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Novel bidentate phosphine modified $Pd(acac)_2/BF_3OEt_2$ catalyst system for the homopolymerization of alkylnorbornenes and copolymerization with norbornene

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Abstract

The $Pd(acac)_2 + nPh_2P(CH_2)_mPPh_2 + 25BF_3OEt_2$, $n = 1–3$, $m = 1–6$, 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 $Pd(acac)_2 + 2Ph_2P(CH_2)_4PPh_2 + 25BF_3OEt_2$. 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 $Pd(acac)_2 + 25BF_3OEt_2$ system switched the carbocationic polymerization mechanism to the coordination Ziegler–Natta polymerization. The simplicity of this catalytic system composition might be of industrial importance.

Keywords: Alkylnorbornene; Bidentate phosphine; Boron trifluoride; Copolymerization; Palladium; Polymerization

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 α-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

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endo-functionalized norbornenes. Palladium and nickel catalysts for the polynorbornenes containing pendant polycycles, alkyls, alkenyls, alkylidenes, 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, $B(C_6F_5)_3$, with or without triethylaluminum (TEA) [17,18]. $Li^+[C_6F_5]_4B^-$ [19], $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ [20] and $[PhNHMe_2]^+[C_6F_5]_4B^-$ [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 BF_3, 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, BF_3OEt_2, 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, PPh_3, 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 $Pd(acac)_2 + 25BF_3OEt_2$ catalyst system modified with bidentate phosphine ligands of the general formula $PPh_2(CH_2)_mPPh_2$, 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, CaH_2. 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 ^{13}C 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.

BF_3OEt_2 (Aldrich, 99%) was distilled over CaH_2 prior to use. Toluene and benzene were distilled with Na/K alloy under dry nitrogen. $Pd(Acac)_2$ (Aldrich) was recrystallized from benzene. Triphenylphosphine (PPh_3, Aldrich), 1,2-bis(diphenylphosphino)methane (DPPM, $m = 1$), 1,2-bis(di-

Table 1
^{13}C NMR chemical shifts (δ, ppm from TMS) of various 5-alkyl-2-norbornenes

R-Nb	*Endo* or *exo*	Carbon no.[a]																
		Norbornene ring							Substituent									
		1	2	3	4	5	6	7	1	2	3	4	5	6	7	8	9	10
H-NB		41.7	135.3	135.3	41.7	24.6	24.6	48.5										
C_3-NB	*Endo*	42.6	136.8	132.4	45.5	39.0	37.2	49.6	32.4	21.8	14.6							
	Exo	42.0	137.4	136.1	46.4	39.0	36.7	45.2	33.1	22.0	14.6							
C_4-NB	*Endo*	42.6	136.7	132.2	45.5	38.8	34.5	49.6	32.5	31.0	23.0	14.1						
	Exo	41.9	137.2	136.0	46.2	38.8	36.6	45.2	33.1	31.2	23.0	14.1						
C_6-NB	*Endo*	42.6	136.8	132.4	45.5	38.9	34.9	49.6	32.5	28.8	29.7	32.0	22.8	14.1				
	Exo	42.0	136.9	136.0	46.4	38.9	36.8	45.3	33.2	29.0	29.7	32.0	22.8	14.1				
C_{10}-NB	*Endo*	42.6	136.8	132.4	45.5	38.9	34.9	49.6	32.5	28.8	30.0	29.0–29.8			29.5	32.1	22.8	14.1
	Exo	42.0	136.9	136.0	46.5	38.9	36.8	45.2	33.2	29.0	30.0	29.7–29.8			29.5	32.1	22.8	14.1

[a] Numbering of carbon atoms is as follows: