pressure had the following effects. The molecular weights of the nanocomposites prepared with 1 bar and rac$[Et(IndH_4)_2]ZrCl_2$ were measured between 300 and 1400 g/mol and were lower than the molecular weights of the nanocomposites produced with 2.5 bar propene and using the same catalyst (1100-3800 g/mol). All used zirconocene complexes were known to produce isotactic polypropylene. The $^{13}C$-NMR investigations showed that the nanofillers have not changed the tacticities of the polymer. $[Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Naph)Ind)_2]ZrCl_2$ gives the highest isotacticity with 96% mmmm pentades. The $Me_2Si(Flu)(Ind)ZrCl_2$ yields an isotacticity of 50%. The lowest isotacticity with a value of 40% is given for rac$[Et(IndH_4)_2]ZrCl_2$.[13] As typical for isotactic polypropene the ratio of mmmr: mmrr: mrrm is 2:2:1.[14]

## Conclusion

PP-nanocomposites with different fillers, filler contents and catalysts were prepared by in-situ polymerization. The activity was strongly influenced by the kind of the nanofiller content. The $Al_2O_3$-nanoparticles were encased by a thin polypropylene film. The melting points, glass temperatures and crystallization temperatures of the PP-nanocomposites were especially influenced by the filler content, but there was nearly no influence of the kind of the fillers. The melting points of the polymers produced with the rac$[Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Naph)Ind)_2]ZrCl_2$-catalyst were higher than the melting points of the other polymers due to the high isotacticity of the polymers obtained with this catalyst system. The polymers synthesized with the catalyst system rac$[Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Naph)Ind)_2]ZrCl_2$ presents the lowest glass temperatures, while nanocomposites produced with rac$[Et(IndH_4)_2]ZrCl_2$ and 1 bar propene pressure presents the highest ones. The crystallinities of the polymers synthesised with the rac$[Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Naph)Ind)_2]ZrCl_2$-catalyst were high and varied between 38 and 43%. The molecular weights and the crystallinities of the polymers which were synthesised with the rac$[Et(IndH_4)_2]ZrCl_2$, $Me_2Si(Flu)(Ind)ZrCl_2$-catalyst-systems were low.

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