Synthesis of Copolymers with Sterically Hindered and Polar Monomers

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Summary: Different highly substituted C_1 symmetric metallocenes have been investigated for the copolymerization of ethene and norbornene. The influence of the feed ratio and the polymerization temperature were varied to characterize the polymer by means of microstructure, thermal properties and catalysts activity. The bulky structured ligands of the catalysts lead to highly stereoregular copolymers with semi-crystalline phases even at low norbornene incorporation. Two different allyl ethers (allyl ethyl and allyl propyl ether) have been used to copolymerize with ethene using metallocene catalyst system (*rac*-[Me_2Si(2-Me-4-(1-Ph)Ind)$_2$]$ZrCl_2$/MAO). In order to investigate the influence to ether incorporation to polymer properties, we have performed experiments varying comonomers concentration in feed, polymerization temperature and ratio $Al_{(MAO)}/Zr$. The higher comonomer incorporation was followed by loss of cristallinity of the produced polymer. Additionally, the catalytic activity and melting point of the polymers also decrease with increase in comonomer concentration in feed.

Keywords: alternating ethene norbornene copolymers; C_1 symmetric metallocenes; cycloolefin-copolymers COC; polar monomers

Introduction

Metallocene catalysts have opened new perspectives due to the possibility to the direct copolymerization of olefins with sterically hindered or functional monomers [1].

Technical copolymers of ethene and norbornene (cyclic olefin copolymers, COCs) are amorphous thermoplastics. The combination of properties like high transparency, glass transition temperature and refractive index, together with an excellent processability, makes them an alternative for materials like polycarbonate and polymethyl methacrylate. Besides amorphous COCs, a major academical and industrial interest is to synthesize semi-crystalline E/N-copolymers [2]. Due to their nano sized crystals these alternating copolymers show high melting temperatures with excellent transparency [3].

Various investigations have been made with C_1 symmetric [4] [5] or constrained geometry catalysts [6] [7] to obtain highly alternating semi-crystalline E/N-copolymers starting with melting points from 230 °C. The aim of this work was the synthesis of highly stereoregular copolymers with exclusively isolated norbornene units which already show crystallization at low norbornene incorporation.

Another way to modify the polymer properties is the introduction of polar groups into non polar materials [1]. These polar groups into the polymer backbone can yield materials with enhanced properties on the polymer surface, such as, barrier properties, adhesion and better compatibility with non olefinic polymers. Metallocene catalysts have opened new perspectives in this area, through the direct copolymerization of olefins with functional monomers [8]. Copo-

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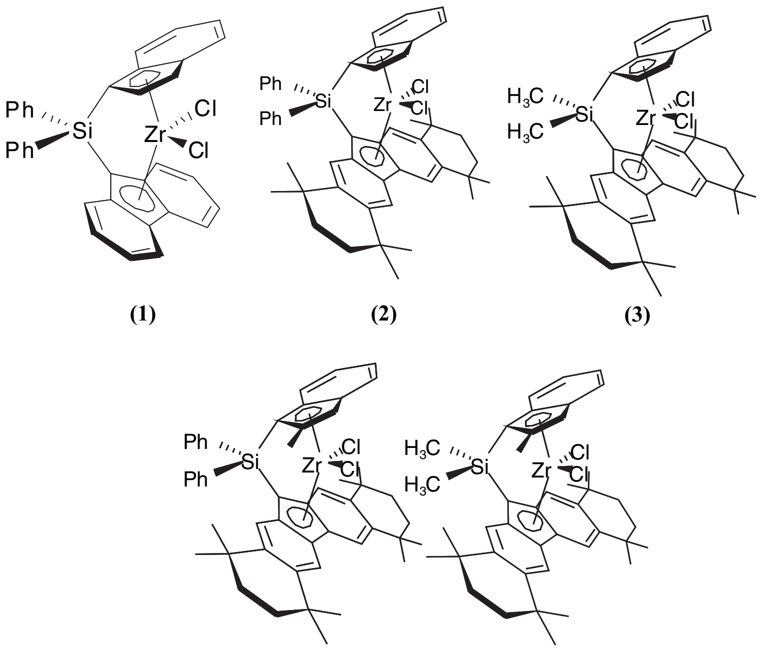
lymerization of olefin with oxygen containing comonomer normally leads to decrease in catalyst activity [9]. One way of reducing the deactivation of metallocene catalyst is the introduction of protecting group that can be easily removed from the produced polymer [10]. In this work, ethene was copolymerized with allyl ethyl ether (AEE) and allyl propyl ether (APE) using metallocene catalyst and TIBA as protecting group. Comonomer incorporation was evidenced by the presence of the polar group and the absence of comonomer vinyl group in the copolymer (^{1}H-NMR).

Experimental

The polymerization experiments were performed using standard Schlenk technique. Argon (Linde) was purified by passing through a Messer Oxisorp cartridge. Ethene (Linde) and toluene were purified by BASF R3-11 catalyst and 3 Å molecular sieve. Norbornene (Acros) was stirred for 48 h with triisobutylaluminum (TIBA) followed by a distillation at 50 °C. A solution in toluene of 6–7 mol L^{-1} was used for polymerizations. A solution in toluene (1 mol L^{-1}) of AEE was dried over molecular sieves for 48 h and stored under argon atmosphere. The same procedure has been done for APE.

Methylalumoxane (MAO) was purchased from Crompton as a solution in toluene containing trimethylaluminum (TMA). The solution was filtered, the solvent condensed, and the residue dried in vacuo yielding solid TMA-free MAO.

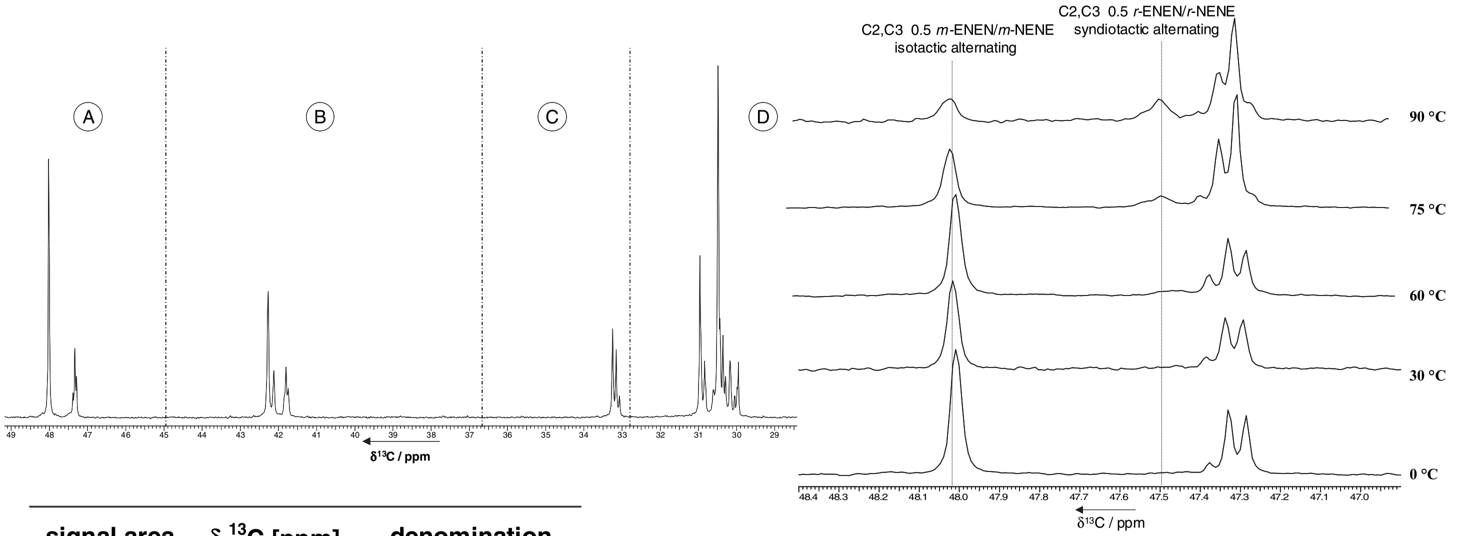
All polymerization runs were performed in a Büchi BEP 280 laboratory autoclave with a Type I glass pressure vessel. Temperature was adjusted with a heat jacket connected to a thermostat allowing adjustment of the polymerization temperature with an accuracy of ±0.5 °C. During the polymerization runs, the ethene pressure was kept constant. The ethene consumption was monitored with a Brooks 5850 TR mass flow meter. For a typical polymerization experiment, the reactor was evacuated at 92 °C for



(1) **(2)** **(3)**

(4) **(5)**

Figure 1.
C_1 symmetric metallocenes used for ethene/norbornene copolymerization.



signal area	δ ^{13}C [ppm]	denomination
A	60 - 44.8	C2, C3
B	44.8 - 36.8	C1, C4
C	36.8 - 32.8	C7
D	32.8 - 10	C5, C6, Cα, Cβ, Cγ, Cδ

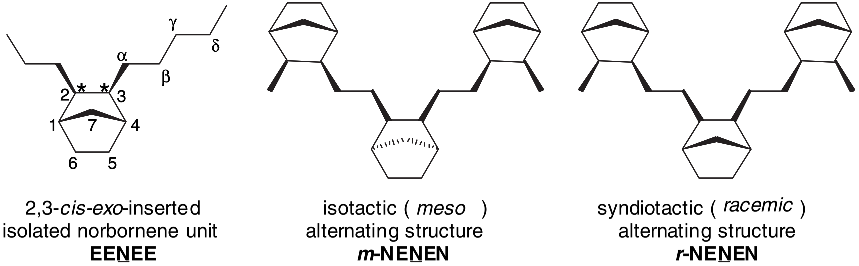


Figure 2.
Signal regions, ^{13}C-NMR assignments and NMR-region A for E/N-copolymers synthesized with [$Ph_2Si(OctHFlu)(Ind)]ZrCl_2$ at different temperatures ($X_N \approx 0.35$).

1 h and then cooled down to the desired temperature. Subsequently, the reactor was charged with MAO, comonomer solution and toluene up to a volume of 200 mL followed by ethene to the desired feed composition. The polymerization was started by injection of the catalyst solution. The reaction was quenched by addition of 5 –10 mL ethanol. All ethene/norbornene-polymer solutions were stirred overnight with 100 mL of diluted hydrochloric acid. In the case of ethene/ether polymers the

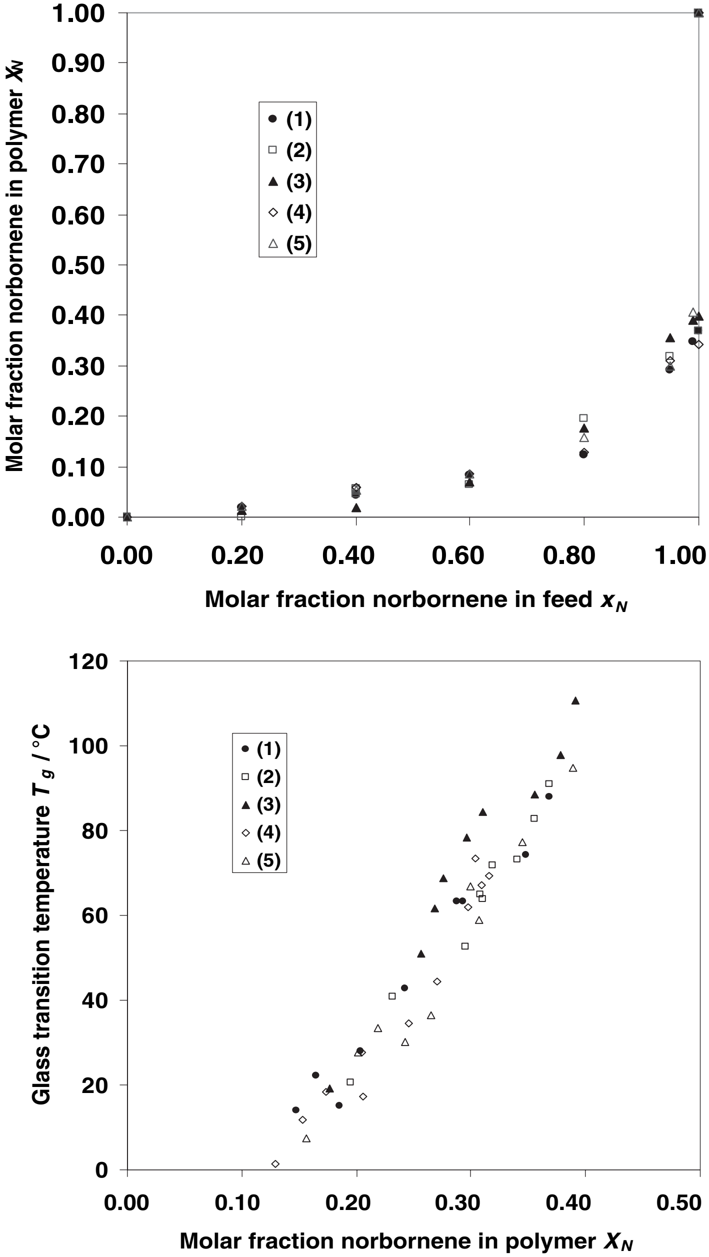


Figure 3.
Copolymerisation diagram and glass transition temperature T_g for different E/N-copolymers produced at 30 °C.

solutions were stirred overnight just with 100 mL ethanol. After phase separation, the organic phase was washed three times with water and reduced to 50–70 mL at the rotary evaporator. The polymer was precipitated with ethanol, filtered off, washed with ethanol, and dried under vacuum at 40 °C until the weight remained constant.

E/N-copolymers were characterized by ^{13}C-NMR recorded on a Bruker Avance 400 Ultrashield spectrometer. Polymer samples were measured at 100.62 MHz and 100 °C using 200 mg of polymer in 2.3 mL of 1,2,4-trichorobenzene and 0.5 ml of 1,1,2,2-tetrachloroethane-*d*$_2$. Chemical shifts are reported referenced to $C_2D_2Cl_4$ (δ 74.24 ppm against TMS for ^{13}C).

The ether incorporation was determined using ^{1}H-NMR. The samples were prepared by dissolving the polymer (10–20 mg) in a mixture of (2.5 mL) 1,2,4-trichorobenzene and (0.5 mL) of 1,1,2,2-tetrachloroethane-*d*$_2$ and measured at room temperature. All chemical shifts were referred to the solvent of TCE-*d*$_2$ at 5.9 ppm.

Differential scanning calorimetry curves were recorded on a Mettler Toledo DSC 821^e instrument. Results of the second thermal cycle are presented exclusively.

High-temperature gel permeation chromatography (GPC) measurements were performed in 1,2,4-trichlorobenzene at 140 °C using a Waters GPCV 2000 instrument with HT 10^6, 10^4, and 10^3 Å columns. The instrument operated with a combined refractive index and viscosity detector unit, which allowed the calculation of appropriate Mark-Houwink constants for each polymer. Calibration was applied using polystyrene standards (PSS).

Table 1.
Polymerization conditions and results ($T_{Pol} = 30$ °C)

Conditions[a]		Results			
Catalyst	x_N[b]	X_N (^{13}C-NMR)[c]	*Activity*[d]	T_g (°C)	T_m (°C)
1	0.000	0.000	39815	*e*	137.6
1	0.200	0.019	348	*e*	104.2
1	0.400	0.043	210	*e*	80.0
1	0.600	0.082	148	*e*	62.8
1	0.800	0.185	23	15.2	*f*
1	0.950	0.293	4	63.2	*f*
1	0.990	0.348	2	74.2	*f*
1	0.999	0.345	2	85.5	*f*
1	1.000	*g*	<1	*h*	*h*
2	0.000	0.000	4499	*e*	139.8
2	0.200	0.000	1154	*e*	111.2
2	0.400	0.057	680	*e*	88.5
2	0.600	0.064	358	*e*	75.7
2	0.800	0.195	212	20.6	*f*
2	0.950	0.319	86	71.8	206.3
2	0.990	0.311	46	63.8	231.2
2	0.999	0.368	18	90.9	238.0
2	1.000	*g*	<1	*h*	*h*
3	0.000	0.000	1985	*e*	137.7
3	0.200	0.013	1556	*e*	110.7
3	0.400	0.019	412	*e*	89.0
3	0.600	0.069	568	*e*	67.4
3	0.800	0.176	231	19.2	*f*
3	0.950	0.321	44	84.6	205.8
3	0.990	0.360	18	110.9	244.5
3	0.999	0.397	66	97.8	249.3
3	1.000	*g*	<1	*h*	*h*
4	0.000	0.000	5002	*e*	135.9
4	0.200	0.020	64	*e*	111.1
4	0.400	0.058	44	*e*	92.5
4	0.600	0.087	49	*e*	71.1
4	0.800	0.129	32	1.2	*f*
4	0.950	0.309	19	67.2	*f*
4	0.990	0.315	12	69.2	220.6
4	0.999	0.341	20	61.8	289.8
4	1.000	*g*	<1	*h*	*h*
5	0.000	0.000	4149	*e*	137.2
5	0.200	0.022	326	*e*	111.5
5	0.400	0.054	210	*e*	91.5
5	0.600	0.086	190	*e*	68.1
5	0.800	0.157	98	7.5	*f*
5	0.950	0.299	24	66.9	*f*
5	0.990	0.407	5	94.8	*f*
5	0.999	0.345	37	77.2	246.4
5	1.000	*g*	<1	*h*	*h*

[a] Total reaction volume: 200 mL (norb. homopolym. 50 mL); T_{pol}: 30°C; concentration co-catalyst: c_{MAO}: 1 gL^{-1}.
[b] Mole fraction of norbornene in the feed.
[c] Mole fraction of norbornene in the polymer (determined by ^{13}*C-NMR*).
[d] Activity: kg_{Pol} mol_M^{-1} h^{-1} (M: Zr).
[e] T_g not detected.
[f] not available.
[g] Polymer insoluble. [h] Polymer decomposes.

Results and Discussion

Ethene/Norbornene-Copolymers

Four different highly substituted C_1 symmetric metallocenes (**2**–**5**), shown in Figure 1, were used to synthesize ethene/norbornene copolymers and were compared with the unsubstituted complex **1** concerning their ability to form high amounts of stereoregular polymers. Due to their sterically hindered structure these catalysts have proven their potential to yield an increase of the percentage of alternating triads in ethene/propene copolymers [11]. To investigate the E/N copolymerization behavior over a wide range, both dominant factors for the polymer properties, the polymerization temperature (0–90 °C) and the feed ratio between ethene and norbornene ($0.0 \leq x_N \leq 1.0$), were varied.

The microstructure was studied by ^{13}C-NMR spectroscopy [12]. The spectra were subdivided into four areas (s. Figure 2, left) to calculate the norbornene content (X_N). The denomination of the carbon atoms is given as well as the corresponding chemical shift. In all cases the measurements show only isolated norbornene units. Described is an example of a copolymer with $X_N = 0.35$ synthesized with catalyst **2** at 0 °C. Caused by only alternating isotactic (*meso*) E/N and isolated norbornene units the spectra look simple compared to spectra with norbornene linkages. The bulky substituents of the catalyst result in highly selective norbornene incorporation. Exclusively isotactic alternating sequences (C2, C3, 0.5*m*NENE/ENEN) could be detected (s. Figure 2, right). The polymerization temperature has to be significantly higher ($T_P > 30$ °C) to detect the first syndiotactic alternating sequences (C2, C3, 0.5*r*NENE/ENEN) caused by misinsertion. Shown is signal region A for a copolymer with X_N of around 0.3 synthesized with catalyst **2** at different temperatures. The higher the temperature the higher the amount of syndiotactic alternating sequences (47.35 ppm).

Figure 3 shows the polymerization diagrams for the ethene/norbornene copolymers. For all catalysts the copolymerization behavior looks similar: A maximum incorporation of norbornene (X_N) is approached with around 0.4. Even at high norbornene fractions in the feed ($x_N = 0.999$) it is impossible to obtain strictly alternating E/N copolymers ($X_N = 0.5$) under this conditions. Surprisingly, norbornene homopolymers could be synthesized with all catalysts.

For all polymers with a molar fraction of norbornene higher than 0.1 glass transition temperatures could be detected. In analogy to [4] they show a linear relationship between T_g and the norbornene incorporation. With X_N of around 0.4 the maximum glass transition temperature is 110 °C. Caused by the incorporation of norbornene into the backbone the regular structure of linear polyethene is disturbed (Table 1). These polymers are semi-crystalline up to X_N of around 0.1 and melting temperatures decreasing to 62 °C for catalyst **1**. While this catalyst does not create any crystalline phases at higher norbornene contents all metallocenes with bulky substituents produce semi-crystalline E/N copolymers starting from around 32 % norbornene resulting in T_m of around 206 °C (catalyst **2**, **3**). Here the catalysts show their excellent ability to form highly stereoregular alternating copolymers causing a semi-crystalline phase at a norbornene incorporation of only 32% which seems to be the lowest reported so far. A deeper insight into the microstructural analysis and the influence of the polymerization temperature will be presented in the near future.

With higher norbornene contents a drastic decrease in activity can be observed. The substituted fluorenyl ligands seem to have a positive effect on the activity at high x_N (compare **1** and **2**) in contrast to the methyl group at the indenyl (compare **2** and **4**).

Ethene/Ether-Copolymers

Copolymerizations of APE with ethylene and AEE with ethene were carried out in presence of *rac*-[$Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Ph)Ind)_2]ZrCl_2$/MAO. It is well know that copolymerization of an olefin with oxygen containing comonomers is usually followed by a loss of catalytic activity. Probable, this undesirable deactivation reaction is caused by the formation of a complexes between the functional monomers and the catalytic electrophilic active center[1]. An alternative way to minimize this effect is to protect the functional group just before its contact with the catalyst. In this work, the protecting agent was triisobutylaluminium (TIBA). A prior reactions of APE and

Polymerization Conditions:	
Catalyst:	c(Kat) $= 2 \cdot 10^{-6}$ mol
Al:Zr - Ratio:	3781
Temperature:	30 °C, 45 °C, 60 °C
Monomer Concentration:	0.02 mol L^{-1} – 0.1 mol L^{-1}
Polymerization time:	30 min

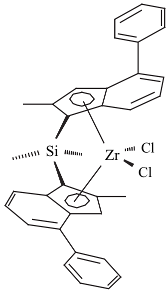


Table 2.
Ethene polymerization with *rac*-[$Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Ph)Ind)_2]ZrCl_2$/ MAO in the presence of ethers[a]

Comonomer Concentration in feed (mol/L), X_{AEE}	APE Incorporation level (% mol)	AEE Incorporation level (%mol)
0.02/0.06	1.0	0.84
0.05/0.15	4.5	4.2
0.075/0.23	5.7	4.1
0.1/0.30	8.2	4.0

[a] Polymerization conditions: polymerisation temperature, 60 °C; monomer pressure, 4 bar, total solvent volume (toluene), 200 mL; polymerisation time, 30 min; Al(MAO)/Zr ratio 3781; catalyst concentration, 2×10^{-6} M.

TIBA and AEE and TIBA at room temperature for 30 minutes using Al/ Comonomer = 0.5, 1.5, 2 have been carried out. Afterwards, the solution was injected into reactor containing the solvent and the cocatalyst. In order to investigate the influence of ether incorporation to polymer properties, we have performed a series of experiments where we modified the following parameters: comonomer concentration, temperature and ratio AL/Zr in polymerization process.

The incorporation rate for both ethers, obtained varying the comonomers concentration in feed are shown below in Table 2.

The effect of comonomer was observed varying its concentration from 0.02 to 0.1 mol L^{-1} in feed. It was observed a steady decrease in polymerisation activity with increasing value of comonomer concentration. The smaller monomer (AEE) also had a lower activity than the analogous APE (see Figure 4).

Similar behaviour was observed with melting points, the higher the concentration of comonomer in feed, the lower the melting point of the copolymer (see Figure 5). The DSC curve of each copolymer shows a melting peaks that shifts towards lower temperatures with increase in comonomers concentration. In both cases, there is a loss of cristallinity with increase of comonomer concentration in feed.

The incorporated AEE and APE contents were determined by ^1H-NMR (Figure 6). The ^1H-NMR characterization of the produced polymer showed the presence of the ether group for all the concentration used. The maximum APE incorporation (8,2% mol) was followed by a significant decrease in catalyst activity. Under the same copolymerisation condition, APE incorporation is slightly higher than that observed for AEE.

Molecular weight determinations by GPC have shown an uniform distribution in all samples. It was observed some broadening of MWD ($2 \le MWD \le 3.5$) with the presence of polar comonomer, although the molecular weights profiles continue as unimodal distribution. These results together with DSC results, suggests some heterogeneity of copolymers at

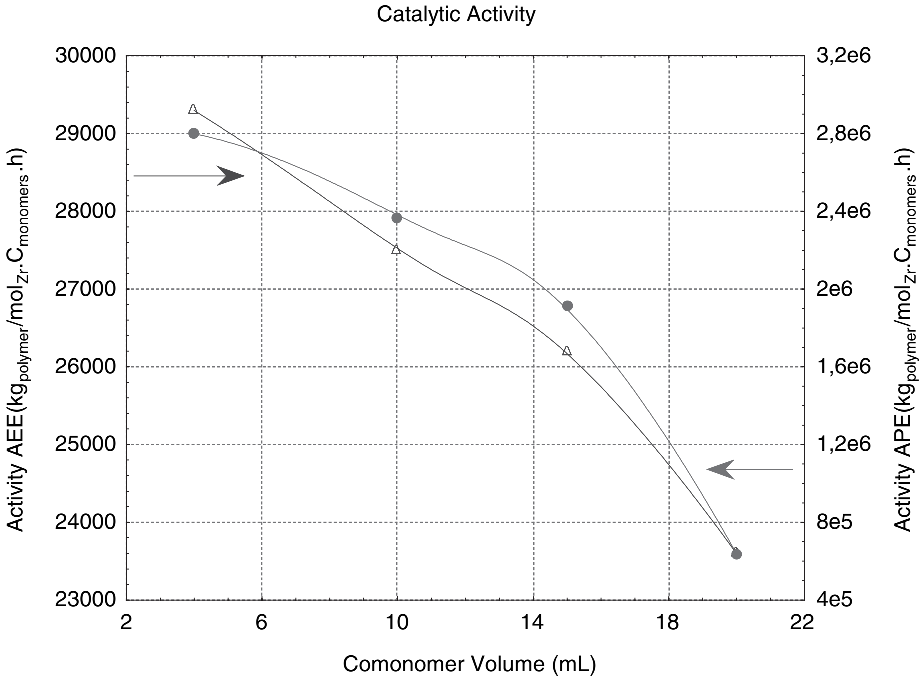


Figure 4.
Reaction activity as a function of comonomer volume (mL) in feed. Polymerization conditions polymerization temperature, 60 °C; monomer pressure, 4 bar, total solvent volume (toluene), 200 mL; polymerisation time, 30 min; $Al_{(MAO)}/Zr$ ratio 3781; catalyst concentration, 2×10^{-6} M.

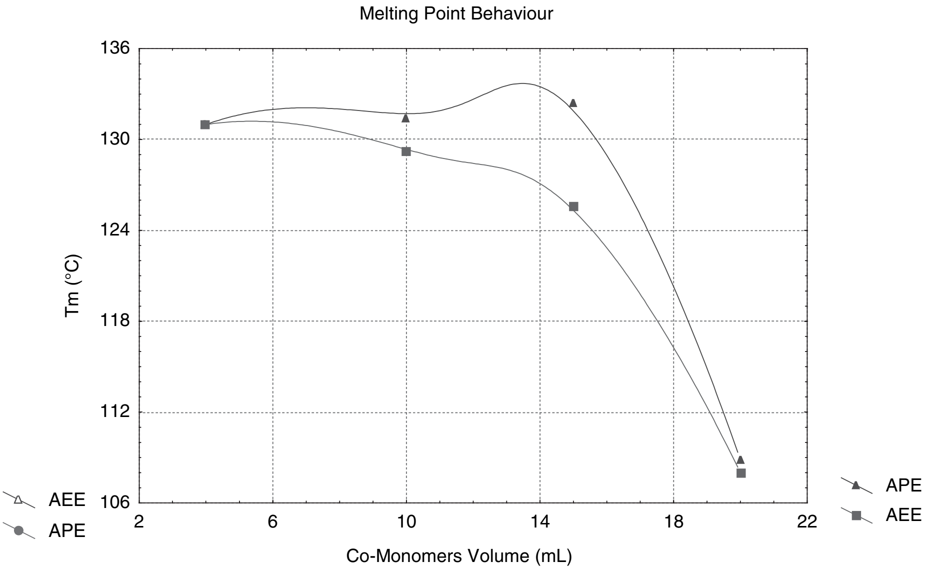


Figure 5.
Melting point behaviour as a function of comonomer volume (mL) in feed. Polymerization conditions polymerization temperature, 60 °C; monomer pressure, 4 bar, total solvent volume (toluene), 200 mL; polymerisation time, 30 min; $Al_{(MAO)}/Zr$ ratio 3781; catalyst concentration, 2×10^{-6} M.

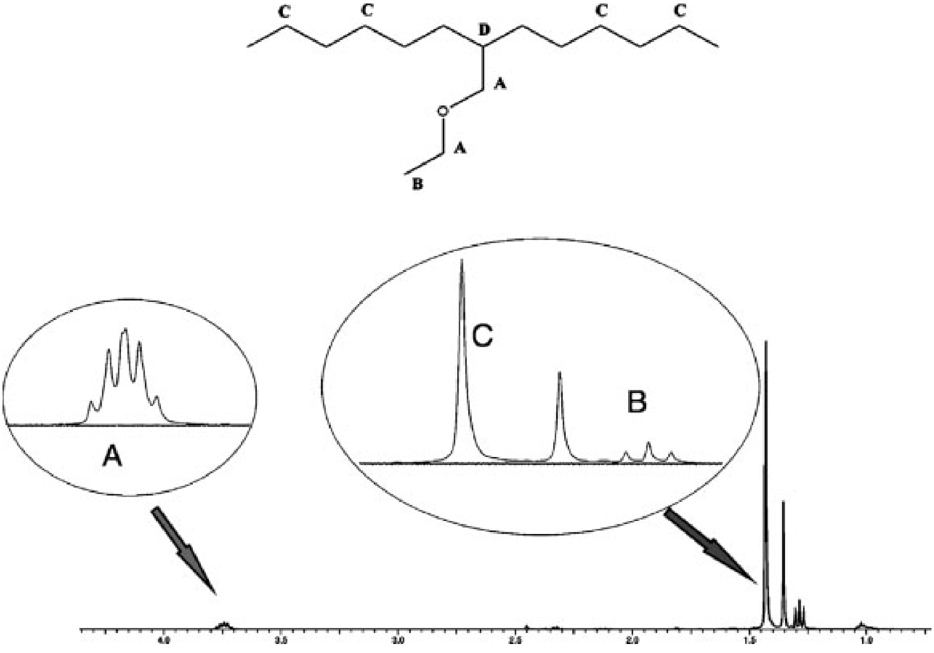


Figure 6.
^{1}H NMR spectrum of ethene/AEE copolymer obtained from (*rac*-[$Me_2Si(2\text{-}Me\text{-}4\text{-}(1\text{-}Ph)Ind)_2$]$ZrCl_2$/MAO) at 60 °C.

higher AEE and APE contents. Aaltonen et al [10] and Deffieux et al [13] have already observed the same behaviour for copolymerization of ethene with 10-Undecenol.

Conclusion

The copolymerization of ethene and norbornene by highly substituted C_1-symmetric metallocenes leads to strongly isotactic alternating E/N copolymers. These polymers show a crystalline phase with a norbornene content of only 32 mol%. Compared to the non substituted [Ph_2Si-(Flu)(Ind)]$ZrCl_2$ which does not produce any crystalline phase at high norbornene contents, the bulky ligands cause a higher stereoregular copolymer. With a melting temperature of around 206 °C these semicrystalline alternating E/N polymers show the lowest value reported in the literature. At polymerization temperatures of 0 °C no syndiotactic sequences could be detected any more.

Using metallocene/MAO catalyst system, ethene was copolymerized with APE and AEE. The catalyst activity is almost independent from the $Al_{(MAO)}$/Zr molar ratio or reaction temperature, but it decreases with the increase of polar monomer concentration in the feed. For both comonomers, APE and AEE, the incorporation values are highly dependent on comonomer concentration in feed. Additionally, the APE copolymer composition is strongly dependent on reaction temperature, it has been seen that reaction activity and comonomer incorporation have reached their optimal values at 45 °C, whereas slightly dependent on $Al_{(MAO)}$/Zr ratio.

In the case of AEE copolymer composition, we have seen that the opposite behaviour. The ratio $Al_{(MAO)}$/Zr exerts influence on the incorporation level while the temperature influence is negligible.

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