

Nickel Catalysts for the Addition Polymerization of Norbornene and Its Derivatives and for Their Copolymerization with Ethylene

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Abstract—The addition polymerization of norbornene and its derivatives has been carried out in the presence of a nickel complex or carboxylate and an electron acceptor to obtain amorphous polymers with bicyclic units. Norbornene copolymers with conjugated dienes or ethylene cannot be obtained with these catalysts because of rapid chain transfer reactions. Norbornene can be copolymerized with ethylene under mild conditions in the presence of nickel phosphorylide chelates without using any cocatalyst. In most cases, the backbone of the resulting copolymer consists of alternating comonomer units. The new catalysts allow ethylene to be copolymerized with norbornene derivatives containing ester substituents.

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High-molecular-weight addition polymers of monocyclic olefins (cyclobutene and cyclopentene) and of norbornene derivatives, whose backbone contains cyclic units, were for the first time synthesized by Kaminsky and his colleagues in the late 1980s [1]. Polymerization was carried out in the presence of catalysts consisting of an *ansa*-zirconocene and methylalumoxane. Later, palladium [2] and nickel [3] complexes were applied to the addition polymerization of norbornene. Since then, a variety of catalysts based on transition metals (Ni, Pd, Co, Cr, Zr, and Ti) have been developed for this process.

Amorphous saturated norbornene polymers containing bicyclic units are interesting because they combine remarkable properties: chemical and thermal stability, high transparency, low hygroscopicity, and good mechanical and dielectric characteristics [4]. However, the addition polymers of norbornene have a high glass transition temperature (T_g) close to their decomposition temperature ($\sim 400^\circ\text{C}$). Therefore, they cannot be processed by conventional methods. In order to introduce flexible units into the very rigid polynorbornene chain and thereby reduce T_g , some laboratories have attempted norbornene copolymerization with olefin monomers. The first success in this approach was norbornene–ethylene copolymerization in the presence of zirconocene catalysts [5]. Later, this technology was refined and commercialized by researchers of Hoechst AG [6]. At present, norbornene–ethylene copolymers are manufactured by Ticona GmbH. (trade mark Topas) [7].

Here, we report norbornene–ethylene copolymerization in the presence of specific nickel catalysts. Furthermore, we present some unpublished results concerning norbornene homopolymerization.

EXPERIMENTAL

Norbornene (Aldrich) was distilled in flowing argon. Norbornene solutions were stored in an argon atmosphere over sodium wire in Schlenk flasks. 5-Hexylnorbornene (BF Goodrich) was distilled in *vacuo*. Ethylaluminum sesquichloride, bis(cyclooctadiene)nickel, methyl diphenylphosphine, dimethylphenylphosphine (all from Aldrich), triphenylphosphine (Fluka), and acetyl methylene triphenylphosphorane (Fluka) were used as received. Bis(π -pentenylnickel chloride) was obtained from pentenyl chloride and $\text{Ni}(\text{CO})_4$ by the Fischer method [8]. Benzoylmethylenetriphenylphosphorane, $\text{PPh}_3=\text{CHC}(\text{O})\text{Ph}$, was synthesized from PPh_3 and phenacyl bromide by a procedure described in [9].

The solvents were purified by standard methods used in organometallic chemistry. All manipulations involved in the preparation of norbornene solutions and catalysts and in the charging of components into the reactor were made in an oxygen- and water-free argon atmosphere. Copolymerization was carried out in a 80-ml stainless steel reactor fitted with a magnetic stirrer.

The composition of resulting copolymers was determined by ^1H NMR spectroscopy in CDCl_3 . NMR spectra were recorded on a Bruker Model MSL-300 spectrometer. IR spectra of the ylides and copolymers synthesized were recorded on a Specord M-82 spectrophotometer. DSC studies were carried out using a Mettler calorimeter (heating rate, 20 K/min). The molecular-weight distribution of copolymers was determined by gel permeation chromatography on a Waters chromatograph.

Table 1. Polymerization of norbornene (NB) in toluene at 20°C with nickel catalysts ([NB] = 2.5 mol/l)

Catalyst	Cocatalyst (CC)	CC/Ni, mol/mol	NB/Ni, mol/mol	Time, h	Polymer yield, %	[η], dl/g
$(C_5H_9NiCl)_2$	No	—	65	72	Traces	—
	$Ni(OCOCCl_3)_2$	2	65	20	100	0.72
	$BF_3 \cdot OEt_2$	1	1000	1	95	0.29
	$Et_3Al_2Cl_3$	3	2000	2	95	0.48
Nickel dinaphthenate	"	5	2000	2	99	0.43
$Ni(OCOCCl_3)_2$	"	5	1300	1	92	0.20
$Ni(SA)_2^*$	"	10	3200	4.5	89	—
$Ni(PSAI)_2^{**}$	"	10	4000	4.5	70	0.80

* $Ni(SA)_2$ = bis(salicylaldehyde)nickel(II).

** $Ni(PSAI)_2$ = bis(N-diisopropylphenylsalicylaldimine)nickel(II).

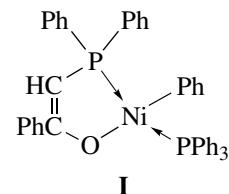
RESULTS AND DISCUSSION

Initially, we tested, in norbornene polymerization, nickel π -allyl complexes, which are known to be effective in the stereospecific polymerization of dienes. π -Pentenylnickel chloride appeared to be almost ineffective: only small amounts of liquid norbornene oligomers were detected. However, complexes obtained by reacting π -pentenylnickel chloride with various electron acceptors, such as nickel trichloroacetate, ether- BF_3 complex, and particularly alkylaluminum chlorides, effectively catalyzed the addition polymerization of norbornene. Later, it was found that the nickel π -allyl complex can be replaced with a nickel carboxylate or a nickel bis chelate. The results obtained are presented in Table 1. In all cases, we prepared saturated amorphous polymers with a relatively high molecular weight and a high T_g value. These polymers are well soluble in chlorinated arenes (chlorobenzene and dichlorobenzene) and cyclohexane and are insoluble in toluene and chloroform. Furthermore, we synthesized addition polymers of some norbornene derivatives (*endo*-dicyclopentadiene, *exo*-dicyclopentadiene, *endo,exo*-tetracyclododecene, and 5-subsituted alkynorbornenes). The activity of these monomers depends strongly on their conformation: the *exo* conformers polymerize much more rapidly than the *endo* conformers, particularly in the case of dicyclopentadiene. In 72 h, dicyclopentadiene containing ~97% *endo* conformer is polymerized into a low-molecular-weight polymer with $M_w = 2800$ in 55% yield. By contrast, specially synthesized *exo*-dicyclopentadiene polymerizes nearly as rapidly as norbornene. In this case, the yield of amorphous polymer is 75% in 1.5 h. This polymer has $M_w = 130000$ and is readily soluble in toluene and chloroform. Like polynorbornene, it does not vitrify up to the decomposition temperature (~400°C).

Our attempts to copolymerize norbornene with conjugated dienes (butadiene and isoprene) or ethylene have been unsuccessful. With dienes, we obtained semiliquid polymers with $M_w = 4000$ –6000 and $M_n =$

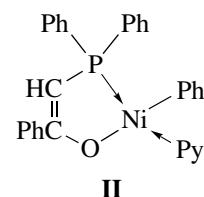
1800–2500 that consisted mainly of norbornene units and contained only one or two diene units. Copolymerization with ethylene resulted only in low-molecular-weight polynorbornene with terminal vinyl groups because of chain transfer occurring at a high rate.

In searching for a norbornene–ethylene copolymerization catalyst, we looked at nickel phosphorylide complexes. Keim et al. [10] reported the ylide complex **I** as an effective catalyst for ethylene oligomerization.



The phosphine ligand ensures chain transfer and the formation of C_8 – C_{30} ethylene oligomers. Later, it was found that replacing PPh_3 in **I** with a less strongly bonded ligand, such as pyridine, results in high-molecular-weight polyethylene rather than oligomers [11].

We assumed that such complexes can initiate norbornene–ethylene copolymerization as well. The pyridine-containing complex **II**,



was synthesized by reacting equimolar amounts of benzoylmethylenetriphosphorane and $(\pi-C_8H_{12})_2Ni(0)$ in the presence of pyridine. At room temperature, this complex was almost inactive in norbornene homopolymerization. In contrast, norbornene–ethylene copolymerization in toluene in the presence of **II** occurred even at low temperatures (Table 2) and did not require any cocatalyst. The use of nickel phosphorylide com-

Table 2. Copolymerization of norbornene (NB) and ethylene in the presence of complex **II**

Run no.	Amount of NB, g	T, °C	Ethylene pressure, atm	Time, h	Polymer yield, g	T _g , °C	NB in the copolymer, mol %	M _w × 10 ³	M _n × 10 ³
1	0.68	20	20	3	0.94	75	29	16.8	8.2
2	0.68	20	5	3.5	0.78	99	36	15.1	7.7
3	0.68	20	1	6	0.12	144	48	13.8	7.6
4*	1.25	50	5	4	0.30	153	50	7.4	2.8
5**	4.4	20	5	4	0.59	125	43	32.5	20.5
6	0.68	80	5	4	0.30	126	43	5.1	1.7

Note: NB : **II** = 300 (mol/mol); the solvent is toluene.

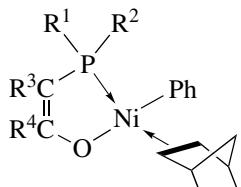
*Copolymerization in molten NB.

An equimolar amount of (C₈N₁₂)₂Ni(0) is added to complex **II.

plexes in norbornene–ethylene copolymerization was patented together with BF Goodrich [12].

Unlike polynorbornene, the copolymers obtained with complex **II** are readily soluble in ordinary organic solvents. According to DSC data, the copolymers are amorphous and show only one phase transition, specifically, a glass transition at 125–150°C. They have a comparatively low molecular weight (usually $M_w \leq 2 \times 10^4$) and a unimodal molecular-weight distribution. Equimolar amounts of (π -C₈H₁₂)₂Ni(0) added to the catalyst allow the molecular weight to be somewhat increased. The composition of the copolymers was derived from ¹H NMR data, making use of the fact that the signals between 1.7 and 2.4 ppm are from two types of protons in the norbornene unit. As a rule, these copolymers contained 40–50 mol % norbornene units. Raising the polymerization temperature to 50–70°C reduces both the activity of the catalyst and the molecular weight of the copolymer.

In some experiments, the catalyst was prepared *in situ* by charging the reactor with solutions of the ylide and (π -C₈H₁₂)₂Ni(0) in the presence of norbornene. In this case, norbornene served as a weakly bonded ligand. In order to study the effect of the structure of the complex on the catalytic activity and on the properties of the copolymer, we synthesized a series of ylides with substituents in different positions of the ylide structure. A series of nickel complexes with general formula **III** was obtained *in situ* from these ylides, and these complexes were tested in norbornene–ethylene copolymerization (Table 3).

**III**

(R¹, R² = Ph, Me; R³ = H, NaO₃S, MeO₃S, HO₃S, C₁₄H₂₉O₃S; R⁴ = Ph, Me, H, OEt)

The nickel ylide complexes show different activities. Relatively high yields of copolymers with moderate molecular weights can be obtained only with a complex prepared from benzylmethyltriphenylphosphorane or acetyl methyltriphenylphosphorane.

Note that the successive replacement of phenyl groups at the phosphorus atom by methyl groups causes a considerable decrease in catalytic activity and, at the same time, increases the proportion of norbornene units in the resulting copolymers from 40–50 to >60 mol %. This is accompanied by an increase in T_g . Spectroscopic data indicate the presence of norbornene–norbornene dyads in these copolymers.

In order to increase the molecular weight of the copolymers, we carried out norbornene–ethylene copolymerization at lower catalyst concentrations (Table 3). Although copolymerization in this case is much slower at room temperature, it affords large amounts of copolymers with molecular weights up to 10⁵.

The ylide catalysts were also used in the synthesis of ethylene–hexylnorbornene copolymers and ternary copolymers of ethylene, norbornene, and substituted norbornene containing hexyl or trimethylsilyl groups.

It was noted above that norbornene–ethylene copolymers obtained in the presence of the nickel ylide catalyst usually contain comonomer units in nearly equimolar proportions. The mechanism of the formation of these copolymers can be viewed as follows: the norbornene molecule coordinated to the Ni atom cannot insert itself into the Ni–phenyl or Ni–norbornyl bond for steric reasons, while the insertion of ethylene into these bonds takes place readily. This yields a copolymer in which comonomer units alternate with a high degree of regularity.

The nickel phosphorylide complexes allow ethylene to be copolymerized with functionalized norbornenes. We synthesized copolymers of ethylene and norbornene with ester substituents, namely, 5-methylcarboxy and 5-*tert*-butylcarboxy groups. These norbornene derivatives copolymerize much slower than unsubstituted norbornene. The copolymer yield is 30–60% in 5–10 days. The copolymers have a low molec-

Table 3. Copolymerization of norbornene (NB) and ethylene at 20°C in toluene with catalyst **III** ($E^3 = H$) obtained in situ

Run no.	R ¹	R ²	R ⁴	NB, g	Ethylene pressure, atm	NB/Ni, mol/nol	Time, h	Copolymer yield, g	T _g , °C	NB in the copolymer, mol %	M _w × 10 ³	M _n × 10 ³
1	Ph	Ph	Me	2.4	7	300 : 1	20	0.87	146	49	27.6	15.7
2	Ph	Ph	Me	16.4	7	800 : 1	20	3.1	143	48	89.3	56.1
3	Ph	Ph	Me	28.0	10	2000 : 1	70	14.0	138	46	99.4	44.7
4	Ph	Ph	Me	25.6	14	3000 : 1	20	13.7	132	45	95.5	30.0
5	Ph	Ph	Me	25.6	14	6000 : 1	40	11.9	125	43	93.0	31.6
6	Ph	Ph	Ph	25.6	14	6000 : 1	40	12.1	123	42	71.7	50.2
7	Ph	Ph	H	6.4	14	6000 : 1	20	0.37	126	43	39.5	16.6
8	Ph	Me	Ph	3.5	2	300 : 1	48	0.40	164	55	25.7	12.4
9	Me	Me	Ph	2.8	7	300 : 1	170	0.38	182	62	53.1	26.2

ular weight of $M_n = 1700$ –2300. The composition of the ethylene–5-methylcarboxynorbornene copolymer was determined by ¹H NMR spectroscopy. The composition of the ethylene–5-*tert*-butylcarboxynorbornene copolymer was determined by IR spectroscopy: the proportion of functionalized norbornene units was estimated by comparing the integrated intensities of the 1460 cm^{–1} band (due to CH₂ in polyethylene) and the 1392 cm^{–1} band (due to the skeletal vibrations of the *tert*-butyl groups) or, independently, the 1152 cm^{–1} band (due to the stretching vibrations of the *tert*-BuO groups). The polymers were found to contain 15–40 mol % bicyclic units, and their T_g was measured to be 51–122°C. Note that the copolymers of ethylene with functionalized norbornenes cannot be obtained with zirconocene catalysts.

Thus, we have demonstrated that norbornene–ethylene copolymers can be synthesized using comparatively simple nickel phosphorylide complexes. Although these copolymerization catalysts are much less active than the systems based on zirconocene and methylalumoxane, they do not require any cocatalyst (e.g., alumoxane, which is an expensive chemical). Moreover, the lower oxophilicity of nickel in the ylide catalysts allows ethylene to be copolymerized with functionalized norbornenes.

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