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Vinyl-Type Addition Polymerization of Norbornene and Synthesis of Norbornene Macromonomers in the Presence of Ethylene Catalyzed by Cobalt(II)−Phosphine Complexes

Giuseppe Leone, Aldo Boglia, Antonella Caterina Boccia, Santolo Taglialatela Scafati, Fabio Bertini, and Giovanni Ricci*

CNR-Istituto per lo Studio delle Macromolecole (ISMAC), via Bassini 15, I-20133 Milano, Italy

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ABSTRACT: The polymerization of norbornene (NB) with catalysts obtained by combining cobalt(II)−phosphine complexes (i.e., $CoCl_2(PR_3)_2$, $CoCl_2(PRPh_2)_2$, R = alkyl or cycloalkyl group, Ph = phenyl) with methylaluminoxane (MAO) is reported. These systems exhibited excellent activity when used in an halohydrocarbon solvent, yielding amorphous, soluble vinyl-type poly(norbornene)s (PNB)s. The NB copolymerization with ethylene (E) was also examined. Norbornene macromonomers (M_n in the range 740−8740 g mol^{-1}) with a terminal vinyl group, likely originating from insertion of one ethylene molecule followed by a β-hydrogen elimination reaction, were obtained in almost 100% yield. By varying the NB starting concentration as well as the time and the polymerization temperature, it was possible to tune the molecular weight of the macromonomers which exhibited different T_g values upon the NB polymerization degree. The PNBs and the macromonomers were fully characterized by NMR analysis, and a reaction mechanism for the formation of the vinyl-end NB macromonomers in the copolymerization of NB with E is proposed.

Introduction

Vinyl-type addition is one of the three polymerization methods commonly used for preparing poly(norbornene)s, the other ones being ring-opening metathesis polymerization (ROMP) and the cationic or radical polymerization.[1] Vinyl-type polymerization of NB results in PNBs consisting of linked strained rings, which exhibit remarkable improvements in physical properties (e.g., excellent dielectric properties and optical transparency, chemical resistance, and mechanical properties) with respect to acyclic polymeric structures, and high T_g values up to 350 °C.[2] However, due to the high viscosity above T_g, vinyl-PNBs cannot be processed from the molten state, so that many researchers have been focused toward the synthesis of a melt-processable vinyl-type PNB in a temperature range above its T_g and below its degradation temperature. To improve processabilty of PNBs, NB was usually copolymerized with ethylene or others α-olefins by means of a coordinative-addition polymerization catalyzed by neutral or cationic metal compounds in combination with a suited cocatalyst activator. Amorphous thermoplastic cyclic olefin copolymers (COCs) with lower rigidity and high refractive indices, which make these materials suitable to be extruded to tubes and pipes and for optical data storage, were obtained.[3] Organometallic complexes containing several early (Ti, Zr, Hf, V), late (Pd, Ni), and rare-earth (Sc, Y) metals were used as catalyst precursors for the vinyl-addition polymerization of NB and E/N copolymerization and are widely described in the literature.[1,4−6] The development of single site metallocene and half-sandwich based catalysts has brought to several catalytic systems which gave E/NB copolymer with sequences of E repeating units, single E units, or even alternating E and NB sequences, depending on the metal precursor as well as on the polymerization conditions.[7−10] On the contrary, few reports have appeared so far on the homo- and copolymerization of NB with cobalt catalysts, for which both ROMP and addition polymerization are in principle possible depending on the reaction conditions as well as on the type of cocatalyst.[11]

In the present investigation we report on the polymerization of NB with the catalytic systems obtained by combining cobalt(II)−phosphine complexes $CoCl_2(PR_3)_2$ (PR_3 = di-*tert*-butylphosphine, P^tBu_2H; di-*tert*-butylmethylphosphine, P^tBu_2Me; tricyclopentylphosphine, $PCyp_3$) and $CoCl_2(PRPh_2)_2$ (R = methyl, Me; isopropyl, ^{i}Pr; cyclohexyl, Cy) (Chart 1) with MAO, yielding soluble, amorphous vinyl-type PNBs. The copolymerization of norbornene with ethylene was also examined. Vinyl-end NB macromonomers were obtained in almost 100% yield within a very short polymerization time. To date, the unique example of Co-catalyzed polymerization of NB in the presence of E yielding vinyl-end NB based macromonomers was reported by Heitz by using bis(benzoylacetonato)- $[(PhC_4H_5O_2)_2]$- and bis(trifluoroacetylacetonato)- $[(C_5H_4F_3O_2)_2]$- Co(II) complexes with MAO; the reported yield in macromonomers was about 25%.[12]

Thus, the results obtained in the polymerization of NB in the presence of E discussed herein clearly indicate the Co−phosphine catalysts as highly active systems (as up to 7900 kg mol Co^{-1} h^{-1}) for the preparation of vinyl-end NB macromonomers. The macromonomers exhibited molecular weights (M_n) in the range from 740 to 8740 g mol^{-1} and high T_g values, in the range 115−210 °C, depending on the M_ns as well as on the polymerization conditions (e.g., NB feedstock composition, polymerization temperature, and time).

An accurate NMR study of the polymers as well as of the macromonomers obtained, with a particular care to the type of chain-end groups, was carried out, allowing to formulate a plausible formation mechanism for the norbornene based macromonomers.

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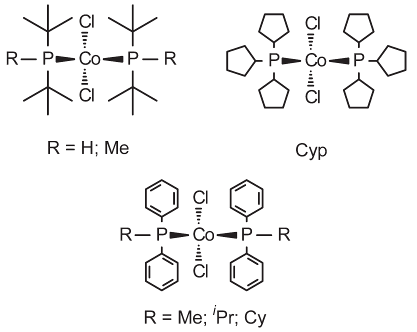
*Corresponding author. E-mail: giovanni.ricci@ismac.cnr.it.

Chart 1. Cobalt(II)−Phoshine Complexes



Experimental Section

Materials. Manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk-line techniques. Toluene (Fluka, >99.5% pure) was refluxed over Na for ca. 8 h and then distilled and stored over molecular sieves under nitrogen. 1,2-*o*-Dichlorobenzene (*o*-DCB) (Sigma-Aldrich, anhydrous grade) was degassed under vacuum and then by bubbling nitrogen, kept over molecular sieves, and used without any further purification. Methylaluminoxane (Crompton, 10 wt % solution in toluene) was used as received. Solid MAO (d-MAO) was prepared by removing toluene and unreacted free trimethylaluminum ($Al(CH_3)_3$) under vacuum from commercially available MAO solution. The resulting white powder was heated further to 50 °C under vacuum overnight. The cobalt alkylphosphine and diphenylalkylphoshine complexes were synthesized according to experimental procedures previous reported in the literature.[13] Norbornene (Aldrich, 99% pure) was stirred over molten potassium at 80 °C under nitrogen for 4 h and then distilled. A stock solution of NB was prepared by dissolving 50 g of freshly distilled NB in 86.21 mL of toluene or *o*-DCB (0.58 mg mL^{-1}). Ethylene was purified flowing through BTS catalysts, molecular sieves, and $CaCl_2$. Deuterated solvent for NMR measurements ($C_2D_2Cl_4$) (Cambridge Isotope Laboratories, Inc.) was used as received.

Polymerization Procedure. The polymerization experiments were carried out in a 25 mL round-bottomed Schlenk flask containing a stirring bar. The polymerization reactor was first dried by heating at 80 °C, and then vacuum was applied for 1 h at 40 °C.

Norbornene Polymerization. Norbornene polymerizations were carried out as follows: a toluene or *o*-DCB solution of the monomer was transferred into the reactor vessel; the solution was brought to the desired polymerization temperature; then MAO, as toluene or as *o*-DCB solution, and the cobalt compound were added in the order. Polymerizations were stopped with methanol containing a small amount of hydrochloric acid; the precipitated polymers were collected by filtration, repeatedly washed with fresh methanol, and then dried in vacuum at room temperature to constant weight.

Norbornene Polymerization in the Presence of Ethylene. The reactor vessel was charged with a solution of norbornene, and the solution was brought to the desired polymerization temperature. MAO was added; the solution was degassed and saturated with ethylene under vigorous stirring for 10 min. The polymerization was started by adding a solution of the cobalt compound under continuous flow of ethylene. Polymerizations were stopped as reported above.

Polymer Characterization. ^{13}C and ^{1}H NMR measurements were carried out on Bruker Avance 400 spectrometer operating at 400 MHz for ^{1}H NMR and at 100.58 MHz for ^{13}C NMR measurements. The spectra were obtained in $C_2D_2Cl_4$ at 103 °C using hexamethyldisiloxane (HMDS) as internal standard. The concentration of the polymer solutions was about 10 wt %. Differential scanning calorimetry (DSC) scans were carried out on a Perkin-Elmer Pyris 1 instrument. Typically, ca. 10 mg of polymer was analyzed in each run, with a scan speed of 20 °C/min under a nitrogen atmosphere. T_g was recorded during a second thermal cycle. The molecular weight averages (M_n) and the molecular weight distribution (M_w/M_n) were obtained by a high-temperature Waters GPCV2000 size exclusion chromatography (SEC) system using two online detectors: a differential viscometer and a refractometer. The experimental conditions consisted of three PL Gel Olexis columns, *o*-DCB as the mobile phase, 0.8 mL/min flow rate, and 145 °C temperature. The calibration of the SEC system was constructed using 18 narrow MWD polystyrene standards with molar weights ranging from 162 to 5.6×10^6 g mol^{-1}.

Results and Discussion

Norbornene Polymerization. The results obtained in the polymerization of NB with catalysts obtained by combining the cobalt−phosphine complexes with MAO are shown in Table 1 and can be summarized as follows.

(i) The Co−phosphine based catalysts were extremely active when the NB polymerization was carried out in *o*-DCB as medium solvent, and high monomer conversions were obtained over a very short polymerization time. Complete monomer conversions can also be obtained by slightly increasing the polymerization time. The NB polymerization activities were instead rather low when the polymerizations were carried out in toluene; nevertheless, quantitative yields could be obtained upon increasing the polymerization time as up to 24 h (Table 1, entries 3 and 5). The above results clearly suggest that the polarity of the solvent plays a fundamental role, strongly affecting the polymerization activities.[11,14] Considering that NB is a sterically encumbered cyclolefin monomer, the higher rate of NB incorporation using a more polar solvent can be associated with the sterically open nature of the active polymerization centers.[15]

(ii) The polymerization activities seem to be dependent on the steric demand of the ligand, being the cobalt complexes with more hindered phosphine ligands the most active systems. Such a behavior could be interpreted as follows: if we admit that the phospine ligand remains coordinated to the cobalt atom, a bulky ligand should favor the sterically open nature of the active polymerization centers and consequently allow a higher incorporation rate of a sterically hindered monomer such as norbornene. This is only a working hypothesis, and we are actually examining the polymerization of NB with other catalysts based on different cobalt−phosphine complexes in order to check this interpretation. For instance, the system $CoCl_2(PMePh_2)_2$−MAO, using a minimally hindered phosphine ligand, gave only polymer traces in toluene (Table 1, entry 7) and exhibited a rather low activity in *o*-DCB solvent (Table 1, entry 8), while the systems based on $CoCl_2(P^iPrPh_2)_2$ and $CoCl_2(PCyPh_2)_2$, having a more hindered phosphine ligand, were much more active (Table 1, entries 10 and 12, respectively). The $CoCl_2(PCyp_3)_2$−MAO catalyst too exhibited a very high polymerization activity as up to 14 760 kg of PNB mol Co^{-1} h^{-1} (Table 1, entry 6). Hence, the choice of a polar solvent as well as of a Co compound with a high hindered phosphine ligand as catalyst component seems to be the right one to afford excellent PNB yields in a very short polymerization time.

(iii) Molecular weights were in general higher for the polymers obtained in toluene, whereas the M_w/M_ns were narrower with respect to PNBs obtained in *o*-DCB as solvent. Thus, these experimental results, in agreement with an enhanced polymerization activity observed in *o*-DCD

Table 1. Polymerization of Norbornene Catalyzed by Cobalt−Phosphine with MAO[a]

entry	solvent (type)	cobalt compound	time (min)	yield (%)	activity[b]	M_n[c] (g mol^{-1})	M_w/M_n[c]
1	toluene	$CoCl_2(P^tBu_2H)_2$	1440	47	4	ns[d]	
2[e]	o-DCB		1	36	8 640	45 800	5.5
3	toluene	$CoCl_2(P^tBu_2Me)_2$	1440	100		846 000	1.7
4	o-DCB		1	87	10 500	121 800	3.4
5	toluene	$CoCl_2(PCyp_3)_2$	1440	100		ns[d]	
6[e]	o-DCB		1	62	14 760	110 000	2.1
7	toluene	$CoCl_2(PMePh_2)_2$	1440	traces			
8	o-DCB		5	78	1 900	nd[f]	
9	toluene	$CoCl_2(P^iPrPh_2)_2$	1440	35	3	ns[d]	
10[e]	o-DCB		5	84	4 032	112 100	4.8
11	toluene	$CoCl_2(PCyPh_2)_2$	1440	19	2	402 300	2.9
12	o-DCB		1	100		89 000	5.2

[a] Polymerization conditions: total volume, 18 mL; NB, 2 g; Co, 1×10^{-5} mol; Al/Co molar ratio = 1000; temperature, 25 °C. [b] Given in kg of PNB mol Co^{-1} h^{-1}. [c] Determined by SEC in o-DCB by using standard polystyrene calibration. [d] Insoluble. [e] Co, 5×10^{-6} mol. [f] Not determined.

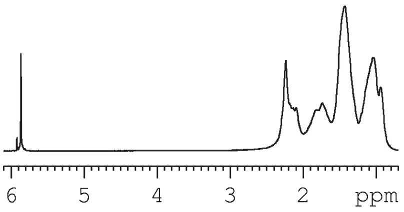
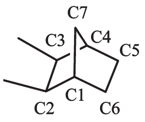


Figure 1. ^1H NMR spectrum of PNB obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 1, entry 10).

ppm	*mr*	*rr*
C5	28.2	30.3 – 28.7
C6	29.0	30.3 – 28.7
C7	33.3	34.9 – 35.5
C4	37.8	36.5 – 37.2
C1	38.6 – 41.0	36.5 – 37.2
C3	45.7	44.1 – 49.7
C2	49.8	44.1 – 49.7



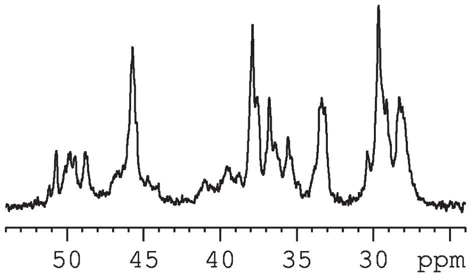


Figure 2. ^{13}C NMR spectrum of PNB obtained with $CoCl_2(P^iPrPh_2)_2$−MAO (Table 1, entry 10). The numbering scheme of *cis*-2,3-*exo*-enchained PNB is also reported.

solvent, seem to suggest the formation of a larger number and type of active centers when the polymerizations were carried out in a polar solvent.

The polymer microstructure was investigated by NMR and IR spectroscopy. The absence of any signal at 5.1 ppm in the ^1H NMR spectra of the PNBs (Figure 1) and of any band at 1680−1620 cm^{-1} in the infrared spectra was indicative of a vinyl-type nature of the polymers.[16]

The ^{13}C NMR spectrum of PNB obtained with $CoCl_2(P^iPrPh_2)_2$−MAO is shown in Figure 2. The peaks were attributed on the basis of ^{13}C DEPT experiments and by comparison with ^{13}C NMR chemical shifts of PNBs already reported in the literature.[17] The NMR spectra of all the other PNBs reported in Table 1 were very similar to those shown in Figures 1 and 2, meaning that the nature of the phosphine ligand bonded to the Co atom has no influence on the polymer microstructure (i.e., on the polymerization selectivity).

The broad unresolved nature of the ^{13}C NMR spectra made it difficult to assign the exact microstructure to PNBs. The carbon atoms are in the following spectral region: C5/C6 (30.8−26.4 ppm); C7 (35.9−32 ppm); C4/C1 (41.7−36.0 ppm); C3/C2 (52.2−43.7 ppm). By studying in details the spectrum of Figure 2, it appears clear that the PNBs under investigation have an atactic structure, with predominance of syndiotactic sequences. Indeed, the spectrum evidence three main sharp resonances assigned, respectively, to C6, C4, and C3, and four broad resonances assigned to C5, C7, C1, and C2 carbon atoms.[18] All the assignments are listed in the table reported in Figure 2, distinguished for tacticity.

PNBs listed in Table 1 were amorphous on wide-angle X-ray scattering investigations, in agreement with the atactic structure suggested by the NMR analysis.

Norbornene Polymerization in the Presence of Ethylene. Experimental data and general polymerization conditions (i.e., NB feedstock composition, polymerization temperature, and time) for some selected NB polymerizations in the presence of E with the catalyst systems based on $CoCl_2(P^tBu_2Me)_2$, $CoCl_2(PCyp_3)_2$, and $CoCl_2(P^iPrPh_2)_2$ are reported in Table 2.

Under the conditions employed, the Co−phosphine catalysts were completely inactive toward the ethylene polymerization, whereas the copolymerizations of NB with E exhibited an excellent activity. Low-M_n products soluble in common organic solvents such as toluene, THF, and benzene were obtained in almost 100% yield.

The polymeric materials obtained were characterized by NMR spectroscopy with the aim to determine their nature and microstructure. The ^1H NMR spectrum shown in Figure 3 evidences signals in the aliphatic region between 0.8 and 2.4 ppm (maxima at 0.94, 1.04, 1.43, 1.70, and 2.37 ppm), very similar to that observed in the PNB spectra (Figure 1). Moreover, two further resonances were detected at low field. The first multiplet, centered at 4.89 ppm, was attributed to $=CH_2$ protons, while the second multiplet, centered at 5.69 ppm, was assigned to the $-CH=$ proton: the relative intensities of the two multiplets were about in a 2:1 ratio. Analogously in the ^{13}C NMR spectrum (Figure 4) two resonances at about 111.9 and 139.9 ppm, respectively, attributable to an olefinic end group $CH_2{=}CH-$, likely arising from a β-hydride elimination chain transfer, were observed. Therefore, since the planar conformation, normally required for β-H elimination, of a Co−polynorbornyl bond intermediate in the *exo* position and of the β-H-carbon

Table 2. Polymerization of Norbornene in the Presence of Ethylene[a]

entry	cobalt compound	NB (mol L^{-1})	T (°C)	time (min)	yield[b] (%)	activity[c]	M_n[d] (g mol^{-1})	M_w/M_n[d]	T_g[e] (°C)
13	$CoCl_2(PCyp_3)_2$	2.54	25	5	77	7920	3394	5.4	nd[f]
14		1.77	25	5	83	5970	2341	4.6	nd[f]
15		1.18	25	5	80	3864	1926	3.3	210
16		0.77	25	5	55	1706	1405	2.3	148
17		0.36	25	5	47	672	981	1.6	126
18		1.18	0	5	82	3960	1775	2.9	167
19		1.18	−20	5	53	2520	1237	1.8	162
20		0.77	0	5	49	1526	1285	1.9	152
21		0.36	25	60	72	86	8741	3.2	nd[f]
22		0.36	25	1	21	300	740	1.4	115
23		0.36	0	5	traces				
24	$CoCl_2(P^tBu_2Me)_2$[g]	1.18	0	20	54	1080	1302	1.8	152
25		1.18	−20	20	29	575	1013	1.6	128
26	$CoCl_2(P^iPrPh_2)_2$[g]	1.18	25	3	24	3200	2011	2.4	187
27		1.18	0	3	21	2800	1288	1.7	150

[a] Polymerization conditions: *o*-DCB as solvent, total volume 18 mL; Co, 5×10^{-6} mol ; Al/Co molar ratio = 1000, $p_E = 1.01$ bar. [b] Based on NB conversion. [c] Given in kg-macromonomer·mol Co^{-1} h^{-1}. [d] Determined by SEC in *o*-DCB by using standard polystyrene calibration. [e] Measured by DSC. [f] Not detected. [g] Co, 3×10^{-6} mol.

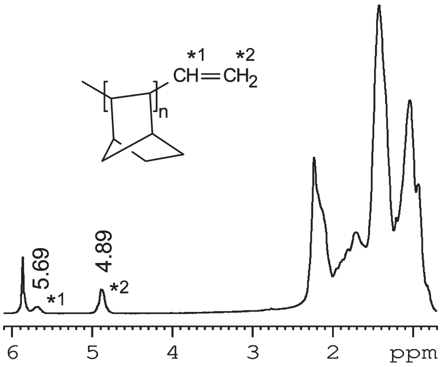


Figure 3. ^1H NMR spectrum of NB macromonomer obtained with $CoCl_2(P^tBu_2Me)_2$−MAO (Table 2, entry 25).

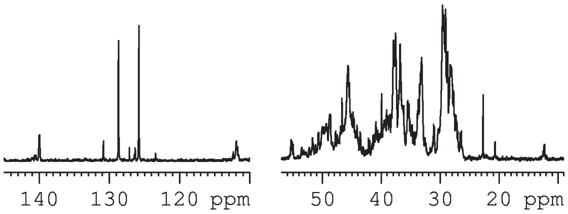


Figure 4. ^{13}C NMR spectrum of NB macromonomer obtained with $CoCl_2(P^tBu_2Me)_2$−MAO (Table 2, entry 25).

bond in the *endo* position is prohibited by Bredt's rule,[7d,19] the vinyl end group $CH_2{=}CH{-}NB{-}$ can be formed only through an insertion of an E molecule into the NB last inserted unit.[20,21] Thus, ethylene acts as an effective transfer agent in the vinyl-type NB polymerization mediated by Co−phosphine catalysts and MAO, yielding low-M_n vinyl-end NB oligomers, as observed by Goodall and Ihm with Ni-transition-metal catalysts.[21,22]

A series of NB/E copolymerizations with the system $CoCl_2(PCyp_3)_2$−MAO were carried out by varying the NB starting concentration (from 0.36 to 2.54 mol L^{-1}), the polymerization temperature (in the range −20 to +25 °C), and the polymerization time, in order to evaluate the influence of the reaction parameters on the polymerization activity, polymer molecular weight (M_n), molecular weight distribution (M_w/M_n), and glass transition temperature (T_g). The following observations can be made.

(i) With increasing the NB starting concentration, the catalytic activity at 25 °C increases linearly within 5 min of polymerization as well as M_n goes from 981 to 3394 g mol^{-1} (Table 2, entries 13−17). Figure 5 displays the SEC curves of NB macromonomers prepared for different NB feedstock composition at 25 °C.

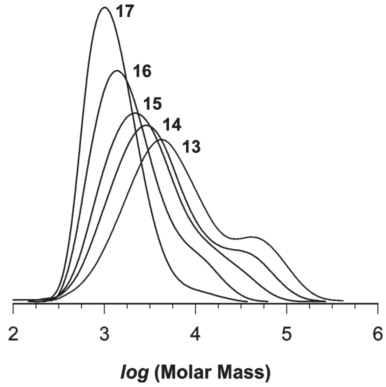


Figure 5. SEC curves of NB macromonomers obtained with $CoCl_2(PCyp_3)_2$−MAO at different NB feedstock composition (Table 2, entries 13−17).

At NB poor feed conditions (0.36 mol NB L^{-1}) a narrow and nearly Gaussian molecular weight distribution was obtained. In contrast, as the charged NB increases, the curve transforms into the broader distribution, while shifting to higher M_ns. Specifically, the SEC curves of the samples prepared at 2.54 and 1.77 mol NB L^{-1} (Figure 5, entries 13 and 14 of Table 2) show a low molecular weight peak at about 4306 and 2964 g mol^{-1}, respectively, and then a broader shoulder tail at higher M_n. As reported above, a maximum ethylene consumption was in general observed in the first minutes of the polymerization, while, after the initial stage, the insertion rate of E seems to decrease. It follows that, in the case of high NB feed concentration, low-M_n macromonomers are most likely formed at the beginning of the polymerization, whereas higher M_n macromonomers are likely obtained after the initial polymerization stage, when the NB concentration is still high and the E insertion rate lower with respect to the initial stage. This fact could explain the bimodal distribution observed at higher NB feedstock concentration.

Therefore, the NB starting concentration significantly affects M_n as well as M_w/M_n; i.e., the catalyst $CoCl_2(PCyp_3)_2$−MAO gave macromonomers with a broader M_w/M_n when the charged NB is in the range 0.77−2.54 mol L^{-1}. In contrast, narrow M_w/M_n resulted by using NB poor starting concentrations (e.g., 0.36 mol NB L^{-1}).

(ii) The polymerization temperature seems to have no effect on the activity when the polymerizations are carried out in the range 0−25 °C (Table 2, entries 15 and 18, 16 and 20, 26 and 27). However, at lower polymerization temperature (−20 °C) a general decreasing of the activity is observed (Table 2, entries 19 and 25), and in the case of very low starting NB concentration (Table 2, entry 24) only polymer traces are obtained also at 0 °C. In addition, a decreasing of the polymer M_n and M_w/M_n with decreasing of the polymerization temperature is also observed, likely due to a higher decreasing of the norbornene polymerization rate with respect to the ethylene insertion rate at low temperature. The higher ethylene insertion rate observed is in agreement with the increase of the ethylene solubility at low temperature.

(iii) The influence of the polymerization time on the molecular weight and molecular weight distribution was also investigated. Some experiments were carried out at a NB feed concentration of 0.36 mol L^{-1} at 25 °C over the range of time from 1 to 60 min (Table 2, entries 21, 17, and 21). As the time of polymerization was raised, the NB conversion resulted increased; the M_n strongly increased as up to 8741 g mol^{-1} for 60 min as well as the M_w/M_n (Table 2, entry 22 M_w/M_n = 1.4 and entry 21 M_w/M_n = 3.2). Upon the increase of the polymerization time to 60 min the SEC curves did not show a bimodal distribution, but a broader tail at lower molecular weight, meaning that, at longer reaction time, the NB propagation step resulted favored with respect to the β-hydrogen abstraction chain transfer. This finding is in agreement with the maximum ethylene consumption observed in the first minutes of the polymerization reaction.

(iv) The T_g values of the macromonomers having a M_n values up to 2000 g mol^{-1} appear to be related to their molecular weight, increasing with increasing the M_n values. The slight deviations in T_g values observed could be also attributable to some differences in stereoregularity which might influence the local stiffness of the NB macromonomer chains and therefore the T_g. For macromonomer M_n greater than 2000 g mol^{-1} nothing can be said, since the measurement of the T_g by DSC technique results difficult, probably due to a degradation pathway of the polymers.

The polymer molecular weights determined by SEC analysis were compared with those obtained through NMR spectroscopy. Being the signals attributable to the vinyl end group well detectable in the ^{1}H NMR spectra of the macromonomers (Figure 3), the polymerization number-average degree P_n was determined by applying the following equation:

$$P_n = (B/A)/5 \tag{1}$$

where $B = I_{Hn}$ is the total area of the peaks in the range 0.7−2.5 ppm, substantially attributed to NB hydrogens (the H—NB— chain was neglected), and $A = I_{Ht}$ is the area of the peak at 4.87 ppm, due to the methylenic hydrogens (=CH_2) of the vinyl end group. Hence, the macromonomer M_ns can be obtained from P_n by applying the following equation:

$$M_n = (P_n \times 94.16 + 27.05)\ \text{g mol}^{-1} \tag{2}$$

In Table 3 some representative results for the M_n of macromonomers calculated by NMR spectroscopy are reported along the M_n obtained by SEC analysis. The number-average molecular weights of the macromonomers determined by ^{1}H NMR spectroscopy agree reasonably well with those determined by SEC analysis. Some differences may be attributable to experimental errors intrinsic to the NMR measurement as well as to the rough determination of the M_n by SEC analysis due to the relationship between the hydrodynamic volume and the molecular weight which is not the same for all polymers (polystyrene standard does not represent a good model for all classes of polymers).

Table 3. Molecular Weights of NB Macromonomers Determined by ^{1}H NMR and SEC

entry[a]	P_n[b] (^{1}H NMR)	M_n[c] (^{1}H NMR)	M_n[d] (SEC)
14	30	2861	2341
15	19	1769	1926
16	17	1627	1405
24	16	1533	1302
25	12	1194	1013
27	16	1524	1288

[a] The numbers correspond to those listed in Table 2. [b] Polymerization number-average degree, determined by eq 1. [c] Determined by eq 2. [d] Determined by SEC in o-DCB by using standard polystyrene calibration.

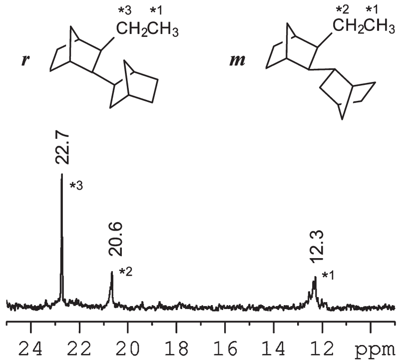


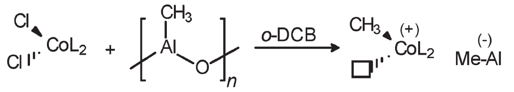
Figure 6. Expanded plot of the ^{13}C NMR spectrum of NB macromonomer obtained with $CoCl_2(P^tBu_2Me)_2$−MAO (Table 2, entry 25).

Chain-End Analysis of Norbornene Macromonomers. As already discussed, the ^{1}H and ^{13}C NMR spectra (Figures 3 and 4, respectively) clearly showed the presence of an unsatured end group in the NB chain as well as the chain-end units due to the polymerization initiation were clearly detectable from the ^{13}C NMR. An expansion of the ^{13}C NMR spectrum (from 25 to 9 ppm) is shown in Figure 6. On the basis of the studies reported by Fujita, Brintzinger, and Sen for the low-M_n E/NB copolymers obtained with catalysts based on bis(pyrrolide-imine) Ti, Zr metallocene, and Ni complexes,[20,21,23] we performed a detailed NMR study which allowed to formulate a possible mechanism of formation of the vinyl-end NB macromonomers under investigation.

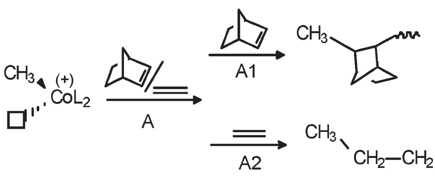
The active species formed upon the reaction of the cobalt−phosphine complex with MAO is likely an alkylated cationic cobalt—methyl (Co—Me) species (Scheme 1.i). Hence, if the polymerization reaction starts with a NB insertion into the Co—Me bond, the resulting polymer should have a chain-end structure such as CH_3—NB— (Scheme 1.ii, route A1). However, the peak at 15.8 ppm attributable to the methyl group bonded to the NB unit was not detected in the ^{13}C NMR spectra (Figure 6). This fact unequivocally suggests that E is the first unit to insert into the Co—Me (Scheme 1.ii, route A2). If the resulting Co−CH_2CH_2 intermediate is able to initiate the polymerization, the macromonomer obtained should have the chain-end structure CH_3—E—NB— (Scheme 1.iii, route B1) or CH_3—E—E— in case of a further E insertion (Scheme 1.iii, route B2). The signals at 14.8 and 14.1 ppm, attributable to the CH_3 of a n-propyl group and of a n-pentyl group, respectively, were not detected in the ^{13}C NMR spectra

Scheme 1. Possible Chain Initiation and Propagation Steps of Polymerization of NB in the Presence of E Derived from Co—Me and Formation of Co−H Active Species (□ = Vacant Coordination Site)

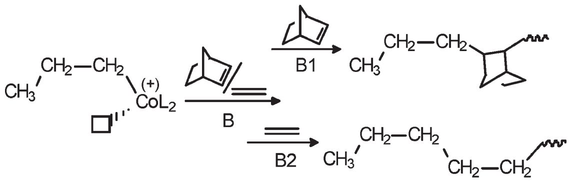
(***i***) Formation of Co-Me active species generated upon the reaction of the Co complex with MAO



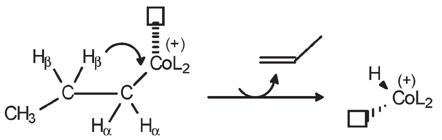
(***ii***) Possible chain initiation derived from Co-Me active species



(***iii***) Possible polymerization propagation step derived from the first E unit inserted into the Co-Me active species



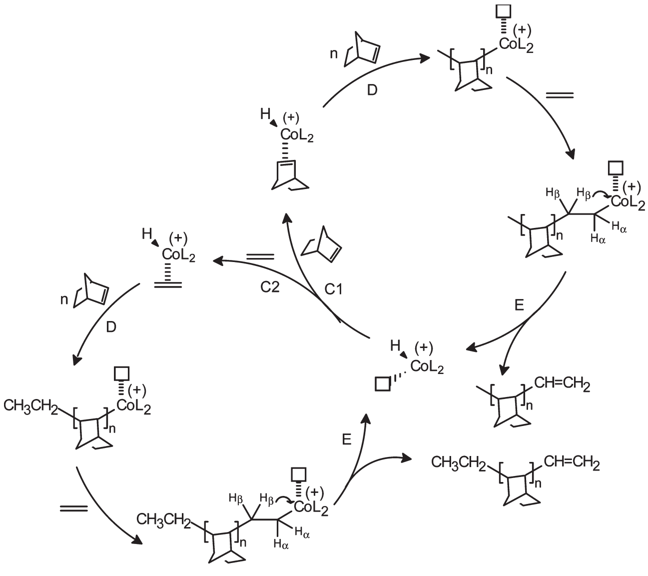
(***iv***) Formation of Co-H active species generated from the 0-H elimination upon the E-last inserted into the Co-Me



(Figure 6);[23,24] it follows that the first insertion of E into the Co—Me species undergoes a β-H transfer leading to a Co—hydride (Co−H) (Scheme 1.iv) active species. The presence of a vinyl-end group can be taken as proof of the existence of a Co−H metal-active species.

In view of these NMR experimental findings, the macromolecular chain growth should occur by insertion of norbornene (Scheme 2, route C1) or by insertion of ethylene (Scheme 2, route C2) into the cobalt−hydride intermediate. Thus, in the case of E as first unit inserted into the Co−H (Scheme 2, route C2), a chain-end structure such as CH_3CH_2—NB— can be considered; vice versa, if norbornene coordination is more favored than ethylene, a polymer chain-end such as NB— structure, resulting from the NB insertion into the Co−H active species, should be taken into account. The ^{13}C NMR signals due to the carbons arising from the NB-terminated polymer chain are not readily detectable because of the complexity of the crude NB macromonomer NMR spectra resulting by the overlap of the terminal units signals with the peaks due to the main NB chained units. On the other hand, the ^{13}C NMR spectrum shown in Figure 6 evidences resonances around 12.3 and 20−23 ppm assignable respectively to the CH_3 and CH_2 of an ethyl end group,[23,24]plausibly arising from E insertion into the Co−H active species (Scheme 2, route C2). Specifically, two signals at about 20.6 and 22.7 ppm related to the β-methylene carbons of the CH_3CH_2—NB— chain-end structure were detected, likely due to the fact that the dyads formed by the first two inserted NB units can be isotactic (*m*) or syndiotactic (*r*) (Figure 6).[25] The coexistence of the two chain-end species (CH_3CH_2—NB— and NB— respectively) was also observed by Goodall upon isolation and GC-MS coupled NMR characterization of NB based vinyl-end dimers obtained with Ni complexes.[6]

Scheme 2. Plausible Mechanism for the Synthesis of Vinyl-End NB Macromonomers by Polymerizing NB in the Presence of E from Co−H Active Species[a]



[a] The chain transfer reaction which can arise from Co—E species formed by E insertion into the Co−H intermediate, resulting into a new Co—hydride active species was omitted for clarity.

Afterward, regardless of the last inserted monomer unit into the Co−H active species, the step of chain propagation proceeds by insertion of NB (Scheme 2, route D) until an E unit is inserted again; a β-hydrogen elimination reaction (Scheme 2, route E) immediately occurs with formation of a terminally unsaturated low-M_n norbornene oligomer and a Co−H active species, which can insert NB or E as first unit and the catalytic cycle rolls on.

The NMR characterization has indeed allowed us to gain insight into the polymerization mechanism of NB in the presence of E with Co−phosphine−MAO catalysts. The results obtained can be summarized as follows. In the copolymerization of norbornene with ethylene, the first monomer inserting on the Co—Me active polymerization site is exclusively ethylene. As soon as E inserts into the Co—Me, the resulting Co−alkyl intermediate undergoes a β-H abstraction chain transfer, generating a Co−H active species. The insertions of NB or E on this active species are both possible, since the signals corresponding to the structures CH_3CH_2—NB— and NB— chain were both detected in the ^{13}C NMR spectra. The polymerization proceeds by further NB additions until E inserts again, leading to the formation of a terminally unsaturated low-M_n norbornene oligomer through a reaction of β-H elimination. Furthermore, the ^{13}C NMR spectroscopy allows us to determined the percentage ratio between the ethyl and vinyl end groups,[26] which was found in the range 30−60 depending on the polymerization conditions (e.g., polymerization temperature and NB concentration in feed).

Hence, before concluding, we would highlight that the presence of a ligand bonded to the Co atom as well as its chemical nature (e.g., N, P, O, or other donor atoms) have a marked effect on the polymerization of NB in the presence of E. Indeed, the use of catalysts based on cobalt−phospine complexes permitted to afford vinyl-terminated NB macromonomers in almost 100% yield, whereas catalysts based on pyridine bis(imine)−$CoCl_2$ complexes gave mixtures of homopolymers,[11d] $CoCl_2$−MAO gave high-M_n PNB,[11d] and catalyst systems based on cobalt complexes with oxygen donor ligands gave a 25% yield of NB macromonomer.[12]

Conclusion

Cobalt(II)−phosphine complexes in combination with MAO were found to be extremely active catalysts for the polymerization of norbornene, giving amorphous, soluble, and high molecular weights ($M_n > 10^5$ g mol^{-1}) PNBs in excellent yield within 1 min of polymerization by using an halohydrocarbon solvent. The steric bulk provided by the substituents on the phosphine ligand donors as well as their chemical nature play a key role in controlling the NB propagation rate, thus influencing both activity, M_n, and M_w/M_n of the polymers.

The same catalysts were used for the copolymerization of norbornene with ethylene, giving vinyl-end, high-T_g phase, NB macromonomers in almost 100% yield. It is worthwhile to note that, as far as we know, cobalt−phosphine complexes in combination with MAO are the first example of catalyst systems giving vinyl-end norbornene macromonomers in quantitative yield.

Furthermore, the presence of a vinyl end group makes these products of some interest. The reactivity of the unsaturated moiety could be useful for any functionalization and further grafting, or at least, these materials could be used as polymerizable building branched blocks monomers for the synthesis of fine chemicals as well as of novel thermoplastic elastomers.

Finally, a possible mechanism of formation of the vinyl-end norbornene macromonomers described in this work, based essentially on their NMR characterization, has been proposed.

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(25) Unpublished results from our laboratory.
(26) The percentage ratio between the ethyl and the vinyl end groups, determined by ^{13}C NMR spectra, was calculated by applying the following equation: $[(I_{\mathrm{ethyl}}/I_{\mathrm{vinyl}}) \times 100] = R_{\mathrm{ethyl/vinyl}}$ %, where I_{ethyl} is the sum of the integrated areas of the peaks at 20.6 and 22.7 ppm corresponding to the β-methylene carbons and I_{vinyl} is the integrated area of the peak centred at 111.9 ppm, corresponding to the olefinic carbon atom ($=CH_2$).