



Ethene–norbornene copolymerizations using two different homogeneous metallocene catalyst systems and investigations of the copolymer microstructure

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Abstract

Ethene–norbornene copolymerizations were carried out at various ethene pressures by using the homogeneous catalyst systems $iPr[(3-iPr-Cp)Ind]ZrCl_2/MAO$ and $rac-iPr[Ind]_2ZrCl_2/MAO$. The copolymer microstructures were analyzed by ^{13}C NMR spectroscopic investigations. On the basis of the obtained results, it could be concluded that copolymers generated with the metallocene $iPr[(3-iPr-Cp)Ind]ZrCl_2$ contain norbornene microblocks with a maximum length of two norbornene units in spite of high norbornene excess in the norbornene and ethene feedstock composition. In the microstructures of copolymers generated with the metallocene $rac-iPr[Ind]_2ZrCl_2$ norbornene microblocks with a length of three norbornene units have been detected. Results have shown that the amount of norbornene triblocks in the copolymer chain as well as the stereochemical connection of the norbornene triblocks depends on the monomer concentration and the polymerization temperature.

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1. Introduction

Ethene–norbornene copolymers have achieved a high status of importance as new amorphous polymer material due to their special thermoplastic properties, for instance, high heat resistance and excellent transparency [1,2]. The most important parameters which are useful for varying and optimizing these properties are monomer feedstock composition and ligand framework of the metallocene catalyst used. By means of using different norbornene content in the feedstock composition, the glass transition tem-

perature of the resultant copolymer, which increases with increasing norbornene content in the copolymer chain, can be adjusted over a wide temperature range (20–220 °C) [3–5]. The glass transition temperature is dependent upon the highest possible norbornene content in the copolymer which is limited by the maximum length of norbornene blocks. The norbornene sequence length could be regulated by the ligand framework of the metallocene catalyst systems used. In general, it can be differentiated between metallocenes which generate copolymers with alternating copolymer structures without any norbornene microblocks (maximal norbornene content 50 mol%) and metallocenes which generate copolymers containing norbornene microblocks up to a length of three norbornene units or even longer norbornene blocks (norbornene content up to 70 mol%).

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^{13}C NMR spectroscopic analysis is the most important analytical method to get information about the copolymer microstructure. The individual resonances can be assigned to the different pentads, tetrads or triads which occur in the copolymer microstructure. Signal assignments of most of the resonances have been described by different research groups in numerous publications [6–10]. Exact signal assignments have been carried out in ^{13}C NMR spectra of ethene–norbornene copolymers with isolated norbornene units and alternating sequences by using ^{13}C enriched monomers [7], comparing ^{13}C NMR spectra of copolymers with various norbornene content [6–8] and using theoretical calculations [9]. These signal assignments are nearly consistent with each other except for some assignments of the ethene pentads. The controversial assignments will be discussed in a further publication [10c]. In addition, most important resonances belonging to norbornene blocks with a length of two norbornene units have been assigned consistently by different research groups [7–9]. Several examples of these assignments can be found in previous publications [9,10]. The assignments of signals belonging to norbornene blocks with a length of three norbornene units are quite difficult due to the low occurrence of this kind of microblock and the low intensity of the corresponding resonances. In addition, due to the chiral centers at the carbon atom C2 and C3, norbornene triblock sequences could be differentiated in three different stereochemical connections of adjacent norbornene units. Fig. 1 shows the scheme of these various norbornene triblocks (NNN—triads) including the usual labeling of the carbon atoms and the stereochemical notation (*rac* or *meso*).

Numerous characteristic norbornene triblocks resonances in ^{13}C NMR spectra obtained from ethene–

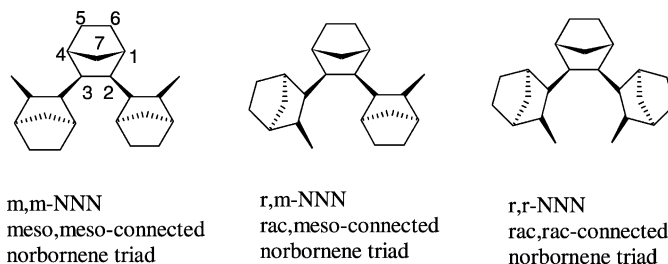


Fig. 1. Scheme of norbornene triblock sequences with various stereochemical connections of the norbornene units. The norbornene unit centered in the *meso,meso*-connected norbornene triblock shows the labeling of the norbornene carbon atoms.

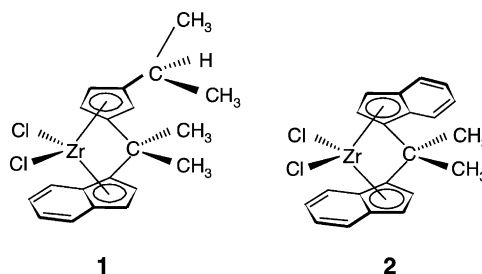


Fig. 2. Scheme of the structures of the homogeneous metallocene-catalysts used for the ethene–norbornene copolymerizations.

norbornene copolymers containing various connected norbornene triblocks have been assigned by our research group. The results have been recently published [10b]. These assignments have been achieved by using $^{13}\text{C}5/^{13}\text{C}6$ enriched norbornene, comparing spectra of copolymers with various norbornene content and with the help of chemical shifts in stereospecific connected norbornene hydrotrimers investigated in the previous works [11]. Assignments of all individual triblock resonances have still not been achieved completely due to overlapping of some signals. However, in the case of *meso,meso*- and *rac,meso*-connected norbornene triblock sequences, a characteristic signal distribution has been determined. Table 1 shows an overview of these assignments. So far, only *rac,rac*-connected norbornene triblock sequences have not been detected in any ^{13}C NMR spectra.

In the current work, ethene–norbornene copolymerizations were carried out using the catalyst systems *iPr*[(3-*iPr*-Cp)Ind] ZrCl_2/MAO (1) and *rac-i-Pr*[Ind] $_2\text{ZrCl}_2/\text{MAO}$ (2), presented in Fig. 2. The monomer feedstock compositions were varied by using various ethene pressures at constant norbornene

Table 1

Ethene–norbornene copolymers containing norbornene triblocks with *meso,meso*- and *rac,meso*-connected norbornene units: ^{13}C NMR signal assignments of the characteristic resonances of the norbornene carbon atoms [10]

Carbon atom ^a	Norbornene triblock resonances: chemical shift (ppm)	
	<i>meso,meso</i> -ENNNE	<i>rac,meso</i> -ENNNE
C5/C6	28.7: ENNNE	28.5: <i>m,r</i> -ENNNE
	31.6: ENNN	29.0–29.6: <i>r,m</i> -ENNNE; ENNN
	32.7: NNNE	32.2: <i>m,r</i> -NNNE
C7	35.2: ENNNE	35.1: <i>m,r</i> -ENNNE
	39.1: ENNN	36.5: <i>m,r</i> -ENNN
	–	37.9: <i>r,m</i> -ENNN
C1/C4	37.1: ENNNE	37.4: <i>m,r</i> -ENNN
	43.0: ENNN	39.1: <i>r,m</i> -ENNN
	43.4: NNNE	40.0: <i>r,m</i> -ENNNE/ <i>m,r</i> -ENNNE
	–	43.2: <i>m,r</i> -NNNE
C2/C3	47.7/50.4: ENNN	44.8: <i>m,r</i> -ENNN
	52.0: NNNE	45.8: <i>m,r</i> -NNNE
	55.0: ENNNE	51.5: <i>m,r</i> -ENNNE
	–	55.6: <i>m,r</i> -ENNNE

^a In the case of the signal groups C5/C6, C1/C4 and C2/C3 the left carbon atom of the underlined norbornene unit is considered.

concentration. The copolymer microstructure has been determined by applying the signal assignments which were described in recently published papers [8–10].

In addition, further copolymerizations were investigated by using the catalyst system *rac*-*i*Pr[Ind]₂ZrCl₂/MAO (**2**) at lower ethene pressure. These copolymerizations were conducted at various pressures and polymerization temperatures in order to evaluate the influence of polymerization conditions on the amount and stereochemical connection of norbornene triblock sequences. In recently published works from our research group, an increasing amount of norbornene triblocks sequences in the copolymer chain with decreasing ethene pressure (monomer concentration) at similar feedstock compositions has been found [10]. The catalyst system used was *rac*-Me₂Si[Ind]₂ZrCl₂/MAO. These results have been evaluated in the current work by using catalyst system (**2**). Additionally, the influence of the polymerization temperature on the microstructure has been investigated.

2. Experimental

All operations were carried out under an argon atmosphere using Schlenk techniques.

2.1. Materials for the polymerization experiments

Natural ethene (Messer-Griesheim, 99.5%) was dried by passing it through columns filled with a 3 Å molecular sieve and NaAlEt₄. Natural norbornene was used as a 85 vol.% solution in toluene. This solution was purified over dried molecular sieves.

Toluene was pre-dried over NaAlEt₄ and then refluxed over NaAlEt₄ and distilled.

The catalyst systems used were the metallocenes *i*Pr[(3-*i*PrCp)Ind]ZrCl₂ and *rac*-*i*Pr[Ind]₂ZrCl₂. The principle syntheses of such metallocenes are described in the literature [12,13].

The co-catalyst methylaluminumoxan (MAO) was purchased from CK Witco (10 wt.% solution in toluene).

2.2. Polymerization experiments at ethene excess pressure between 4 and 25 bar

The ethene–norbornene copolymerizations at high ethene pressure were carried out in a 11 steel autoclave (Büchi) with a stirrer (6.7 rps) at constant ethene pressure. The autoclave was charged with a concentrated solution of norbornene in toluene (7.6 mol/l) and MAO in toluene (total volume of: 0.4 l). The solution was heated to 70 °C and saturated with ethene. The pre-activated catalyst system was injected into the reactor with an argon overpressure. The consumption of ethene was detected by thermal mass flowmeters (Brooks Instrument). After 5–20 min polymerization time (depends on the activity), the copolymerization was stopped by rapidly cooling the reaction mixture and carefully blowing off excess ethene. The reaction mixture was poured into 2 l acetone and stirred overnight. The polymer was separated off, washed with fresh acetone and dried in a vacuum oven.

2.3. Polymerization experiments at low ethene pressure

The ethene–norbornene copolymerizations at low pressure were carried out in a 250 ml Büchi glass autoclave with a speed stirrer (20.0 rps) under constant

ethene pressure. The polymerization temperature was varied between 20 and 80 °C. The reactor was charged with the solution of norbornene and MAO in toluene (total volume of: 130 ml). The consumption of ethene was detected by thermal mass flowmeters (Brooks Instrument). The copolymerization was stopped by blowing off excess ethene and adding some methanol. The reaction mixture was poured into 600 ml of a diluted solution of hydrochloric acid in methanol and stirred overnight. The polymer was separated off, washed with fresh methanol and dried in a vacuum oven.

2.4. Characterization of the copolymers

The ^{13}C NMR spectra were measured in 10 mm NMR tubes with proton broad-band decoupling at 120 °C on a Bruker AMX 300 spectrometer at 75 MHz. The samples of the copolymers (200–300 mg) were dissolved in 3 ml of a mixture of 1,2,4-trichlorobenzene/1,1,2,2-tetrachloroethane- d_2 (volume ratio: 2.5/1). The chemical shifts were determined relative to the $-\text{CDCl}_2$ peak of the 1,1,2,2-tetrachloroethane- d_2 solvent and converted to the TMS scale ($\delta_{\text{C}} = 74.2$). The norbornene content was determined by using the formula according to a previous publication [6].

The molar mass measurements were carried out at 155 °C in 1,2,4-trichlorobenzene using a water-gel permeation chromatograph 150-C equipped with a viscosity detector (viscotek) [14].

The melting points or glass transition temperatures of the copolymers were measured on a Mettler-Toledo DSC 820 calorimeter according to [15].

3. Results and discussion

In the current work, ethene–norbornene copolymerizations were carried out between 4 and 25 bar ethene excess pressure at constant norbornene concentration using the catalyst systems $i\text{Pr}[(3-i\text{Pr-Cp})\text{Ind}]\text{ZrCl}_2/\text{MAO}$ (**1**) and $rac-i\text{Pr}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ (**2**). Table 2 shows the results of these copolymerizations.

One could note the expected decreasing polymerization activity with decreasing ethene pressure due to decrease of the entire monomer concentration.

The molecular weights of the copolymers increase with rising norbornene content in the feedstock composition and in the resultant copolymer. This tendency could be particularly observed when using the catalyst system $rac-i\text{Pr}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ (**2**). The increasing molecular weights with increasing norbornene content have already been found in previous investigations of ethene–norbornene copolymerizations using other metallocene catalyst systems. These results have been explained through the lower occurrence of chain transfer and chain termination reactions during the polymerization [14]. In the case of norbornene, as last inserted monomer unit which is inserted stereospecific *cis*-2,3-*exo* [16], β -hydrid-elimination reactions and β -hydrid transfer reactions to another monomer are

Table 2

Results of ethene–norbornene copolymerizations at various ethene pressures using the catalyst systems $i\text{Pr}[(3-i\text{Pr-Cp})\text{Ind}]\text{ZrCl}_2/\text{MAO}$ (**1**) and $rac-i\text{Pr}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ (**2**)

Metallocene and sample no.	p (Ethene) (bar)	Norbornene/ethene ratio in feedstock	Activity (kg/(mol h))	Molecular weight (M_w , g/mol $\times 10^{-3}$)	Norbornene (mol%) in copolymer (^{13}C NMR)
1a	19.7	82/18	250000	260	46.9
1b	11.4	90/10	46000	260	49.1
1c	8.2	93/7	37000	305	52.2
1d	4.4	97/3	22000	304	54.6
2a	24.3	79/21	72000	470	43.7
2b	15.3	86/14	36000	570	50.0
2c	10.0	92/8	19000	780	54.2
2d	8.2	93/7	25000	950	59.0
2e	4.5	97/3	8000	1000	62.6

Polymerization conditions: $[\text{Zr}] = 3 \times 10^{-6}$ mol/l (**1**) and $[\text{Zr}] = 5 \times 10^{-6}$ mol/l (**2**); $[\text{Al}]_{\text{MAO}}/[\text{Zr}] = 2200$; $[\text{norbornene}] = 7.5$ mol/l; $T_{\text{p}} = 70$ °C.

impossible due to the endo-position of the β -H-atom in the norbornene.

On the basis of the results in terms of copolymer compositions obtained by using the catalyst system $i\text{Pr}[(3-i\text{Pr-Cp})\text{Ind}]\text{ZrCl}_2/\text{MAO}$ (**1**), only a low increase of the norbornene content in the copolymer chain could be obtained with a high increase of norbornene/ethene ratio in the feedstock composition (decreasing ethene pressure). The 55 mol% norbornene content in the copolymer could not be exceeded. In the case of using catalyst system $rac-i\text{Pr}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ (**2**), an increasing norbornene content in the feedstock composition leads to an increasing norbornene content in the polymer chain of up to 63 mol% (see Table 2).

The copolymer composition corresponds with the glass transition temperatures of the copolymers depending on the norbornene content in the copolymer chain. Fig. 3 shows the glass transition temperatures of the ethene–norbornene copolymers as a function of the ethene pressure at constant norbornene concentration (norbornene/ethene feedstock ratio). It could be noted that in the case of using metallocene $i\text{Pr}[(3-i\text{Pr-Cp})\text{Ind}]\text{ZrCl}_2/\text{MAO}$ (**1**), the glass transition temperatures of the resultant copolymers reach a maximum limit at approximately 155 °C between 10 and 4 bar ethene pressure. In the case of the copolymers

resulting from metallocene $rac-i\text{Pr}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ (**2**), the glass transition temperatures can be increased up to 210 °C on decreasing the ethene pressure down to 4 bar.

3.1. Microstructure of ethene–norbornene copolymers when using $i\text{Pr}[(3-i\text{Pr-Cp})\text{Ind}]\text{ZrCl}_2/\text{MAO}$ (**1**) for copolymerization

Initial investigations concerning the microstructure of the ethene–norbornene copolymers give the obtained results of Fig. 3. In the case of metallocene $i\text{Pr}[(3-i\text{Pr-Cp})\text{Ind}]\text{ZrCl}_2/\text{MAO}$ (**1**) the occurrence of norbornene block sequences with more than two norbornene units would not be expected in the copolymer chain due to the limited increase in glass transition temperature with increasing norbornene excess in the feedstock composition. In order to investigate the microstructure, Fig. 4 shows two ^{13}C NMR spectra of copolymers with various norbornene content generated with metallocene (**1**). The most important resonances have been designated according to the pentad assignments published in previous works [7–10].

In both spectra presented in Fig. 4, no resonances could be detected which arise from norbornene

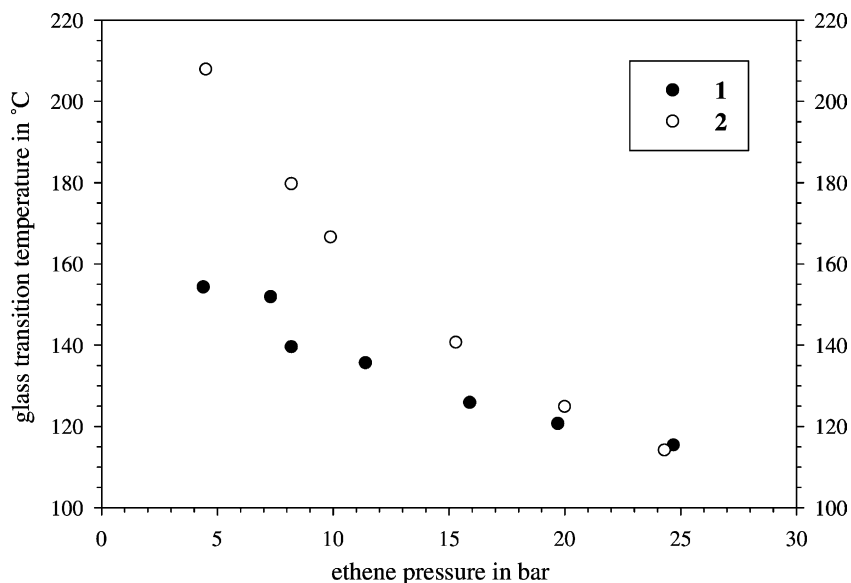


Fig. 3. Ethene–norbornene copolymers: glass transition temperatures of the copolymers as a function of the ethene pressure used at constant norbornene concentration. For polymerization conditions: see Table 1.

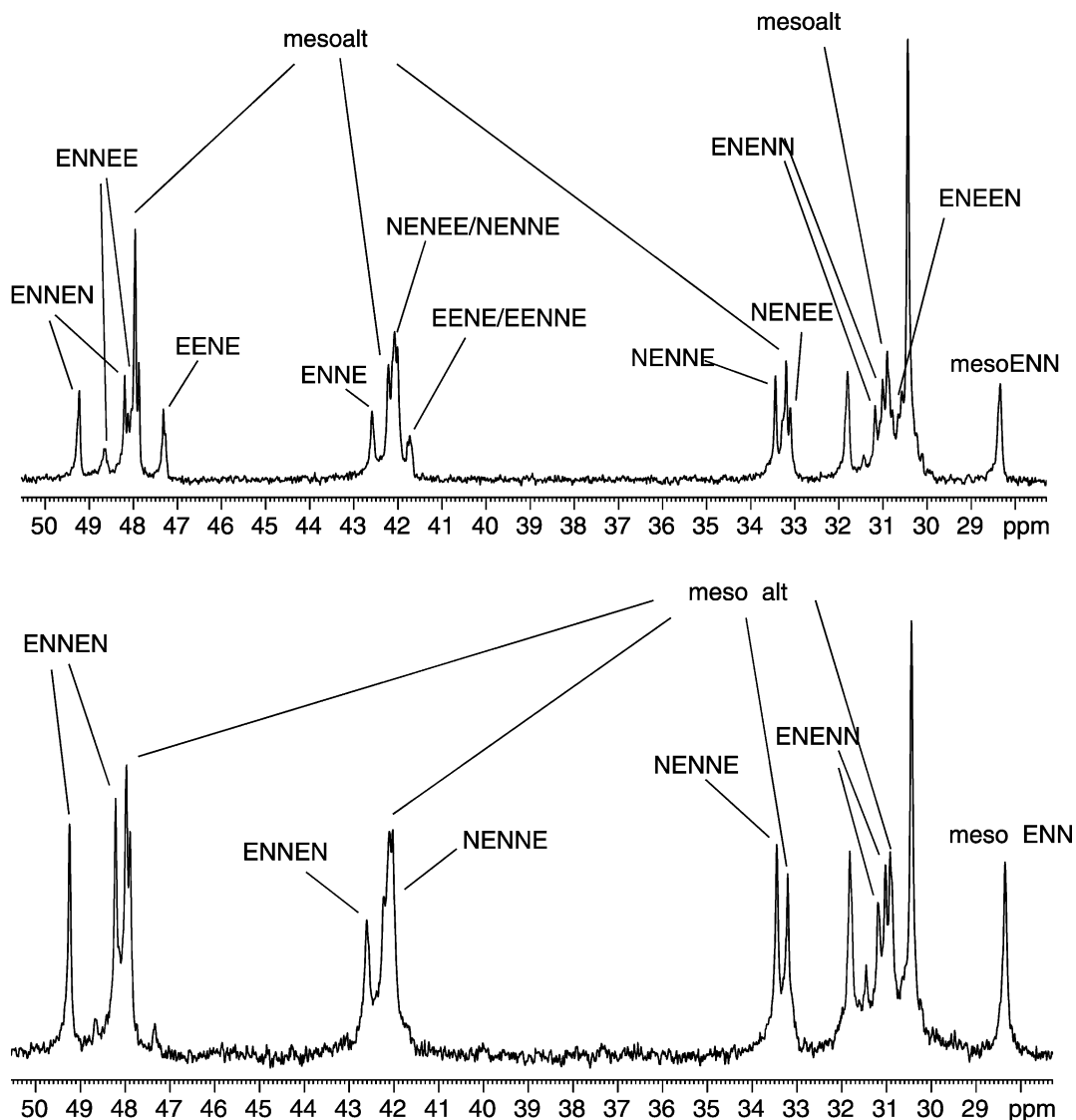


Fig. 4. ^{13}C NMR spectrum of an ethene–norbornene copolymer including the assignments of characteristic resonances to pentads. Catalyst system: $i\text{Pr}[(3\text{-}i\text{Pr-Cp})\text{Ind}]\text{ZrCl}_2/\text{MAO}$. Above: 46.9 mol% norbornene content; polymerization conditions: see Table 2, sample **1a**. Below: 54.6 mol% norbornene content; polymerization conditions: see Table 2, sample **1d**.

triblocks or longer norbornene block sequences. Therefore, it can be concluded that catalyst system $i\text{Pr}[(3\text{-}i\text{Pr-Cp})\text{Ind}]\text{ZrCl}_2/\text{MAO}$ (**1**) forms similar copolymer microstructures as the catalyst system $i\text{Pr}[(3\text{-}tert\text{-But-Cp})\text{Ind}]\text{ZrCl}_2$ investigated in a previous work [6]: resultant copolymers contain norbornene microblocks with a maximum length of two units as well as alternating sequences and sequences

with ethene diblocks. The maximum norbornene content of the copolymers obtained with both catalyst systems at high norbornene excess in the feedstock composition was approximately 55 mol%. However, some certain information concerning pentad assignments could be obtained by comparison of both spectra presented in Fig. 4. In the ^{13}C NMR spectrum of the copolymer with a norbornene content

of 46.9 mol%, besides the isotactic alternating pentads (*meso*-alt) several resonances were assigned to pentads containing ethene diblocks as well as pentads or triads containing *meso*-connected norbornene diblocks. In the case of pentads with norbornene diblocks, it has been assumed, that the signals of pentads containing both, norbornene and ethene diads (i.e. EENNE) show lower intensities in comparison with signals containing a norbornene diad with an adjacent alternating sequence (i.e. ENNEN) due to the lower probability of occurrence [7]. In the spectrum of Fig. 4 coming from the copolymer with a norbornene content of 54.6 mol%, all typical resonances assigned to ethene diblock pentads and tetrads (i.e. NEENE) have disappeared. Therefore, all signals which have been assigned to sequences containing norbornene diblocks which have decreased or disappeared in the spectra of the copolymer with higher norbornene content should be assigned to pentads containing adjacent norbornene and ethene diads. On the basis of these results, it has been concluded that at high norbornene excess in the feedstock, the catalyst system $i\text{Pr}[(3-i\text{Pr-Cp})\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ (**1**) generates ethene–norbornene copolymer microstructures with alternating norbornene units and norbornene diads which are separated by ethene units. The maximum norbornene content of such kind of copolymers should be around 60 mol%. This prediction meets the experimental results.

3.2. Microstructure of ethene–norbornene copolymers when using $rac-i\text{Pr}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ (**2**) for copolymerisation

On the basis of the norbornene content in copolymers generated by using the catalyst system $rac-i\text{Pr}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ (**2**) it can be proposed that the resultant copolymer microstructure contains norbornene diblocks as well as norbornene triblocks. In fact, even in the ^{13}C NMR spectra of copolymers containing only 45 mol% norbornene, characteristic NNN-resonances between 35–40 ppm as well as >50 ppm could be detected. On the basis of the signal assignments published in [10] both, *meso,meso*- and *rac,meso*-connected norbornene triblocks could be identified in the ^{13}C NMR spectra.

The microstructures of copolymers obtained by using a metallocene compound with the same ligand

structure, $rac-\text{Me}_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$, has already been investigated and published in [10]. Copolymers were generated at 2 bar ethene excess pressure as well as at 0.8 bar ethene absolute pressure (lower monomer concentration at similar feedstock composition). As a result of the signal assignments, in the ^{13}C NMR spectrum of copolymers generated at 0.8 bar ethene absolute pressure only norbornene triblock signals which are characteristic for *meso,meso*-connected norbornene units could be detected. However, investigations of ^{13}C NMR spectra of copolymers generated at 2 bar ethene excess pressure at similar ethene/norbornene feedstock ratio when using the catalyst system $rac-\text{Me}_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$ show a significantly lower intensity of the norbornene triblock resonances. Therefore, it has been assumed that catalyst systems like $rac-\text{Me}_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$ show a tendency to produce larger amounts of norbornene triblocks with decreasing ethene pressure or lower monomer concentration [10].

In order to investigate these results more precisely, ethene–norbornene copolymerizations using the catalyst system $rac-i\text{Pr}[\text{Ind}]_2\text{ZrCl}_2$ (**2**) (same ligand framework as $rac-\text{Me}_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$) were additionally carried out in a lab glass autoclave using low ethene pressure between 0.3 and 1.5 bar with similar norbornene/ethene ratios in the feedstock composition as has been used at higher ethene pressure. Fig. 5 shows a representative comparison of two ^{13}C NMR spectra obtained from copolymers which have been generated at 0.3 bar (glass autoclave) and 15.3 bar ethene excess pressure (steel autoclave). Both copolymers have a similar norbornene content.

In the NMR spectrum of the copolymer generated at low pressure, the typical resonances of *meso,meso*-connected norbornene triblocks (*m,m*-NNN) could be noted. These resonances show lower intensities in the spectrum of the copolymer generated at 15.3 bar. However, in these spectrum some additional triblock resonances with low intensity could be observed which are characteristic for norbornene triblocks with *meso,rac*-connection. On the basis of these results, it can be concluded that increasing monomer concentration in the feedstock of ethene norbornene copolymerizations in general leads to a lower tendency of forming norbornene triblocks. Additionally, with increasing monomer concentration the stereospecific control of *meso,meso*-connection is reduced

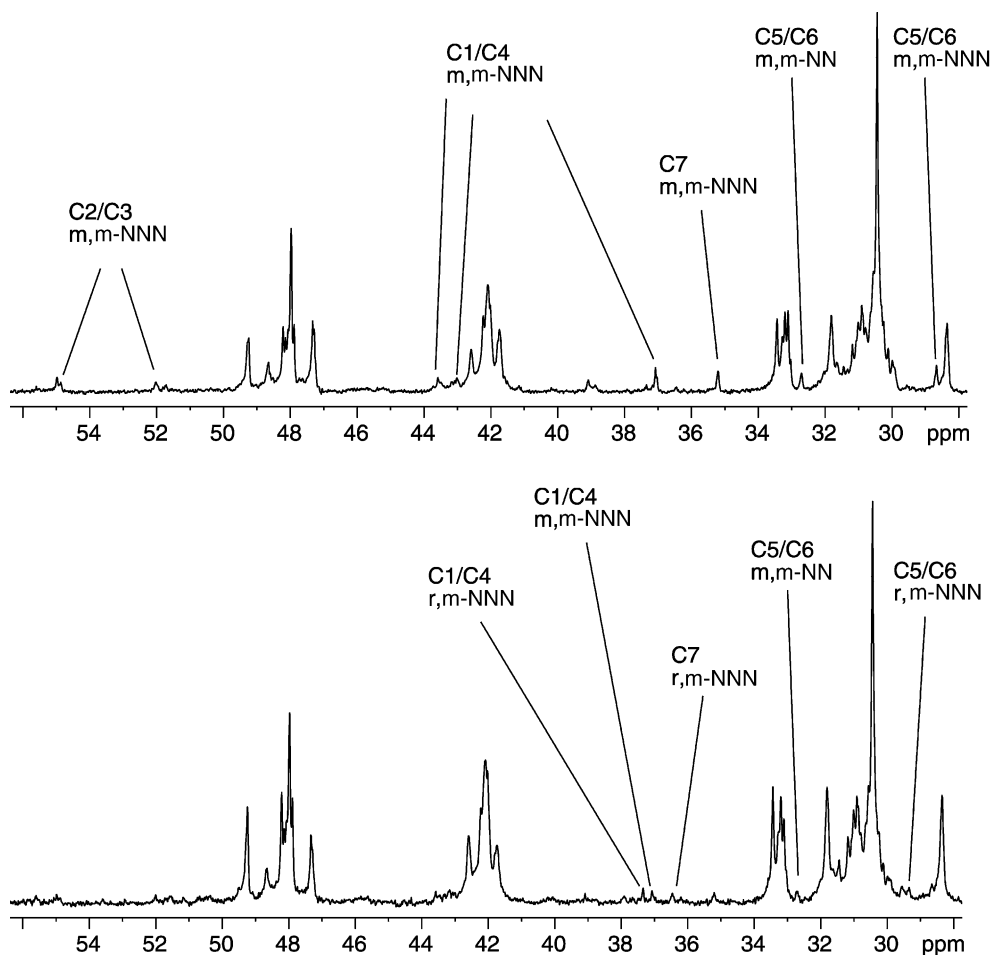


Fig. 5. ^{13}C NMR spectrum of an ethene–norbornene copolymer including the assignments of characteristic norbornene triblock resonances. Catalyst system: *rac*-*i*Pr[Ind] $_2$ ZrCl $_2$ /MAO (2). Above: 48.0 mol% norbornene content; polymerization conditions: 0.3 bar ethene excess pressure (glass autoclave); [norbornene]/[ethene] = 9.1; T_p = 40 °C. Below: 50.0 mol% norbornene content; polymerization conditions: 15.3 bar ethene pressure, see Table 2, sample 2b.

in the case of forming a triblock sequence by comparison of copolymers generated at different high monomer concentrations. By analysis of the copolymers generated between 0.3 and 1.5 bar at 40 °C, a slight decrease in norbornene triblock sequences with increasing ethene pressure could be observed. These results confirm the results obtained by using catalyst system *rac*-Me $_2$ Si[Ind] $_2$ ZrCl $_2$. The higher stereospecific formation of *meso,meso*-connected triblocks with lower monomer/metallocene ratio could be explained through the lower activity of the norbornene insertion in comparison to the ethene insertion. In previous

publications, it has been shown that in comparison to ethene, norbornene is coordinated to the catalyst center longer before insertion into the polymer chain [17]. Therefore, at higher concentration of both monomers an exchange of coordinated norbornene against ethene becomes more probable than at lower monomer concentration. In the case of a norbornene diblock as the last inserted sequences in the polymer chain, this kind of exchange should have a higher probability due to the high steric demand at the catalyst center.

In the current work, the influence of the polymerization temperature on the microstructure was

Table 3

Results of ethene–norbornene copolymerizations at various ethene pressure and polymerization temperatures in a glass autoclave using the catalyst systems *rac*-iPr[Ind]₂ZrCl₂/MAO (2)

Norbornene/ethene ratio in feedstock	<i>p</i> (Ethene) (bar)	Polymerization temperature (°C)	Activity (kg/(mol h))	Norbornene (mol%) in copolymer (¹³ C NMR)	Glass transition temperature (°C)
88/12 a	0.3	20	570	45.6	124
92/8 b	0.3	40	2200	48.1	115
92/8 b	0.3	60	5000	47.0	105
97/3 b	0.3	80	7300	47.2	–
91/9 a	0.5	20	570	47.5	138
90/10 b	0.5	60	5400	48.2	114
89/11 b	0.8	20	850	47.8	143
91/9 b	0.8	60	9800	49.4	110

Polymerization conditions: (a) [Zr] = 3 × 10⁻⁵ mol/l or (b) [Zr] = 6 × 10⁻⁵ mol/l; [Al]_{MAO}/[Zr] = 2200.

investigated by using catalyst system *rac*-iPr[Ind]₂ZrCl₂ (2). Therefore, ethene–norbornene copolymerizations were carried out between 20 and 80 °C at low ethene pressure in a glass autoclave. Table 3 shows the results of these copolymerization experiments.

In spite of some noticeable slight differences between the monomer feedstock compositions, which have been determined by using ethene saturation curves for each polymerization, all obtained copolymers show a similar norbornene content. Therefore, a comparison of the ¹³C NMR spectra of the copolymers generated at various temperatures in order to investigate the influence on the microstructure should be possible. Fig. 6 shows a comparison of ¹³C NMR spectra obtained from copolymers which have been generated at 0.3 bar ethene excess pressure and different polymerization temperatures.

The comparison of the ¹³C NMR spectra in Fig. 6 shows an increasing intensity of norbornene triblock signals with increasing polymerization temperature. The resonances with increasing intensity can be assigned to *meso,meso*-connected norbornene sequences (see Table 1). In accordance to this result, a decreasing intensity of the signals assigned to norbornene diblock sequences with increasing polymerization temperature can be noted. Same results have been obtained in the case of NMR comparisons conducted with copolymers which have been generated at 20 and 80 °C at an excess ethene pressure of 0.5 and 0.8 bar, respectively (see Table 3). Therefore, it can be concluded, that microstructures of ethene–norbornene copolymers generated using the catalyst system *rac*-iPr[Ind]₂ZrCl₂ contain an increasing amount of stereospecific *meso,meso*-connected norbornene

triblock sequences with increasing polymerization temperature and decreasing monomer concentration (low ethene pressure, monomer/metallocene ratio relative low). The increasing amount of norbornene triblock sequences with increasing polymerization temperature gives an indication that either the formation of norbornene triblock sequences requires a high amount of activation energy or the high temperature leads to a more open ligand system which enables better formation of norbornene triblocks with high steric demand. However, a strongly increasing monomer concentration (monomer/metallocene ratio) leads to a decreasing amount of norbornene triblock sequences even at high polymerization temperature. Ethene–norbornene copolymers generated between 4 and 20 bar ethene excess pressure at 80 °C show low intensities of norbornene triblock resonances, which indicates the presence of both, *meso,meso*- as well as *meso,rac*-connected norbornene triblocks (see Fig. 5). Therefore, stereospecific *meso,meso*-connection is lost at high pressure even at high temperature.

The various amount of norbornene triblock sequences inside the polymer chain seems to also have an influence on the glass transition temperature of ethene–norbornene copolymers. On the basis of the analytical data of Table 3, increasing glass transition temperatures with decreasing polymerization temperature could be noted. Therefore, decreasing amount of norbornene triblock resonances seems to have an increasing effect on the glass transition temperature. This result may be caused by the different microstructure: if two copolymer chains have approximate the same norbornene content (e.g. 50 mol%) but different contents of norbornene triblock sequences,

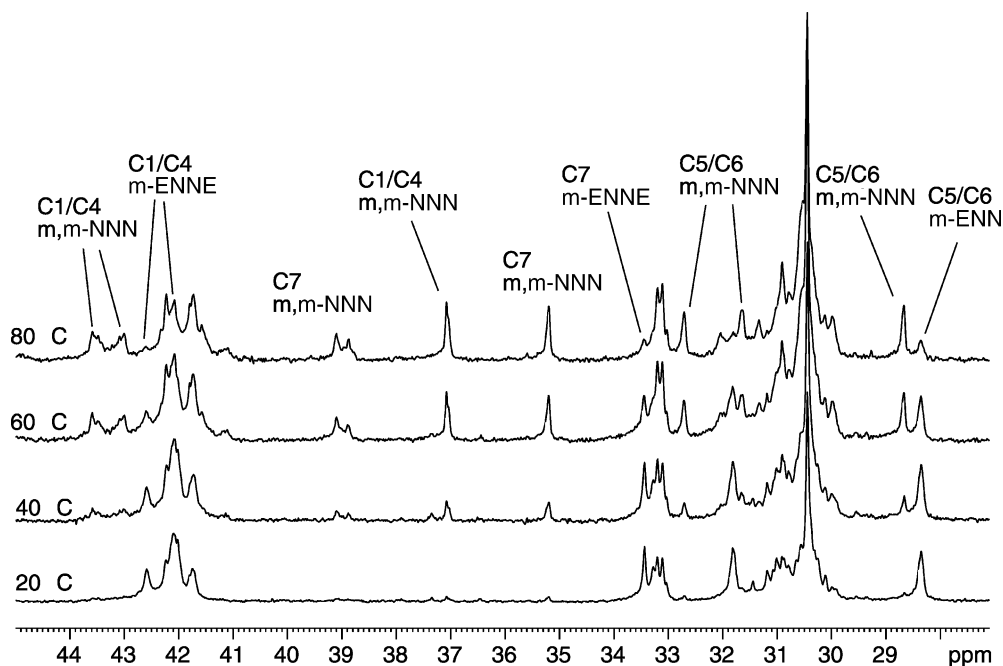


Fig. 6. Part of ^{13}C NMR spectra of ethene–norbornene copolymers generated at various polymerization temperatures using the catalyst system $\text{rac-}i\text{Pr}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ (2): comparison of the characteristic norbornene tri- and di-block resonances of the carbon atoms C5/C6, C7 and C1/C4. For polymerization conditions: see Table 3.

the copolymer with a higher amount of triblocks should also have a higher amount of ethene di- and tri-blocks. It can be assumed that the polymer chain agility is higher in the case of more ethene blocks. Therefore, such kind of polymer should show a glass transition at lower temperature. On the basis of this discussion, a lower glass transition temperature in ethene–norbornene copolymers with higher amounts of norbornene triblock sequences but constant norbornene content could be explained.

4. Conclusion

Based on the results of ethene–norbornene copolymerizations investigated in the current work, the influence of various catalyst ligand frameworks on the copolymer microstructure which has already been discussed in the previous works can be verified. The catalyst system $i\text{Pr}[(3-i\text{Pr-Cp})\text{Ind}]\text{ZrCl}_2/\text{MAO}$ (1) generates copolymer chains which contain norbornene blocks with a maximum length of two units,

like the catalyst system $i\text{Pr}[(3\text{-tert-But-Cp})\text{Ind}]\text{ZrCl}_2$ investigated in a previous work [6]. However, a slightly higher norbornene content could be achieved with the $i\text{Pr}$ -substituted metallocene. Therefore, the polymer microstructure can be described as a kind of quasi-alternating structure with isolated norbornene units and norbornene diblocks separated by ethene units. When using the catalyst system $\text{rac-}i\text{Pr}[\text{Ind}]_2\text{ZrCl}_2$ (2) ethene–norbornene copolymer microstructures containing norbornene triblocks have been generated. It has been shown that the amount of triblock sequences inside the polymer chain depends on monomer concentration in general as well as polymerization temperature. The amount of triblock sequences increases with increasing temperature and decreasing of total monomer concentration (monomer/metallocene ratio). With the increasing tendency to generate triblock sequences, the tendency of stereospecific *meso,meso*-connection inside the norbornene triblock sequences is also favored. Therefore, in the case of using a catalyst system like $\text{rac-}i\text{Pr}[\text{Ind}]_2\text{ZrCl}_2$, the polymer microstructure can

be regulated by variation of polymerization temperature and monomer/metallocene ratio.

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