

Copolymerization of Propene with Phenylnorbornene Using *ansa*-Bridged Metallocene Catalysts

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ABSTRACT: Propene was copolymerized with phenylnorbornene using methylaluminumoxane (MAO)-activated metallocene dichlorides exhibiting different symmetry: C_2 -Symmetric *rac*-ethylenebis(1-indenyl)zirconium dichloride (**1**), *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride (**2**), *rac*-ethylenebis(1-indenyl)hafnium dichloride (**6**), C_s -symmetric isopropylidene(cyclopentadienyl-9-fluorenyl)zirconium dichloride (**3**), *meso*-ethylenebis(1-indenyl)zirconium dichloride (**4**), and C_1 -symmetric ethylene(1-fluorenyl-1-phenyl-2-indenyl)zirconium dichloride (**5**) were chosen to evaluate the influence of the symmetry in copolymerization reactions. Experiments were done as batch polymerizations to produce homogeneous copolymers. By this setup, blend formation was avoided. The copolymers were characterized by NMR, GPC, and DSC. Catalysts **1** and **2** were the most active to copolymerize random, amorphous, copolymers with good activity. C_s -symmetric, **3**, showed decreased activity compared with **1** and **2** and produced a bimodal copolymer. Catalyst **4** showed even lower activity than that of **3**. The activity of the hafnium complex **6**, which produced a semicrystalline polymer with a high molecular weight (116,000 g/mol) was 320 kg/mol. Catalyst **1** produced the highest comonomer content (42%) in the copolymers measured by NMR. The least active catalyst was **5** (phenyl group in the bridge), producing only 290 kg copolymer per mole of catalyst. All polymers had elevated glass transition temperatures compared to polypropylene. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2743–2752, 2002

Key words: metallocene; propene; cyclic olefin; copolymer

INTRODUCTION

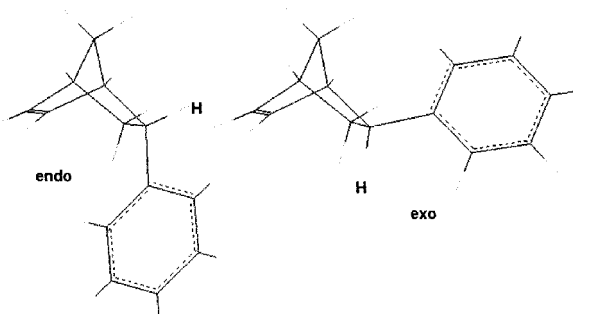
During last two decades, research of homogeneous coordination polymerization catalysts and cocatalysts has been intensive, especially that of group 4 metallocenes activated with methylaluminum oxane (MAO). Fundamental work in this area done by Kaminsky, Brintzinger, and others has introduced a versatile tool to the polymer

synthesis to control molar mass and chain tacticity together with very high catalytic activity.^{1–3} Metallocenes also have the ability to copolymerize a high variety of monomers, which was not possible earlier using traditional Ziegler–Natta catalysts and, therefore, many new polymer materials have been introduced.⁴

Norbornene and ethene can be copolymerized with metallocenes, producing amorphous random copolymers with a high incorporation of norbornene.² Bulky norbornene units randomly distributed along the polymer chain elevate the glass transition temperatures linearly with increasing

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Scheme 1 Endo and exo regioisomers of phenylnorbornene.

comonomer content. The softening temperature of these copolymers can be increased to 200°C and even higher. These copolymers can be used in optical applications, packaging, and automotive parts. Hoechst (Frankfurt, Germany) and the Exxon Chemical Co. (Houston, TX) have been very active based on their patents issued in this research area.⁵⁻⁷

Substituted and higher cyclic olefins such as phenylnorbornene and indanylnorbornene can also be polymerized via olefinic double bonds with metallocenes, providing many new monomer-comonomer combinations to be polymerized.⁸ Phenylnorbornene (5-phenyl-bicyclo[2,2,1]hept-2-ene) elevates the T_g of ethene-phenylnorbornene copolymers and also increases the impact strength of the material compared to norbornene.⁹ Phenylnorbornene, presented in Scheme 1, exists in two enantiomers, named endo and exo forms, depending of the position of the phenyl group related to the cyclohexyl ring plane. Propene can be polymerized with norbornene to yield relatively low

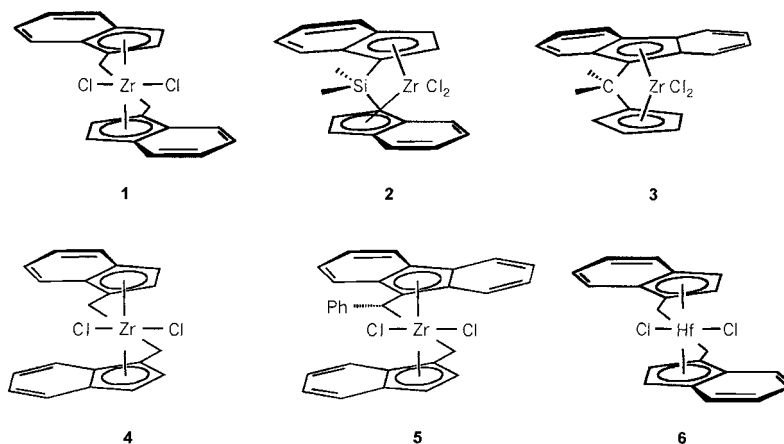
molar mass amorphous copolymers with a high content of norbornene and high T_g .¹⁰ In this work, we synthesized propene-phenylnorbornene copolymers using different MAO-activated metallocene dichlorides to study the polymerization behavior of phenylnorbornene and the properties of the copolymer. Polymerization conditions were controlled to avoid blend formation during the copolymerization.¹¹

To study the influence of catalyst symmetry in copolymerizations, six different metallocenes, presented in Scheme 2, were chosen: C_1 -symmetric *meso*-ethylenebis(1-indenyl)ZrCl₂ (**4**), ethylene(1-fluorenyl-1-phenyl-2-indenyl)ZrCl₂ (**5**), C_2 -symmetric *rac*-ethylenebis(1-indenyl)ZrCl₂ (**1**), *rac*-dimethylsilylbis(1-indenyl)ZrCl₂ (**2**), *rac*-ethylenebis(1-indenyl)HfCl₂ (**6**), and C_s -symmetric isopropylidene(1-fluorenyl-1-cyclopentadienyl)ZrCl₂ (**3**). Complexes **1** and **2** are highly active catalyst precursors for isotactic polypropene and **3** was reported to be the first metallocene catalyst to produce syndiotactic polypropene.¹ *meso*-Zirconocenes, such as **4**, are known to polymerize propene to a low molar mass atactic polypropene with low activity.¹²

EXPERIMENTAL

Materials

Toluene was purified by refluxing on sodium and was distilled under argon. Phenylnorbornene was obtained from the Optatech Corp. (Espoo, Finland), distilled on CaH₂ under reduced pressure, and stored on molecular sieves. All catalysts, cocatalysts, and comonomers were handled under a dry argon atmosphere using standard Schlenk



Scheme 2 Used metallocene catalyst precursors.

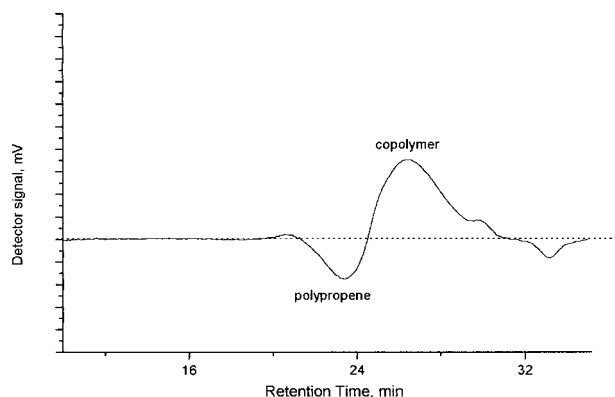


Figure 1 GPC chromatogram of polypropylene/poly(propene-*co*-phenylnorbornene) blend measured with refractive index (RI) detector. Polymerization conditions: propene pressure, 3.8 bar; temperature, 40°C; catalyst **1**, 2 μmol ; polymerization time, 50 min; comonomer feed, 10.3 mol %; Al : Zr = 15,000.

techniques. Catalysts were pretreated with MAO for about 20 min before injecting them into the autoclave. Catalysts **2** and **3** were purchased from the Boulder Scientific Co. (Mead, CO) and catalysts **1**, **4**, **5**, and **6** were made according to refs. 12–14. MAO was used as a 30% solution in toluene and purchased from the Albemarle Co. (Houston, TX).

Polymerization Procedure

The polymerizations were done in a thermostatic 1.0-L Büchi glass autoclave. The reactor was

filled with 200 mL toluene and the required amount of the cocatalyst and then saturated with propene at 3.8 bar. The propene pressure, reactor temperature, and monomer consumption were followed by an on-line analyzing system connected to a computer. The polymerizations were stopped by passing the polymerization solution into 600 mL of a HCl–methanol solution.

Preliminary polymerizations with catalysts **1** and **2** were done at a constant propene pressure maintained by a controlled flow of propene to the autoclave. This led to inhomogeneous incorporation of the comonomer into the copolymer and blend formation, which can be seen in the GPC and DSC measurements. Figure 1 presents how a differential refractive index (DRI) detector separates the responding peaks of the blend components on the both sides of the chromatographic baseline due to the contrasting refractive index change of polypropylene and phenyl containing copolymer against 1,2,4-trichlorobenzene. In DSC, the inhomogeneity of the copolymer can be seen as very broad T_g temperature interval, while blend formation can be seen as a clear T_g of the copolymer and a sharp melting peak of the homopolymer. Figure 2 shows thermograms of a blend and a pure copolymer. Searching for the optimal conditions for copolymerizations, we made a batch copolymerization using 7.3 mol % of the comonomer and recorded the propene pressure drop from an initial 3.8–0.0 bar versus time (Fig. 3). In this procedure, we made an assump-

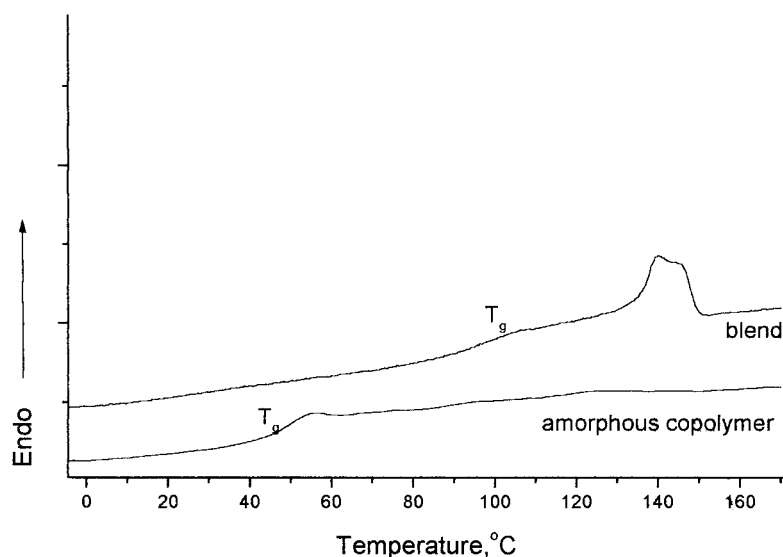


Figure 2 DSC thermograms of poly(propene-*co*-phenylnorbornene)/polypropylene blend and homogeneous copolymer.

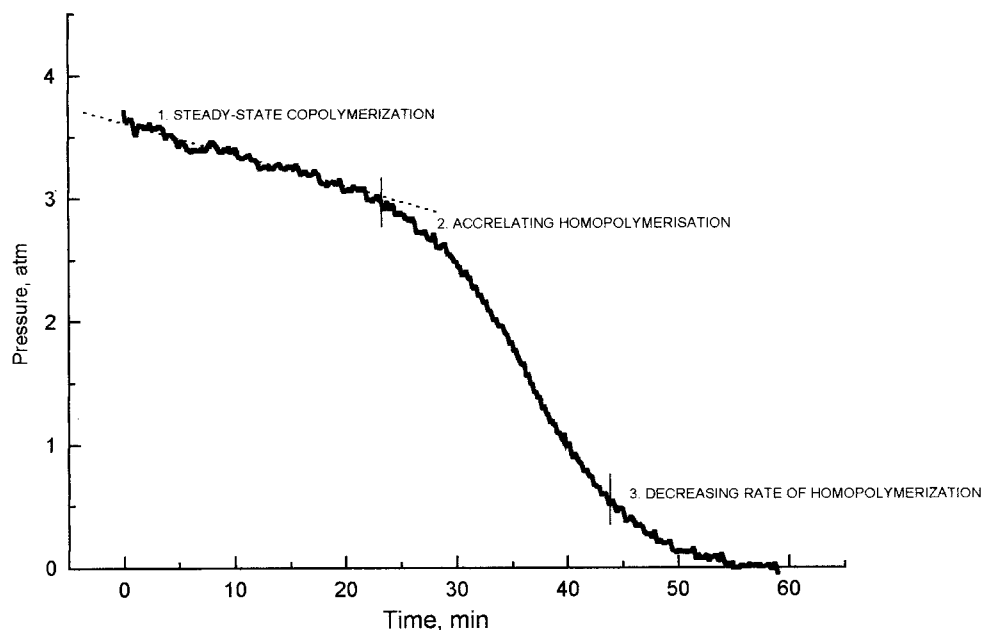


Figure 3 Pressure drop during propene–phenylnorbornene batch copolymerization. Reactor conditions: propene pressure, 3.8–0.0 bar; temperature, 40°C; comonomer feed, 3.8 mol %; catalyst **1**, 5 μmol .

tion that the propene insertion rate, $k_i = -(d[M_{\text{ins}}]/dt)$, is equal to the time-dependent pressure drop ($-dp_{\text{prop}}/dt$) of propene during the polymerizations. At the beginning of the polymerization $-dp_{\text{prop}}/dt$ is constant and copolymerization is close to a steady-state equilibrium condition. When the comonomer concentration was decreased to zero, the propene homopolymerization accelerates and this can be seen in Figure 3 as a faster drop of propene pressure. The use of a steady-state pressure area in batch copolymerizations yielded homogeneous copolymers with a monomodal GPC peak and clearly detectable glass transition temperatures.

Copolymer Characterization

The molar mass determinations were done with a Waters ALC-GPC 150C apparatus at 135°C using Waters HT3, HT4, and HT5 columns and 1,2,4-trichlorobenzene as an eluent. Copolymers with a low detector response against 1,2,4-trichlorobenzene were measured at room temperature using toluene or chloroform as the eluent. GPC was calibrated with narrow polystyrene standards.

The determination of the comonomer content in the copolymer was done by $^1\text{H-NMR}$ spectroscopy.¹⁵ The copolymers in Table I were recorded

Table I Results of Copolymerizations of Propene and Phenylnorbornene Using Catalysts 1–6

Catalyst	$n_{\text{catalyst}}/(\mu\text{mol})$	Al : Me	Activity [kg/(mol _{Zr} h)]	M_w (g/mol)	M_w/M_n	T_m (°C)	T_g (°C)	Comonomer Incorporation (%)
1	5.1	6000	1900	23,500	1.8	Amorphous	51	21.6
2	5.4	6000	1200	21,400	2.9	Amorphous	32	17.8
3	5.4	6000	790	8100	2.5	107	10	7.1
4	5.0	6000	460	8200	2.4	Amorphous	−3	7.9
5	10.0	3000	290	23,800	1.9	Amorphous	2	6.5
6	18.0	2000	320	103,000	1.6	105	7	15.2

Copolymerization conditions: batch polymerizations; toluene, 200 mL; temperature, 40°C; initial pressure of propene, 3.8 bar; comonomer feed, 6.2 mol %.

Table II Results of Copolymerizations of Propene and Phenylnorbornene Using **1** with Different Comonomer Feed Ratios

Catalyst	Polymerization Time (s)	PhNB in Feed (mol %)	Activity ($\text{kg mol}_{\text{Zr}}^{-1} \text{h}^{-1}$)	M_w (g/mol)	M_w/M_n	T_m ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)	Comonomer Content (mol %)
1	1602	3.3	4221	16,100	1.9	109	12.0	10.5
1	2018	7.4	3028	20,800	2.0	Amorphous	19.3	23.4
1	3763	10.7	2202	21,000	2.4	Amorphous	31.0	33.8
1	5106	13.8	1911	21,200	2.5	Amorphous	72.3	40.0
1	7668	16.7	1646	21,400	2.4	Amorphous	73.3	42.1

Copolymerization conditions: batch polymerizations; toluene, 200 mL; temperature, 40 $^{\circ}\text{C}$; initial pressure of propene, 3.8 bar; Al : Zr = 2000; n_{catalyst} 5.0 μmol .

with a Varian Gemini 200-MHz spectrometer at ambient temperature using 1,1,2,2-tetrachloroethane- d_2 as a solvent. An acquisition time of 2.0 s, a pulse interval of 4.0 s, and a pulse width of 90 $^{\circ}$ were used and 16 free-induction decays were recorded in the spectrum consisting of 22,500 data points in the spectral window of 3000 Hz. The copolymers referred to in Table II were measured with a 500-MHz spectrometer at 80 $^{\circ}\text{C}$ in 1,1,2,2-tetrachloroethane- d_2 . An acquisition time of 1.8 s, pulse intervals of 20 s, and a pulse width of 45 $^{\circ}$ were used and 64 free-induction decays were recorded in the spectrum of 30,300 data points in the spectral window of 8000 Hz. The comonomer content in the copolymer was determined by using integrated areas of aliphatic, A_1

(0–3.5 ppm), and aromatic, A_2 (6.6–8.4 ppm), regions in the proton spectra. The molar percentage of the comonomer was calculated using eq. (1).

^{13}C -NMR spectra, 50 MHz, were measured at ambient temperature in 1,1,2,2-tetrachloroethane- d_2 using 1.5 s acquisition times, 4.0 s pulse intervals, and 45 $^{\circ}$ pulse widths. More than 10,000 free-induction decays were collected in the spectrum of 37,500 data points in the spectral window of 12,500 Hz. Full NOE with a WALZ16 decoupler mode was used to increase the signal-to-noise ratio in the measurement. According to earlier published procedures, these parameters are valid for quantitative analysis of pentad sequences for the tacticity determination of polypropenes.¹⁶

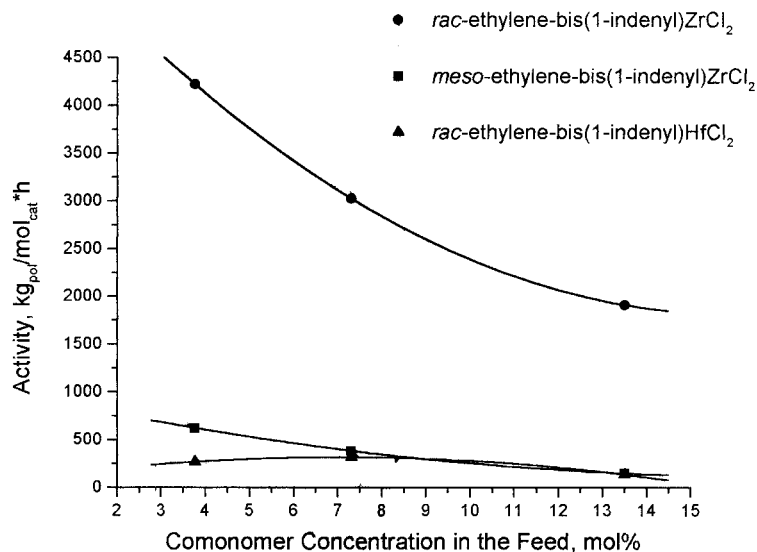


Figure 4 Dependence of copolymerization activities of comonomer feed of 3.8, 7.3, and 13.5 mol % with catalysts **1**, **4**, and **6**. Batch copolymerization; temperature, 40 $^{\circ}\text{C}$; initial pressure of propene, 3.8 bar, and final, 3.3 bar.

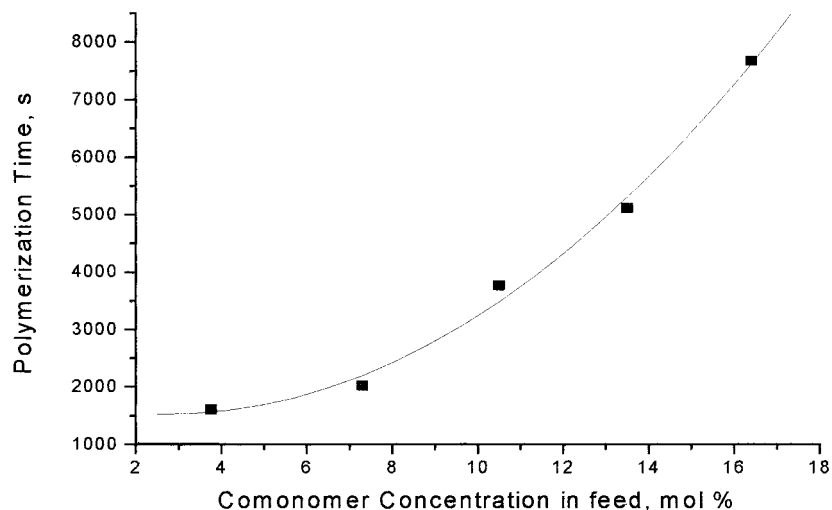


Figure 5 Propene phenylnorbornene copolymerization time plotted against comonomer feed in batch polymerizations with constant pressure change from 3.8 to 3.3 bar of propene. Catalyst **1**, 5 μmol ; temperature, 40°C; Al : Zr = 2000.

$$phNB\% = \frac{\frac{1}{5} * A_1}{\frac{1}{6} \left(A_2 - \frac{9}{5} * A \right) + \frac{1}{5} * (A_1)} * 100 \quad (1)$$

Differential scanning calorimetry (DSC) measurements were carried out with a Perkin–Elmer DSC-2 calorimeter equipped with a digital data acquisition system. Thermograms were determined from the second temperature scan from

–20 to 200°C after cooling from 200 to –20°C with cooling rate of 320°C/min.

RESULTS

Activities of Different Catalysts

Results of comparable polymerizations with different catalyst precursors **1–6** are summarized in Table I. In this series, the *rac* catalyst **1** was the

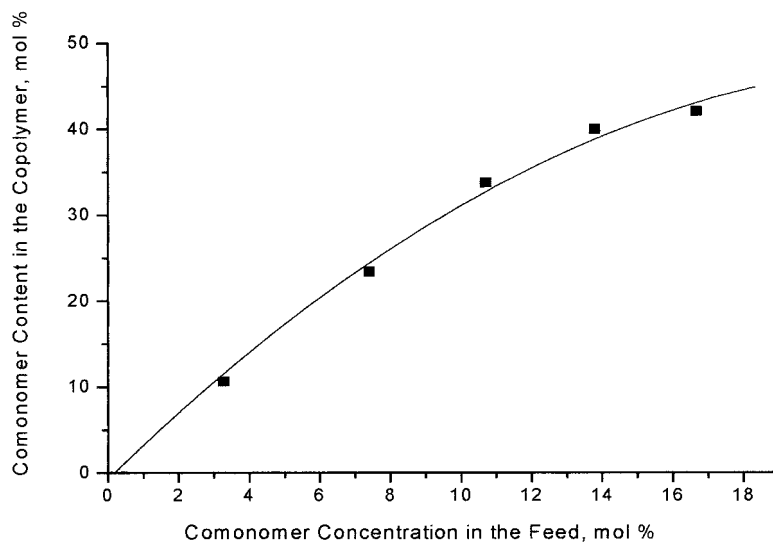


Figure 6 Phenylnorbornene content in the poly(propene-*co*-phenylnorbornene) synthesized with catalyst **1** using comonomer feed of 3.8, 7.5, 10.5, 13.5, and 16.3 mol %.

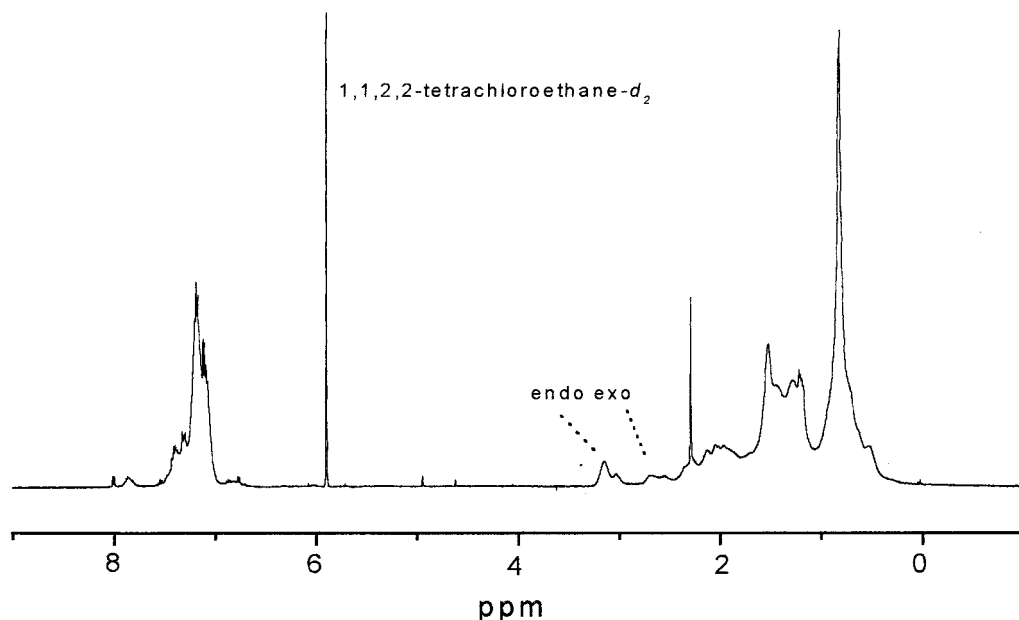


Figure 7 $^1\text{H-NMR}$ spectra, 500 MHz, of poly(propene-*co*-phenylnorbornene) copolymerized with catalyst **1**.

most active in copolymerizations with an activity of $1930 \text{ kg mol}_{\text{cat}}^{-1} \text{ h}^{-1}$. Its *meso* derivative **4** showed an activity of $460 \text{ kg mol}_{\text{cat}}^{-1} \text{ h}^{-1}$. The C_s -symmetric, **3**, had 40% of the activity of **1**. In this series, the sterically most hindered catalyst, **5**, had the lowest activity. The hafnium analog of the catalyst, **1**, *rac*-ethylenebis(1-indenyl)- HfCl_2 , **6**, produced a copolymer with an activity of $320 \text{ kg mol}_{\text{cat}}^{-1} \text{ h}^{-1}$. Polymerization activities of catalysts **1**, **4**, and **6** were scaled also with different comonomer feed ratios and fitted to the exponential decay curves in Figure 4. The results of the copolymerizations with catalyst **1** using five different comonomer feed ratios are presented in Table II. The decrease in the rate of the copolymerization as the phenylnorbornene concentration in the comonomer feed increased using the most active catalyst can be seen in Figure 5. This indicates that the insertion of the bulky phenylnorbornene unit into the polymer chain is controlling the rate of the copolymerization. Figure 6 illustrates how the comonomer content in the copolymer chain depends on the phenylnorbornene concentration in the feed in the copolymers synthesized with catalyst **1**.

Chemical Structure of the Copolymer

The 500-MHz $^1\text{H-NMR}$ spectra of the copolymer made with catalyst **1** using 7.2 mol % of the phe-

nylnorbornene comonomer in the feed is presented in Figure 7. Resolution of aliphatic protons in the polypropene segments and norbornene rings is diminished due to the many overlapping peaks, but the methine protons connected to the phenyl ring separate into two peaks: 2.65 ppm for *exo* phenylnorbornene and 3.15 for *endo* isomer. This indicates that both regioisomers of the comonomer are inserted into the copolymer.¹⁵ Figure 8 presents 500-MHz $^1\text{H-NMR}$ spectra of olefinic regions of the copolymers made with cat-

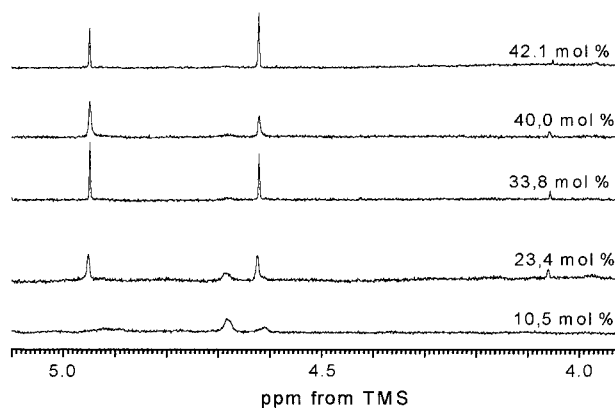


Figure 8 Olefinic region of $^1\text{H-NMR}$ spectra of five poly(propene-*co*-phenylnorbornene)s. Copolymerized with catalyst **1** using comonomer feed of 3.8, 7.5, 10.5, 13.5, and 16.3 mol %.

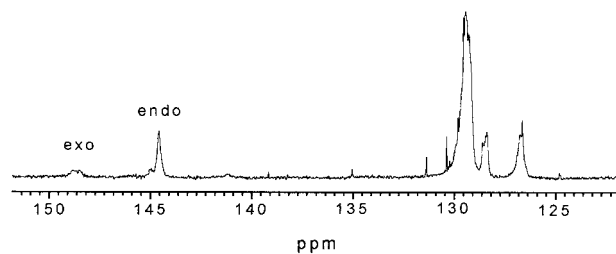


Figure 11 Aromatic region of ^{13}C -NMR-spectra of poly(propene-co-phenylnorbornene) copolymerized with catalyst **1**.

mer. The copolymer made with catalyst **1** shows a sharp peak at 21.96 in the methyl region, indicating a high fraction of isotactic *mmmm* pentads in the enchainment. Respectively, the copolymer made with catalyst **5** shows eight peaks of the different pentads typical for atactic polypropene (Fig. 10). The nonprotonated aromatic carbon in the downfield region of the spectrum (143–148.5 ppm) of the copolymer with 21.6 % of phenylnorbornene shows two separate peaks for the *exo/endo* isomers (Fig. 11).

Molar Mass and Molar Mass Distributions

The molar mass of copolymers made with zirconocenes **1–5** at 40°C varied from 8100 to 24,700 g/mol. The molar mass distribution of the copolymer made with complex **3** was bimodal, which can be due to two different coordination sites for phe-

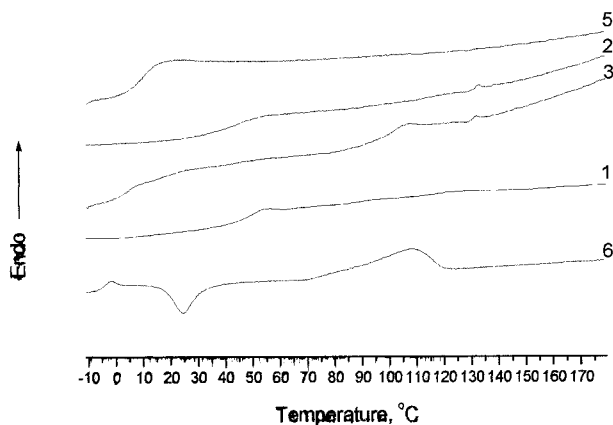


Figure 13 DSC thermograms of poly(propene-co-phenylnorbornene) copolymers synthesized with catalysts **1–3**, **5**, and **6**. Comonomer feed, 7.3 mol %.

nylnorbornene. The hafnium catalyst **6** produced a copolymer with a significantly higher molar mass, 103,000 g/mol, with a narrow molecular weight distribution of 1.6. The molar mass dependence of the polymerization temperature with catalyst **1** is plotted in Figure 12.

Glass Transition Temperatures

Some thermograms of different copolymers measured with DSC are presented in Figure 13. All the copolymers had elevated glass transition temperatures compared to that of the polypropylene

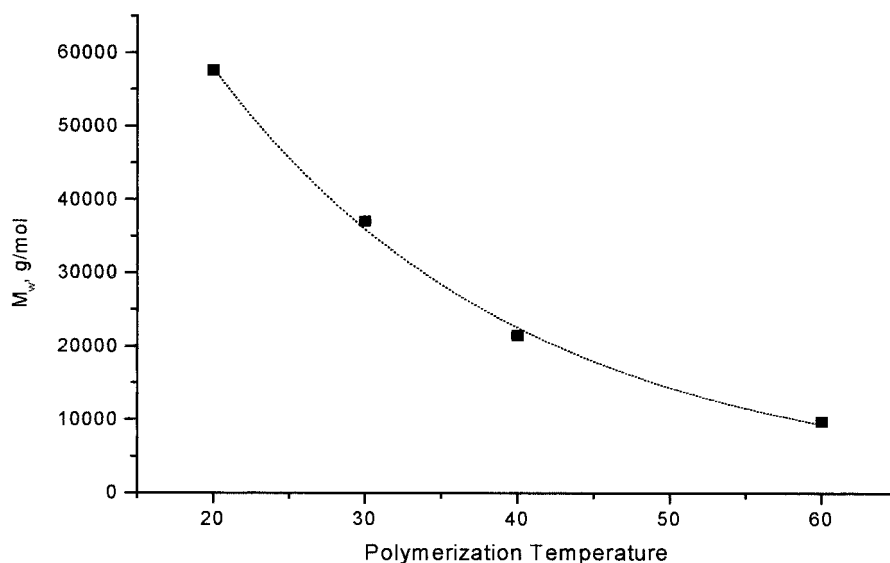


Figure 12 Dependence of weight-average molar mass, M_w , on the copolymerization temperature in copolymerizations done at 20, 30, 40, and 60°C with catalyst **1**.

homopolymer. The T_g increased almost linearly with comonomer incorporation into the polymer chain. The tacticity of the propene segments and the molar masses of the copolymers are different depending on the catalyst used and this can be seen as variations in the glass transition temperatures in the copolymers with the same amount of incorporated comonomer. Most of the copolymers obtained were totally amorphous and no melting peaks were detected. Partially crystalline polymers had broad melting peaks around 100°C.

CONCLUSIONS

In well-optimized copolymerization conditions, catalysts **1** and **2** produce a pure amorphous copolymer with good activity and more than 40% of phenylnorbornene units in the copolymer. With highly purified monomers, no catalyst deactivation was recognized during the polymerization—only a decreasing rate of the copolymerization with higher comonomer feeds due to the slow insertion rate of phenylnorbornene. The coordination equilibrium and insertion rates for propene and phenylnorbornene vary between each active catalyst and this leads to the different composition of the copolymer chain. Excluding the copolymer made with the hafnium complex, the molar masses of synthesized copolymers are rather low. According to the ^{13}C -NMR measurements, the tacticity of the propene segments can vary from purely isotactic to atactic. A higher incorporation of phenylnorbornene than 42.1 % was not detected and this confirms that insertion of phenylnorbornene into a copolymer chain is possible only after insertion of propene. The increasing amount of phenylnorbornene units in the copolymer chain increases the T_g , decreases the crystallinity of poly(propene-*co*-phenylnorbornene), and

results in a glassy, polymeric material with softening temperatures to 90°C.

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