Novel bidentate phosphine modified \( \text{Pd(acac)}_2 / \text{BF}_3\text{OEt}_2 \) catalyst system for the homopolymerization of alkylnorbornenes and copolymerization with norbornene

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Abstract

The \( \text{Pd(acac)}_2 + n\text{Ph}_2\text{P(CH}_2)_m\text{PPh}_2 + 2\text{BF}_3\text{OEt}_2, n = 1–3, m = 1–6, \) catalyst system has been successfully employed for the homopolymerization of 5-alkyl-2-norbornenes and their copolymerization with norbornene. For this series, the most efficient catalyst system was \( \text{Pd(acac)}_2 + 2\text{Ph}_2\text{P(CH}_2)_4\text{PPh}_2 + 2\text{BF}_3\text{OEt}_2 \). The activity of the catalyst system is comparable to that of most active late transition metal catalysts described in the literature. Bidentate phosphines containing bridges larger than 1,4-butane are likely to act as monodentate ligands. The incorporations of flexible alkyl groups onto the main chain of norbornene, as well as copolymerization of 5-alkyl-2-norbornenes with norbornene, represent a useful method for lowering the glass transition temperature \( (T_g) \), i.e. improving the processability. The introduction of bidentate phosphine ligand to the \( \text{Pd(acac)}_2 + 2\text{BF}_3\text{OEt}_2 \) system switched the carbocationic polymerization mechanism to the coordination Ziegler–Natta polymerization. The simplicity of this catalytic system composition might be of industrial importance.

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1. Introduction

Recent developments in transition metal catalysis have led to a wide range of polyolefinic materials; transition metal catalysts were particularly important for the polymerization of cycloolefins. Norbornene (NB) (bicyclo[2.2.1]hept-2-ene) and its derivatives can be polymerized via ring-opening olefin metathesis (ROMP), cationic or radical polymerization and also by addition polymerization. The best known polymerization of norbornene is the ROMP; the corresponding polymer contains one double bond in each repeating unit [1]. Little is known about the cationic and the radical polymerization of norbornene, which mostly result in a low molecular weight material with 2,7-enchainity of the monomer [2,3]. The addition polymerization is less developed than ROMP. Catalysts containing the metals titanium, zirconium, cobalt, chromium, nickel and palladium are described in the literature for the addition polymerization of norbornene [4]. The norbornene addition polymer with 2,3-enchainity displays a characteristic rigid random coil conformation, which shows restricted rotation about the main chain and exhibits strong thermal stability. In addition, it has excellent dielectric properties, optical transparency and unusual transport properties [5]. Therefore, norbornene addition polymer and its derivatives are attractive materials for the manufacture of microelectronic and optical devices. However, norbornene addition polymers have some disadvantages, such as poor processability and lower solubility in common organic solvents. One way to improve the processability of polynorbornene is copolymerization of norbornene with \( \alpha \)-olefins [6–14]. Copolymers of norbornene with ethene have been prepared on a semicommercial basis [6–10]. Recent objectives to improve the properties of polynorbornenes have focused on incorporating pendant functional substituents onto the polycyclic backbone, enabling this class of polymer to be utilized for a wide variety of uses. Transition metal-catalyzed addition polymerization of functional norbornenes has proved to be difficult. This is especially true for the
endo-functionalized norbornenes. Palladium and nickel catalysts for the polynorbornenes containing pendant polycycles, alkyls, alkenyls, alkyldienes, silyls, carboxyls, amines, sulfonamides and esters have been described in the literatures [15–24]. Some of the palladium and nickel complexes employed in these reactions are cationic systems with non-coordinating counter ions [16,23,24]. Neutral palladium and nickel complexes have to be activated with cocatalysts such as methylalumoxane (MAO) [15]. Another possibility to activate late transition-metal complexes was to use tris(pentafluorophenyl)borane, B(C₆F₅)₃, with or without triethylaluminum (TEA) [17,18]. Li⁺[C₆F₅]₄B₀ [19], Na⁺[3,5-(CF₃)₂C₆H₃]₄B₀ [20] and [PhNHMe₂]⁺[C₆F₅]₄B₀ [21] also were used to activate palladium complexes. Due to the high production costs of MAO and organoborane cocatalysts, it is desirable to find some novel activators, which can be used as substitutes for MAO and organoboranes. A simple Lewis acid BF₃, in the form of boron trifluoride etherate, was applied in the polymerization of norbornene-type monomers as a “third component” and in combination with TEA, but not as a cocatalyst [17,18].

In the case of homogeneous catalyst systems, it is frequently possible to vary the catalyst composition and thereby to improve the efficiency of the catalyst. In the past decade, considerable progress has been made in the use of bidentate phosphine ligands (DP) for the catalytic formation of carbon-to-carbon bonds [25]. We have recently shown that boron trifluoride etherate, BF₃OEt₂, can be successfully used as a cocatalyst towards bis(acetylacetonate)palladium, Pd(acac)₂, precursor for the polymerization of norbornene [26]. Modification of this system with triphenylphosphine, PPh₃, enabled us to polymerize 5-alkyl-2-norbornenes (alkNB) to some extent [27]. In the present paper, we report the homopolymerization of 5-alkyl-2-norbornenes and their copolymerization with norbornene with Pd(acac)₂ + 25BF₃OEt₂ catalyst system modified with bidentate phosphate ligands of the general formula PPh₂(CH₂)ₘPPh₂, where m = 1–6.

2. Experimental

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

2.1. Materials

Norbornene (99%, Aldrich) was purified by distillation over calcium hydride, CaH₂. 5-Propyl-2-norbornene (PrNB, b.p. = 85 °C/13 mmHg, endo/exo = 76/24), 5-butyl-2-norbornene (BuNB, b.p. = 100 °C/7 mmHg, endo/exo = 78/22), 5-hexyl-2-norbornene (HexNB, b.p. = 90 °C/3 mmHg, endo/exo = 78/22) and 5-decyl-2-norbornene (DecNB, b.p. = 136 °C/3 mmHg, endo/exo = 80/20) were synthesized by the Diels–Alder reactions of cyclopentadiene with the corresponding 1-alkenes (1-pentene, 1-hexene, 1-octene and 1-dodecene) as described elsewhere [3]. endo/exo mole ratios of 5-alkyl-2-norbornenes were determined from 13C NMR spectra. The carbon peaks were assigned in comparison with that reported early [3] and their assignment are listed in Table 1. 5-Alkyl-2-norbornenes were twice distilled in vacuum directly before use. BF₃OEt₂ (Aldrich, 99%) was distilled over CaH₂ prior to use. Toluene and benzene were distilled with Na/K alloy under dry nitrogen. Pd(acac)₂ (Aldrich) was recrystallized from benzene. Triphenylphosphine (PPh₃, Aldrich), 1,2-bis(diphenylphosphino)methane (DPPM, m = 1), 1,2-bis(di-
phenylphosphino)ethane (DPPE, \( m = 2 \)), 1,2-bis(diphenylphosphino)propane (DPPP, \( m = 3 \)), 1,2-bis(diphenylphosphino)butane (DPPB, \( m = 4 \)), 1,2-bis(diphenylphosphino)pentane (DPPPe, \( m = 5 \)), and 1,2-bis(diphenylphosphino)hexane (DPPH, \( m = 6 \)) (all from Strem Chemicals), were used as obtained from suppliers.

2.2. Polymerization of 5-alkyl-2-norbornenes and copolymerization with norbornene

Polymerizations were carried out in a 10 ml glass reactor equipped with a magnetic stirrer. The reactor was first purged in vacuum and then filled with nitrogen, and finally was filled with monomer and phosphine as solutions in toluene. The solution was kept at the desired temperature for 15 min and then the solution of Pd(acac)\(_2\) in toluene was added. Polymerizations were initiated by the injection of boron compound. After the mixture was stirred for a time needed, the polymers that formed were precipitated in acidified ethanol. In standard runs, the amount of palladium precursor was 5.0 \( \times \) 10\(^{-6}\) mol, the AlkNB/Pd ratio was 4500, the B/Pd ratio was 25, the DP/Pd ratio was 2, the reaction time was 30 min, and the total reaction volume was 7.0 ml, unless otherwise stated. Copolymerization runs were carried out in the same way with equimolar mixtures of norbornene and 5-alkyl-2-norbornene. Polymerization and copolymerization runs were carried out at least three times to ensure reproducibility.

2.3. Characterization of polymers

NMR spectra were recorded at room temperature on a Bruker AMX-500 spectrometer with frequencies of 500 MHz for \(^1\)H NMR and 125 MHz for \(^{13}\)C NMR. Each polymer sample was dissolved in 1,2,4-trichlorobenzene up to a concentration of 10 wt.% in NMR tubes (5 mm o.d.). Tetramethyl silane (TMS) was used as the internal standard. Viscosity measurements were carried out in 1,2,4-trichlorobenzene at 65 °C using an Ubbelohde viscometer. Gel permeation chromatography (GPC) analysis was carried out on a WATERS 150 HPLC instrument with 10 \( \mu \)m MIXED-B columns (300 mm \( \times \) 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 polyalkynorbornene 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 20 °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

Sagane and Mizuno [3] have synthesized 5-alkyl-2-norbornenes with AlEtCl\(_2\)/tert-butylchloride catalyst system and have investigated the effect of an alkyl substituent on monomer reactivity, polymer structure and thermal properties. A further improvement in the polymerization of 5-alkyl-2-norbornenes has been achieved through use of late transition metal catalysts [15,16,20,21].

The polymerization of 5-butyl-2-norbornene (BuNB) as a representative member of 5-alkyl-2-norbornenes with Pd(acac)\(_2\) + 25BF\(_3\)OEt\(_2\) catalyst system at the B/Pd ratio of 25 at room temperature for 48 h yielded a conversion of 20%. For the addition polymerization of functionalized norbornene derivatives \textit{endo}-substituted norbornenes are polymerized more slowly [18,20–24]; therefore this conversion was probably owing to a consumption of \textit{exo} isomer. At temperatures of 35 °C and higher, the catalyst system decomposed due to its low thermal stability [26]. However, in the case of homogeneous catalyst systems, it is frequently possible to vary the catalyst composition and thereby to improve the efficiency of the catalyst. The effects of phosphine ligands in catalysis have been known for quite some time and the crucial role that the bidentate phosphine ligands play in homogeneous catalysis is well recognized. It has been demonstrated that in the catalytic carbon-to-carbon bond formation, both the steric properties and the bite angle of the associated diphosphine ligands exert a profound influence on the catalytic activity [25]. Generally, a diphosphine ligand can change the steric bulk around the metal center, modify the electronic properties of the metal, and enforce the bite angle preferred by the ligand. Therefore, it was attractive to modify the Pd(acac)\(_2\) + 25BF\(_3\)OEt\(_2\) catalyst system with bidentate phosphine ligands. We have performed a series of experiments on the homopolymerization of 5-butyl-2-norbornene over Pd(acac)\(_2\) + \( n \)PPh\(_3\)(CH\(_2\))\(_n\)PPh\(_3\) + 25BF\(_3\)OEt\(_2\) catalyst system, \( n = 1–3 \), \( m = 1–6 \), at 65 °C. Our results are listed in Table 2. The B/Pd ratio of 25 and the reaction temperature of 65 °C were employed, as they were optimized for the homopolymerization of 5-alkyl-2-norbornenes with Pd(acac)\(_2\) + \( n \)PPh\(_3\) + 25BF\(_3\)OEt\(_2\) catalyst system [27]. Experiments with monodentate PPH\(_3\) ligand were included in Table 2 for the comparison.

As can be seen in Table 2, when going from DPPM to DPPH, the conversion passed through a maximum at \( m = 4 \) (DPPB) at given DP/Pd ratio. The optimum conversion of 84.6% was found with DPPB ligand at DP/Pd ratio of 2. At the same time, intrinsic viscosities for DPPPe, DPPP and DPPB were approximately the same at given DP/Pd ratios, whereas for DPPPe and DPPH ligands intrinsic viscosities were substantially decreased to nearly equal to those values with monodentate PPH\(_3\) ligand. Additionally, for DPPPe, DPPH and PPH\(_3\) ligands the conversions were almost the same at given DP/Pd ratios. In the series DPPPe, DPPP, and DPPB, the latter was by far the fastest catalyst, i.e. the conversion was increased with increasing natural bite angle of the diphosphine. Palladium(II)
d⁸, 16-electron species would be expected to be square-planar and with bidentate phosphine ligands DPPE, DPPP, and DPPB the two phosphine groups are likely to bind exclusively in a cis configuration to a single palladium center [28]. In this case, the active species can contain no more than one diphosphine ligand in the coordination sphere. Then the role of the second diphosphine ligand at DP/Pd ratio of 2 should only be an “additional” stabilization of the unstable palladium complex at higher temperatures. Many proposed reaction mechanisms at such species are commonly believed to proceed via a transition state different from square-planar (mainly trigonal-bipyramidal) [29]. It is thought, therefore, that an important requirement for the bidentate ligand is that it should stabilize both the square-planar ground state and the transition state; for efficient catalysis, there should be a low energy barrier between the two states. Clearly, the chain length (m), or the bite angle, would be expected to influence this transformation, and it would seem that, for high reaction rates, a chain length of four carbon units with the bite angle of 98° satisfies this requirement better than shorter or longer chains due to its enhanced flexibility. It should be noted that, for the square-planar complexes the “metal-preferred” P–M–P angle is 90°/C₂, while tetrahedral complexes

Table 2
Effect of bidentate phosphine ligands on the polymerization of 5-butyl-2-norbornene over Pd(acac)₂ + nPh₂P(CH₂)ₘPPh₂ + 25BF₃OEt₂ catalyst system

<table>
<thead>
<tr>
<th>Phosphine</th>
<th>Ph₃ a (°)</th>
<th>BuNB/Pd ratio</th>
<th>DP/Pd ratio</th>
<th>Yield (g)</th>
<th>Conversion (%)</th>
<th>[η] (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh₃</td>
<td>–</td>
<td>4500</td>
<td>1</td>
<td>1.93</td>
<td>54.8</td>
<td>0.62</td>
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<tr>
<td></td>
<td>4500</td>
<td>2</td>
<td>2.66</td>
<td>75.6</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4500</td>
<td>3</td>
<td>2.52</td>
<td>62.5</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4500</td>
<td>4</td>
<td>1.68</td>
<td>44.7</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>Ph₂P(CH₂)ₙPPh₂</td>
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<td>4500</td>
<td>1</td>
<td>0.00</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>4500</td>
<td>2</td>
<td>0.00</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>4500</td>
<td>3</td>
<td>0.00</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ph₂P(CH₃)ₙPPh₂</td>
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<td>4500</td>
<td>1</td>
<td>0.35</td>
<td>10.4</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>4500</td>
<td>2</td>
<td>0.00</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>4500</td>
<td>3</td>
<td>0.00</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ph₂P(CH₃)ₙPPh₂</td>
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<td>4500</td>
<td>1</td>
<td>1.60</td>
<td>47.4</td>
<td>1.03</td>
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<tr>
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<td>4500</td>
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<td>1.92</td>
<td>56.9</td>
<td>1.20</td>
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<td>4500</td>
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<td>0.20</td>
<td>0.6</td>
<td>1.00</td>
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<td>Ph₂P(CH₃)ₙPPh₂</td>
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<td>68.4</td>
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<td>28.6</td>
<td>84.7</td>
<td>1.17</td>
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<tr>
<td></td>
<td>4500</td>
<td>3</td>
<td>0.26</td>
<td>7.7</td>
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<td>Ph₂P(CH₃)ₙPPh₂</td>
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<td>50.7</td>
<td>0.83</td>
</tr>
<tr>
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<tr>
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</tr>
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<td>44.1</td>
<td>0.79</td>
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</tr>
<tr>
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<td>4500</td>
<td>3</td>
<td>1.71</td>
<td>50.7</td>
<td>0.68</td>
<td></td>
</tr>
</tbody>
</table>

Experimental conditions: Pd amount 5 × 10⁻⁶ mol, 65 °C, 30 min, 3.375 g of BuNB, total volume 7 ml.

* Natural bite angles βₘ are taken from Ref. [25].

Table 3
Effect of the reaction time on the homopolymerization of 5-butyl-2-norbornene (BuNB) over Pd(acac)₂ + 25BF₃OEt₂ and Pd(acac)₂ + 25BF₃OEt₂ catalyst systems

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>DP/Pd ratio</th>
<th>Conversion (%)</th>
<th>Activity (kg BuNB/mol Pd h) [η] (dl/g)</th>
<th>DPPH</th>
<th>Conversion (%)</th>
<th>Activity (kg BuNB/mol Pd h) [η] (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1</td>
<td>22.5</td>
<td>3040</td>
<td>0.39</td>
<td>16.0</td>
<td>2160</td>
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<tr>
<td></td>
<td>2</td>
<td>28.1</td>
<td>3800</td>
<td>0.52</td>
<td>8.3</td>
<td>1120</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>40.9</td>
<td>3313</td>
<td>0.70</td>
<td>25.5</td>
<td>2064</td>
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<td></td>
<td>2</td>
<td>46.5</td>
<td>3768</td>
<td>0.83</td>
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<tr>
<td>10</td>
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<td>53.6</td>
<td>2172</td>
<td>0.95</td>
<td>37.3</td>
<td>1512</td>
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<tr>
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<td>2</td>
<td>66.4</td>
<td>2688</td>
<td>1.10</td>
<td>52.7</td>
<td>2136</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>65.5</td>
<td>1768</td>
<td>1.00</td>
<td>43.0</td>
<td>1160</td>
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<td>2000</td>
<td>1.15</td>
<td>60.4</td>
<td>1632</td>
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<td>1.02</td>
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<td>596</td>
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<td>84.7</td>
<td>1144</td>
<td>1.17</td>
<td>66.7</td>
<td>900</td>
</tr>
</tbody>
</table>

Experimental conditions: [Pd] = 5 × 10⁻⁶ M, 65 °C, 3.375 g of BuNB, BuNB/Pd = 4500, total volume 7 ml.
will prefer P–M–P angles of 109° and the trigonal–bipyramidal structure requires an angle of 120°. Concerning DPPPe and DPPH ligands, they can act as monodentate phosphines or can form bimetallic complexes, having the phosphines in trans dispositions [30]. The results in Table 2 tend to indicate that the behavior of DPPPe and DPPH ligands is similar to that of monodentate ones. This suggestion was additionally supported by the kinetic studies. The polymerization kinetics of 5-butyl-2-norbornene for DPPB and DPPH ligands at DP/Pd ratios of 1 and 2 are presented in Table 3 and Fig. 1.

In all runs, the intrinsic viscosity increased rapidly within the first 5 min and then increased slightly with longer reaction times. That is, in the beginning of the polymerization, the rate of chain transfer is on the order of the reaction time, whereas in the longer period, the molecular weight is controlled by chain transfer. In the case of DPPB ligand, the polymer yield increased linearly during the first 5–10 min and increased more slightly for longer reaction times at DP/Pd ratios of both 1 and 2. The same behavior was observed for DPPH ligand at the DP/Pd ratio of 1. For DPPB ligand a maximum catalytic activity of 3800 kg BuNB/mol Pd h was observed at the DP/Pd ratio of 2 and reaction time of 3 min. The commensurate high activities were achieved by Goodall and co-workers [19] and Sen et al. [20,21] using Pd(II) precursors containing anionic hydrocarbyl ligand and one equivalent of monodentate phosphine in combination with Li+[C6F5]4B– and Na+[3,5-(CF3)2C6-H3]4B– or [PhNHMe2][B(C6F5)4] complexes, respectively.

Further decrease of catalytic activity in these cases is mainly due to hindered monomer diffusion to the active species, since an increase of the monomer feed, that is of the reaction volume at a fixed catalyst amount, resulted in an increased polymer yield. However, a partial catalyst deactivation is not excluded to be a secondary reason. The kinetic behavior for DPPH ligand at a DP/Pd ratio of 2 was quite different from that for other values. In this case, three distinct periods can be observed in the conversion profile. Careful analysis of kinetic data showed an induction period within the first 3–5 min of the reaction. After the induction period, the conversion increased linearly within 10 min and almost leveled off during the next period. Due to this induction period, a maximum catalytic activity of 2136 kg BuNB/mol Pd h was recorded at the reaction time of 10 min (Fig. 1).

Clearly, if the insertion of monomer into the palladium–polymer bond involves the adjacent in-plane sites, it is only in the cis-form that chain growth can occur. Two monodentate phosphine can coordinate with both cis and trans stereochemistry. The observed induction period (Table 3) might be caused by a transformation of initially formed inactive trans-isomer to the active, cis-structure. Such transformations are commonly believed to proceed via a trigonal–bipyramidal transition state, as depicted in Scheme 1 [31]. From the data obtained above, one may conclude that the increased thermal stability of the Pd(acac)2 + nDP + 25BF3OEt2 system compared to that without phosphine ligand may be due to the incorporation of phosphine ligand into the inner coordination sphere of the active complex, thus preventing easy decomposition and aggregation of palladium particles.

The temperature dependence of the conversion and intrinsic viscosity for the polymerization of 5-butyl-2-norbornene over Pd(acac)2 + 2DPPB + 25BF3OEt2 catalyst system is shown in Table 4. As was anticipated, a maximum conversion was observed at the reaction temperature of 65 °C.

The reaction temperature affected considerably the catalytic activities and intrinsic viscosities (molecular weights) of polymers. With an increase of the temperature, an increase of the activity was obtained and, a significant decrease of the intrinsic viscosity was observed. The further slight decrease of the activity after reaching a maximum value at 65 °C is probably due to thermal decomposition of active species. The accepted explanation for the decrease of intrinsic viscosity at higher temperatures is that the activation energy for chain transfer is greater than that for propagation and that the
decrease of molecular weight is due to an increased rate of chain termination at higher temperatures.

We have carried out the homopolymerization of other 5-alkyl-2-norbornene monomers over Pd(Acac)₂ + 2DPPB + 25BF₃OEt₂ catalyst system at standard conditions and the results are summarized in Table 5.

The introduction of an alkyl group into the 5-position of the norbornene ring remarkably reduced monomer conversion and decomposition temperature. In the series of alkyl chain lengths from propyl to decyl the conversion decreased from 94.3 to 65.3%. At the same time, the decomposition and glass transition temperatures decreased from 309 to 272 and 197 to 128°C, respectively. Such an increasing difference between the decomposition and glass transition temperatures is essential for improving the processability of the polymers. It is clear that norbornene has much higher reactivity compared to the values of alkyl substituted ones. The small deviation from a quantitative yield for norbornene polymerization might be due to a loss of product during workup. Concerning the tailormaking of the properties of norbornene-type polymers, except the copolymerization with α-olefins, it is well known that the incorporation of pendant groups onto the polycyclic backbone enables one to modify various properties of polymers. More specifically, incorporation of flexible alkyl groups onto the main chain represents a useful method for lowering the glass transition temperature (T_g) of the polymers. As shown in Table 4, the glass transition temperatures of the polymers decrease substantially with increasing alkyl substituent length at approximately similar average polymerization degrees (P_n).

The average polymerization degree and molar mass distributions of 5-alkyl-2-norbornenes did not display any marked difference between the types of monomers. The molecular weight distribution Q = M_w/M_n for the polymer samples is rather narrow and close to a value of 2. A dispersity Q ≈ 2 indicates a single-site character, that is, a highly homogeneous structure of the active catalyst species. For 5-alkyl-2-norbornene monomers, the decrease of reactivity and polymerizability might be explained by an unfavorable interaction between the substituent and the vinylic hydrogen.

### Table 4
Effect of the reaction temperature on the polymerization of 5-butyl-2-norbornene (BuNB) over Pd(Acac)₂ + 2DPPB + 25BF₃OEt₂ catalyst system

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>BuNB/Pd ratio</th>
<th>Catalyst (10⁻⁶ mol)</th>
<th>Yield (g)</th>
<th>Conversion (%)</th>
<th>Activity (kg BuNB/mol Pd h)</th>
<th>[η] (dl/g)</th>
</tr>
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<tr>
<td>25</td>
<td>4500</td>
<td>5</td>
<td>0.05</td>
<td>1.5</td>
<td>20</td>
<td>1.53</td>
</tr>
<tr>
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<td>5</td>
<td>0.50</td>
<td>15.0</td>
<td>200</td>
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<tr>
<td>45</td>
<td>4500</td>
<td>5</td>
<td>0.86</td>
<td>25.5</td>
<td>344</td>
<td>1.34</td>
</tr>
<tr>
<td>55</td>
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<td>5</td>
<td>1.86</td>
<td>55.1</td>
<td>744</td>
<td>1.26</td>
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<tr>
<td>65</td>
<td>4500</td>
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<td>2.86</td>
<td>84.7</td>
<td>1144</td>
<td>1.17</td>
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<tr>
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<td>2.78</td>
<td>82.4</td>
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<td>0.83</td>
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</table>

Experimental conditions: 0.5 h, 3.375 g of BuNB, total volume 7 ml.

### Table 5
Polymerization of 5-alkyl-2-norbornenes over Pd(Acac)₂ + 2DPPB + 25BF₃OEt₂ catalyst system

<table>
<thead>
<tr>
<th>Type of R</th>
<th>AlkNB/Pd ratio</th>
<th>Yield (g)</th>
<th>Conversion (%)</th>
<th>M_w (g/mol)</th>
<th>M_w/M_n</th>
<th>P_n</th>
<th>T_g (°C)</th>
<th>T_dec (°C)</th>
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<tr>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>128</td>
<td>272</td>
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</table>

Experimental conditions: [Pd] = 5 × 10⁻⁶ M, 65 °C, 30 min, total volume 7 ml.

a Not soluble in 1,2,4-trichlorobenzene.

The introduction of an alkyl group into the 5-position of the norbornene ring remarkably reduced monomer conversion and decomposition temperature. In the series of alkyl chain lengths from propyl to decyl the conversion decreased from 94.3 to 65.3%. At the same time, the decomposition and glass transition temperatures decreased from 309 to 272 and 197 to 128 °C, respectively. Such an increasing difference between the decomposition and glass transition temperatures is essential for improving the processability of the polymers. It is clear that norbornene has much higher reactivity compared to the values of alkyl substituted ones. The small deviation from a quantitative yield for norbornene polymerization might be due to a loss of product during workup. Concerning the tailormaking of the properties of norbornene-type polymers, except the copolymerization with α-olefins, it is well known that the incorporation of pendant groups onto the polycyclic backbone enables one to modify various properties of polymers. More specifically, incorporation of flexible alkyl groups onto the main chain represents a useful method for lowering the glass transition temperature (T_g) of the polymers. As shown in Table 4, the glass transition temperatures of the polymers decrease substantially with increasing alkyl substituent length at approximately similar average polymerization degrees (P_n). The decrease of the T_g’s with increasing number of carbons of the substituent was explained on the basis of the mobility of the substituent, which acts as an “internal diluent” [3]. The average polymerization degree and molar mass distributions of 5-alkyl-2-norbornenes did not display any marked difference between the types of monomers. The molecular weight distribution Q = M_w/M_n for the polymer samples is rather narrow and close to a value of 2. A dispersity Q ≈ 2 indicates a single-site character, that is, a highly homogeneous structure of the active catalyst species. For 5-alkyl-2-norbornene monomers, the decrease of reactivity and polymerizability might be explained by an unfavorable interaction between the substituent and the vinylic hydrogen.

![Scheme 2. Steric compression in the insertion of endo-BuNB.](image)
that is being rehybridized from sp² to sp³ upon coordination of monomer to palladium in the endo isomer even for coordination to palladium through the exo face, as described by Sen and co-workers (Scheme 2) [21].

Apparently, the bigger the size of the substituent is, the greater this interaction will be.

The 1H and 13C NMR spectra of polynorbornene obtained with Pd(acac)₂ + 2DPPB + 25BF₃OEt₂ system showed 2,3-enchained structure of the polymer (Fig. 2). In the 1H NMR spectrum (Fig. 2a) bridgehead CH groups (protons 1 and 4) appear at 2.10 ppm. The resonance at 1.73 ppm is due to backbone-connecting CH groups (protons 2 and 3). The resonances between 0.7 and 1.6 ppm are attributed to non-bridge CH₂ groups (protons 5, 6, and 7). No resonances are displayed from 5.0 to 6.0 ppm in the 1H NMR spectrum, which usually indicate the presence of ROMP structures. The 13C NMR spectrum of polynorbornene in Fig. 2b presents four groups of resonances in the region from 25 to 56 ppm. The peaks in the region of 25–34 ppm are non-bridging CH₂ groups (carbons 5 and 6). The resonance between 34 and 37 ppm represent a bridge CH₂ group (carbon 7). The resonance between 37 and 45 ppm are bridgehead CH groups (carbons 1 and 4) and the resonance peaks between 45 and 56 ppm are backbone-connecting CH groups (carbons 2 and 3).

Taking into consideration these results, one might expect the 2,3-repeating units for other poly(5-alkyl-2-norbornene)s. Previously, it has been shown that the interaction of (acac)Pd(C₃-acac)₂(PR₃) with BF₃OEt₂ in the presence of 1-hexene can afford catalytically active tetracoordinated palladium hydride species [32]. We have not carried out detailed mechanistic studies of the interaction of Pd(acac)₂, bidentate phosphine ligand and BF₃OEt₂ in the presence of norbornene or 5-alkyl-2-norbornenes. However, taking in consideration 2,3-connectivity of repeating units, which is characteristic to addition polymerization of norbornene derivatives, we can presume that palladium hydride species are responsible for the catalytic activity in the polymerization of norbornene and 5-alkyl-2-norbornenes.

An additional proof of the coordination mechanism has been obtained using a cationic inhibitor. The homopolymerization of norbornene or 5-butyl-2-norbornene over the Pd(Acac)₂ + 2DPPB + 25BF₃OEt₂ system was not retarded by the addition of 5 equiv. of the cationic inhibitor 2,6-di-tert-butylpyridine. Thus, the introduction of an ancillary bidentate phosphine ligand to the Pd(acac)₂ + 25BF₃OEt₂ system switches the carbocationic polymerization mechanism to the coordination Ziegler–Natta polymerization. Such a phenomenon of switching of polymerization mechanism is well known for the metal-catalyzed polymerization of alkenes [33].

Our interest next turned to the copolymerization of 5-alkyl-2-norbornenes with norbornene using the Pd(Acac)₂ + 2DPPB + 25BF₃OEt₂ system. In the copolymerization runs equimolar mixtures of 5-alkyl-2-norbornene and norbornene were employed and the (AlkNB + NB)/Pd ratio was 4500, similar to homopolymerization runs. The copolymers of 5-alkyl-2-norbornenes with norbornene were characterized using NMR, GPC, TGA and DSC methods; these results and elemental analysis results are summarized in Table 6.

The 13C NMR spectra of the copolymer of 5-butyl-2-norbornene with norbornene and poly(5-butyl-2-norbornene) are shown in Fig. 3 as an example. The only difference in these spectra is integral intensities in the region from 55 to 25 ppm. When the peaks at 14.16 ppm attributable to CH₃ groups are normalized, it was possible to determine the composition of the copolymer: subtraction of the integral intensity of the poly(5-propyl-2-norbornene) from that of the copolymer gives the

---

Table 6

<table>
<thead>
<tr>
<th>Type of R</th>
<th>NB/AlkNB mole ratio</th>
<th>Yield (observed) (g)</th>
<th>Yield (theoretical) (g)</th>
<th>Mₙ (g/mol)</th>
<th>Mₘ (g/mol)</th>
<th>Mₘ/Mₙ</th>
<th>Tₙ (°C)</th>
<th>Tₐdec (°C)</th>
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</table>

Experimental conditions: [Pd] = 5 × 10⁻⁶ M, (AlkNB + NB)/Pd = 4500, equimolar mixture of AlkB and NB, 65 °C, 30 min, total volume 7 ml.
content of norbornene units in the copolymer. The determined compositions of the copolymers were confirmed by the elemental analysis.

As may be seen from Table 6, the observed yields of copolymers were in agreement and a little lower than the values expected theoretically based on the assumption of complete consumption of norbornene. This small deviation is, again, due to a loss of products during workup. In the series of alkyl chain lengths from propyl to decyl, the incorporation of 5-alkyl-2-norbornene into the copolymer decreased from 47 to 32% due to their lowering reactivity. At the same time, the decomposition and glass transition temperatures were reduced with increasing number of carbons of the substituent. Unimodal molecular weight distributions with an apparent $M_w/M_n$ ratio close to 2 for the copolymers indicate that the copolymerization occurs at the single active site and that the polymers are "true" copolymers without homopolymers. Indeed, the copolymers all showed single glass transition and decomposition temperatures (Figs. 4 and 5).

The difference between the decomposition temperatures and the glass transition temperatures of the copolymers substantially increased with increasing chain length of alkyl substituent, which is essential for the polymer processability.

4. Conclusion

The Pd(acac)$_2$ + $n$Ph$_2$P(CH$_2$)$_m$PPh$_2$ + 25BF$_3$OEt$_2$, $n$ = 1–3, $m$ = 1–6, catalyst system was successfully employed for the homopolymerization of 5-alkyl-2-norbornenes and their copolymerization with norbornene. For this series, the most efficient catalyst system was Pd(acac)$_2$ + 2Ph$_2$P(CH$_2$)$_4$PPh$_2$ + 25BF$_3$OEt$_2$. The activity of the catalyst system is comparable to that of most active late transition metal catalysts described in the literature. Bidentate phosphines containing bridges larger than 1,4-butane are likely to act as monodentate ligands. The incorporations of flexible alkyl groups onto the main chain of norbornene, as well as copolymerization of 5-alkyl-2-norbornenes with norbornene, represent a useful method for lowering the glass transition temperature ($T_g$) of the polymers. For both
homo- and copolymers, the difference between the decomposition and glass transition temperatures substantially increased with increasing chain length of alkyl substituent, which is essential for the polymer processability. The molar mass distribution indicates a single-site, highly homogeneous character of the active catalyst species. According to NMR spectroscopy data, the polymers possess 2,3-enched repeating units of polymer backbone. The introduction of bidentate phosphine ligands to the Pd(acac)2 + 25BF3OEt2 system switches the carbocationic polymerization mechanism to the coordination Ziegler–Natta polymerization. The simplicity of catalytic system composition might be of industrial importance.

Acknowledgement

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References