

The Pd₂(CH≡CC₆H₅)₂(C₅H₇O₂)₃(BF₃)₂BF₄ catalyst for the polymerization of norbornene

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Abstract

Pd₂(CH≡CC₆H₅)₂(C₅H₇O₂)₃(BF₃)₂BF₄ and Pd(acac)₂ + 2PhA + 4BF₃OEt₂ are active catalysts for the polymerization of norbornene. For the Pd₂(CH≡CC₆H₅)₂(C₅H₇O₂)₃(BF₃)₂BF₄ a “particular” catalyst activity up to 17,600 kg polynorbornene per mol Pd for an hour and viscosity average molar masses up to 520,000 g/mol were observed. IR and NMR spectroscopy study of the polymer showed the microstructure presented by the *rr* and *mr* triads with low diisotacticity.

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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 by addition polymerization [1]. The norbornene addition polymer with 2,3-enchaind repeating units displays a characteristic rigid random coil conformation, shows restricted rotation about the main chain, and exhibits strong thermal stability, excellent dielectric properties, optical transparency and unusual transport properties [2,3]. Therefore, norbornene addition polymer 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 palladium and nickel complexes are commonly activated with methylalumoxane, MAO [4–20], except for the cationic ones [21,22]. The Lewis acid tris(pentafluorophenyl)borane, B(C₆F₅)₃ with or without triethylaluminum was recently applied as a

cocatalyst system to the activation of palladium and nickel complexes [23,24]. We have shown that the combination of palladium acetylacetonate, Pd(acac)₂ (**1**) with boron trifluoride etherate, BF₃OEt₂, successfully catalyzes the vinyl polymerization of norbornene [25]. In this work, we report on the catalytic activity of the complex Pd₂(CH≡CC₆H₅)₂(C₅H₇O₂)₃(BF₃)₂BF₄ (**2**) as a product of the interaction between Pd(acac)₂, phenylacetylene (PhA) and BF₃OEt₂ in the polymerization of norbornene.

2. Experimental

All manipulations for air sensitive compounds were carried out under a stream of dry argon using standard inert techniques. Norbornene (99%) was supplied by Aldrich. BF₃OEt₂ (Aldrich, 99%) was freshly distilled over calcium hydride prior to use. Toluene was purified according to standard procedure. The reaction of Pd(acac)₂ (**1**) with PhA and BF₃OEt₂ was performed under argon atmosphere in a glass vessel with a magnetic stirrer. The vessel was filled on stirring with the following reagents at 20 °C: benzene (50 ml), Pd(acac)₂ (**1**) (0.7799 g, 2.56 × 10⁻³ mol), PhA (0.2615 g, 2.56 × 10⁻³ mol), and BF₃OEt₂ (1.8163 g, 12.8 × 10⁻³ mol). The precipitate of complex **2** formed

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was filtered under argon, washed five times with benzene, and dried in vacuum (20 °C, 100 Pa) for 5 h. Anal. Calcd. for Pd₂C₃₁H₃₃B₃F₁₀O₆: Pd-22.7; C-39.7; H-3.6; B-3.5; F-20.3. Found: Pd-22.1; C-38.5; H-3.7; B-3.8; F-8.25.

Polymerizations were carried out in a 10 ml glass reactor equipped with a magnetic stirrer. The reactor was preliminary purged in vacuum and filled with argon and then was filled with norbornene as a solution in toluene. The solution was kept at desired temperature for 15 min. Polymerizations were initiated by the injection the solution of **2** in toluene. The polymers formed were precipitated in acidified ethanol, separated by filtration, washed with an excess amount of ethanol and dried in vacuum.

NMR spectra were recorded at room temperature on a Bruker AMX-500 spectrometer with a frequency of 500 MHz for ¹H NMR and 125 MHz for ¹³C NMR. The IR spectrum of the polymer 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. Viscosity average molecular weights were calculated from intrinsic viscosity by using the Mark–Houwink coefficients: $\alpha = 0.679$, $K = 9.872 \times 10^{-5}$ dL/g [10].

3. Results and discussion

The structure of **2** was determined using IR, ¹H, ¹³C NMR spectroscopy and elemental analysis methods Eq. (1). The IR spectrum of **2** exhibits a broad absorbance band in the region 3400–3000 cm⁻¹ with the maximum at 3200 cm⁻¹, the bands at 1685, 1610, 1580, 1560, 1520, 1380, 885, 840, 767, 582, 525 cm⁻¹, and a series of the broad bands in the region 1220–1000 cm⁻¹ (Fig. 1).

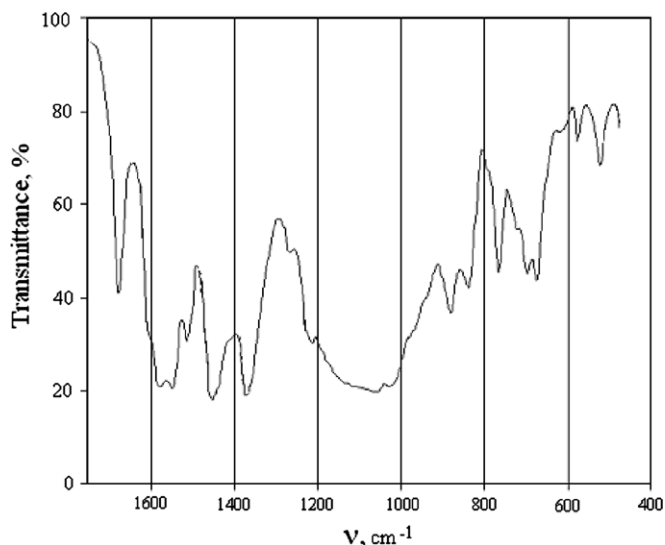
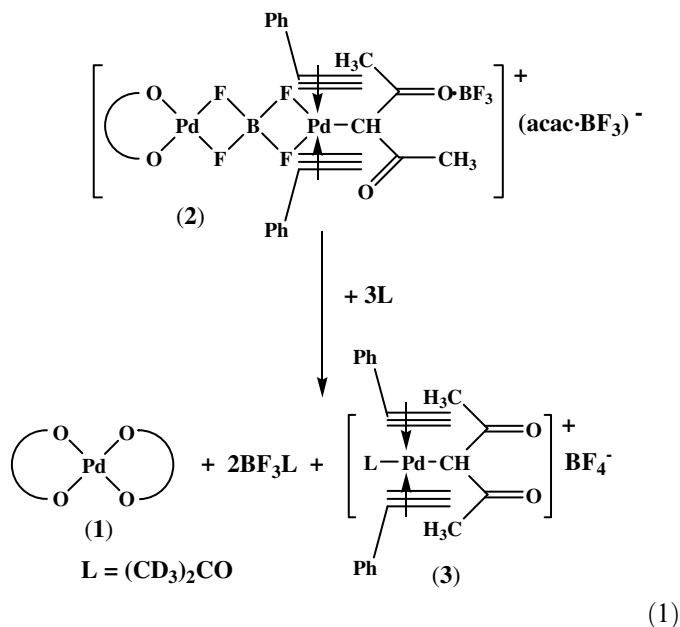


Fig. 1. IR spectrum of **4** in Nujol.



The bands at 1560 and 1520 cm⁻¹ are due to stretching vibrations of the C=O and C=C bonds in chelate bonded acac group, respectively [26]. The band at 1685 (C=O) and 1580 cm⁻¹ (C=O · BF₃) characterize the acac ligand bound to Pd in monodentate keto mode [27]. The stretching vibrations of the B–F and B–O bonds in the C=O · BF₃ group appear at 1380, 885, 840, 767 cm⁻¹, and as a broad band in the range of 1170–1000 cm⁻¹ [28]. The band at 582 cm⁻¹ can be assigned to the stretching vibrations of the Pd–C bond [29]. The anion (acac · BF₃)⁻ appears at 1610 cm⁻¹ [29]. The bands at 525 as well as at 1220–1150 cm⁻¹ are apparently due to bridging BF₄ moiety [30]. The confirmation of the π-coordination of PhA to Pd comes from the ¹³C NMR spectra of **2** and PhA in deuterioacetone (Table 1).

As is seen in Table 1, the resonances of the C_α and C_β carbons of the C≡C bond of PhA in **2** are significantly deshielded as compared to those in a free PhA as a result of the coordination. According to ¹¹B NMR data in deuterioacetone **2** decomposes affording **3**, Pd(acac)₂ and BF₃[(CD₃)₂CO] Eq. (1). The ¹¹B NMR spectrum of **2** in deuterioacetone exhibits resonances at 0.00 ppm from BF₃[(CD₃)₂CO] and at -0.58 ppm from BF₄⁻ anion in the intensity ratio BF₃[(CD₃)₂CO]:BF₄⁻ of 2:1. The resonance of the BF₄⁻ anion appears as a quintet with the intensities ratio 1:4:6:4:1 due to interaction of ¹¹B with four equivalent ¹⁹F nuclei (J_{B-F} = 1.1 Hz). Additionally, the ¹H NMR spectrum of **2** in deuterioacetone shows resonances specific to only two modes of acac ligands, particularly, the chelate (δ_{CH₃} = 2.00 ppm, δ_{CH} = 5.52 ppm) and monodentate keto (δ_{CH₃} = 2.10 ppm, δ_{CH} = 3.88 ppm) ones.

Table 1
Chemical shifts of PhA carbons (ppm)

C _β	C _α	C ₁	C _{2,6}	C _{3,5}	C ₄	
100.9	102.1	123.0	132.0	129.0	129.5	PhA in complex 2
77.1	83.5	122.5	132.0	127.9	128.2	Free PhA

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