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# Oligomers and soluble polymers from the vinyl polymerization of norbornene and 5-vinyl-2-norbornene with cationic palladium catalysts

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## ABSTRACT

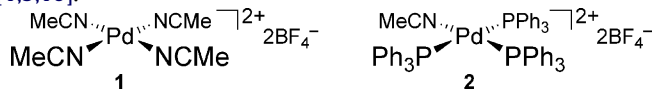
Oligomeric vinyl polynorbornene (2 to ~12 monomer units) was obtained via hydrooligomerization of norbornene (NB) using the cationic palladium complexes  $[\text{Pd}(\text{PPh}_3)_n(\text{NCCH}_3)_{4-n}](\text{BF}_4)_2$  [ $n=0$  (**1**), 3 (**2**)] at different hydrogen pressures. The vinyl polymerization of norbornene (NB) in the ionic liquid *N*-butyl-*N*-trimethylammonium bis(trifluoromethylsulfonyl)imide ( $\text{BtMA}^+\text{NTf}_2^-$ ) with  $[\text{Pd}(\text{NCCH}_3)_4](\text{BF}_4)_2$  led to soluble polynorbornenes (with several hundred monomer units) at different temperatures and molar NB:Pd ratios. The norbornene derivative 5-vinyl-2-norbornene (VNB) was oligomerized in high yield with **1** in  $\text{CH}_3\text{NO}_2$  primarily through the (endocyclic) norbornene double bond but also through both the norbornene and (exocyclic) vinyl double bond for about every second monomer (by  $^1\text{H}$  NMR). A 2D  $^1\text{H},^{13}\text{C}$ -HSQC NMR analysis suggests a  $\beta$ -hydrogen elimination after insertion of a norbornene double bond as chain-termination mechanism. The conversion of NB or VNB increased with temperature and a lower NB:Pd and VNB:Pd ratio, respectively. The vinyl double bond in VNB slowed down the insertion rate drastically when compared with NB (activity decrease by a factor of  $10^2$ ).

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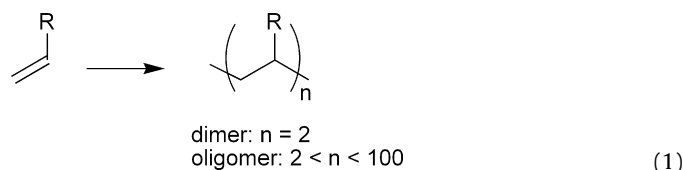
## 1. Introduction

Bicyclo[2.2.1]hept-2-ene, better known as norbornene (NB) can be polymerized by three different mechanisms (Fig. 1) [1].

Vinyl polynorbornene (PNB) is of special interest [2] due to its good mechanical strength, heat resistivity, and optical transparency, for example, for deep ultraviolet (193 nm) photoresist binder resins in lithographic processes [3], interlevel dielectrics in microelectronics applications, or as a cover layer for liquid-crystal displays [4,5]. Nickel and palladium complexes initiate the vinyl polymerization of norbornene in combination with methylaluminoxane (MAO) or the Lewis acid tris(pentafluorophenyl)borane  $[\text{B}(\text{C}_6\text{F}_5)_3]$  with or without triethylaluminum as cocatalysts [1,6]. An exception is cationic palladium(II) complexes, such as  $[\text{Pd}(\text{NCCH}_3)_4](\text{BF}_4)_2$  (**1**) and  $[\text{Pd}(\text{PPh}_3)_3(\text{NCCH}_3)](\text{BF}_4)_2$  (**2**), which require no cocatalyst for their activation towards the vinyl polymerization of norbornene because of the weakly bound acetonitrile ligands [1,7–9]. Also, palladium and nickel catalysts in particular allow the polymerization of functionalized norbornene monomers [1,3,10].



The use of olefin oligomers as intermediates for specialty chemicals, versatile feedstocks and building blocks drives the interest in the catalytic oligomerization (e.g., SHELL-higher-olefin-process, SHOP) [11–13]. In addition, olefin oligomerization is used to study mechanistic aspects because of the homogeneity of the reaction mixture (no heterogenation through polymer precipitation) and because in some aspects the oligomeric products are easier to investigate than high-molar-mass polymers [13,14]. The formation of olefin chains according to Eq. (1) is categorized as follows: dimerization when  $n=2$ , oligomerization when  $2 < n < 100$  and polymerization when  $n > 100$  [11].



Norbornene was oligomerized with the system  $\text{TiCl}_4/\text{AlEt}_2\text{Cl}$  at  $0^\circ\text{C}$  [15]. The hydrooligomerization of norbornene, that is, the norbornene C–C bond coupling in the presence of  $\text{H}_2$ , with *rac*- $\text{Me}_2\text{C}(\text{Ind}')_2\text{ZrCl}_2/\text{MAO}$  or *rac*- $\text{C}_2\text{H}_4(\text{Ind}'\text{H}_4)_2\text{ZrCl}_2/\text{MAO}$  was used to deliberately obtain oligomers in order to gain insight into the microstructure of polynorbornene. The X-ray crystal structure of a norbornene pentamer (Fig. 2) showed that in-between the regular *cis*-2,3-*exo* vinyl/addition insertions a metallocene-catalyzed  $\sigma$ -bond metathesis can take place. The *syn*-hydrogen on C7 (the

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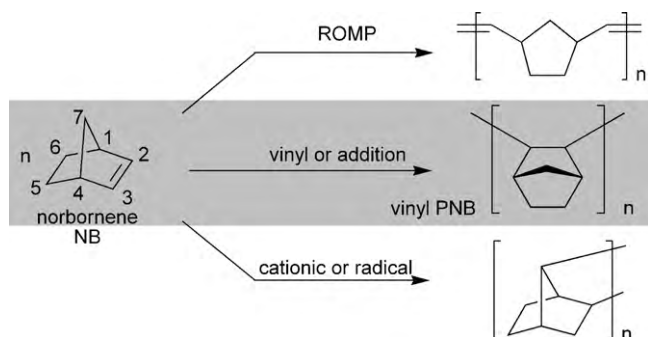


Fig. 1. Schematic representation of the three different types of polymerization of norbornene.

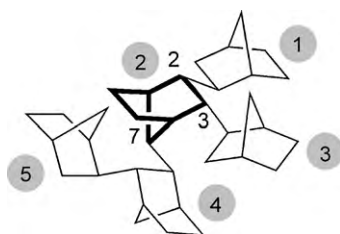


Fig. 2. Norbornene pentamer from a hydroooligomerization. The norbornene which was part of the  $\sigma$ -bond metathesis is highlighted for better visibility; the order of monomer insertion is given in the gray circles [16].

bridgehead) of the previous to last inserted monomer interacts with the Zr atom which in the  $\sigma$ -bond metathesis becomes now bound to C7. Thus, the chain continues with the next insertion on the C7-bridgehead carbon atom of the previous to last monomer [16].

Recent work on the more difficult vinyl polymerization of functionally substituted norbornenes shows that generally the *endo*-functionalized norbornenes are polymerized more slowly compared to the *exo*-analogues because of the possible coordination of the donor-containing substituent to the metal atom (Fig. 3), which attenuates the polymerization activity. Since the synthesis of substituted norbornenes is accomplished in a Diels–Alder reaction, always a mixture of *endo*- and *exo*-isomers is obtained [17].

The often encountered insolubility of PNBs obtained with palladium catalysts [2,6,7,9,18] makes a characterization of the polymer molar mass and mass distribution by gel permeation chromatography (GPC) impossible [1]. The origin of this insolubility is still not quite clear. One possibility may be chain cross-linking due to partial cationic polymerization. The targeted preparation of norbornene oligomers or soluble polymers with palladium catalysts may help to clarify the polymerization mechanisms.

We report here three concepts to obtain oligomeric or soluble vinyl polynorbornene with palladium catalysts: (1) the hydroooligomerization of norbornene in  $\text{CH}_3\text{NO}_2$ . (2) The vinyl polymerization of norbornene in ionic liquids [19]. (3) The vinyl

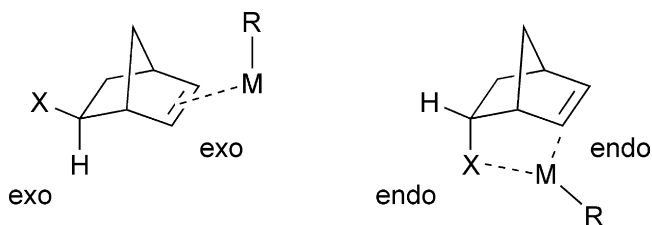


Fig. 3. Bonding modes for functionalized norbornene derivatives (X = coordinating functionality).

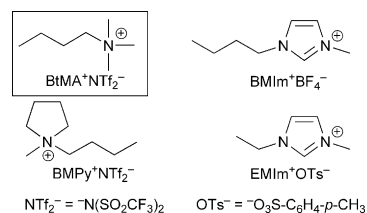


Fig. 4. Overview over the used ionic liquids (ILs). The only IL which allowed for a norbornene C–C bond coupling (BtMA<sup>+</sup>NTf<sub>2</sub><sup>-</sup>) is highlighted.

oligomerization of the  $\alpha$ -olefin substituted norbornene derivative 5-vinyl-2-norbornene [20].

## 2. Experimental

### 2.1. General procedures

All works involving air- and/or moisture-sensitive compounds were carried out by using standard vacuum, Schlenk or drybox techniques. IR spectra (KBr pellet) were measured on a Bruker Optik IFS 25. Gel permeation chromatography (GPC) analyses were performed on a PL-GPC 220 (2 columns, PL gel 10  $\mu\text{m}$  MIXED-B) with polymer solutions in 1,2,4-trichlorobenzene (concentration 2 mg/ml). The polymer solutions were filtered (Sartorius, Minisart RC 15, RC-membrane, PP-housing, pore size 0.45  $\mu\text{m}$ ) prior to the GPC measurements. The GPC was measured at 140  $^{\circ}\text{C}$  with an injection volume of 200  $\mu\text{l}$  and with a flow rate of 1 ml/min. Gas chromatography–mass spectroscopic (GC–MS) investigations were performed on a Hewlett Packard 5890 GC (equipped with an Ultra2 column, stationary phase cross-linked Ph–Me–silicon, length 50 m, outer diameter 0.2 mm, inner diameter: 0.11 mm; He carrier gas) connected with a mass-spectrometer (HP 5989A). Sample solutions in acetone (0.5  $\mu\text{l}$ ) were injected with a glass syringe. Electron impact mass spectra (EI-MS) were obtained on a Thermolectron TSQ 700. The 1D and 2D NMR experiments with VNB and oligo-VNB were performed on a Bruker Avance II 400 WB spectrometer (400 MHz for <sup>1</sup>H).

### 2.2. Materials

*N*-Butyl-*N*-trimethylammonium bis(trifluoromethylsulfonyl) imide (BtMA<sup>+</sup>NTf<sub>2</sub><sup>-</sup>), 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPy<sup>+</sup>NTf<sub>2</sub><sup>-</sup>), 1-butyl-3-methyl-imidazolium tetrafluoroborate (BMIm<sup>+</sup>BF<sub>4</sub><sup>-</sup>) and 1-ethyl-3-methyl-imidazolium tosylate (EMIm<sup>+</sup>OTs<sup>-</sup>) (Fig. 4) were obtained from IoLiTec and used without further purification. Palladium powder (~200 mesh, Aldrich), acetonitrile (Fluka), nitrosonium tetrafluoroborate (Aldrich) and triphenylphosphine (Aldrich) were used as received. Nitromethane (Merck-Schuchardt) was dried over P<sub>4</sub>O<sub>10</sub>, distilled twice, degassed and stored under argon. Norbornene (Aldrich) was purified by distillation and stored under argon.

#### 2.2.1. Tetrakis(acetonitrile)palladium(II)-bis(tetrafluoroborate), [Pd(NCCH<sub>3</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (1)

The complex was prepared according to the method from Schramm and Wayland [21] by oxidation of Pd-powder with NO<sup>+</sup>BF<sub>4</sub><sup>-</sup> in CH<sub>3</sub>CN solution. An air-sensitive yellow solid (turning brown within minutes upon air contact) was obtained which was stored in a glove box under argon. Yield 61%. IR (cm<sup>-1</sup>): 2322  $\nu(\text{CN})$ , 1100–1000, 765  $\nu(\text{BF}_4)$ .

### 2.2.2. Mono(acetonitrile)tris(triphenylphosphine)palladium(II)-bis(tetrafluoroborate), [Pd(PPh<sub>3</sub>)<sub>3</sub>(NCCH<sub>3</sub>)](BF<sub>4</sub>)<sub>2</sub> (**2**)

The catalyst was prepared as described in the literature [8c] yielding a yellow solid which did not seem air-sensitive but was also stored in a glove box under argon. Yield 71%. IR (cm<sup>-1</sup>): 2330  $\nu$ (CN), 1100–1000  $\nu$ (BF<sub>4</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.4–7.2 (45 H, m), 1.9 (3 H, s).

### 2.3. Polymerization procedures

#### 2.3.1. General

Each oligomerization at a chosen set of parameters (catalyst, temperature, time, pressure, and molar NB: Pd ratio) was carried out three times to ensure reproducibility of the catalytic activities. Hydroooligomerizations were run at room temperature with Pd complexes **1** and **2** at different hydrogen pressures. For the norbornene oligomerizations in the ionic liquids different reaction temperatures, reaction times and monomer/catalyst ratios were used with complex **1**. The oligomers were *inter alia* analyzed by infrared spectroscopy to check for the absence of double bonds in the region of 1620–1680 cm<sup>-1</sup> to ascertain that a vinyl polymerization instead of a ring opening metathesis polymerization (ROMP) took place [22].

#### 2.3.2. Reaction of norbornene and hydrogen with compound **1**

A 120 ml glass Büchi Miniclave was flushed with argon, charged with 8 ml of a 1.325 mol/l solution of norbornene (1.0 g, 10.6 mmol) in CH<sub>3</sub>NO<sub>2</sub> and pressurized to 2 bar hydrogen pressure under stirring to saturate the solution. After depressurizing, a solution of **1** (9 mg, 0.02 mmol) in CH<sub>3</sub>NO<sub>2</sub> (2 ml) was quickly added with a syringe through a ball valve against a positive pressure of hydrogen, followed by immediate re-pressurizing to a preset starting value of 0.5 bar, 1 bar, 2 bar or 4 bar. A grey precipitate developed. After 1 h the pressure was released. The grey suspension was filtered and the highly viscous grey residue in the filter paper was treated three times with 15 ml each of methanol to remove the catalyst residues. The clear yellow filtrate was analyzed by GC–MS.

#### 2.3.3. Hydroooligomerization of norbornene with compound **2**

The Büchi Miniclave was prepared as before with a solution of **2** (22.2 mg, 0.02 mmol) in CH<sub>3</sub>NO<sub>2</sub> (2 ml) and hydrogen pressures to a preset starting value of 0.5 bar, 1 bar, 2 bar or 4 bar. After 1 h the pressure was released. The yellow suspension was filtered and the highly viscous colorless residue in the filter paper was treated three times with 15 ml of methanol each to remove the catalyst residues. The highly viscous colorless oil was dried *in vacuo* for 5 h and analyzed by GC– and EI–MS.

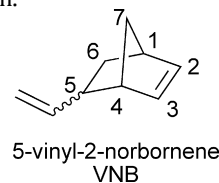
#### 2.3.4. Poly-/oligomerization of norbornene in ionic liquids

A 25 ml Schlenk-flask was charged with norbornene (0.5 g, 5.3 mmol) and the respective ionic liquid (2 ml) and thermostated to a specified temperature in an oil bath. Then, a defined but variable amount of the solid complex **1** (1.0 mg, 0.0023 mmol; 4.5 mg, 0.0101 mmol; 9.0 mg, 0.0202 mmol) was added against a positive pressure of argon. The polymerization was stopped after different reaction times by addition of methanol (10 ml). The yellow suspension was filtered and washed three times with 15 ml each of methanol to remove the catalyst residues. The colorless solid was dried *in vacuo* for 5 h.

#### 2.3.5. Oligomerization of 5-vinyl-2-norbornene

A Schlenk-flask was charged with 5-vinyl-2-norbornene (1.28 g, 10.6 mmol), nitromethane (8 ml) was added and thermostated to a specified temperature in an oil bath. Then, a defined amount of complex **1** (15.0 mg, 0.033 mmol; 30.0 mg, 0.066 mmol; 60.0 mg, 0.135 mmol or 120.0 mg, 0.265 mmol) was added as a solution

in nitromethane (2 ml) to start the polymerization reaction. The polymerization was stopped after 24 h by adding a methanol–HCl mixture (10:1, 30 ml). After an additional stirring for 30 min the polymer was separated by filtration, washed with methanol and dried in vacuum for 5 h.



## 3. Results and discussion

### 3.1. Hydroooligomerization of norbornene

Under hydroooligomerization conditions catalyst **1** proved unstable. The palladium(II) atom was rapidly reduced by hydrogen to metallic palladium(0), indicative by the formation of a grey precipitate. Metallic palladium then functions as a hydrogenation catalyst towards double bonds. A GC–MS product analysis indicated the formation of norbornane (Fig. 5). Thus, the norbornene hydroooligomerization was not investigated further with catalyst **1**.

Complex **2** did not show signs of Pd(II) reduction. A product analysis by GC–MS did not indicate norbornane formation. Norbornene hydroooligomerization with **2** was carried out at different hydrogen pressures from 0.5 bar to 4 bar. Preliminary experiments indicated that after 1 h quantitative norbornene oligomerization had been reached. A sample drawn after this time and analyzed without workup by GC–MS did not show traces of the norbornene monomer anymore. Thus, the reaction time was set to 1 h. The oligomer product was worked up and analyzed by GC–MS for the low molar mass dimer and trimer fraction (Fig. 6) and by EI–MS for the higher oligomers ( $n \geq 4$ ) (Fig. 7). The dimers and trimers were also seen in the EI–MS, but their intensity could not be determined accurately due to peak overlap with low molar mass fragmentation products.

For each hydrogen pressure the lowest mass oligomer of norbornene was the dimer followed by the trimer. Higher chain lengths were identified bei EI–MS. Fig. 7 illustrates the intensities from EI–MS as a function of monomer units at different hydrogen pressures. We want to make it very clear that this does not reflect the oligomer

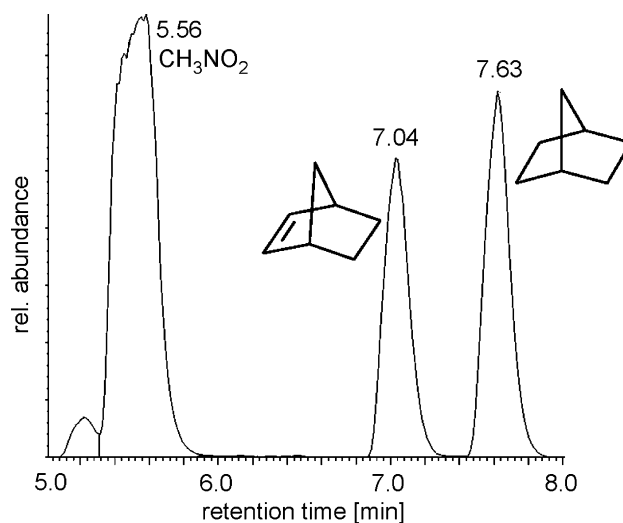


Fig. 5. Chromatogram from GC–MS of the product from **1**/H<sub>2</sub> in nitromethane indicating the norbornane formation. Peaks were assigned from the MS fragmentation pattern.

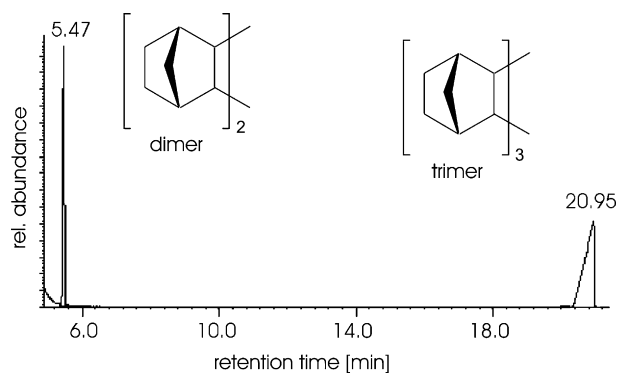


Fig. 6. GC-MS graph shows the dimers and trimers of norbornene obtained by the hydrooligomerization of norbornene with **2**/ $H_2$ .

distribution. The intensity of the higher oligomers will be lower because of their lower vapor pressure and their easier fragmentation in the EI mode. Thus, oligomers with more than 12 monomer units were of very low intensity and are not included anymore in Fig. 7. We will also refrain from discussing any intensity variation for oligomers with the same value of  $n$  for different hydrogen pressures. We just displayed the oligomer intensities to show that an increase in hydrogen pressure reduces the oligomer chain length. For a pressure of 4 bar the longest oligomer chain consisted of 9 norbornene monomer units. At a pressure of 2 bar the longest oligomer found by EI-MS contained 11 monomer units. Only at lower  $H_2$  pressures of 0.5 and 1 bar oligomers with 12 (and more) norbornene units were found with significant intensities. This is reasoned by the rate increase of the hydrogen-transfer chain-termination reaction with increasing  $H_2$  pressures which leads to shorter oligomer chains.

### 3.2. Polymerization of norbornene in ionic liquids (ILs)

Pre-screening experiments showed compound **1** to be much more active than compound **2** in norbornene polymerization experiments. Furthermore, only in the IL *N*-butyl-*N*-trimethylammonium bis(trifluoromethylsulfonyle)imide ( $BtMA^+NTf_2^-$ ) could an active polymerization catalyst be generated with compound **1**. In the ILs  $BMPy^+NTf_2^-$ ,  $BMI^+BF_4^-$  and  $EMI^+OTf^-$  no polymerization activity was observed with **1** at a temperature of 22 °C (no higher temperatures investigated), even after a polymerization time of 24 h. The catalyst inactivity in these ILs could be due to immiscibility of these more polar ILs with the

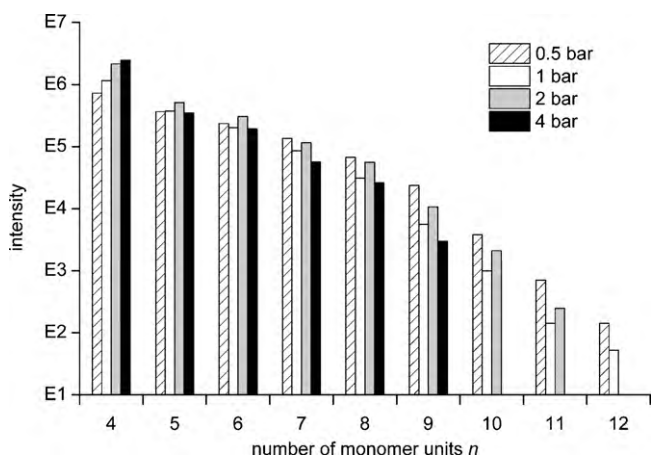


Fig. 7. Influence of the different hydrooligomerization conditions on the chain lengths of the obtained norbornene oligomers.

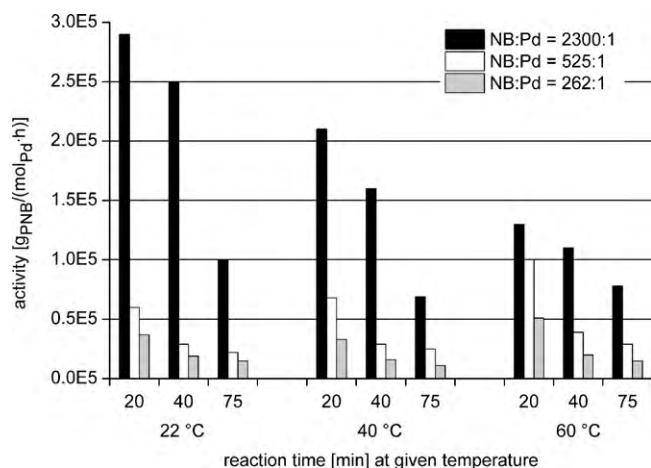


Fig. 8. Polymerization activities for the system **1**/ $BtMA^+NTf_2^-$  at different polymerization temperatures (22 °C, 40 °C, and 60 °C), reaction times (20 min, 45 min, and 75 min) and molar monomer:catalyst (NB:Pd) ratios (2300:1, 525:1, and 262:1).

NB monomer. In other catalytic applications the dependence of the activity on the IL chemical structure is noted [23]. Reaction temperatures, reaction times and monomer/catalyst ratios were varied with complex **1**/IL. The results of the homopolymerization of norbornene in the IL  $BtMA^+NTf_2^-$  are summarized in Table 1 and Fig. 8.

Polymer yields or conversions increase only slightly with extending the reaction times from 20 min over 45 to 75 min at a given temperature and NB:Pd ratio (Table 1). As the reaction mixture becomes more viscous with time and concomitant monomer conversion the reaction rate decreases through the decrease of monomer and the increased hindered diffusion of the NB monomer to the active center. The NB polymerization is truly homogeneous only at the very beginning. With PNB formation the active complex becomes more and more imbedded in the polymer matrix which represents a transfer to a heterogeneous phase, that is, a heterogeneous active complex form, and this leads to a hindered diffusion and diffusion-controlled reaction [24]. Consequently, the activity decreases strongly with time when the only slightly higher yields are divided by the more than doubled or tripled reaction time (Fig. 8).

There is a trend of increased conversion upon lowering the NB:Pd ratio from 2300:1 over 525:1 to 262:1 at otherwise identical reaction conditions. The NB:Pd ratio was lowered by keeping the NB amount and concentration the same, and increasing the amount of catalyst and, hence, its concentration. Thus, more catalytic centers became available per reaction volume. Still, the conversion did at most increase by a factor of about 1.5. Thus, the activity decreased as a mathematical artefact due to the division of the slightly increased yield by the quadrupled 2300 to 525) and further doubled (525 to 262) molar catalyst amount.

The variation of activity with temperature depended on the molar NB:Pd ratio. For an NB:Pd ratio of 2300:1 the activity decreased with rising temperatures. For an NB:Pd ratio of 525:1 there is a clear trend of increased activity with increasing temperature. This is reasoned by the opposing effects of increased polymerization rate and catalyst decomposition in the IL upon increased temperature. This decomposition is most pronounced for the smallest catalyst amount, that is, the NB:Pd ratio of 2300:1.

The molar mass determination by GPC is really only meaningful for the fully soluble polymers at NB:Pd ratios of 262:1. At higher NB:Pd ratios the PNB was only partially soluble. Understandably the soluble molar mass fractions then covered a rather narrow  $M_n$  range from  $1.2 \times 10^4$  g/mol to  $4.7 \times 10^4$  g/mol. One can qualitatively note an increased molar mass for higher NB:Pd. Presumably, the

**Table 1**  
Polymerization of norbornene with **1** in BtMA<sup>+</sup>NTf<sub>2</sub><sup>-</sup> <sup>a</sup>.

Entry	Time (min)	Temp. (°C)	NB:Pd ratio	Conversion (%)	Activity (g <sub>PNB</sub> /mol <sub>Pd</sub> h)	M <sub>n</sub> (×10 <sup>4</sup> g/mol)	M <sub>w</sub> (×10 <sup>4</sup> g/mol)	Q = M <sub>w</sub> /M <sub>n</sub>
1	20	22	2300:1	44	2.9 × 10 <sup>5</sup>	2.3	12	5.2
2	45	22	2300:1	52	2.5 × 10 <sup>5</sup>	3.0	11	3.7
3	75	22	2300:1	58	1.0 × 10 <sup>5</sup>	2.5	14	5.6
4	20	40	2300:1	32	2.1 × 10 <sup>5</sup>	4.0	9.7	2.4
5	45	40	2300:1	54	1.6 × 10 <sup>5</sup>	3.8	9.8	2.6
6	75	40	2300:1	40	6.9 × 10 <sup>4</sup>	3.1	9.7	3.1
7	20	60	2300:1	20	1.3 × 10 <sup>5</sup>	3.7	14	3.8
8	45	60	2300:1	39	1.1 × 10 <sup>5</sup>	3.9	13	3.3
9	75	60	2300:1	45	7.8 × 10 <sup>4</sup>	4.7	15	3.2
10	20	22	525:1	40	6.0 × 10 <sup>4</sup>	2.0	7.2	3.6
11	45	22	525:1	44	2.9 × 10 <sup>4</sup>	2.3	11	4.8
12	75	22	525:1	56	2.2 × 10 <sup>4</sup>	2.6	9.7	3.7
13	20	40	525:1	46	6.8 × 10 <sup>4</sup>	1.7	7.2	4.2
14	45	40	525:1	43	2.9 × 10 <sup>4</sup>	3.2	11	3.4
15	75	40	525:1	64	2.5 × 10 <sup>4</sup>	1.8	6.6	3.7
16	20	60	525:1	69	1.0 × 10 <sup>5</sup>	1.6	6.1	3.8
17	45	60	525:1	60	3.9 × 10 <sup>4</sup>	1.7	6.7	3.9
18	75	60	525:1	73	2.9 × 10 <sup>4</sup>	1.8	6.5	3.6
19	20	22	262:1	50	3.7 × 10 <sup>4</sup>	1.2	4.8	4.0
20	45	22	262:1	57	1.9 × 10 <sup>4</sup>	1.7	6.8	4.0
21	75	22	262:1	77	1.5 × 10 <sup>4</sup>	1.5	7.2	4.8
22	20	40	262:1	44	3.3 × 10 <sup>4</sup>	1.6	5.5	3.4
23	45	40	262:1	49	1.6 × 10 <sup>4</sup>	1.5	4.9	3.3
24	75	40	262:1	59	1.1 × 10 <sup>4</sup>	1.4	5.8	4.1
25	20	60	262:1	70	5.1 × 10 <sup>4</sup>	1.2	3.3	2.8
26	45	60	262:1	60	2.0 × 10 <sup>4</sup>	1.3	4.1	3.2
27	75	60	262:1	75	1.5 × 10 <sup>4</sup>	1.7	6.2	3.6

<sup>a</sup> Norbornene (NB, 0.5 g, 5.3 mmol), ionic liquid (2 ml), different amounts of solid **1** (1.0 mg, 0.0023 mmol; 4.5 mg, 0.0101 mmol; 9.0 mg, 0.0202 mmol) to give the different molar NB:Pd ratios. The polymerization was stopped after different reaction times by addition of methanol (10 ml). Conversion and subsequent activity data are the average from three polymerization runs. Molar mass determinations by GPC were carried out on a selected sample out of these three runs. The PNB obtained for a NB:Pd ratio of 2300:1 was partly soluble, for a NB:Pd ratio of 525:1 was soluble for the most part and for a NB:Pd ratio of 262:1 was completely soluble in 1,2,4-trichlorobenzene. GPC analyses were carried out at 140 °C.

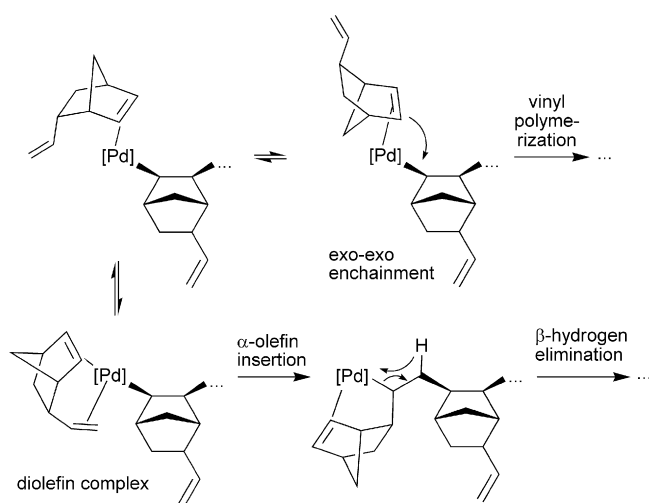
insoluble PNB fraction contained even longer chains. Yet, there is no clear trend of the molar mass with reaction time or temperature even for the soluble PNB obtained at NB:Pd ratios of 262:1. This may be due to opposing trends of differently increased polymerization rate and chain-termination rates with a decrease in IL viscosity.

At NB:Pd ratios of 262:1 the range of M<sub>n</sub> values between 1.2 × 10<sup>4</sup> g/mol and 1.7 × 10<sup>4</sup> g/mol translates into average PNB chain lengths of 127–180 monomer units. Together with a polymer dispersion (M<sub>w</sub>/M<sub>n</sub>) between 3 and 4 and a monomer conversion of typically less than 70% (less than 185 NB out of 262 NB molecules) this indicates that the majority of Pd complexes are polymerization

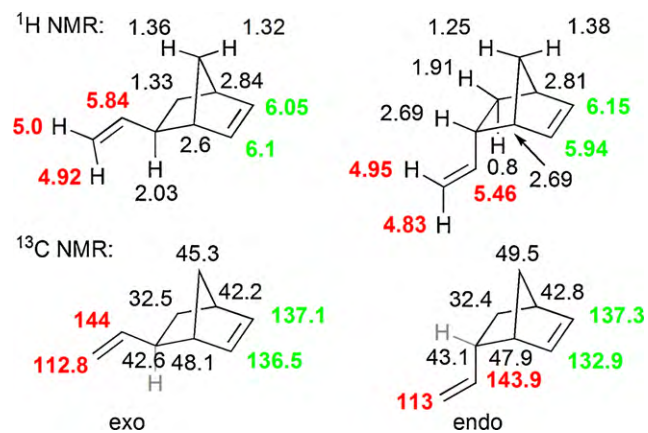
active under these conditions contrary to other reports on Ni/MAO catalysts [25]. Also, each Pd atom gives rise to about one chain. It remains noteworthy that in the IL BtMA<sup>+</sup>NTf<sub>2</sub><sup>-</sup> soluble PNBs could be obtained with a Pd catalyst.

### 3.3. Oligomerization of 5-vinyl-2-norbornene

It is well established that functionalized norbornene derivatives are polymerized more slowly because donor functionalities like a C=C double bond slow down the chain propagation through metal coordination (cf. Fig. 3) [17,26]. Also with an inert substituent in the 5-position, such as in 5-phenyl-2-norbornene, predominantly the *exo*-isomer undergoes the polymerization reaction, that is, the



**Fig. 9.** Competition in the VNB double bonds coordinating to Pd; the formulation [Pd] indicates that additional ligands can be present. The VNB–diolefin complex may be a resting state. An *exo*–*exo* enchainment was suggested for the insertion of the ring double bond in the vinyl NB polymerization [29].



**Fig. 10.** NMR assignment of *exo*- and *endo*-VNB in CDCl<sub>3</sub>. The norbornene and vinyl olefinic resonances are highlighted in green and red color, respectively, conforming to the green and red rectangles in Figs. 11 and 12. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

**Table 2**  
Polymerization of 5-vinyl-2-norbornene (VNB) with **1** in nitromethane<sup>a</sup>.

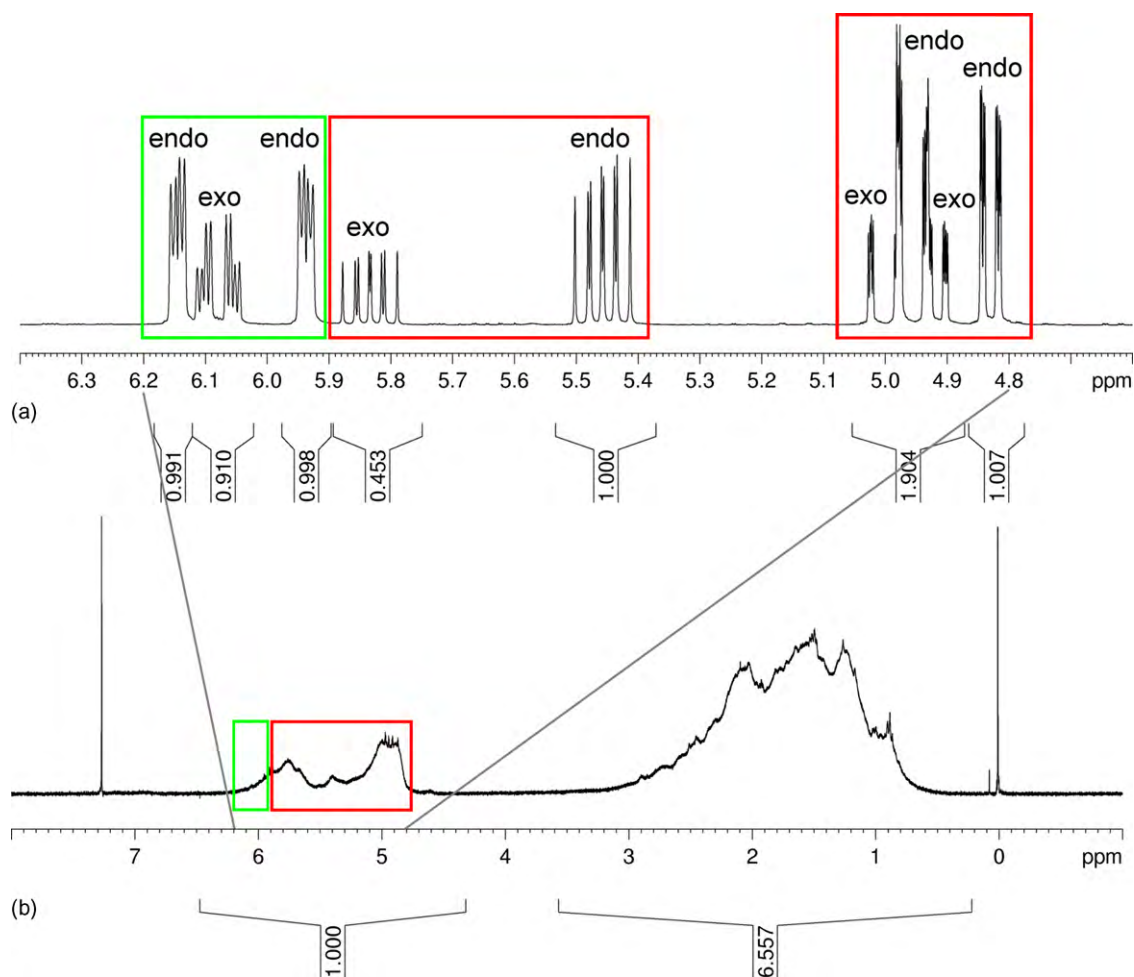
Entry	Temp. (°C)	VNB: Pd ratio	Conversion (%)	Activity (g <sub>polymer</sub> /mol <sub>Pd</sub> h)	$M_n$ ( $\times 10^3$ g/mol)	$M_w$ ( $\times 10^3$ g/mol)	$Q = M_w/M_n$
1	22	320:1	15	250	n.a.	n.a.	n.a.
2	40	320:1	25	393	n.a.	n.a.	n.a.
3	60	320:1	35	561	n.a.	n.a.	n.a.
4	22	160:1	32	256	n.a.	n.a.	n.a.
5	40	160:1	43	345	n.a.	n.a.	n.a.
6	60	160:1	55	440	2.4	3.4	1.4
7	22	80:1	42	169	2.9	4.3	1.5
8	40	80:1	65	260	2.4	3.5	1.5
9	60	80:1	79	316	2.3	3.1	1.4
10	22	40:1	60	120	2.6	4.2	1.6
11	40	40:1	75	150	n.a.	n.a.	n.a.
12	60	40:1	87	178	2.1	3.2	1.5

<sup>a</sup> 5-Vinyl-2-norbornene (VNB, 1.28 g, 10.6 mmol), nitromethane (8 ml), different amounts of **1** (15.0 mg, 0.033 mmol; 30.0 mg, 0.066 mmol; 60.0 mg, 0.135 mmol; 120.0 mg, 0.265 mmol) as a solution in nitromethane (2 ml), reaction time 24 h, quenching by addition of a methanol–HCl mixture (10:1, 30 ml). Conversion and subsequent activity data are the average from three polymerization runs. Molar mass determinations by GPC were carried out on a selected sample out of these three runs. n.a., not available. For entries 1–5 the polymer was little soluble at room temperature. GPC analyses were carried out at room temperature.

*endo*-isomer is polymerized more slowly [27]. In addition,  $\alpha$ -olefins are known as chain-transfer agents in the vinyl polymerization of norbornene to control the molar mass [27]. The insertion of the  $\alpha$ -olefin into the metal–chain end can terminate the chain propagation process by a  $\beta$ -hydride elimination (Fig. 9) [4,28]. The vinyl

group in the norbornene derivative 5-vinyl-2-norbornene is an intramolecular  $\alpha$ -olefin functionality.

Reaction temperatures and monomer:catalyst ratios were varied with complex **1** in CH<sub>3</sub>NO<sub>2</sub>. Because of lower activities the reaction time was kept constant at 24 h. Table 2 shows the results



**Fig. 11.** <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of (a) the olefinic region of the VNB monomer and (b) of oligo-VNB obtained under the conditions of Table 2, entry 12. Primarily the vinyl olefinic protons (red rectangles) of the monomer can still be seen in the oligomer. The two sets of signals for each olefinic proton in the monomer with a ratio of about 1:0.45 are due to the *endo*- and *exo*-configuration of the vinyl group (cf. Fig. 10). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

for the polymerization of 5-vinyl-2-norbornene (VNB) with **1**. First, the obtained activities are low, which is a consequence of the above mentioned lower polymerization propagation of *endo* 5-vinyl-2-norbornene and the therefore chosen long reaction time of 24 h. The monomer conversions increased clearly with a decrease in the molar VNB: Pd ratio and increasing reaction temperatures, so that the highest conversion of 87% was observed for a molar VNB: Pd ratio of 40 and a polymerization temperature of 60 °C. A dependency between the average molar mass of the oligo-VNB and both the molar VNB: Pd ratio and the temperature is not very apparent. In each polymerization series with constant molar VNB: Pd ratios the  $M_n$  values decreased slightly with higher temperatures (for example entries 7–9). The same effect was observed for a constant temperature but decreasing VNB: Pd ratios (for example entries 6, 9 and 12). Furthermore, the available GPC data showed that the  $M_n$  values covered a range from  $2.1 \times 10^3$  g/mol to  $2.9 \times 10^3$  g/mol depending on the reaction conditions. Together with  $M_w < 4.3 \times 10^3$  g/mol and with the molar mass of the VNB monomer (120.19 g/mol) these results clearly indicate the existence of oligo-VNB with chain lengths of an average of 20 monomer units. The values for the molecular weight dispersion  $Q$  are around 1.5, which argue for relative narrow molecular weight dispersion. A dispersity of  $Q < 2$  is common for oligomers and can be explained by a chain length-dependent insertion mechanism [14,30]. The resulting molecular weight dispersion is consistent with a Poisson-dispersion.

Oligo-VNB can be analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. For comparison, the NMR assignment of the VNB monomer is provided in Fig. 10.

The  $^1\text{H}$  NMR spectrum of oligo-VNB (Table 2, entry 12) shows a ratio of aliphatic protons to olefinic protons of 6.6:1 (Fig. 11). For a sole oligomerization through either the (*endo*-cyclic) norbornene double bond or the (*exocyclic*) vinyl double bond a ratio of the aliphatic to the olefinic proton resonances in oligo-VNB of 3:1 or 5:1, respectively, would be expected (not considering the end groups) (Fig. 12). The surplus of aliphatic resonances compared to the olefinic ones leads to the assumption, that some 5-vinyl-2-norbornene monomers are oligomerized through both the norbornene and the vinyl double bond, thereby leading to a fully saturated repeat unit with no olefinic protons. This suggests that oligomerization can proceed through either of the two double bonds or through both of them.

Yet, a comparison between the  $^1\text{H}$  NMR of the VNB monomer and oligo-VNB in Fig. 11a and b, respectively shows that the norbornene double bond was preferred for the oligomerization. The corresponding  $^1\text{H}$  resonances of the norbornene double bond (green rectangles) have almost disappeared in oligo-VNB. For the most part, the resonances in the olefinic region of oligo-VNB can be attributed to the protons of the vinyl double bond (red rectangles). An aliphatic to olefinic ratio of 7:1 is calculated if each second VNB monomer is polymerized through both double bonds and the other monomer through only the norbornene double bond (Fig. 12 bottom).

Furthermore, the prominent peak for the vinyl  $-\text{CH}=\text{CH}_2$  proton of the *endo*-isomer at 5.46 ppm is much less pronounced in oligo-VNB. This leads us to conclude that it is primarily the major *endo*-isomer (*endo/exo* ratio of about 2/1) which is oligomerized also through its vinyl double bond.

A  $^1\text{H},^{13}\text{C}$ -Heteronuclear Single Quantum Coherence (HSQC [31]) spectrum of the oligo-VNB (Fig. 13) provided further support on the preferential oligomerization route in VNB and also on the end-group structure. The  $^{13}\text{C}$  resonances for the norbornene and the vinyl double bond in VNB appear in well separated regions of  $\sim 132$ – $138$  ppm and around 113/144 ppm, respectively (cf. Fig. 10). The  $^1\text{H},^{13}\text{C}$ -HSQC spectrum of the same

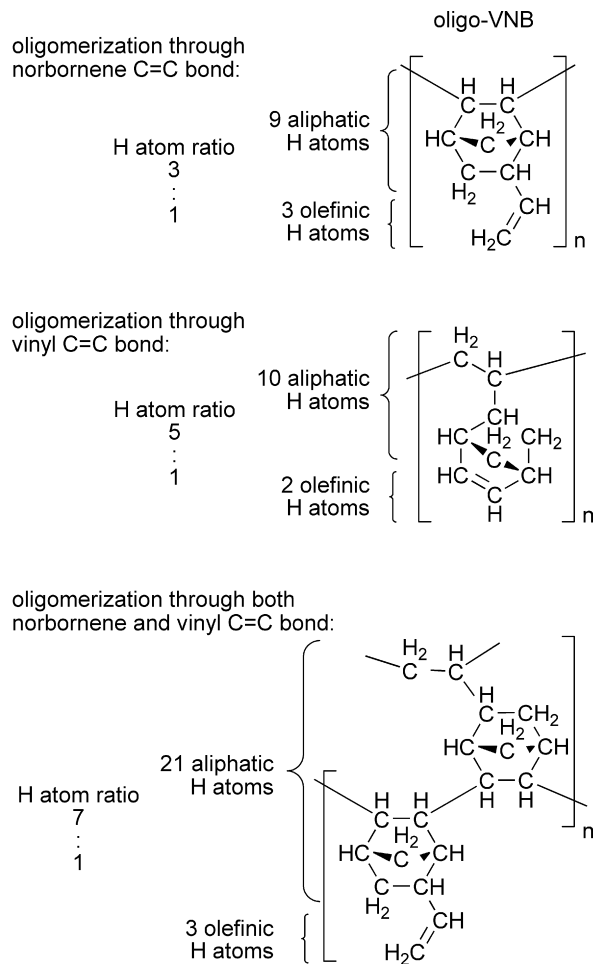
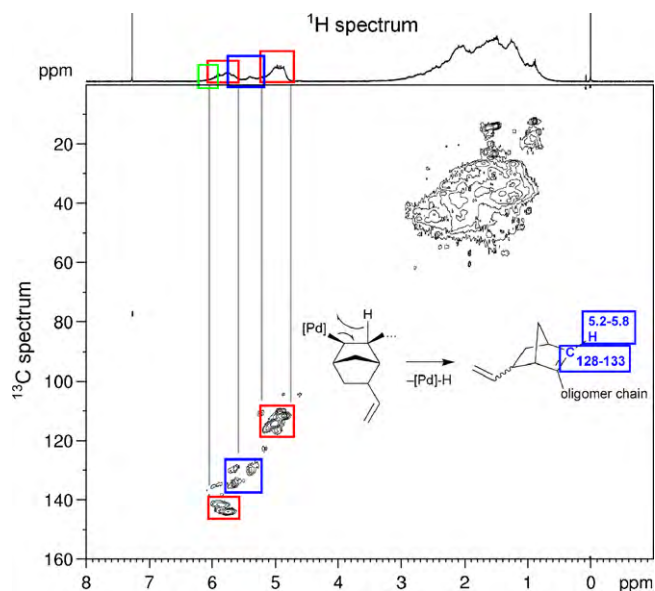


Fig. 12. Oligomerization modes for 5-vinyl-2-norbornene (VNB) with the resulting H atom ratio of the aliphatic and olefinic protons.

oligo-VNB as for the above  $^1\text{H}$  NMR (Table 2, entry 12) shows resonances both for the norbornene and vinyl olefinic carbon atoms (Fig. 13, blue and red rectangles, respectively, in the 2D spectrum).

The vinyl olefinic carbon resonances clearly arise from (correlate with) the vinyl olefinic hydrogen atom resonances (dashed lines to red rectangles in the  $^1\text{H}$  spectrum of Fig. 13). Yet, the norbornene olefinic C resonances do not arise from any possibly remaining H resonances of a norbornene- $\text{HC}=\text{CH}$ - double bond. There is no correlation to H atom resonances above 5.9 ppm (cf. Fig. 11). Instead, the norbornene- $\text{C}=\text{C}$ - resonances arise from weak H atom resonances in the region of 5.2–5.8 ppm (blue rectangle in the  $^1\text{H}$  spectrum of Fig. 13). Norbornene olefinic hydrogen resonances in this region are due to a  $-\text{HC}=\text{C}(\text{R-chain})-$  moiety, that is, a norbornene end group arising from a  $\beta$ -hydrogen elimination after insertion (see insert in Fig. 13). This assignment is supported by a  $^1\text{H}$  NMR spectrum generator [32] and, for example, the 5.5 ppm  $^1\text{H}$  NMR chemical shift of H-3 in 2-methyl-norbornene [33]. The spread from  $\sim 5.2$  ppm to 5.8 ppm for the H and  $\sim 128$ – $133$  ppm for the C atom resonances is due to two regioisomers each for the *endo*- and *exo*-isomer.

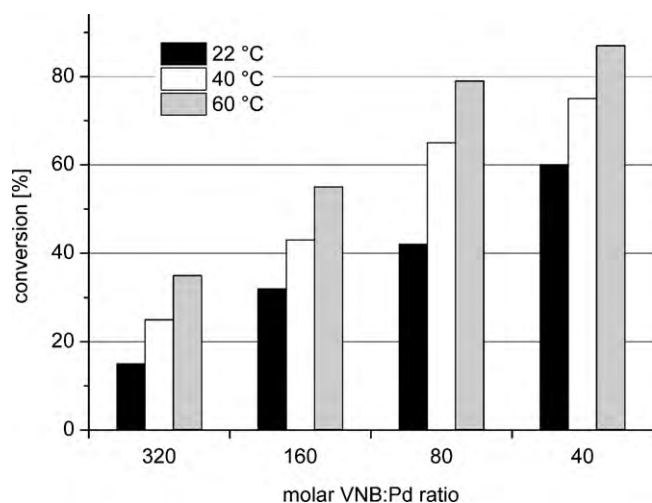
The monomer conversion increases with temperature and with lowering of the molar VNB: Pd ratio (Fig. 14). The rather linear increase with temperature is reasoned with the increased insertion rate. There is no indication of catalyst decomposition up to 60 °C, different from what was seen in ILs.



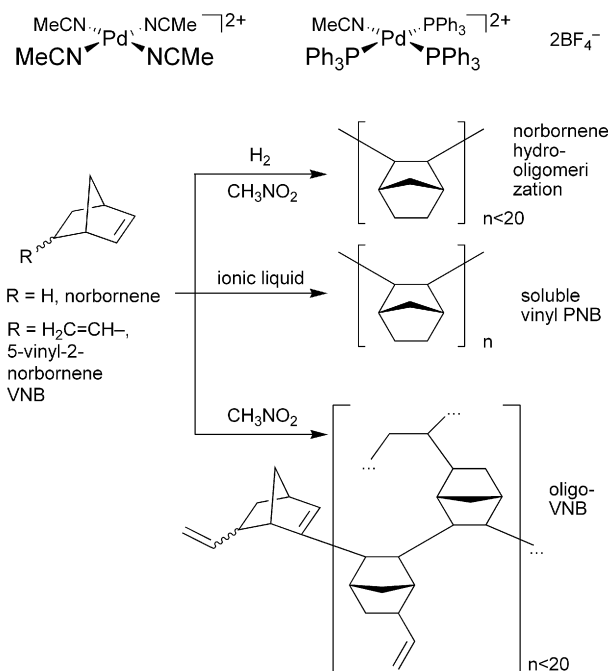
**Fig. 13.**  $^1\text{H},^{13}\text{C}$ -HSQC spectrum of the oligo-VNB (entry 12 in Table 2) in  $\text{CDCl}_3$ . The horizontal axis is the  $^1\text{H}$  spectrum, the vertical axis is the  $^{13}\text{C}$  spectrum. The Heteronuclear Single Quantum Coherence (HSQC [31]) is a 2D experiment, which correlates resonances of nuclei with the resonances of other nuclei by means of the one-bond coupling between them. Crosspeak carbon signals from the norbornene-type double bond are surrounded by a blue rectangle, those of the vinyl double bond by a red rectangle. In the  $^1\text{H}$  spectrum the green rectangle surrounds the norbornene- $\text{HC}=\text{CH}$ -olefinic proton region, the red rectangles the vinyl- $\text{CH}=\text{CH}_2$  olefinic protons and the blue rectangle the protons for the norbornene chain end group - $\text{HC}=\text{C}(\text{R-chain})$ - (see insert). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The VNB:Pd ratio was lowered by keeping the VNB amount and concentration constant and increasing the amount of catalyst and, hence, its concentration. Thus, more catalytic centers became available per reaction volume. Starting with a low conversion the increase was a factor of up to 2 (entries 1 and 4) but typically the increase in conversion was less. The activity decreased as a mathematical artefact due to the division of the somewhat increased yield by the doubled molar catalyst amount (320 to 160 to 80 to 40:1) at each stage.

As noted above, the overall activities for the oligomerization of VNB are much lower than for unsubstituted NB, because of the possible coordination of the vinyl substituent to the metal atom (cf. Figs. 3 and 9).



**Fig. 14.** Influence of the reaction temperature and molar VNB:Pd ratio on the oligomerization of 5-vinyl-2-norbornene.



**Fig. 15.** Summary of the routes and conditions to oligonorborene, soluble poly-norbornene (PNB), and oligo(5-vinyl-2-norbornene) (oligo-VNB) with cationic palladium catalysts.

#### 4. Conclusion

Soluble and oligomeric polynorbornenes with the palladium catalysts  $[\text{Pd}(\text{NCCH}_3)_4](\text{BF}_4)_2$  (**1**) or  $[\text{Pd}(\text{PPh}_3)_3(\text{NCCH}_3)](\text{BF}_4)_2$  (**2**) could be obtained by three different routes (Fig. 15): (1) the hydrooligomerization of norbornene with **2** in nitromethane; (2) by employing the ionic liquid *N*-butyl-*N*-trimethylammonium bis(trifluoromethylsulfonyl)imide ( $\text{BtMA}^+\text{NTf}_2^-$ ) as reaction medium for the norbornene polymerization with **1**, and (3) by using the NB derivative 5-vinyl-2-norbornene (VNB) with **1** in  $\text{CH}_3\text{NO}_2$  where a vinyl double bond slows down the insertion rate and is also opened as part of the C–C bond formations. The oligo- and polynorbornene products were obtained under variation of the reaction conditions like hydrogen pressure, temperature (22 °C, 40 °C, and 60 °C), reaction time (20 min, 45 min, and 75 min) and molar monomer/Pd ratio. The short chain hydrooligomers were analyzed by GC–MS, EI–MS, the longer oligomers and polymers by GPC. Analysis of the chain length for poly-/oligomers formed in the IL and from 5-vinyl-2-norbornene (VNB) shows that each Pd atom is catalytically active and gives rise to about one chain. An NMR analysis of oligo-VNB reveals that primarily the norbornene double bond is opened but that simultaneously also the vinyl double bond, mostly of the *endo*-isomer, is polymerized. A  $\beta$ -hydrogen elimination after insertion of a norbornene double bond is a possible chain-termination mechanism.

#### References

- (a) F. Blank, C. Janiak, *Coord. Chem. Rev.* 253 (2009) 827–861; (b) C. Janiak, P.-G. Lassahn, V. Lozan, *Macromol. Symp.* 236 (2006) 88–99; (c) C. Janiak, P.-G. Lassahn, *J. Mol. Catal. A: Chem.* 166 (2001) 193–209; (d) B.L. Goodall, L.H. McIntosh, L.F. Rhodes, *Macromol. Symp.* 89 (1995) 421–432.
- Recent work: (a) A. Sachse, S. Demeshko, S. Dechert, V. Daebel, A. Lange, F. Meyer, *Dalton Trans.* 39 (2010) 3903–3914; (b) P. Hao, S. Zhang, J.-J. Yi, W.-H. Sun, *J. Mol. Catal. A: Chem.* 302 (2009) 1–6; (c) H.-Y. Gao, L. Pei, Y. Li, J.-K. Zhang, Q. Wu, *J. Mol. Catal. A: Chem.* 280 (2008) 81–86; (d) X. Meng, G.-R. Tang, G.-X. Jin, *Chem. Commun.* (2008) 3178–3180;



- (e) W.-G. Jia, Y.-B. Huang, Y.-J. Lin, G.-X. Jin, *Dalton Trans.* (2008) 5612–5620;  
 (f) W. Zuo, W.-H. Sun, S. Zhang, P. Hao, A. Shiga, *J. Polym. Sci.: Part A: Polym. Chem.* 45 (2007) 3415–3430;  
 (g) J. Hou, S. Jie, W. Zhang, W.-H. Sun, *J. Appl. Polym. Sci.* 102 (2006) 2233–2240.
- [3] (a) C. Chang, J. Lipian, D.A. Barnes, L. Seger, C. Burns, B. Bennett, L. Bonney, L.F. Rhodes, G.M. Benedikt, R. Lattimer, S.S. Huang, V.W. Day, *Macromol. Chem. Phys.* 206 (2005) 1988–2000;  
 (b) K.H. Park, R.J. Twieg, R. Ravikiran, L.F. Rhodes, R.A. Shick, D. Yankelevich, A. Knoesen, *Macromolecules* 37 (2004) 5163–5178.
- [4] B. Berchtold, V. Lozan, P.-G. Lassahn, C. Janiak, *J. Polym. Sci.: Part A: Polym. Chem.* 40 (2002) 3604.
- [5] (a) H. Ito, H.D. Truong, L.F. Rhodes, C. Chang, L.J. Langsdorf, H.A. Sidaway, K. Maeda, S. Sumida, *J. Photopolym. Sci. Technol.* 17 (2004) 609–614;  
 (b) T. Hoskins, W.J. Chung, A. Agrawal, J. Ludovice, C.L. Henderson, L.D. Seger, L.F. Rhodes, R.A. Shick, *Macromolecules* 37 (2004) 4512–4518;  
 (c) X.Q. Wu, H.A. Reed, Y. Wang, L.F. Rhodes, E. Elce, R. Ravikiran, R.A. Shick, C.L. Henderson, S.A.B. Allen, P.A. Kohl, *J. Electrochem. Soc.* 150 (2003) H205–H213;  
 (d) X.Q. Wu, H.A. Reed, L.F. Rhodes, E. Elce, R. Ravikiran, R.A. Shick, C.L. Henderson, S.A.B. Allen, P.A. Kohl, *J. Appl. Polym. Sci.* 88 (2003) 1186–1195;  
 (e) N.R. Grove, P.A. Kohl, S.A.B. Allen, S. Jayaraman, R. Shick, *J. Polym. Sci.: Part B: Polym. Phys.* 37 (1999) 3003;  
 (f) A. Hideki, A. Satoshi, M. Hiroshi, M. Junichi, patent EPO445755, Equivalents DE69129600, JP4063807, Idemitsu Kosan Co. (Jpn.) (1991);  
 (g) T.F.A. Haselwander, W. Heitz, S.A. Krügel, J.H. Wendorff, *Macromol. Chem. Phys.* 197 (1996) 3435, and references therein.
- [6] (a) F. Blank, H. Scherer, J. Ruiz, V. Rodríguez, C. Janiak, *Dalton Trans.* 39 (2010) 3609–3619;  
 (b) T. Yamamoto, C. Shikada, S. Kaita, T. Olivier, Y. Maruyama, Y. Wakatsuki, *J. Mol. Catal. A: Chem.* 300 (2009) 1–7;  
 (c) G.-R. Tang, Y.-J. Lin, G.-X. Jin, *J. Polym. Sci.: Part A: Polym. Chem.* 46 (2008) 489–500;  
 (d) Y.-B. Huang, G.-R. Tang, G.-Y. Jin, G.-X. Jin, *Organometallics* 27 (2008) 259–269;  
 (e) W.-J. Zhang, W.-H. Sun, B. Wu, S. Zhang, H.-W. Ma, Y. Li, J. Chen, P. Hao, *J. Organomet. Chem.* 691 (2006) 4759–4767;  
 (f) T. Hu, Y.-G. Li, Y.S. Li, N.-H. Hu, *J. Mol. Catal. A: Chem.* 253 (2006) 155;  
 (g) J. Hou, W.-H. Sun, D. Zhang, L. Chen, W. Li, D. Zhao, H. Song, *J. Mol. Catal. A: Chem.* 213 (2005) 221–233;  
 (h) T.J. Woodman, Y. Sarazin, S. Garratt, G. Fink, M. Bochmann, *J. Mol. Catal. A: Chem.* 235 (2005) 88;  
 (i) H. Gao, J. Zhang, Y. Chen, F. Zhu, Q. Wu, *J. Mol. Catal. A: Chem.* 240 (2005) 178;  
 (j) H. Yang, Z. Li, W.-H. Sun, *J. Mol. Catal. A: Chem.* 206 (2003) 23.
- [7] (a) A. Sen, T.-W. Lai, R.R. Thomas, *J. Organomet. Chem.* 358 (1988) 567;  
 (b) T.-W. Lai, A. Sen, *Organometallics* 1 (1982) 415.
- [8] (a) N. Seehof, C. Mehler, S. Breunig, W. Risse, *J. Mol. Catal.* 76 (1992) 219;  
 (b) C. Mehler, W. Risse, *Makromol. Chem. Rapid Commun.* 12 (1991) 255;  
 (c) T.-W. Lai, A. Sen, *Organometallics* 3 (1984) 866.
- [9] (a) J.A. Casares, P. Espinet, G. Salas, *Organometallics* 27 (2008) 3761–3769;  
 (b) R. López-Fernández, N. Carrera, A.C. Albéniz, P. Espinet, *Organometallics* 28 (2009) 4996–5001.
- [10] (a) J. McDermott, C. Chang, L.F. Martin, L.F. Rhodes, G.M. Benedikt, R.P. Lattimer, *Macromolecules* 41 (2008) 2984–2986;  
 (b) M. Yamashita, I. Takamiya, K. Jin, K. Nozaki, *Organometallics* 25 (2006) 4588–4595;  
 (c) J. Lipian, R.A. Mimna, J.C. Fondran, D. Yandulov, R.A. Shick, B.L. Goodall, L.F. Rhodes, J.C. Huffman, *Macromolecules* 35 (2002) 8969–8977;  
 (d) A.D. Hennis, J.D. Polley, G.S. Long, A. Sen, D. Yandulov, J. Lipian, G.M. Benedikt, L.F. Rhodes, J. Huffman, *Organometallics* 20 (2001) 2802–2812.
- [11] (a) C. Janiak, *Coord. Chem. Rev.* 250 (2006) 66–94;  
 (b) C. Janiak, F. Blank, *Macromol. Symp.* 236 (2006) 14–22.
- [12] (a) J. Skupinska, *Chem. Rev.* 91 (1991) 613;  
 (b) D. Vogt, in: B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Complexes*, VCH, Weinheim, Germany, 2000, pp. 245–258, ch. 2.3.1.3;  
 (c) K. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry, Important Raw Materials and Intermediates*, Verlag Chemie, Weinheim, Germany, 1978;  
 (d) G.W. Parshall, S.D. Ittel, *Homogeneous Catalysis, The Applications and Chemistry by Soluble Transition Metal Complexes*, 2nd ed., Wiley, New York, 1992.
- [13] Recent work related to SHOP:  
 (a) Y. Yang, P. Yang, C. Zhang, G. Li, X.-J. Yang, B. Wu, C. Janiak, *J. Mol. Catal. A: Chem.* 296 (2008) 9;  
 (b) L.L. de Oliveira, R.R. Campedelli, M.C.A. Kuhn, J.-F. Carpentier, O.L. Casagrande Jr., *J. Mol. Catal. A: Chem.* 288 (2008) 58;  
 (c) A. Kermagoret, F. Tomicki, P. Braunstein, *Dalton Trans.* (2008) 2945;  
 (d) A. Kermagoret, P. Braunstein, *Dalton Trans.* (2008) 1564;  
 (e) P. Kuhn, D. Sémeril, D. Matt, M.J. Chetcuti, P. Lutz, *Dalton Trans.* (2007) 515;  
 (f) C. Bianchini, G. Giambastiani, I.G. Rios, G. Mantovani, A. Meli, A.M. Segarra, *Coord. Chem. Rev.* 250 (2006) 1391;  
 (g) F. Speiser, P. Braunstein, L. Saussine, *Acc. Chem. Res.* 38 (2005) 784–793.
- [14] (a) C. Janiak, K.C.H. Lange, P. Marquardt, R.-P. Krüger, R. Hanselmann, *Macromol. Chem. Phys.* 203 (2002) 129;  
 (b) C. Janiak, K.C.H. Lange, P. Marquardt, *J. Mol. Catal. A: Chem.* 180 (2002) 43;  
 (c) C. Janiak, K.C.H. Lange, P. Marquardt, R.-P. Krüger, R. Hanselmann, in: J. Sun, C. Janiak (Eds.), *Advances on Organometallic Catalysts and Olefin Polymerization in China and Germany*, Chemical Industry Press, Beijing, 2001, pp. 117–142, ch. 12.
- [15] L. Porri, V.N. Scalera, M. Bagatti, A. Famulari, S.V. Meille, *Macromol. Rapid Commun.* 27 (2006) 1937.
- [16] (a) M. Arndt, M. Gosmann, *Polym. Bull.* 41 (1998) 433;  
 (b) C. Karfilidis, H. Hermann, A. Ruffińska, B. Gabor, R.J. Mynott, G. Breitenbruch, C. Weidenthaler, J. Rust, W. Joppek, M.S. Brookhart, W. Thiel, G. Fink, *Angew. Chem. Int. Ed.* 43 (2004) 2444.
- [17] (a) M. Kang, A. Sen, *Organometallics* 23 (2004) 5396;  
 (b) J.K. Funk, C.E. Andes, A. Sen, *Organometallics* 23 (2004) 1680.
- [18] A. Sen, T.-W. Lai, *J. Am. Chem. Soc.* 103 (1982) 4627.
- [19] (a) H. Olivier-Bourbigou, Y. Chauvin, *J. Mol. Catal. A: Chem.* 214 (2004) 9;  
 (b) J.S. Wilkes, *J. Mol. Catal. A: Chem.* 214 (2004) 11–17;  
 (c) V. Calò, A. Nacci, A. Monopoli, *J. Mol. Catal. A: Chem.* 214 (2004) 45–56;  
 (d) P. Wasserscheid, C. Hilgers, W. Keim, *J. Mol. Catal. A: Chem.* 214 (2004) 83–90;  
 Selected articles from the special issue on "ionic liquids as promising alternative media for organic synthesis and catalysis" which provide an overview or report regioselective C–C bond forming and oligomerization reactions.
- [20] E.V. Novikova, G.P. Belov, W.-H. Sun, V.R. Flid, *Polym. Sci. Ser. A* 48 (2006) 462–469.
- [21] R.F. Schramm, B.B. Wayland, *J. Chem. Soc., Chem. Commun.* (1968) 898.
- [22] T. Saegusa, T. Tsujino, J. Furukawa, *Makromol. Chem.* 78 (1964) 231.
- [23] (a) S.A. Forsyth, J.M. Pringle, D.R. MacFarlane, *Aust. J. Chem.* 57 (2004) 113;  
 (b) J.M. Pringle, *Aust. J. Chem.* 62 (2009) 287.
- [24] C. Janiak, K.C.H. Lange, U. Versteeg, D. Lentz, P.H.M. Budzelaar, *Chem. Ber.* 129 (1996) 1517.
- [25] C. Janiak, P.-G. Lassahn, *Polym. Bull.* 47 (2002) 539.
- [26] (a) S. Liu, S. Borkar, D. Newsham, H. Yennawar, A. Sen, *Organometallics* 26 (2007) 210–216, and references therein;  
 (b) T. Hasan, T. Ikeda, T.J. Shiono, *Polym. Sci.: Part A: Polym. Chem.* 45 (2007) 4581;  
 (c) B. Liu, Y. Li, B.-B. Shin, D.Y. Yoon, I. Kim, L. Zhang, W. Yan, *J. Polym. Sci.: Part A: Polym. Chem.* 45 (2007) 3391;  
 (d) K. Mueller, S. Kreiling, K. Dehnicke, J. Allgaier, D. Richter, L.J. Fetters, Y. Jung, D.Y. Yoon, A. Greiner, *Macromol. Chem. Phys.* 207 (2006) 193;  
 (e) M.K. Boggiano, D. Vellenga, R. Carbonell, V.S. Ashby, J.M. DeSimone, *Polymer* 47 (2006) 4012;  
 (f) B.-G. Shin, M.-S. Jang, D.Y. Yoon, W. Heitz, *Macromol. Rapid Commun.* 25 (2004) 728;  
 (g) D.P. Sanders, E.F. Connor, R.H. Grubbs, R.J. Hung, B.P. Osborn, T. Chiba, S.A. MacDonal, C.G. Willson, W. Conley, *Macromolecules* 36 (2003) 1534;  
 (h) G.M. Benedikt, E. Elce, B.L. Goodall, H.A. Kalamirides, L.H. McIntosh, L.F. Rhodes, K.T. Selvy, C. Andes, K. Oylar, A. Sen, *Macromolecules* 35 (2002) 8978;  
 (i) R.A. Wendt, G. Fink, *Macromol. Chem. Phys.* 201 (2000) 1365.
- [27] (a) A.S. Abu-Surrah, K. Lappalainen, M. Kettunen, T. Repo, M. Leskelä, H.A. Hodali, B. Rieger, *Macromol. Chem. Phys.* 202 (2001) 599–603;  
 (b) C. Mehler, W. Risse, *Macromol. Chem., Rapid Commun.* 13 (1992) 455.
- [28] PCT Int. Appl. WO 9514048, 1995, B.F. Goodrich Company (USA), invs.: B.L. Goodall, G.M. Benedikt, L.H. McIntosh, D.A. Barnes, L.F. Rhodes, Equivalents: Patent US 5468819, 1995, B.F. Goodrich Co. (US); *Chem. Abstr.* 123 (1995) 341322 p.
- [29] (a) S. Ahmed, S.A. Bidstrup, P.A. Kohl, P.J. Ludovice, *J. Phys. Chem. B* 102 (1998) 9783–9790;  
 (b) S. Ahmed, P.J. Ludovice, P. Kohl, *Comp. Theor. Polym. Sci.* 10 (2000) 221–233;  
 (c) C. Janiak, P.G. Lassahn, *Macromol. Rapid Commun.* 22 (2001) 479–492.
- [30] C. Janiak, K.C.H. Lange, P. Marquardt, *Macromol. Rapid Commun.* 16 (1995) 643–650.
- [31] G. Bodenhausen, D.J. Ruben, *Chem. Phys. Lett.* 69 (1980) 185–189.
- [32] ACD/HNMR Spectrum Generator, Version 4.0 for Microsoft Windows, copyright 1994–1999 by Advanced Chemistry Development Inc., Toronto, Canada.
- [33] (a) W. Hüchel, H.-J. Schneider, H. Schneider-Berndlöhr, *Liebigs Ann. Chem.* (1975) 1690–1695;  
 (b) J. San Filippo Jr., G.M. Anderson, *J. Org. Chem.* 39 (1974) 473–477;  
 (c) J.A. Duncan, R.T. Hendricks, K.S. Kwong, *J. Am. Chem. Soc.* 112 (1990) 8433–8442.