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Homopolymerization of 5-alkyl-2-norbornenes and their copolymerization with norbornene over novel $Pd(acac)_2/PPh_3/BF_3OEt_2$ catalyst system

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Abstract

The homopolymerization of 5-alkyl-2-norbornenes and their copolymerization with norbornene have been successfully carried out employing $Pd(acac)_2/PPh_3/BF_3OEt_2$ catalyst system. The activity of the catalyst system is comparable to that of most active late-transition metal catalysts described in the literature. The molecular weight distributions of homo- and copolymers indicate a single-site, highly homogeneous character of the active catalyst species. The incorporation of flexible alkyl groups onto the main chain of norbornene as well as copolymerization of 5-alkyl-2-norbornenes with norbornene represent useful methods for lowering the glass transition temperature (T_g), i.e. improving the processability. The simplicity of catalytic system composition might be of industrial importance.

Keywords: Alkylnorbornene; Palladium; Polymerization

1. Introduction

The homopolymerization of bicyclic olefins such as norbornene (NB) can be effected by three commonly known routes: ring-opening metathesis polymerization (ROMP), cationic polymerization, or vinyl addition polymerization. Vinyl addition of norbornene yields a completely unsaturated polymer with no rearranged norbornene units. Reviews of routes to vinyl addition polymers have recently appeared [1,2]. The vinyl homopolymers of norbornene display a characteristic rigid random coil conformation, show restricted rotation about the main chain, and exhibit strong thermal stability, excellent dielectric properties, optical transparency and unusual transport properties and they are attractive materials for the manufacture of microelectronic and optical devices [3,4]. On the other hand, here exists a need in the microelectronics industry for a thermally stable, non-corrosive, low dielectric constant polymer with good solvent resistance, high glass transition temperatures, good mechanical performance, and good adhesive properties. The improvement of chemical and physical properties of polynorbornenes can be achieved by copolymerization of norbornene with α-olefins (especially ethene and propene) or by incorporation of pendant groups onto the polycyclic backbone. 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. However, 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, alkylidenes, silyls, carboxyls, amines, sulfonamides and esters have been described in the literature [5–13].

Typical late transition-metal palladium and nickel complexes employed in norbornene polymerization are cationic systems with non-coordinating counter ions [1 (references 83–106 cited therein), 6]. These cationic complexes are polymerization-active without a cocatalyst. Neutral palladium and nickel complexes have to be

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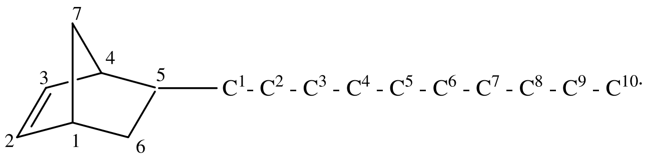
Table 1
^{13}C NMR chemical shifts (δ, ppm from TMS) of various 5-alkyl-2-norbornenes

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:



activated with cocatalysts such as methylalumoxane (MAO) [5,14–21]. Another possibility to activate late transition-metal complexes is to use tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, with or without triethylaluminum (TEA) [7,8,22–26]. $Li^+[C_6F_5]_4B^-$ [9], $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ [10] and $[PhNHMe_2]^+[C_6F_5]_4B^-$ [11] also were used to activate late transition-metal complexes. 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, was applied in the polymerization of norbornene-type monomers as a ‘third component’ and in combination with TEA, but not as a cocatalyst [7,8].

We have recently shown that boron trifluoride etherate, BF_3OEt_2, can be successfully used as a cocatalyst towards tetrakis(triphenylphosphine)nickel, $Ni(PPh_3)_4$, and bis(acetylacetonate)palladium, $Pd(acac)_2$, precursors for the polymerization of norbornene [27,28]. In the present paper, we report the homopolymerization of 5-alkyl-2-norbornenes and their copolymerization with norbornene over $Pd(acac)_2/BF_3OEt_2$ catalyst system modified with monodentate triphenylphosphine ligand, PPh_3.

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 (bp = 85 (°C/13 mm Hg, *endo*/*exo* = 76/24), 5-butyl-2-norbornene (bp = 100 °C/7 mm Hg, *endo*/*exo* = 78/22), 5-hexyl-2-norbornene (bp = 90 °C/3 mm Hg, *endo*/*exo* = 78/22) and 5-decyl-2-norbornene (bp = 136 °C/3 mm Hg, *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 [29]. *Endo*/*exo* mole ratios of 5-alkyl-2-norbornenes were determined from ^{13}C NMR spectra in deuterocloroform. The carbon peaks were assigned in comparison with that reported early [29] and summarized 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. PPh_3 (99%) was used as obtained from Aldrich.

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

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 nitrogen, and then was filled with monomer and phosphine as solutions in toluene. The solution was kept at desired temperature for 15 min and the solution of Pd(acac)$_2$ 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. In standard runs the amount of palladium precursor was 5.0×10^{-6} mol, the monomer to palladium ratio was 4500, the B/Pd ratio was 25, the P/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 Ubbelohde viscometer. Gel permeation chromatography (GPC) analysis was carried out on a WATERS 150 HPLC instrument with 10 µm MIXED-B columns (300×7.5 mm^2) using 1,2,4-trichlorobenzene solvent at 135 °C and polystyrene standard. Here, it should be noted that the molecular weights determined are only apparent due to different hydrodynamic volume for a polystyrene chain and a polyalkylnorbornene chain. However, the molecular weights might be compared to that determined by the same method and described in the literature. Thermogravimetric analysis (TGA) was done using a Setaram Inc. TG/DTA 92-18 instrument. 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. 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 analysis was done on a VarioEL CHNS instrument.

3. Results and discussion

Sagane et al. [29] have synthesized 5-alkyl-2-norbornenes with AlEtCl$_2$/*tert*-butylchloride catalyst system and 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 [5,6,10,11].

The polymerization of 5-butyl-2-norbornene (BuNB) as a representative member of 5-alkyl-2-norbornenes with Pd(acac)$_2$/ BF$_3$OEt$_2$ catalyst system at the B/Pd ratio of 25 at room temperature for 48 h yielded a conversion of 20%. The B/Pd = 25 ratio was chosen as it was optimized for the homopolymerization of norbornene [28]. Since for the addition polymerization of functionalized norbornene derivatives *endo*-substituted norbornenes are polymerized more slowly [8,10–13], this conversion was probably owing to a consumption of *exo* isomer. At temperatures of 35 °C and higher the catalyst system decomposed due to its low thermal stability [28]. 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 therefore it was attractive to modify Pd(acac)$_2$/25BF$_3$OEt$_2$ catalyst system with trivalent phosphorus ligand PPh$_3$. The temperature dependence of the conversion and intrinsic viscosity for the polymerization of 5-butyl-2-norbornene over Pd(acac)$_2$/ 1PPh$_3$/25BF$_3$OEt$_2$ catalyst system is shown in Table 2.

As one can see, the reaction temperature affects considerably the catalytic activities and intrinsic viscosities (molecular weights) of polymers. With an increase of the temperature, a drastic increase of the activity was obtained and, a significant decrease of the intrinsic viscosity was observed. When the reaction temperature was 65 °C a

Table 2
Effect of the reaction temperature on the polymerization of 5-butyl-2-norbornene (BuNB) over Pd(acac)$_2$/1PPh$_3$/25BF$_3$OEt$_2$ catalyst system

Temperature (°C)	BuNB/Pd (ratio)	Catalyst (10^6 mol)	Yield (g)	Conversion (%)	Activity (kg BuNB/(mol Pd h))	[η] (dL/g)
25	4500	5	0.22	6.5	88	0.97
35	4500	5	0.77	22.8	308	0.93
45	4500	5	1.38	40.9	552	0.83
55	4500	5	1.77	52.4	708	0.75
65	4500	5	1.85	54.8	740	0.62
75	4500	5	1.83	54.2	732	0.42

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

maximum activity of 740 kg BuNB/(mol Pd h) and a lower intrinsic viscosity of 0.62 dL/g were obtained. 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 in molecular weight is due to an increased rate of chain termination at higher temperatures. The results obtained demonstrated the possibility to polymerize 5-alkyl-2-norbornenes using $Pd(acac)_2/PPh_3/BF_3OEt_2$ catalyst system.

The effect of P/Pd ratio on the conversion of 5-butyl-2-norbornene and intrinsic viscosity (molecular weight) of polymers over $Pd(acac)_2/nPPh_3/25BF_3OEt_2$ system at 65 °C is depicted in Fig. 1. In a range of P/Pd ratio from 1 to 4 an optimum conversion at P/Pd = 2 and a higher intrinsic viscosity at P/Pd = 3 were obtained. Lower and higher P/Pd ratios revealed to a significant decrease of both values.

The polymerization kinetics of 5-butyl-2-norbornene at P/Pd ratios of 1 and 2 is summarized in Table 3 and Fig. 2. For both P/Pd ratios of 1 and 2 the intrinsic viscosity increased rapidly within first 5 min and then increased slightly with longer reaction time. 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 P/Pd = 1, in the first period, about 5–10 min, the polymer yield increased almost linearly and a maximum catalytic activity of 2640 kg BuNB/(mol Pd h) was observed at the reaction time of 3 min. In the second period, the polymer yield increased very slightly and leveled off. By contrast, in the case of P/Pd = 2 three distinct periods can be observed in the conversion profile. Careful analysis of kinetic data showed an induction period within 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.

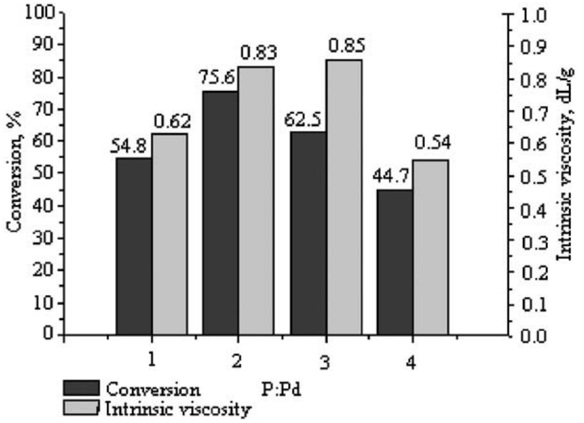


Fig. 1. Effect of P/Pd ratio on the conversion and intrinsic viscosity ([Pd] = 5×10^{-6} M, BuNB/Pd = 4500, B/Pd = 25, 65 °C, 30 min, total volume 7 ml).

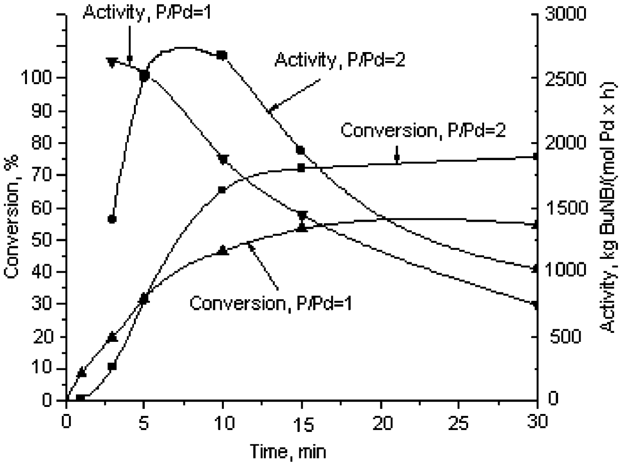


Fig. 2. Effect of the reaction time on the polymerization of 5-butyl-2-norbornene.

Due to this induction period, a maximum catalytic activity of 2676 kg BuNB/(mol Pd h) was recorded at the reaction time of 10 min. Further, decrease of catalytic activity 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 especially in the case of P/Pd = 1. The commensurate and higher activities were achieved by Goodall et al. [9] and Sen et al. [10,11] using Pd(II) precursors containing anionic hydrocarbyl ligand and 1 equivalent of monodentate phosphine in combination with $Li^+[C_6F_5]_4B^-$ and $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ or $[PhNHMe_2][B(C_6F_5)_4]$ complexes, respectively. The main differences of the $Pd(acac)_2/PPh_3/BF_3OEt_2$ system from these are high availability and ease of manipulation of the catalyst components.

Polymerizations of other 5-alkyl-2-norbornenes were carried out over $Pd(acac)_2/2PPh_3/25BF_3OEt_2$ catalyst system at standard conditions and the results are presented in Table 2.

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 length from propyl to decyl the conversion decreased from 89.0 to 59.5%. At the same time, the decomposition and glass transition temperatures decreased from 326 to 294 °C and from 190 to 130 °C, respectively, increasing by this way the difference between them, that is, improving the processability of the polymers. It is clear that norbornene is much higher reactivity compared to alkyl substituted ones. The small deviation from a quantitative yield for norbornene polymerization might be due to loss of product during workup. Concerning the tailor-making 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,

Table 3
Effect of the reaction time on the polymerization of 5-butyl-2-norbornene (BuNB) over $Pd(acac)_2/nPPh_3/25BF_3OEt_2$ catalyst system

Time (min)	P/Pd (ratio)	Catalyst (10^6 mol)	Yield (g)	Conversion (%)	Activity (kg BuNB/(mol Pd h))	[η] (dL/g)
3	1	5	0.66	19.6	2640	0.30
	2	5	0.35	10.4	1400	0.66
5	1	5	1.06	31.4	2544	0.40
	2	5	1.04	30.8	2496	0.75
10	1	5	1.57	46.5	1884	0.48
	2	5	2.23	65.2	2676	0.78
15	1	5	1.80	53.3	1440	0.53
	2	5	2.43	72.0	1944	0.80
30	1	5	1.85	54.8	740	0.62
	2	5	2.55	75.6	1020	0.83

Experimental conditions: 65 °C, 3.375 g of BuNB, BuNB/Pd = 4500, total volume 7 ml.

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' [29]. The average polymerization degree and molar mass distributions of 5-alkyl-2-norbornenes did not display a 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 $Q \approx 2$ indicates a single-site character, that is, a highly homogeneous structure of the active catalyst species.

The ^1H and ^{13}C NMR spectra of polynorbornene obtained with the $Pd(acac)_2/2PPh_3/25BF_3OEt_2$ catalyst system showed 2,3-enchained structure of the polymer (Fig. 3). In the ^1H NMR spectrum (Fig. 3(a)) bridgehead CH groups (protons 1 and 4) appear at 2.10 ppm. The resonance 1.53 ppm is backbone connecting CH groups (protons 2 and 3). The resonances between 0.7 and 1.4 ppm are attributed to non-bridging CH_2 groups (protons 5, 6, and 7).

The ^{13}C NMR spectrum of polynorbornene in Fig. 3(b) presents four groups of resonances in the region from 25 to 56 ppm. The peaks in the region of 25 to 34 ppm are non-bridging CH_2 groups (carbons 5 and 6). The resonances present between 34 and 37 ppm represent a bridge CH_2 group (carbon 7). The resonance between 37 and 47 ppm are bridgehead CH groups (carbons 1 and 4) and the resonance peaks between 47 and 56 ppm are backbone connecting CH groups (carbons 2 and 3). Taking into consideration these results, same 2,3-repeating units might be expected for other

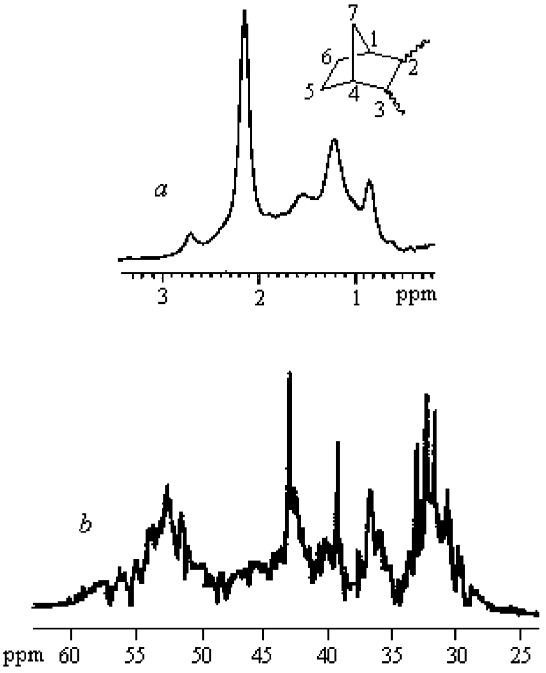


Fig. 3. NMR spectra of polynorbornene obtained with $Pd(acac)_2/2PPh_3/25BF_3OEt_2$: ^1H NMR spectrum (a); ^{13}C NMR spectrum (b).

Table 4
Polymerization of 5-alkyl-2-norbornenes over $Pd(acac)_2/2PPh_3/25BF_3OEt_2$ catalyst system

Type of R	AlkNB/Pd (ratio)	Yield (g)	Conversion (%)	M_w (g/mol)	M_w/M_n	P_n	T_g (°C)	T_{dec} (°C)
H	4500	2.01	95.3	74000	2.18	360	285	335
C_3H_7	4500	2.74	89.0	70000	1.43	360	190	326
C_4H_9	4500	2.55	75.6	82000	1.49	370	183	320
C_6H_{11}	4500	2.81	70.1	91000	1.36	380	140	307
$C_{10}H_{21}$[a]	4500	3.16	59.5	–	–	–	130	294

Experimental conditions: $[Pd] = 5 \times 10^{-6}$ M, 65 °C, total volume 7 ml.

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

poly(5-alkyl-2-norbornene)s. Previously, it has been shown that the interaction of (acac)Pd(C^3-acac)$_2$·PR$_3$ with BF$_3$OEt$_2$ in the presence of 1-hexene can afford catalytically active tetracoordinated palladium hydride species [30]. We have not carried out detailed mechanistic studies of the interaction of Pd(acac)$_2$ and PPh$_3$ ligand with BF$_3$OEt$_2$ in the presence of norbornene and 5-alkyl-2-norborenes. However, taking in consideration 2,3-connectivity of repeating units, which is characteristic to addition polymerization of norbornene derivatives, we can presume palladium hydride species to be responsible for the catalytic activity in the polymerization of norbornene and 5-alkyl-2-norbornenes. An additional evidence of the coordination mechanism has been obtained using a cationic inhibitor. The homopolymerization of norbornene or 5-butyl-2-norbornene over the Pd(acac)$_2$/2PPh$_3$/25BF$_3$OEt$_2$ system was not retarded by the addition of 5 equivalents of the cationic inhibitor 2,6-di-*tert*-butylpyridine. Thus, the introduction of an ancillary phosphine ligand PPh$_3$ to the Pd(acac)$_2$/BF$_3$OEt$_2$ system switches the carbocationic polymerization mechanism to the coordination Ziegler–Natta polymerization. The phenomenon of switching of polymerization mechanism is well known for the metal-catalyzed polymerization of alkenes [31].

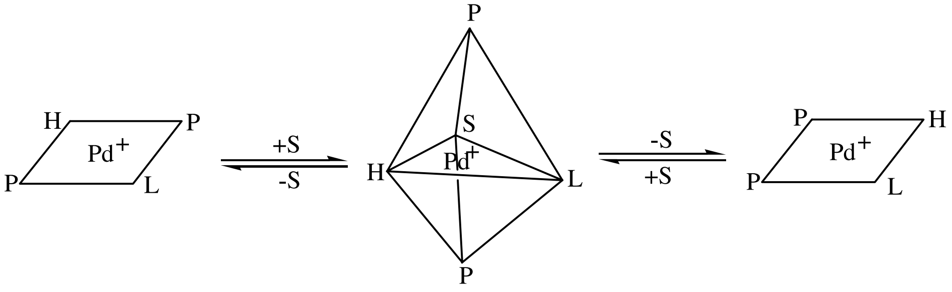
Clearly, if the insertion of monomer into the palladium–polymer bond involves the adjacent in-plane sites, it is only in the *cis*-form that chain growth can occur. Two monodentate phosphine can coordinate with both *cis* and *trans* stereochemistry. The observed induction period (Table 3) might be caused 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 [32]. From the data obtained above, it may be concluded that the increased thermal stability of the Pd(acac)$_2$/PPh$_3$/BF$_3$OEt$_2$ system compared with that without phosphine ligand may be addressed to the incorporation of phosphine ligand into the inner coordination sphere of the active complex thus preventing easy decomposition and aggregation of palladium particles.

In the case of 5-alkyl-2-norbornene monomers, the decrease of reactivity and polymerizability for the 5-alkyl-2-norbornenes might be explained by an unfavorable interaction between the substituent and the vinylic hydrogen that is being rehybridized from sp^2 to sp^3 upon coordination of monomer to palladium in the *endo* isomer even for coordination to palladium through the *exo* face, as described by Sen et al. (Scheme 2) [11]:

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

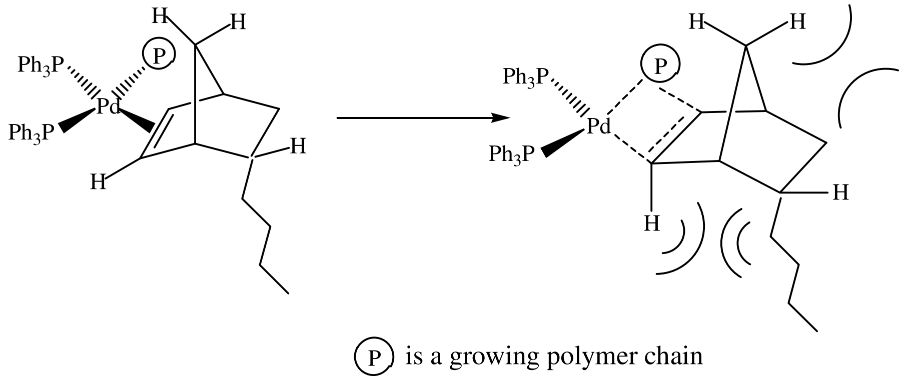
The results obtained prompted us to test the Pd(acac)$_2$/2PPh$_3$/25BF$_3$OEt$_2$ system in the copolymerization of 5-alkyl-2-norbornenes with norbornene. In the copolymerization runs equimolar mixtures of 5-alkyl-2-norbornene and norbornene were employed and the (AlkNB + NB)/Pd ratio was 4500, similar to homopolymerization runs. The copolymers of 5-alkyl-2-norbornenes with norbornene were characterized using NMR, GPC, TGA and DSC methods and elemental analysis and results are summarized in Table 5. The ^{13}C NMR spectra of the poly(5-propyl-2-norbornene) and copolymer of 5-propyl-2-norbornene with norbornene are shown in Fig. 4 as an example. The only difference in these spectra is the integral intensity ratio in the region from 55 to 25 ppm. When the peaks at 14.4 ppm attributable to CH$_3$ groups are normalized, it was possible to determine the composition of the copolymer: subtraction the integral intensity of the poly(5-propyl-2-norbornene) from that of the copolymer gives the content of norbornene units in the copolymer. The determined compositions of the copolymers were confirmed by the elemental analysis.

As can be seen from Table 5, the observed yields of copolymers were in agreement and little lower than that expected theoretically based on the assumption of complete consumption of norbornene. This small deviation is, again, due to loss of products during workup. In the series of alkyl chain length from propyl to decyl the incorporation of 5-alkyl-2-norbornene into the copolymer decreased from 50 to 33% due to their lowering reactivity. A decrease of the decomposition and glass transition temperatures, as well as of the molecular weights was observed with increasing number of carbons of the substituent. Unimodal molecular



S is solvent or ligand

Scheme 1. *Trans* to *cis* isomerization of active species.



Scheme 2. Steric compression in the insertion of *endo*-BuNB.

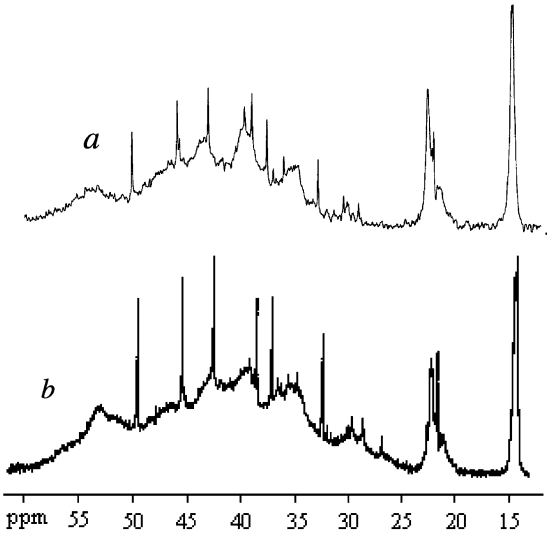


Fig. 4. ^{13}C NMR spectra of poly(5-propyl-2-norbornene) (a) and copolymer of 5-propyl-2-norbornene and norbornene (b).

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 the polymers are 'true' copolymers without homopolymers. Indeed, the copolymers all showed single glass transition and decomposition temperatures (Figs. 5 and 6).

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

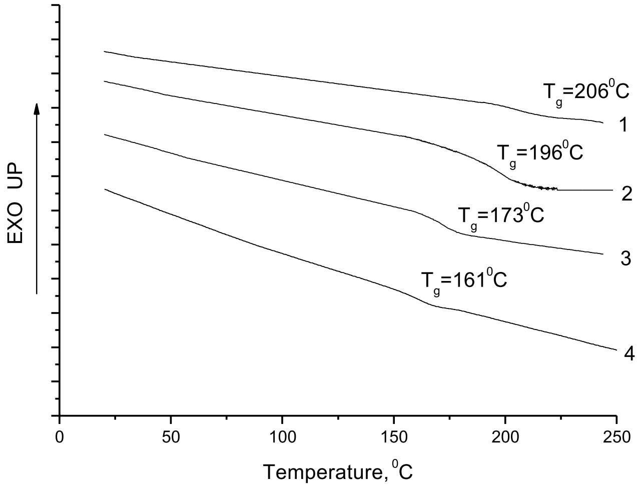


Fig. 5. DSC analyses of copolymers of 5-alkyl-2-norborbornenes with norbornene: PrNB–NB (1); BuNB–NB (2); HexNB–NB (3); DecNB–NB (4).

4. Conclusion

The homopolymerization of 5-alkyl-2-norbornenes and their copolymerization with norbornene were successfully carried out using Pd(acac)$_2$/PPh$_3$/BF$_3$OEt$_2$ catalyst system. The activity of the catalyst system is comparable to that of most active late transition metal catalysts described in the literature. The incorporation 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

Table 5
Copolymerization of 5-alkyl-2-norbornenes (AlkNB) and norbornene (NB) over Pd(acac)$_2$/2PPh$_3$/25BF$_3$OEt$_2$ catalyst system

Type of R	NB/AlkNB (mol ratio)	Yield (obs.) (g)	Yield (theor.) (g)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_g (°C)	T_{dec} (°C)
H	50/50	2.01	2.12	34000	74000	2.18	285	335
C_3H_7	50/50	2.52	2.59	73000	94000	1.29	206	285
C_4H_9	56/44	2.25	2.39	29000	58000	2.00	196	315
C_6H_{11}	60/40	2.24	2.40	15000	37000	2.47	173	284
$C_{10}H_{21}$	67/33	2.10	2.36	6700	16500	2.46	161	278

Experimental conditions: [Pd] = 5×10^{-6} M, (AlkNB + NB)/Pd = 4500, equimolar mixture of AlkNB and NB, 65 °C, total volume 7 ml.

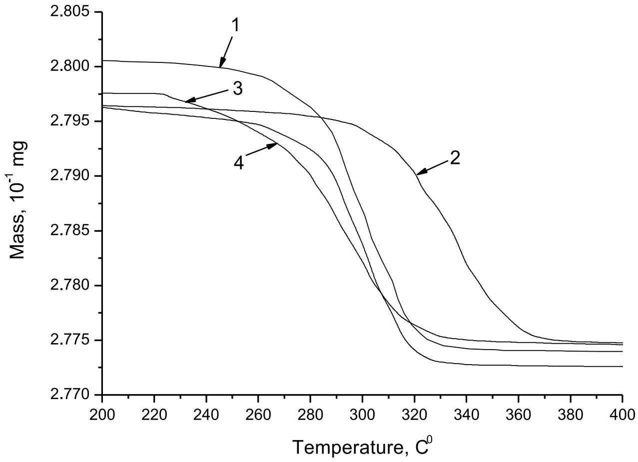


Fig. 6. TGA analyses of copolymers of 5-alkyl-2-norborbornenes with norbornene: PrNB–NB (1); BuNB–NB (2); HexNB–NB (3); DecNB–NB (4).

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 almost certainly possess 2,3-enchained repeating units of polymer backbone. The introduction of an ancillary phosphine ligand PPh_3 to the $Pd(acac)_2/BF_3OEt_2$ system switches the carbocationic polymerization mechanism to the coordination Ziegler–Natta polymerization. The simplicity of catalytic system composition might be of industrial importance.

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