

# Influence of Polymerization Conditions on Microstructure of Norbornene-Ethylene Copolymers Made Using Metallocene Catalysts and MAO

CHRISTER H. BERGSTRÖM,<sup>1</sup> TAITO L. J. VÄÄNÄNEN,<sup>2</sup> JUKKA V. SEPPÄLÄ<sup>3</sup>

<sup>1</sup>Optatech Corporation, Ahventie 4 B 33, FIN-02170, Espoo, Finland

<sup>2</sup>Neste Corporate Technology, P.O. Box 310, FIN-06101, Porvoo, Finland

<sup>3</sup>Helsinki University of Technology, Department of Chemical Engineering, FIN-02150, Espoo, Finland

Received 27 June 1996; accepted 28 June 1996

**ABSTRACT:** When characterized with <sup>13</sup>C-NMR, it was found that norbornene-ethylene copolymers had a more complicated microstructure when dimethylsilyl bis(indenyl) zirconium dichloride was used as the catalyst compared to ethylene bis(indenyl) zirconium dichloride. One could see more block sequences but less alternating sequences. For both catalysts the highest amounts of block sequences were obtained for high norbornene concentrations, medium to high Al/Zr ratios, and low polymerization temperatures. There were also more alternating sequences for high norbornene concentrations and high polymerization temperatures. The isolated norbornene units (separated by more than one ethylene unit) were all exoconfiguration. No unsaturation was seen.

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## INTRODUCTION

By incorporating rigid cyclic monomers in a polymer chain, the chain becomes stiffer, which increases the glass transition temperature ( $T_g$ ) and decreases the degree of crystallinity.<sup>1</sup> Therefore, if a cyclic monomer like norbornene is copolymerized with ethylene using a metallocene catalyst and methylaluminoxane (MAO) as cocatalyst a copolymer with elastomeric properties<sup>2</sup> is obtained for low (10 mol %) incorporations of norbornene. And with increasing amounts of norbornene the  $T_g$  increases so that engineering plastic properties<sup>3</sup> are obtained. When the norbornene incorporation is about 35 mol % a  $T_g$  as high as 150°C is obtained, which is on the same level as polycarbonate. Such norbornene-ethylene copolymers are amorphous and transparent and are therefore used in optical applications like compact disks.<sup>4</sup>

When looking at the <sup>13</sup>C-NMR spectra of such norbornene-ethylene copolymers made under different conditions, one notices that there are significant differences in their microstructures.<sup>5</sup> The intention of this publication is to provide information about the influence of the polymerization conditions on the microstructures obtained by different monomer sequences. These monomer sequences are isolated norbornene units (IS), which are separated by more than one ethylene unit, and alternating (ALT) and block sequences (BL), which are expected to contribute more to the stiffness of the polymer chain ( $T_g$ ). Due to the objective of this work a systematic sequence analysis was not made. Such a sequence analysis would also have required polymerization conditions that provided very low conversions of norbornene.

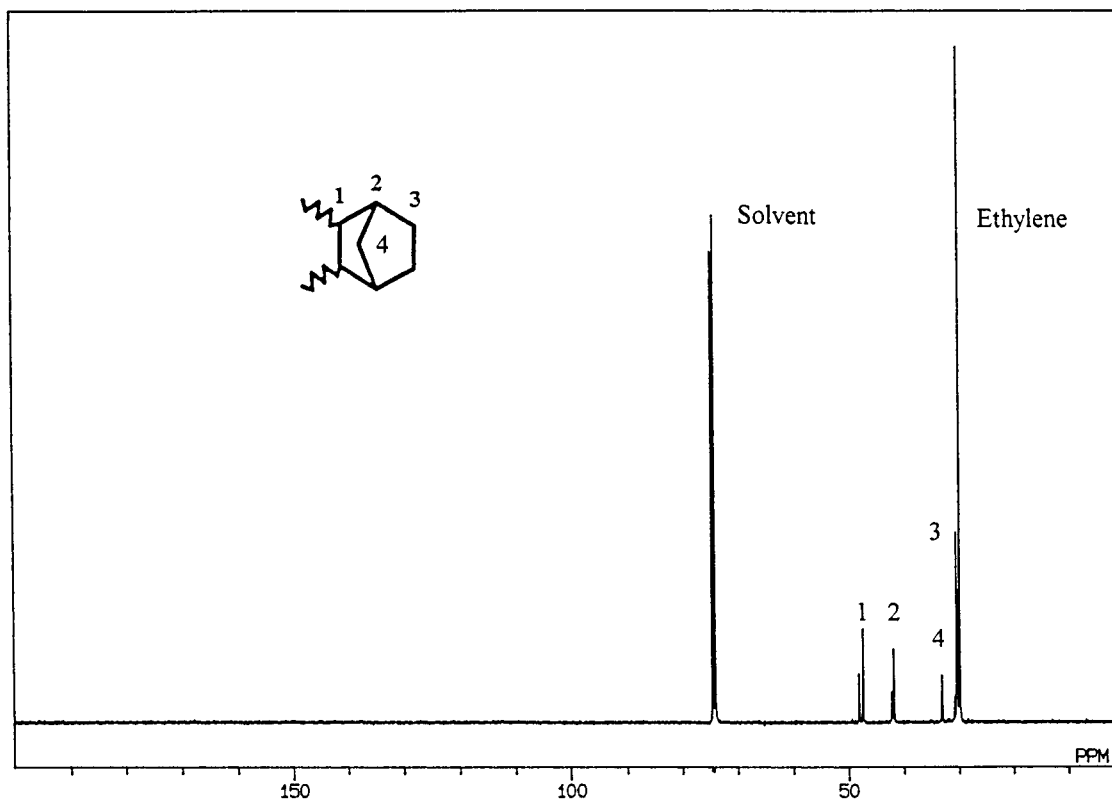
## EXPERIMENTAL

### Apparatus and Polymerization Method

The copolymerization of norbornene and ethylene was done using a semiflow method and a reactor

Correspondence to: C. H. Bergström

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**Figure 1** Assignment of the  $^{13}\text{C}$ -NMR resonances for a norbornene-ethylene copolymer made with a metallocene catalyst and MAO.

system described in detail in an earlier article by our group.<sup>6</sup> The appropriate amount of norbornene was dissolved in toluene and diluted so that a 250-mL solution was obtained. The solution was dried with molecular sieves overnight and poured into a thermostated 500-mL stainless steel reactor equipped with a stirrer. After purging with nitrogen and ethylene the ethylene pressure and the temperature of the reactor content were set at the chosen values and ethylene was supplied until the toluene solution was saturated and the ethylene flow stopped. After that the MAO-toluene solution was pumped to the reactor and the

mixing continued for 15 min after which the catalyst-toluene solution was pumped to the reactor. After the addition of catalyst ( $2\text{ mg} = 19 \cdot 10^{-6}\text{ mol/L}$  or  $4\text{ mg} = 38 \cdot 10^{-6}\text{ mol/L}$ ) the polymerization was allowed to continue for 60 or 30 min so that the ethylene consumed in the polymerization was constantly replaced and the pressure and temperature were automatically controlled. No hydrogen or other chain transfer agents were used in this study. When the chosen polymerization time was finished the ethylene supply was shut off, the reactor vented, and the reactor content poured into 300 mL ethanol. Then hydrochloric acid was added to deactivate the MAO and the sample was kept that way until the next day when it was filtered, washed, with acetone, filtered again, and dried in a vacuum oven.

**Table I Ethylene Dissolved in Toluene (mol/L) at Different Ethylene Pressures and Temperatures**

Pressure (atm)	Temperature ( $^{\circ}\text{C}$ )			
	10	30	50	70
2	0.374	0.266	0.195	0.143
4	0.761	0.544	0.405	0.310
6	1.159	0.825	0.618	0.477

### Chemicals

The catalysts were the soluble metallocene catalysts ethylene bis(indenyl) zirconium dichloride, EURECEN 5036, and dimethylsilyl bis(indenyl) zirconium dichloride, TA 02720, from Witco and the cocatalyst was 10 wt % MAO in toluene

**Table II Influence of Norbornene Content (Low Levels) and Polymerization Temperature on Properties of Norbornene-Ethylene Copolymer**

Run	Norbornene Added (mol %)	Temperature (°C)	Yield (g)	Activity (10 <sup>6</sup> g/mol Zr h atm)	Norbornene (mol %)	T <sub>g</sub> (°C)	BL/ALT/IS (%)
1	30	30	15.5	0.8	13	<0	0/19/81
2	30	70	21.1	1.1	4	<0	0/19/81
3	50	30	16.1	0.9	23	<0	5/42/53
4	50	70	17.4	0.9	13	<0	2/30/68
5	70	30	22.3	1.2	28	90	10/57/33
6	70	70	38.4	2.0	24	<0	9/48/43

Copolymer was polymerized at 4 atm ethylene pressure for 60 min using  $19 \cdot 10^{-6}$  mol/L ethylene bis(indenyl) zirconium dichloride and 3000 Al/Zr as MAO in toluene.

(Witco). The Al content of the cocatalyst was 4.5–5.5 wt %.

The comonomer norbornene (bicyclo-2,2,1-hept-2-ene) was obtained from Fluka (14351) and its purity was 97%.

The ethylene used was AGA's grade 2.7, which was further purified in columns containing molecular sieves, CuO, and Al<sub>2</sub>O<sub>3</sub> before entering the reactor; the toluene used was Riedel-de-Häen's grade RG.

### Polymer Characterization

The glass transition temperatures were measured using a Perkin–Elmer DSC 7. The sample was first heated to 200°C, then cooled to 0°C (20°C/min), and after that heated again to 200°C (10°C/min). The data used in this publication were taken from the second heating.

The <sup>13</sup>C-NMR spectra were measured using a Jeol GSV-400 NMR spectrometer. The spectra were recorded at 110–130°C with 1,1,2,2-tetrachloro-ethane-*d*<sub>2</sub> as solvent. A spectral width of 25,000 Hz, an acquisition time of 1.3 s with 32,768 data points, a preparation time of 8.0 s, a 45° pulse of 5.0 μs, and complete decoupling were used to accumulate 1000–2000 scans. All spectra were baseline corrected and calculations were done using integrated intensities (peak areas). The assignment of resonances<sup>7</sup> is shown in Figure 1. The amount of norbornene was calculated using eq. (1).

$$\text{norbornene (mol \%)} = \frac{(A_1 + A_2)/2}{A_{\text{CH}_2} + A_3} \cdot 100. \quad (1)$$

A<sub>1</sub> is the area of the region at 47–49 ppm, A<sub>2</sub> is the area of the region at 41–42 ppm, and A<sub>CH<sub>2</sub></sub> + A<sub>3</sub> is the area of the region at 30 ppm including

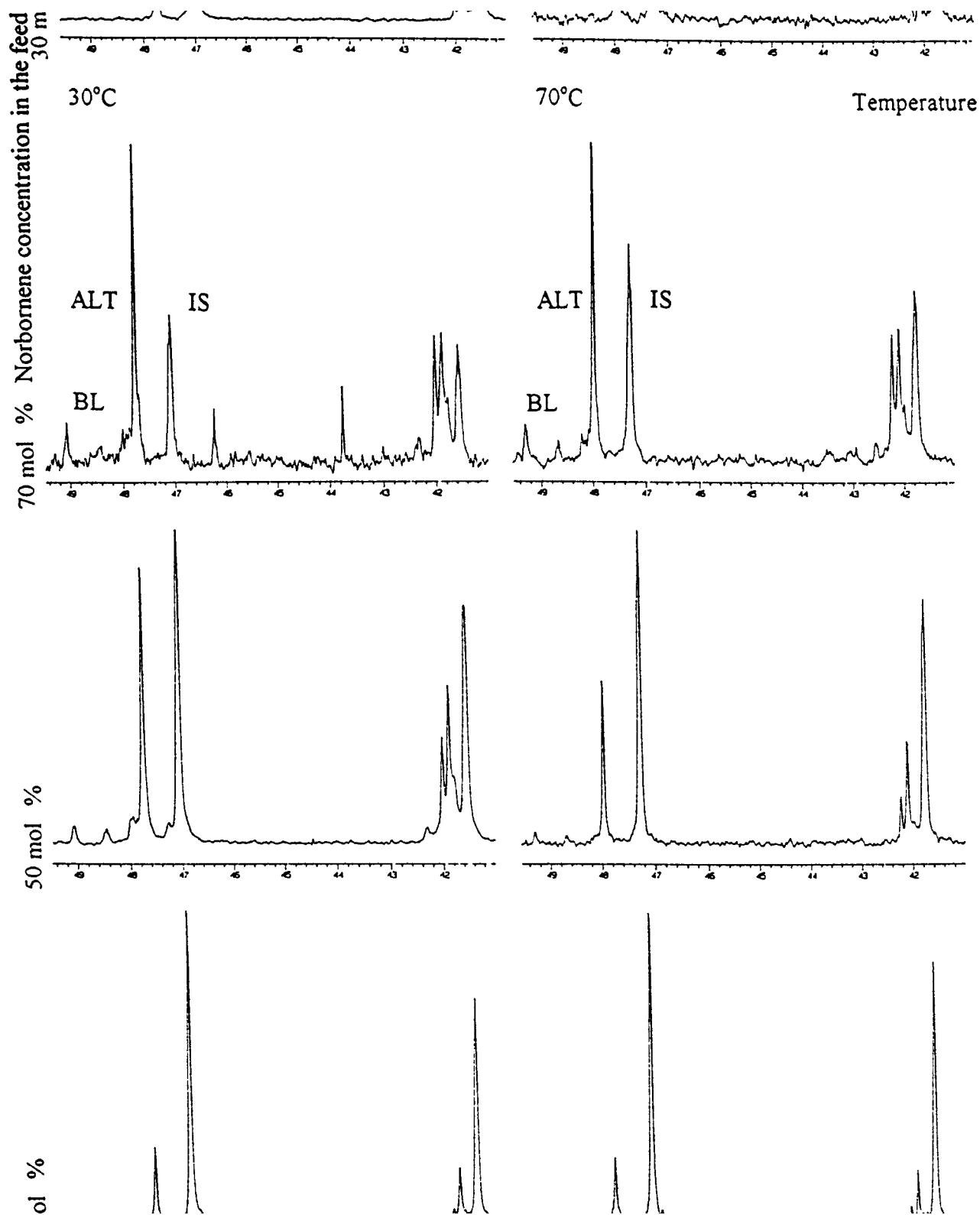
ethylene and carbon 3. The region at 47–49 ppm, which represents carbon 1, can be further divided into IS in exoconfiguration,<sup>7</sup> ALT,<sup>8</sup> and BL. Any unsaturation that would appear in the 120–140 ppm region could not be seen. Because the sequences partly overlap each other the proportions of IS, ALT, and BL should not be considered as absolute values.

## RESULTS AND DISCUSSION

### Low Level Norbornene Content and Polymerization Temperature

To obtain general information and specific data on the influence of norbornene concentration and polymerization temperature on the microstructure of norbornene-ethylene copolymers, the initial monomer mixtures of 30, 50, and 70 mol % norbornene were polymerized at 30 and 70°C. The ethylene pressure was 4 atm, the catalyst 2 mg ethylene bis(indenyl) zirconium dichloride, the Al/Zr-ratio 3000, and the polymerization time 1 h. The amount of ethylene in mols/liter dissolved in toluene at different temperatures and pressures are presented in Table I, which is based on Henry's law and provided by the Borealis Company. Based on these data and assuming that the solubility of ethylene in diluted solutions is approximately the same as in pure solvent, the chosen amounts of norbornene could be calculated for each combination of temperature and pressure. In Table II the results obtained for the investigation described above are presented.

It can be seen that for very small amounts of norbornene (30 mol %) no BL's could be identified. This is very natural because at low comonomer levels mostly random copolymers are obtained



**Figure 2** Influence of norbornene concentration and polymerization temperature on the  $^{13}\text{C}$ -NMR resonances for norbornene in isolated (IS), alternating (ALT), and block (BL) sequences in norbornene-ethylene copolymers made under the conditions presented in Table II.

**Table III Influence of Type of Catalyst and Al/Zr Ratio on Properties of Norbornene-Ethylene Copolymer**

Run	Catalyst	Al/Zr	Yield (g)	Activity (10 <sup>6</sup> g/mol Zr h atm)	Norbornene (mol %)	T <sub>g</sub> (°C)	BL/ALT/IS (%)
7	A	1500	10.5	1.1	29	84	8/55/37
8	A	3000	12.9	1.4	31	90	12/57/31
9	A	6000	13.1	1.4	31	93	9/57/34
10	B	1500	4.7	0.5	29	73	0/50/50
11	B	3000	7.1	0.8	29	78	15/47/38
12	B	6000	2.5	0.3	29	—	15/47/38

Catalysts were 19 · 10<sup>-6</sup> mol/L A, ethylene bis(indenyl) zirconium dichloride or B, dimethylsilyl bis(indenyl) zirconium dichloride. The copolymer was polymerized for 30 min at 30°C and 4 atm starting from 70 mol % norbornene in toluene.

(—) T<sub>g</sub> could not be seen with DSC.

(IS). When adding more norbornene to the reaction mixture the amounts of BLs as well as ALTs increased, and these structures could be further increased by decreasing the polymerization temperature. Furthermore it can be said about these results that the yields and activities increased at higher polymerization temperatures because the polymerization of ethylene increased. This on the other hand had decreasing effects on the norbornene content in the polymer and T<sub>g</sub>. The influences of initial norbornene/ethylene ratio and polymerization temperature on the <sup>13</sup>C-NMR spectra are demonstrated in Figure 2.

#### Type of Catalyst, Al/Zr Ratio, and Polymerization Time

It can be seen from the results in Table III that for 70 mol % norbornene in the reaction mixture, BLs and ALTs can be seen for both catalysts and that the amount increased with increasing Al/Zr ratio. The amounts of BLs were on the same level

as when polymerizing for 60 min (Table II, runs 5 and 6) with ethylene bis(indenyl) zirconium dichloride. For dimethylsilyl bis(indenyl) zirconium dichloride it is interesting to note that it caused less alternating sequences compared to ethylene bis(indenyl) zirconium dichloride, which seems to have had a decreasing effect on the T<sub>g</sub>. Also the yields and activities were lower for dimethylsilyl bis(indenyl) zirconium dichloride.

#### High Level Norbornene Contents

It can be seen from the results in Table IV that for higher incorporations of norbornene the contents of BLs increased significantly and that this effect was more stressed when using dimethylsilyl bis(indenyl) zirconium dichloride as catalyst. It can also be seen that when adding more norbornene less isolated norbornene units and higher T<sub>g</sub>s were obtained. For both catalysts the yields decreased with increasing amounts of norbornene added. High amounts of norbornene seemed to

**Table IV Influence of Norbornene Content (High Levels) on Properties of Norbornene-Ethylene Copolymers**

Run	Catalyst	Norbornene Added (g)	Yield (g)	Activity (10 <sup>6</sup> g/mol Zr h atm)	Norbornene (mol %)	T <sub>g</sub> (°C)	BL/ALT/IS (%)
13	A	50	9.1	1.0	32	104	18/60/22
14	A	70	6.1	0.6	38	114	20/60/20
15	A	90	3.9	0.4	34	123	19/65/16
16	B	50	3.5	0.4	40	98	29/45/26
17	B	70	2.4	0.3	33	117	23/56/21
18	B	90	1.4	0.2	35	150	27/60/13

Polymers were polymerized for 30 min at 30°C and 4 atm using 19 · 10<sup>-6</sup> mol/L A, ethylene bis(indenyl) zirconium dichloride or B, dimethylsilyl bis(indenyl) zirconium dichloride, and 3000 Al/Zr as MAO in toluene.

**Table V Influence of Al/Zr Ratio, Polymerization Temperature, and Amount of Catalyst**

Run	Catalyst (10 <sup>-6</sup> mol/L)	Al/Zr	Temperature (°C)	Yield (g)	Activity (10 <sup>6</sup> g/mol Zr h atm)	Norbornene (mol %)	T <sub>g</sub> (°C)	BL/ALT/IS (%)
19	A, 19	1500	30	1.6	0.2	36	124	19/61/20
20	A, 19	6000	30	3.3	0.3	37	117	18/64/18
21	A, 19	3000	50	13.7	1.4	37	115	19/69/12
22	A, 38	3000	30	3.5	0.2	37	155	19/67/14
23	B, 19	1500	30	1.8	0.2	34	125	22/63/15
24	B, 19	6000	30	2.1	0.2	34	135	25/61/14
25	B, 19	3000	50	3.3	0.3	38	147	25/65/10
26	B, 38	3000	30	2.8	0.1	33	135	22/61/17

Values are when copolymerizing 90 g norbornene with ethylene for 30 min at 4 atm with A, ethylene bis(indenyl) zirconium dichloride or B, dimethylsilyl bis(indenyl) zirconium dichloride as catalyst and MAO as cocatalyst.

deactivate the active sites of the catalysts, and this effect was more strongly seen for dimethylsilyl bis(indenyl) zirconium dichloride.

#### Type and Amount of Catalyst, Al/Zr Ratio, and Polymerization Temperature for High Level Norbornene Contents

The results in Table V show that very different polymer properties can be obtained when starting the polymerization with a 250-mL toluene solution containing 90 g norbornene and maintaining an ethylene pressure of 4 atm. As was the case in Table IV (runs 15 and 18) the yields obtained were very low for both catalysts but with a tendency of lower yields for dimethylsilyl bis(indenyl) zirconium dichloride. It can also be seen that the yields decreased with decreasing Al/Zr ratio and increased with increasing catalyst content and increasing polymerization temperature. These same tendencies were also seen for low norbornene contents and are presented in Tables II and III. The amounts of incorporated norbornene, however, were higher for 50°C than for 30°C, but the T<sub>g</sub>s were lower. The amounts of BLs were in general higher for dimethylsilyl bis(indenyl) zirconium dichloride, which caused higher T<sub>g</sub>s in relation to the norbornene contents measured with <sup>13</sup>C-NMR. The amounts of isolated norbornene units decreased when using higher polymerization temperatures. When using higher catalyst concentrations the norbornene incorporation and T<sub>g</sub> increased for ethylene bis(indenyl) zirconium dichloride but decreased for dimethylsilyl bis(indenyl) zirconium dichloride.

## CONCLUSIONS

One can clearly see which polymerization conditions cause BLs, ALTs, and ISs based on <sup>13</sup>C-NMR for characterization of the microstructure of norbornene-ethylene copolymers. The amounts of BLs and ALTs increase when using higher norbornene concentrations, higher Al/Zr ratios, and higher polymerization temperatures. One can also conclude that dimethylsilyl bis(indenyl) zirconium dichloride cause more BLs but less ALTs than ethylene bis(indenyl) zirconium dichloride. Within the scope of this publication only the influence of the polymerization conditions on the microstructure was studied. A closer identification of the block sequences will be presented in a future publication.

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