

Polymerization of norbornene using novel palladium carboxylate/boron trifluoride etherate catalyst system

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Abstract

The vinyl polymerization of norbornene with Pd(carboxylate)₂/BF₃OEt₂ catalyst system has been investigated by varying the molar cocatalyst/metal ratio, the norbornene/metal ratio, the metal concentration and the reaction temperature. The effects on the catalyst activity were explained on the basis of complexation equilibrium for the active homogeneous complex. A “particular” activity of 154 100 kg NB per mole Pd for an hour has been achieved at B/Pd = 25 and 25 °C. The molecular weights M_w from 77 700 to 293 800 g/mol and glass transition temperatures T_g from 240 to 262 °C were observed for the representative samples of polynorbornene. The molar mass distribution indicates a single-site, highly homogeneous character of the active catalyst species. Catalytic activity and polymer molecular weight can be controlled by varying the reaction parameters over a wide range. NMR and IR spectroscopic studies of the polymer showed 2,3-enchainment repeating units of polymer backbone with low diisotacticity. The simplicity of catalyst system composition might be of industrial importance.

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1. Introduction

Starting from norbornene (NB) and its derivatives, different classes of polymers can be obtained by selecting polymerization conditions that drive the reaction by cationic or radical pathways, by ring-opening metathesis, or by insertion routes [1]. Little is known about the cationic and the radical polymerizations of norbornene, which mostly result in a low molecular weight material with 2,7-enchainment of the monomer [2,3]. The best known polymerization of norbornene is the ROMP and the corresponding polymer contains one double bond in each repeating unit [4]. The increasing interest in the addition polymerization of norbornene (bicyclo[2.2.1]hept-2-ene) and its derivatives is due to the attractive properties of these polymers, which show high glass transition temperatures, high

optical transparency, low dielectric constant and low birefringence [5]. The norbornene addition polymer with 2,3-enchainment displays a characteristic rigid random coil conformation, which shows restricted rotation about the main chain and exhibits strong thermal stability. Therefore the addition polymers of norbornene and its derivatives are attractive materials for the manufacture of microelectronic and optical devices. The late transition-metal palladium and nickel catalysts lead to vinyl addition polymerization of norbornene. The types of catalysts include: (i) single component cationic nickel and palladium complexes with weakly coordinating counteranions, [6,7], (ii) neutral complexes in combination with methylalumoxane (MAO) cocatalysts, [8–23], (iii) neutral complexes in combination with organo-Lewis acid tris(pentafluorophenyl)borane, B(C₆F₅)₃, with or without triethylaluminum (TEA), [24–30], (iv) palladium complexes in combination with Li⁺[C₆F₅]₄B⁻ [31], Na⁺[3,5-(CF₃)₂C₆H₃]₄B⁻ [32] or [PhNHMe₂]⁺[C₆F₅]₄B⁻ [33]. It is noteworthy that the complex [(1,5-COD)(CH₃)Pd(Cl)] in combination with a monodentate phosphine ligand and

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$\text{Na}^+[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_4\text{B}^-$ is allowed to reach a polymerization rate of 1000 tons norbornene per mole Pd for an hour [32].

However, one of the main drawbacks of these systems is represented by the high production costs of MAO and organoborane cocatalysts. Therefore, it is desirable to find the novel activators which can be used as substitutes for MAO and organoboranes. A simple Lewis acid BF_3 , in the form of boron trifluoride etherate, BF_3OEt_2 , was applied in the polymerization of norbornene type monomers as a “third component” in combination with TEA, but not as cocatalyst [34].

We have recently shown that boron trifluoride etherate, BF_3OEt_2 , can be successfully used as a cocatalyst towards palladium acetylacetonate, $\text{Pd}(\text{acac})_2$, and tetrakis(triphenylphosphine)nickel, $\text{Ni}(\text{PPh}_3)_4$, precursors for the polymerization of norbornene [35,36]. In this work, we report upon new catalytic systems based on palladium carboxylates and BF_3OEt_2 for the polymerization of norbornene. It should be noted that previously a number of late transition-metal carboxylates had been reported as active catalysts for the polymerization of norbornene [26,27,34].

2. Experimental

All manipulations for air sensitive compounds were carried out under a stream of dry nitrogen using standard inert techniques.

2.1. Materials

Inert gases were purified before feeding to the reactor by passing them through columns packed with oxygen scavenger (Fisher REDOX) and molecular sieve 5A (Aldrich), respectively. Norbornene (99%, Aldrich) was purified by distillation under reduced pressure over sodium. BF_3OEt_2 (Aldrich, 99%) was freshly distilled over CaH_2 prior to use. Toluene (Sigma–Aldrich, 99.8%) was used as received. Benzene (Aldrich) was distilled with sodium/potassium alloy Na/K under dry nitrogen. $\text{Pd}(\text{OAc})_2$ was supplied by Aldrich. $\text{Pd}(\text{propionate})_2$ (brown), $\text{Pd}(\text{benzoate})_2$ (dark green), $\text{Pd}(\text{heptanoate})_2$ (brown) and $\text{Pd}(\text{stearate})_2$ (mustard) were synthesized as described elsewhere [37], characterized by elemental analyses and recrystallized from benzene.

2.2. Polymerization of norbornene

Polymerizations were carried out in a 10 mL glass reactor equipped with a magnetic stirrer. The reactor was preliminarily purged in vacuum and filled with nitrogen, and then was filled with norbornene as a solution in toluene. The solution was kept at desired temperature for 15 min and the solution of palladium precursor in toluene was added. Polymerizations were initiated by the injection of boron compound. After stirring for a time needed, the polymers formed were precipitated in acidified ethanol. The precipitated polymers were washed three times with ethanol, and dried in vacuum at 80 °C for 6 h. Polymerization runs were carried out at least three times to ensure reproducibility. In standard runs the amount of

palladium precursor was 1.0×10^{-6} mol, the B/Pd ratio was 25, the NB/Pd ratio was 50 000, the reaction time was 30 min, and the total reaction volume was 7 mL, unless otherwise stated.

2.3. Characterization of polymers

NMR spectra were recorded at room temperature on a Bruker AMX-500 spectrometer with frequencies of 500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR. Each polymer sample was dissolved in CDCl_3 up to a concentration of 10 wt.% in NMR tubes (5 mm o.d.). Tetramethyl silane (TMS) was used as the internal standard. The IR spectrum was recorded using a KBr pellet technique with a Nicolet Fourier transform infrared (FT-IR) spectrometer. Viscosity measurements were carried out in chlorobenzene at 25 °C using an Ubbelohde viscometer. Gel permeation chromatographic (GPC) analysis was carried out on a WATERS 150 HPLC instrument with 10 μm MIXED-B columns (300 \times 7.5 mm) using 1,2,4-trichlorobenzene solvent at 135 °C and a polystyrene standard. Here, it should be noted that the molecular weights determined are only apparent due to different hydrodynamic volumes for a polystyrene chain and a norbornene chain. However, the molecular weights might be compared to those determined by the same method and described in the literature. Thermogravimetric analysis (TGA) was done using a Setaram Inc. TG/DTA 92-18 instrument. A suitable amount (10–15 mg) of each sample was heated from 40 to 800 °C using a heating rate of 10 °C/min under nitrogen atmosphere. Calorimetric analysis (DSC) was performed on a DSC Q100 instrument. Typically, 3–3.5 mg of each sample was tested from 10 to 400 °C using a heating rate of 10 °C/min under nitrogen atmosphere. Elemental analyses were done on a VarioEL CHNS instrument.

3. Results and discussion

The amount of BF_3OEt_2 (B hereinafter) was essential for the polymerization. A set of polymerizations were carried out using a fixed amount of $\text{Pd}(\text{OAc})_2$ with the B/Pd ratios from 10 to 60 at 25 °C and the results are presented in Table 1. The polymer yield showed a shallow maximum at the B/Pd ratios from 25 to 40 and a further slight decrease at the ratio of 60. At the same time, the intrinsic viscosity (molecular weight) increased from 0.43 to 1.40 dL/g, while the B/Pd ratio

Table 1
Effect of the B/Pd ratio on the polymerization of norbornene (NB) over $\text{Pd}(\text{OAc})_2/\text{BF}_3\text{OEt}_2$ catalyst system

B/Pd (ratio)	NB/Pd (ratio)	Catalyst (10^6 mol)	Yield (g)	Conversion (%)	Activity (kg NB/(mol Pd h))	$[\eta]$ (dL/g)
5	50 000	1	0.20	4.2	400	0.43
10	50 000	1	0.58	12.3	1160	0.68
15	50 000	1	1.28	27.2	2560	1.18
20	50 000	1	1.50	31.8	3000	1.24
25	50 000	1	1.59	33.8	3180	1.29
40	50 000	1	1.56	33.1	3120	1.40
60	50 000	1	1.53	32.5	3060	1.34

Experimental conditions: 25 °C, 30 min, 4.71 g NB, total volume 7 mL.

changed from 5 to 40 and slightly decreased to 1.34 dL/g at the B/Pd ratio of 60.

The pattern was quite similar to that observed for the Pd(acac)₂/BF₃OEt₂ system; in this case the results obtained were explained by the equilibrium between a fluorine-bridged inactive and an active, tightly associated ion pairs of the palladium species [35]. The interaction of Pd(acac)₂ with BF₃OEt₂ in the presence of 1-hexene led to catalytically active complexes, in which BF₃ can be bonded to Pd as a complexed BF₄⁻ anion or via a fluorine atom as F·BF₃ [38]. Moreover, a rapid exchange between the bridging and the terminal fluorine atoms of coordinated BF₄⁻ (anion “spinning”) and a presence of a tightly associated contact ion pair had been shown for the polymerization of norbornene derivatives with (η³-allyl)Pd(II) catalysts [39]. We have not carried out detailed mechanistic studies of the interaction of Pd(OAc)₂ and BF₃OEt₂ in the presence of norbornene. However, we presume the palladium hydride species to be responsible for the catalytic activity in the case of palladium carboxylates in analogous to those for palladium β-diketonates [35,38]. The ¹⁹F NMR spectrum of the interaction of Pd(OAc)₂ and BF₃OEt₂ in toluene exhibited a signal at -147.2 ppm, which is characteristic of free BF₄⁻ anion [39]. Additionally, a resonance at -0.79 ppm for BF₄⁻ anion was detected in the ¹¹B NMR spectrum. This signal was assigned in comparison with the ¹¹B NMR spectrum of [(acac)Pd(PPh₃)₂]₂BF₄. On the other hand, a formation of σ-alkylpalladium compounds via the insertion of coordinated alkene into Pd–OAc bond and further β-elimination to afford Pd–H species are well described in the literature [40]. Therefore, we are inclined to explain the data obtained again by the equilibrium between an inactive and an active, tightly associated ion pairs of the palladium species. The increasing amount of BF₃ cocatalyst shifts the equilibrium to the active form and increases the ionic character of active species. The increased ionic character of active species resulted in increased chain propagation rate, i.e. in increased intrinsic viscosity (molecular weight), which is in agreement with data reported by Janiak and coworkers [26–28]. The decrease of activity towards higher amounts of BF₃OEt₂ could be explained by a deactivating interaction of BF₃ with the active complex in general.

For the transition metal catalysts, the activity and selectivity in the transformation of alkenes are greatly dependent on the nature of ligands around the metal. In this context, it appeared to be of considerable interest to study the effect of carboxylate

Table 2

Effect of the nature of carboxylate ligand on the polymerization of norbornene (NB) over Pd(carboxylate)₂/BF₃OEt₂ catalyst system

Carboxylate (C _n)	Acidity ^a (pK _a)	NB/Pd (ratio)	Catalyst (10 ⁶ mol)	Yield (g)	Conversion (%)	[η] (dL/g)
Benzoate, C ₇	4.20	50 000	1.0	1.49	31.6	1.09
Acetate, C ₂	4.76	50 000	1.0	1.59	33.8	1.29
Propionate, C ₃	4.87	50 000	1.0	1.52	32.3	1.32
Heptanoate, C ₇	4.89	50 000	1.0	1.63	34.6	1.36
Stearate, C ₁₈	10.15	50 000	1.0	1.61	34.2	1.68

Experimental conditions: B/Pd = 25, 25 °C, 30 min, 4.71 g NB, total volume 7 mL.

^a The values of pK_a are taken from Refs. [44,45].

Table 3

Effect of reaction temperature on the polymerization of norbornene (NB) over Pd(OAc)₂/BF₃OEt₂ catalyst system

Temp. (°C)	NB/Pd (ratio)	Catalyst (10 ⁶ mol)	Yield (g)	Conversion (%)	Activity (kg NB/(mol Pd h))	[η] (dL/g)
15	50 000	1	1.67	35.5	3340	1.37
25	50 000	1	1.59	33.8	3180	1.29
35	50 000	1	1.45	30.8	2900	1.10
45	50 000	1	1.19	25.3	2380	0.88
55	50 000	1	0.95	20.2	1900	0.28
65	50 000	1	0.82	17.4	1640	0.19

Experimental conditions: B/Pd = 25, 4.71 g NB, total volume 7 mL.

ligands at palladium on the polymerization of norbornene. The results are summarized in Table 2. The nature of carboxylate ligands did not affect the conversion of norbornene within experimental errors. However, almost a linear dependency of intrinsic viscosity of polynorbornene on the acidity of carboxylate ligands was observed.

It might be thought that the nature of catalytically active species formed in these systems is same and not dependent on the ligand in palladium. Probably, a degree of acidity of carboxylate ligands might cause a change of the equilibrium between an inactive and active species as well as of the electrophilicity of latter, thus resulting in changes of intrinsic viscosity. The real reason for this observation is a subject of special studies.

Table 3 lists results of the polymerization as a function of reaction temperature. The polymerization temperature can affect the conversion and intrinsic viscosity greatly.

When the reaction temperature increased from 15 to 65 °C, a substantial drop of catalytic activity from 3340 to 1640 kg NB/(mol Pd h) and intrinsic viscosity from 1.37 to 0.19 dL/g was obtained. It indicates that the active species show very low thermal stability. The decreased intrinsic viscosity at higher temperatures might be explained by the fact that the activation energy for chain transfer is greater than that for propagation. It means that the rate of chain termination increases faster than that for chain propagation with increasing temperature.

The polymerization kinetics is presented in Table 4 and Fig. 1. Both the intrinsic viscosity and polymer yield increased rapidly within first 5 min and then increased slightly with longer reaction times. It means that in the beginning of the polymerization the rate of chain transfer is on the order of the reaction time, and in the longer period the molecular weight is controlled by chain transfer. The maximum catalytic activity

Table 4

Effect of reaction time on the polymerization of norbornene (NB) over Pd(OAc)₂/BF₃OEt₂ catalyst system

Time (min)	NB/Pd (ratio)	Catalyst (10 ⁶ mol)	Yield (g)	Conversion (%)	Activity (kg NB/(mol Pd h))	[η] (dL/g)
3	50 000	1	0.63	13.4	12 600	0.64
5	50 000	1	0.92	19.5	11 040	0.84
10	50 000	1	1.18	25.0	7080	0.98
15	50 000	1	1.43	30.4	5720	1.15
20	50 000	1	1.54	32.7	4620	1.23
30	50 000	1	1.59	33.8	3180	1.29

Experimental conditions: B/Pd = 25, 25 °C, 4.71 g NB, total volume 7 mL.

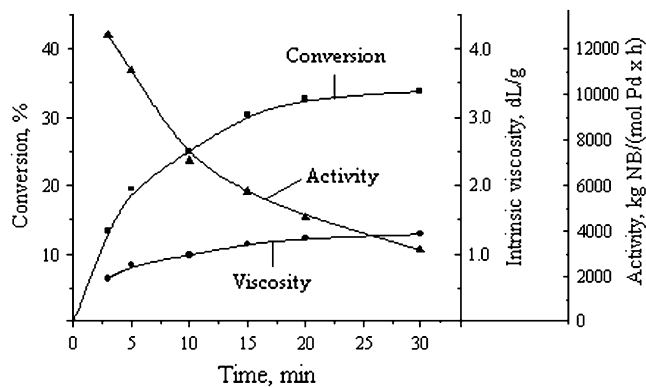


Fig. 1. Effect of reaction time on the polymerization of norbornene over $\text{Pd}(\text{OAc})_2/\text{BF}_3\text{OEt}_2$ catalyst system ($\text{B}/\text{Pd}=25$, 25°C , 4.71 g of NB, total volume 7 mL).

of 12 600 kg NB/(mol Pd h) was observed at the reaction time of 3 min. Further decrease of catalytic activity in these cases is mainly due to hindered monomer diffusion into the active species. However, a partial catalyst deactivation could be another reason.

The effect of NB/Pd ratio (reaction volume and catalyst amount were kept constant) on the polymerization is shown in Table 5. The conversion of monomer was not dependent on the NB/Pd ratio within experimental errors, thus indicating zero order of the reaction rate with respect to monomer. However, the increase of NB/Pd ratio from 25 000 to 100 000 led to a remarkable decrease of intrinsic viscosity from 1.45 to 1.18 dL/g.

For the norbornene polymerization catalyzed by late transition-metal compounds no direct correlation between the monomer/catalyst ratio, catalyst activity and molecular weights of polymers has been reported. In one case an increase of monomer/nickel ratio may lead to a decrease of polymer yield combined with increase of intrinsic viscosity [13]. On the other hand, the higher monomer/catalyst ratios might be also resulted in both increased polymer yield and molecular weight [26]. In the case under study, the decrease of intrinsic viscosity at higher monomer/catalyst ratios might be explained by an increased chain termination rate.

The effect of the $\text{Pd}(\text{OAc})_2$ precatalyst amount on the polymer yield and intrinsic viscosity is presented in Table 6. As is shown, an increase of precatalyst amount led to the increase of polymer yield and decrease of intrinsic viscosity. At the

Table 5
Effect of NB/Pd ratio on the polymerization of norbornene (NB) over $\text{Pd}(\text{OAc})_2/\text{BF}_3\text{OEt}_2$ catalyst system

NB/Pd (ratio)	Catalyst (10^6 mol)	Time (min)	Yield (g)	Conversion (%)	Activity (kg NB/(mol Pd h))	$[\eta]$ (dL/g)
25 000	1	30	1.62	34.4	3240	1.45
37 500	1	30	1.61	34.2	3220	1.41
50 000	1	30	1.59	33.8	3180	1.29
67 500	1	30	1.58	33.5	3160	1.24
100 000 ^a	1	30	1.57	33.3	3140	1.18

Experimental conditions: $\text{B}/\text{Pd}=25$, 25°C , 4.71 g NB, total volume 7 mL.

^a Total volume 10 mL.

Table 6
Effect of precatalyst amount on the polymerization of norbornene (NB) over $\text{Pd}(\text{OAc})_2/\text{BF}_3\text{OEt}_2$ catalyst system

[Pd] (10^6 mol)	NB/Pd (ratio)	Time (min)	Yield (g)	Activity (kg NB/(mol Pd h))	$[\eta]$ (dL/g)
0.5	100 000	30	1.11	4440	1.36
1.0	50 000	30	1.59	3180	1.29
2.0	25 000	30	2.47	2470	1.23
3.0	16 700	30	4.70	3140	0.69
5.0	10 000	1	3.11	37 320	1.1
10.0	5000	<10 s	4.28	>154 100	0.56

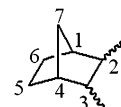
Experimental conditions: $\text{B}/\text{Pd}=25$, 25°C , 4.71 g NB, total volume 7 mL.

precatalyst amount of 1.0×10^{-5} mol, a “particular” activity of more than 154 100 kg polynorbornene per mole Pd for an hour was achieved. This activity is comparable to that for the most active catalyst systems described in the literature [11–14,18–20,25], except for that reported in Ref. [32]. For comparison, a “particular” activity of 20 220 kg/(mol Pd h) has previously been obtained using the $\text{Pd}(\text{acac})_2/\text{BF}_3\text{OEt}_2$ catalyst system [35]. The increase of precatalyst amount from 5×10^{-7} to 1.0×10^{-5} mol was followed by a decrease of intrinsic viscosity from 1.36 to 0.56 dL/g.

It is noteworthy that the reaction became exothermic starting from the precatalyst amount of 3.0×10^{-6} mol. The entry with precatalyst amount of 1.0×10^{-5} mol was extremely exothermic. Immediately after the addition of the boron compound, the polymer started forming and precipitated from the solution as a white powder to give a solid white “cake” within few seconds, and the formation of palladium blacks was observed visually during the reaction. Such an abnormal increase of activity is difficult to explain in the absence of a more knowledge of the active species.

The structure of the polynorbornene obtained has been studied by NMR and IR spectroscopic methods. The polymer was a vinyl addition in nature since no olefinic resonances were observed in the ^1H NMR spectrum. The IR spectrum of the polymer also proves the absence of any double bond absorbance at $1620\text{--}1680\text{ cm}^{-1}$. Additionally, the IR spectrum exhibited a strong absorbance at $1452\text{--}1474\text{ cm}^{-1}$ due to $\delta_{\text{H-C-H}}$ stretching modes for a bridge CH_2 group [41]. The ^{13}C spectrum of the polymer is plotted in Fig. 1 and it showed that the polymer was *exo* enchainment. The spectrum did not exhibit resonances in the 20–24 ppm region. The presence of such resonances was used as an evidence of *endo* enchainment [42].

Assignment of methylene and methine ^{13}C NMR resonances of the polymer is readily made using DEPT editing of the ^{13}C NMR spectrum (Fig. 2). The peaks between about 55 and 38 ppm are assigned to methine carbons, and those peaks between about 38 and 27 ppm are assigned to methylene carbons. With the help of assignments reported by Arndt et al. [43] for hydrotrimer of norbornene and integration of the DEPT spectrum, assignments of carbons 1–7, based on the following numbering scheme, can be made.



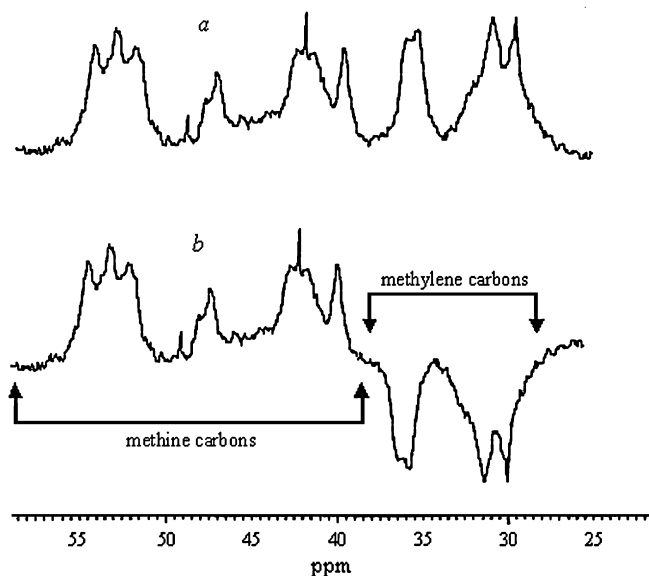


Fig. 2. ^{13}C NMR spectra of polynorbornene: (a) full spectrum; (b) DEPT edited (pulse angle 135°).

The peaks in the region of 28–34 ppm are non-bridging CH_2 groups (C5 and C6). The resonances present between 34 and 38 ppm represent a bridge CH_2 group (C7). The resonances between 38 and 45 ppm are bridgehead CH groups (C1 and C4) and the resonance peaks between 45 and 55 ppm are backbone connecting CH groups (C2 and C3). The peak assigned to C7 appears as a single group of peaks. This observation is consistent with a microstructure containing a composite of two norbornene triads with overlapping peaks due to C7. This is possible for the *rr* and *mr* triads given the close proximity of their C7 resonances. The dearth of substantial population of *mm* triads is confirmed by the absence of peaks near 39 ppm [42]. The ^{13}C NMR spectrum is essentially identical to that reported by Barnes et al. [30] and the microstructure of the polynorbornene obtained might be best described as containing low diisotacticity. Further indications of the low diisotacticity come from the solid state CPMAS- ^{13}C NMR spectrum (Fig. 3). This spectrum is identical to those reported by Arndt and Gosmann [11] and Barnes et al. [30] for

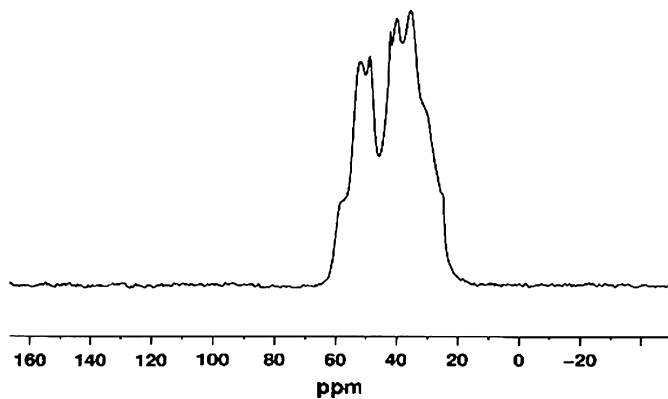


Fig. 3. Solid state CPMAS- ^{13}C NMR spectrum of polynorbornene produced with $\text{Pd}(\text{OAc})_2/\text{BF}_3\text{OEt}_2$ catalyst system.

Table 7

GPC and thermal analyses data for the polymerization of norbornene (NB) over $\text{Pd}(\text{OAc})_2/\text{BF}_3\text{OEt}_2$ catalyst system

$[\eta]$ (dL/g)	Temp. ($^\circ\text{C}$)	Catalyst (10^6 mol)	Time (min)	M_w (g/mol)	Q (M_w/M_n)	T_d ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)
1.40 ^a	25	1.0	30	293 800	2.27	324	262
1.29	25	1.0	30	179 100	2.14	324	258
1.10	25	5.0	1	141 900	2.72	319	252
0.56	25	10.0	<10 s	92 900	3.02	317	245
1.19	45	1.0	30	174 900	3.10	313	256
0.19	65	1.0	30	77 700	3.51	313	240

Experimental conditions: B/Pd = 25, 4.71 g NB, total volume 7 mL.

^a B/Pd = 40.

polynorbornenes for which microstructures of low diisotacticity were claimed. For comparison, the CPMAS- ^{13}C NMR spectrum of polynorbornene produced with the $\text{Ni}(\text{PPh}_3)_4/\text{BF}_3\text{OEt}_2$ system is included in Supplementary data and possesses remarkable difference from that obtained with the $\text{Pd}(\text{OAc})_2/\text{BF}_3\text{OEt}_2$ catalyst system.

The GPC, DSC and TG analyses of the polynorbornene were carried out for representative samples with various intrinsic viscosities, covering all the range of observed values, and results are presented in Table 7.

The molar mass distribution $Q = M_w/M_n$ for the polymer samples is rather narrow and close to a value of 2 at the pre-catalyst amount of 1×10^{-6} mol and at 25°C . A dispersity $Q \approx 2$ indicates a single-site character, that is, a highly homogeneous structure of the active catalyst species. An increase of both catalyst precursor amount and reaction temperature led to a broadened dispersity due to partial decomposition of the active species and increased chain termination rate. The glass transition temperatures T_g ranged from 240 to 262°C at M_w from 77 700 to 293 800 g/mol. The polymer samples decomposed in the range from 313 to 324°C . A $T_g(\infty)$ of 270°C for polynorbornene can be extrapolated by means of the Bueche equation (Eq. (1)):

$$T_g(\infty) = T_g + K/M \quad (1)$$

where $T_g(\infty)$ is the glass transition temperature of a polymer with a very large molecular weight.

4. Conclusion

The vinyl polymerization of norbornene with $\text{Pd}(\text{carboxylate})_2/\text{BF}_3\text{OEt}_2$ catalyst system has been investigated. The effects of cocatalyst amount on the catalyst activity were explained on the basis of complexation equilibrium for the active homogeneous complex. A “particular” catalytic activity up to 154 100 kg/(mol Pd h) and weight average molar masses up to 293 800 g/mol were observed. The molar mass distribution indicates a single-site, highly homogeneous character of the active catalyst species. According to NMR and IR spectroscopic data, the polymers possess 2,3-enriched repeating units of polymer backbone with low diisotacticity. Catalytic activity, polymer yield and polymer molecular weight can be controlled by

varying the reaction parameters. The simplicity of catalytic system composition might be of industrial importance.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.polymer.2006.10.009](https://doi.org/10.1016/j.polymer.2006.10.009).

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