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Polymerization of norbornene by novel bis(acetylacetonate)palladium/boron trifluoride etherate catalyst system

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Abstract

The boron trifluoride etherate, BF_3OEt_2, was used as an activator towards bis(acetylacetonate)palladium precursor in the polymerization of norbornene. The catalyst system $Pd(Acac)_2/BF_3OEt_2$ was highly active in the polymerization of norbornene, resulting in completely soluble polymers. Catalytic activity up to 20,220 kg/(mol Pd·h) and intrinsic viscosities up to 2.64 dL/g were observed, respectively. Catalytic activity, polymer yield and polymer molecular weight can be controlled by varying the reaction parameters. The molar mass distribution indicates a single-site, highly homogeneous character of the active catalyst species. Glass transition temperatures (T_g) ranged from 346 to 365 °C. NMR spectroscopy study of the polymer showed exclusively 2,7-enchained repeating units of polymer backbone.

Keywords: Boron trifluoride; Norbornene; Palladium

1. Introduction

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 and 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. 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 [4,5]. Therefore, norbornene addition polymer and its derivatives are attractive materials for the manufacture of microelectronic and optical devices. Conventional Ziegler–Natta catalysts can cause ROMP or vinyl addition polymerization of norbornene depending on reaction conditions applied [6]. The late-transition metal palladium and nickel catalysts lead to vinyl addition polymerization of norbornene. Some of the nickel and palladium complexes can be used alone as active catalysts for the polymerization of norbornene [7,8]. Most of them have to be activated with methylalumoxane (MAO) cocatalysts [9–16]. Another possibility to activate late-transition metal complexes is to apply the organo-Lewis acid tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, with or without triethylaluminum (TEA) [17–23]. It is also noteworthy that $[(1,5\text{-cyclooctadiene})(CH_3)Pd(Cl)]$ in combination with a monodentate phosphine ligand and $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ complex allowed to reach a polymerization rate of 1000 tons norobornene per mol Pd for an hour [24].

Due to the high production costs of MAO and organoborane cocatalysts, 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 a cocatalyst [25,26].

Recently we have shown that boron trifluoride etherate, BF_3OEt_2, can be successfully used as a cocatalyst towards

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Table 1
Effect of cocatalyst/palladium ratio on the polymerization of norbornene (NB) over $Pd(Acac)_2/BF_3OEt_2$ catalyst system

Cocat/B/Pd ratio	NB/Pd ratio	Catalyst (10^6 mol)	Time (h)	Yield (g)	Activity (kg NB/(mol Pd·h))	[η] (dL/g)
10	22350	5	0.5	2.14	960	1.16
20	22350	5	0.5	2.75	1100	1.22
25	22350	5	0.5	2.94	1180	1.25
30	22350	5	0.5	2.92	1168	1.30
40	22350	5	0.5	2.91	1164	1.37
60	22350	5	0.5	2.58	1032	1.36

Experimental conditions: 25 °C, 10.52 g of NB, total volume 30 ml including toluene as solvent.

tetrakis(triphenylphosphine)nickel, $Ni(PPh_3)_4$, for the polymerization of norbornene [27]. In this study, a novel cocatalysts, BF_3OEt_2, towards bis(acetylacetonate)palladium, $Pd(Acac)_2$, catalyst was examined for the polymerization of norbornene in term of reaction parameters and physical properties.

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 calcium hydride, CaH_2. Boron trifluoride etherate (Aldrich, 99%) was freshly distilled over CaH_2 prior to use. Toluene and benzene were distilled with sodium/potassium alloy (NaK) under dry nitrogen. $Pd(Acac)_2$ was supplied by Aldrich and recrystallized from benzene.

2.2. Polymerization of norbornene

Polymerizations were carried out in a 50 ml glass reactor equipped with a magnetic stirrer. The reactor was preliminary 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 bis(acetylacetonate)palladium 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 5.0×10^{-6} mol, the NB/Pd ratio was 22,350, the reaction time was 30 min, and the total reaction volume was 30 ml.

2.3. Characterization of polymer

NMR spectra were recorded at room temperature on a Bruker AMX-500 spectrometer with a frequency 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. 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 1,2,4-trichlorobenzene at 25 °C using Ubbelohde viscometer. Gel permeation chromatography (GPC) analysis were carried out on a WATERS 150 HPLC instrument with 10 μm MIXED-B columns (300 × 7.5 mm) using 1,2,4-trichlorobenzene solvent at 135 °C and polystyrene standard. Calorimetric analysis (DSC) was done using a DSC Q100 instrument.

3. Results and discussion

For the polymerization of norbornene preliminary experiments were made to check the polymerization activity for each of two single components of the system, $Pd(Acac)_2$ and BF_3OEt_2. Neither $Pd(Acac)_2$ nor BF_3OEt_2 was active in norbornene polymerization. This indicates that only through the combination of $Pd(Acac)_2$ with BF_3OEt_2 can catalytically active species be generated. The polymers obtained were completely soluble in 1,2,4-trichlorobenzene and could be investigated by NMR, GPC and viscometry methods.

For the catalysts system $Pd(Acac)_2/BF_3OEt_2$, the yield and molecular weight of polynorbornene, as well as the catalyst activity depend, significantly on the reaction parameters applied such as cocatalyst/catalyst ratio (B/Pd), reaction temperature, catalyst concentration and monomer/catalyst ratio (NB/Pd).

To investigate the effect of the amount of cocatalyst, a set of polymerizations was carried out with the B/Pd ratios from 10 to 60 at 25 °C. As one may see in Table 1, the polymer

Table 2
Effect of reaction temperature on the polymerization of norbornene (NB) over $Pd(Acac)_2/BF_3OEt_2$ catalyst system

Cocat/Temp. (°C)	NB/Pd ratio	Catalyst (10^6 mol)	Time (h)	Yield (g)	Activity (kg NB/(mol Pd·h))	[η] (dL/g)
15	22350	5	0.5	2.98	1190	2.64
25	22350	5	0.5	2.94	1180	1.25
35	22350	5	0.5	1.89	756	1.00
45	22350	5	0.5	1.35	540	0.77
55	22350	5	0.5	0.8	320	0.33
65	22350	5	0.5	0.72	290	0.17

Experimental condition: B/Pd = 25, 10.52 g of NB, total volume 30 ml.

yield showed a shallow maximum at B/Pd ratios from 25 to 40 and a further decrease at a ratio of 60. At the same time, the intrinsic viscosity (molecular weight) increased from 1.16 to 1.37 dL/g, while the ratio B/Pd changed from 10 to 40 and slightly decreased to 1.36 dL/g at a ratio B/Pd of 60. Similar curves of activity versus cocatalyst/metal ratio for norbornene homopolymerization were reported previously [13,18,19], and the increase of activity with increasing cocatalyst/metal ratio was explained by an equilibrium formation of the active complex from inactive precatalyst and cocatalyst [18,19], i.e. by an increasing number of active species [13].

The interaction of $Pd(Acac)_2$ with BF_3OEt_2 in the presence of hexene-1 leads to catalytically active complexes, in which BF_3 can be bonded to Pd as a complexed BF_4^- anion or via a fluorine atom as $F{\cdot}BF_3$ [28]. Moreover, a rapid exchange between the bridging and the terminal fluorine atoms of coordinated BF_4^- (anion 'spinning') and a presence of a tightly associated contact ion pair had been shown for the polymerization of norbornene derivatives with (η^3-allyl)Pd(II) catalysts [29]. Therefore the results obtained might be explained by the equilibrium between a fluorine-bridged inactive and an active, tightly associated ion pairs of the palladium species. The increasing amount of BF_3 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 [18,19]. The decrease of activity towards higher amounts of BF_3OEt_2 could be explained by a deactivating interaction of BF_3 with the active complex in general. Consequently, an excess of cocatalyst BF_3OEt_2 is not necessary to obtain good polymerization activities.

A series of polymerization runs was performed at temperatures between 15 and 65 °C. The results are presented in Table 2.

The increase of temperature from 15 to 65 °C resulted in drastic drop of catalytic activity from 1190 to 290 kg NB/(mol Pd·h) and intrinsic viscosity from 2.64 to 0.17 dL/g. It indicates that the active species show very low thermal stability. The accepted explanation for the decreased intrinsic viscosity is that the activation energy for chain transfer is greater than that for propagation and that the decrease in molecular weight is due to an increased rate of chain termination at higher temperatures.

The effect of NB/Pd ratio on the norbornene polymerization is shown in Table 3. For norbornene polymerization, the activity of catalyst system is not dependent on the NB/Pd ratio. At the same time, intrinsic viscosity increased from 1.15 to 1.41 dL/g until NB/Pd ratio increased from 11,200 to 33,525 and then decreased to 0.98 at NB/Pd ratio of 44,700. 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. Borkar and Saxena [12] reported for the norbornene polymerization over the Ni(salen)/MAO catalyst system that the increase of monomer/nickel ratio led to the decrease of polymer yield combined with increase of intrinsic viscosity.

On the other hand, the higher monomer/catalyst molecular ratios might be resulted also in both increased polymer yield and molecular weight [18]. In case under study, the increment of intrinsic viscosity might be explained that the chain propagation rate increased at higher monomer concentration. However, at the higher value of NB/Pd = 44,700, intrinsic viscosity of the polymer decreased. The most probable explanation for the decreased intrinsic viscosity is that, due to the modest solubility of the

Table 3
Effect of monomer/palladium ratio on the polymerization of norbornene (NB) over $Pd(Acac)_2/BF_3OEt_2$ catalyst system

NB feed (mol-%)	NB/Pd ratio	Catalyst (10^6 mol)	Time (h)	Yield (g)	Activity (kg NB/(mol Pd·h))	[η] (dL/g)
20	11200	5	0.5	2.83	1132	1.15
40	22350	5	0.5	2.94	1180	1.25
60	33525	5	0.5	2.88	1152	1.41
80	44700	5	0.5	2.96	1184	0.98

Experimental conditions: 25 °C, B/Pd = 25, 10.52 g of NB, total volume 30 ml.

Table 4
Effect of reaction time on the polymerization of norbornene over $Pd(Acac)_2/BF_3OEt_2$ catalyst system

Time (min)	NB/Pd ratio	Catalyst (10^6 mol)	Yield (g)	Conversion (%)	Activity (kgNB/(mol Pd·h))	[η] (dL/g)
5	22350	5	0.48	4.7	1152	0.64
10	22350	5	1.77	16.8	2124	1.0
20	22350	5	2.52	24.0	1512	1.20
30	22350	5	2.94	27.9	1180	1.25
60	22350	5	4.25	40.4	850	1.25

Experimental conditions: B:Pd = 25, 25 °C, 10.52 g of NB, total volume 30 ml.

Table 5
Effect of precatalyst amount on the polymerization of norbornene (NB) over $Pd(Acac)_2/BF_3OEt_2$ catalyst system

Cocat/ [Pd] 10^6 mol	NB/Pd ratio	Time (h)	Yield (g)	Activity (kg NB/(mol Pd·h))	[η] (dL/g)
2	56000	0.5	0.39	390	1.42
5	22350	0.5	2.94	1180	1.25
10	11200	0.5	5.52	1100	1.05
15	7450	0.5	8.89	1185	0.83
20	5600	1 min	6.74	20220	0.62

Experimental conditions: 25 °C, B/Pd = 25, NB 10.52 g, total volume 30 ml.

growing chain, the diffusion of the monomer to the active center is impeded and the propagation rate is decreased. In this case, the chain termination and transfer become more favorable, which allows the restart of faster propagation.

The effect of reaction time on the conversion, activity and intrinsic viscosity is summarized in Table 4 and Fig. 1. As one can see, the polymer yield increased with time almost linearly, while the intrinsic viscosity increased logarithmically. The catalytic activity showed a maximum at reaction time of 10 min.

This is opposite to that for the $Ni(PPh_3)/BF_3OEt_2$ catalyst system, where the polymer yield increased with time logarithmically, while the intrinsic viscosity remained constant [27]. The observed data indicate different types of catalytically active species formed in each catalyst system.

The effect of the precatalyst amount on the polymer yield and intrinsic viscosity is presented in Table 5. As is shown, the increase of the precatalyst amount led to the increase of polymer yield and decrease of intrinsic viscosity. At the precatalyst amount of 2.0×10^{-5} mol, the catalytic activity of 20,220 kg polynorbornene per mol Pd for an hour was achieved. This is comparable to that of the most active catalyst systems, described in literature [10–12,14,17–21], except for that reported in [24]. One also can note that the increase of the precatalyst amount from 2.0×10^{-6} to 2.0×10^{-5} mol followed by the decrease of intrinsic viscosity from 1.42 to 0.62 dL/g.

It is noteworthy that the entry with precatalyst amount of 2.0×10^{-5} mol was extremely exothermic. Immediately after adding the boron compound, the polymer started forming and precipitating from the solution as a white powder to give a solid white ‘cake’ within several seconds, and the formation of palladium blacks was observed visually during the reaction. Such an abnormal increase of

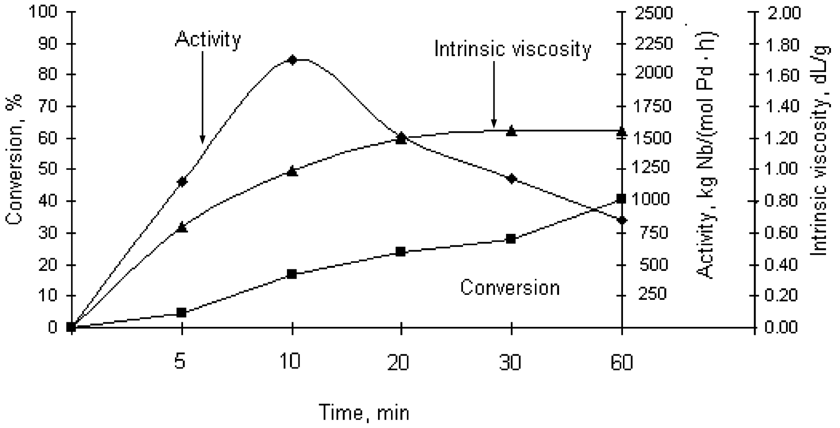

Fig. 1. Effect of reaction time on the polymerization of norbornene over $Pd(Acac)_2/BF_3OEt_2$ catalyst system (B:Pd = 25, 25 °C, 10.52 g of NB, total volume 30 ml).

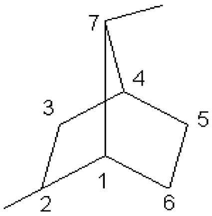

Fig. 2. 2,7-enchained polynorbornene unit.

activity is difficult to explain in the absence of a more knowledge of the active species. However, the in situ formation of a sufficient number of highly active 'naked' Pd^{2+} species is quite possible at some higher limiting precatalyst amount due to negligible effect of impurities and moisture in the reaction medium. Experimental evidence for the formation of this kind of active species as well as simple $PdCl_2$ species well presented by Janiak and coworkers [20,21]. In this case, one should presume a cationic mechanism for the polymerization of norbornene, as is suggested for the polymerization and oligomerization of olefins by Sen and coworkers [30].

Indeed, we found that the catalysts system $Pd(Acac)_2/BF_3OEt_2$ produces a polymer with exclusively 2,7-enchained repeating norbornene units, as is shown in Fig. 2.

To the best of our knowledge, this type of polynorbornene structure has been reported only once in a patent of the B.F. Goodrich Company (USA) [26]. The ^{13}C NMR spectrum of polynorbornene in Fig. 3(a) presents five groups of resonances in the region from 25 to 55 ppm. The resonance peaks at 28–34 ppm are non-bridging CH_2 groups (carbons 5 and 6). The resonance peak 34–38 ppm is a remaining CH_2 group (carbon 3). The peaks between 38 and 44 ppm are bridgehead CH groups (carbons 1 and 4). The resonance peaks at 45–49 ppm and 50–55 ppm are backbone connecting CH groups (carbons 2 and 7) [22]. In the ^{1}H NMR spectrum (Fig. 3(b)) the resonance peaks at 0.8–1.8 ppm are non-bridging and remaining CH_2 groups (protons at 6, 5 and 3 positions). The peak at 1.93 ppm is backbone connecting CH groups (protons 2 and 7). The resonance peak at 2.30 ppm is bridgehead CH groups (protons 1 and 4) [31]. The IR spectrum of the polymer proves the absence of the double bond at 1620–1680 cm^{-1}.

Table 6
GPC analysis data for the polymerization of norbornene (NB) over $Pd(Acac)_2/BF_3OEt_2$ catalyst system

[η] (dL/g)	M_n (g/mol)	M_w (g/mol)	Q (M_w/M_n)	T_g (°C)
2.64	179650	307400	1.71	365
1.41	169300	278500	1.64	364
1.25	159000	258250	1.62	363
0.62	84650	142650	1.69	358
0.33	50400	76300	1.51	346

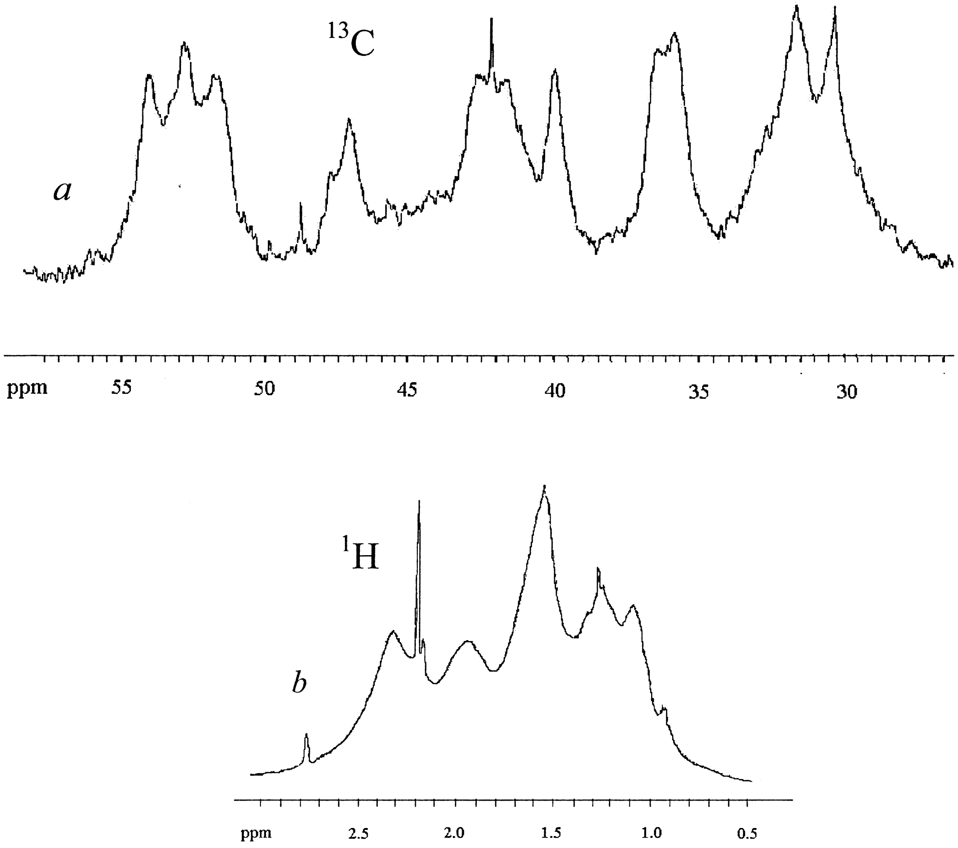

Fig. 3. NMR spectra of polynorbornene: ^{13}C NMR (a), ^{1}H NMR (b).

The GPC and DSC analyses of the polynorbornene were carried out for representative samples with various intrinsic viscosity, covering all the range of observed values, and results are presented in Table 6.

The molar mass distribution $Q = M_w/M_n$ for the polymer samples is rather narrow and close to a value of 2. The value of $Q = 2$ is the theoretical dispersity for a Schultz-Flory-type distribution arising from an ideally behaved polymerization reaction with a chain termination reaction. A dispersity $Q \approx 2$ indicates a single-site character, that is, a highly homogeneous structure of the active catalyst species. The glass transition temperatures were obtained by DSC measurements. T_g ranged from 346 to 365 °C (M_w =76300 − 307400 gmol). A $T_g(\infty)$ of 371 °C for polynorbornene can be extrapolated by means of the Bueche equation (Eq. (1)),

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

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

4. Conclusion

In this work, it was shown that the catalyst system $Pd(Acac)_2/BF_3OEt_2$ is highly active in the polymerization of norbornene to afford soluble polymers. Catalytic activity up to 20220 kg/(mol Pd·h) and intrinsic viscosities up to 2.64 dL/g were observed, respectively. Catalytic activity, polymer yield and polymer molecular weight might be controlled by varying the reaction parameters. The molar mass distribution indicates a single-site, highly homogeneous character of the active catalyst species. Glass transition temperatures ranged from 346 to 365 °C. NMR spectroscopy study of the polymer showed exclusively 2,7-enchained repeating units of polymer backbone.

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