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Polymerization of Norbornene with Co(II) Complexes

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Summary: The norbornene polymerization was studied in the presence of 6 pyridine bis(imine) cobalt(II) complexes activated with methylaluminoxane (MAO). Norbornene was also polymerized with $CoCl_2$ associated to MAO. All these catalytic systems generate an addition polymerization of norbornene, yielding fully saturated polymers. It was shown that the polymerization yield and the molar masses are highly dependant on several reaction parameters (monomer concentration, [Al]/[Co] ratio, polymerization temperature and time) and the frame of the ligand.

Keywords: addition polymerization; catalysts; cobalt; norbornene; pyridine bis(imine)

Introduction

Bicyclo[2.2.1]hept-2-ene (norbornene) can be polymerized in three different ways (Scheme 1), each route leading to its own polymer structure. The most studied polymerization process is the Ring-Opening Metathesis Polymerization (ROMP), yielding polyalkenamers exhibiting good solubility in a wide variety of organic solvents. Cationic norbornene polymerization results in low molar mass oligomeric materials with 2,7-connectivity of the monomer. The addition polymerization of norbornene yields saturated polymers (2,3-insertion), showing high chemical resistance and very good optical properties.[1] Many catalysts based on early or late transition metals were described for this latter process.[2-5] However, few examples of cobalt based catalysts were mentioned in the literature. Cobalt acetylacetonate or cobalt neodecanoate generate ROMP process when associated to trialkylaluminum or addition process when associated to methylaluminoxane (MAO).[6] Some cobalt catalysts based on diphosphine or cyclopentadienyl ligands were developed by Heitz and coworkers.[7, 8] They lead to high molar mass addition polynorbornenes, when associated to MAO. The authors also mentioned a higher polymerization rate when the reactions were performed in chlorobenzene compared to toluene.

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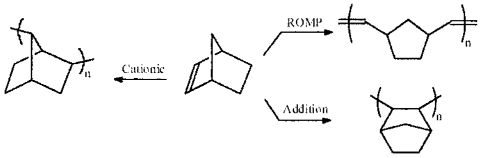
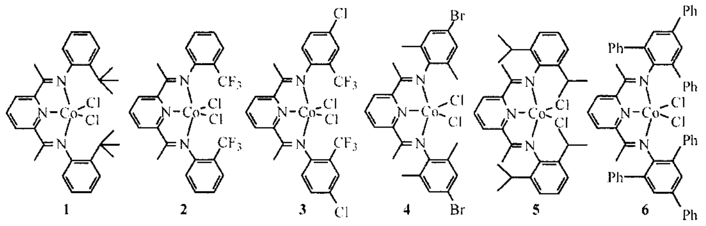


Scheme 1. Polynorbornene structure versus polymerization process.

On another hand, one of the latest breakthroughs in the olefin polymerization field was the discovery of pyridine bis(imine) iron or cobalt complexes as highly active catalysts for ethylene polymerization. Upon addition of various activators, highly linear polyethylenes of tunable molecular weight can be obtained.[9-12] Nevertheless, these catalytic systems revealed much less active towards propylene and higher α-olefins.[13-15] In a previous report with pyridine bis(imine) cobalt complexes, these catalysts proved to be not very active for norbornene polymerization under the used conditions.[16] In this paper, the ability of $CoCl_2$ and selected pyridine bis(imine) cobalt dichloride complexes (PBICo) to polymerize norbornene is studied. The influence of several reaction conditions on the polymerization is examined.

Results and Discussion

The polymerization of norbornene was investigated with 6 pyridine bis(imine) cobalt complexes and $CoCl_2$ activated with MAO. Different substituents were introduced onto the aryl group of the imine function in order to modify either the electron density on the metal or the steric hindrance around the catalytic site (Scheme 2). Their syntheses were already published.[14, 17]

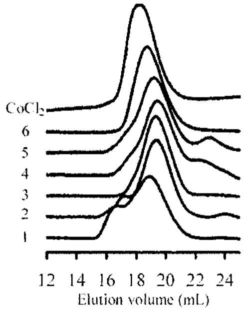


Scheme 2. Pyridine bis(imine) cobalt dichloride complexes.

All polymerizations were performed in chlorobenzene. MAO, purchased as a 10 wt.-% solution in toluene, was dried and used as a white powder (5 mol.-% of trimethylaluminum is still present). Some results are summarized in Table 1 and Figure 1. Pretty good yields were obtained within a couple of hours for all complexes. Catalyst **6** is among the most active, whereas it has revealed inactive for the ethylene polymerization (Figure 1). Moreover, to our knowledge, we were the first to describe $CoCl_2$ as an efficient catalyst for the addition polymerization of norbornene.[17] These complexes are as active as recently described palladium and nickel based complexes activated with MAO,[18, 19] but less active than some others exhibiting activities up to $5 \cdot 10^4$ g/mmol.h.[20-25] It was also checked that MAO alone was not able to polymerize norbornene under the conditions listed in Table 1. Besides, polymerization reactions were also conducted with the iron complexes and whatever the ligand or the reaction conditions, no polymer was detected. Molar masses of the polymers were determined by size exclusion chromatography (SEC) in chlorobenzene at 30°C. As indicated in Table 1, polynorbornenes exhibit high molar masses (ranging from $3.0 \cdot 10^5$ to $2.4 \cdot 10^6$ g/mol) with monomodal or bimodal distribution depending on the ligand.

Table 1. Polymerization of norbornene with several PBICo catalysts and $CoCl_2$.

Catalyst	Loading (µmol)	t_{Pol} (h)	Yield (%)	Activity (g/$mmol_{Cat}$.h)	$M_{w\,LS}$$^{a)}$ (g/mol)	MWD$^{b)}$
1	9.0	4	28	9.7	$2.4\ 10^6$	$3.9^{c)}$
2	9.0	4	38	13.3	$1.0\ 10^6$	$2.6^{c)}$
3	9.1	4	27	9.6	$3.0\ 10^5$	1.4
4	9.0	5	17	4.7	$4.9\ 10^5$	2.1
5	9.8	5	25	6.7	$6.0\ 10^5$	3.3
6	10.0	5	46	12.0	$4.2\ 10^5$	1.4
$CoCl_2$	9.2	5	81	23.0	$1.2\ 10^6$	4.0



$T_{Pol.}$=35 °C; Solvent: Chlorobenzene (12 mL); [Al]/[Co]=400; [NBE]/[Co]=1500; [NBE]=1 mol/L
$^{a)}$ Molar mass measured by SEC in chlorobenzene at 30°C with light scattering online
$^{b)}$ Molecular Weight Distribution
$^{c)}$ Bimodal distribution

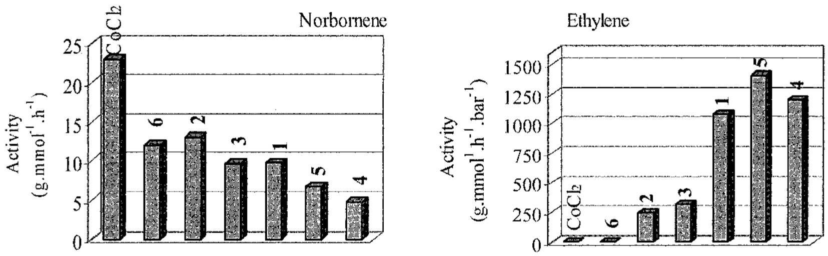


Figure 1. Comparison of ethylene and norbornene polymerization activities with several PBICo and CoCl$_2$.

Polynorbornenes were also characterized by ^{1}H and ^{13}C NMR spectroscopy. As shown on Figure 2, no peaks attributable to ethylenic protons due to a metathesis process were detected. It can thus be assumed that the polynorbornenes were obtained through an addition process.

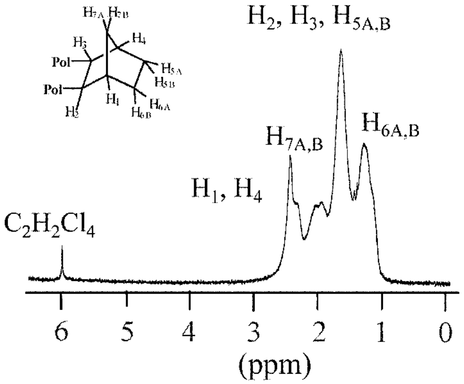


Figure 2. ^{1}H NMR spectrum of a polynorbornene synthesized with catalyst **1**/MAO (400 MHz, $C_2D_2Cl_4$, 120°C).

Influence of monomer concentration

The evolution of the polymerization yield as well as the molar masses of the resulting polymers with norbornene concentration was studied. Results are summarized in Figure 3. As it can be seen, the polymerization yield increases linearly with norbornene concentration and no difference was observed for the molar masses. These observations are different from those made with nickel-based catalysts bearing phosphoraneiminato ligands.[25] Indeed, with these complexes, the molar masses were highly dependent on the monomer concentration.

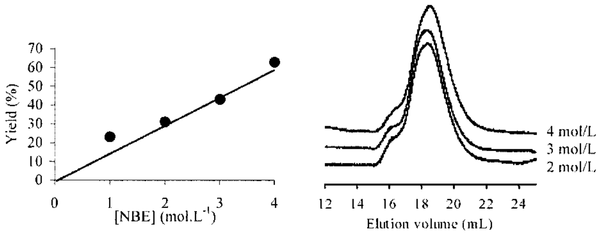


Figure 3. Evolution of norbornene polymerization yield and polynorbornene molar mass with monomer concentration (Catalyst **1** loading: 3.6 μmol; [Al]/[Co]=500; [NBE]/[Co]=1500; $T_{Pol.}$=35 °C; $t_{Pol.}$=1 h; Solvent: Chlorobenzene).

Influence of the [Al]/[Co] ratio

The influence of the [Al]/[Co] ratio on the polymerization yield was also investigated. Results are summarized in Figure 4. A different behavior is observed for the PBICo complexes and $CoCl_2$. Indeed, it appears clearly that $CoCl_2$ is fully activated for lower [Al]/[Co] ratios than the PBICo. With $CoCl_2$, a maximal activity is reached for low [Al]/[Co] ratios (around 100) and, after staying constant for ratios up to 1000, the activity decreases rapidly with increasing ratios. The decrease of $CoCl_2$ activity may be attributed to a poison effect of excess MAO. That may also be due to a poison effect of excess TMA (still present in solid MAO). With catalyst **1**, a fast increase of the activity is observed with increasing ratios up to 500 and then a slight increase is still noticeable for higher ratios. In the presence of catalyst **2**, the activity increases for [Al]/[Co] ratios up to 500 and then a plateau seems to be reached. Similar results have already been mentioned for palladium or nickel based complexes. [20, 25]

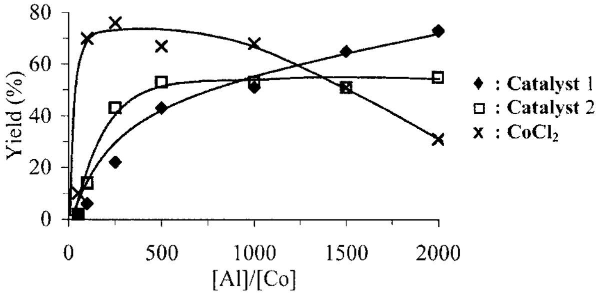


Figure 4. Evolution of norbornene polymerization yield with [Al]/[Co] ratio (Catalyst loading: 3.6 μmol; [NBE]=3 mol/L; [NBE]/[Co]=1500; $T_{Pol.}$=35 °C; $t_{Pol.}$=1 h; Solvent: Chlorobenzene).

The evolution of the molar masses with the [Al]/[Co] ratio was also investigated and results are shown in Figure 5. For catalyst **2** and $CoCl_2$, the molar mass distribution is always monomodal and the molar mass decreases with [Al]/[Co] ratio, probably due to increasing transfer reactions with higher amount of aluminum compounds. Unfortunately, the molar masses were too high to allow chain end determination by NMR spectroscopy. The molar mass distribution of polymers obtained with catalyst **1** is always bimodal and the proportion of the high molar mass fraction increases with the [Al]/[Co] ratio. Presently, we do not know exactly how these high molar mass polymer chains were produced. Nevertheless, it is probably the sign of the presence of at least two kinds of active sites in the polymerization medium.

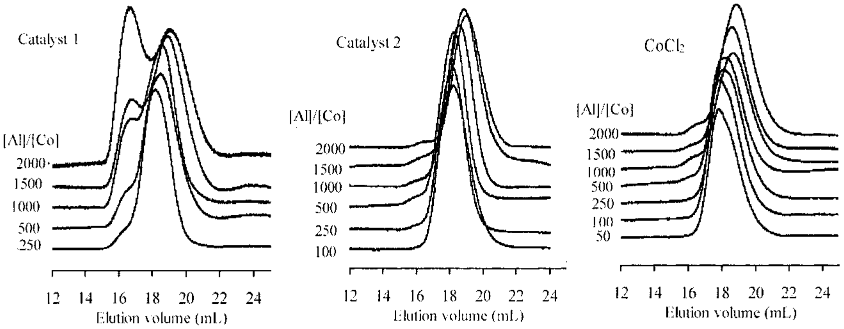


Figure 5. Evolution of polynorbornene molar masses with [Al]/[Co] ratio for catalysts **1** and **2** and $CoCl_2$.

Influence of the polymerization temperature

The influence of the polymerization temperature was also examined. Results are summarized in Figure 6. Each catalyst exhibits a peculiar behavior. With $CoCl_2$, the activity increases with temperature and reaches a plateau around 40°C. In the case of catalyst **1** the yield, quite large even for the lowest temperatures, increases with temperature to reach around 80°C the same plateau as the one observed with $CoCl_2$. With catalyst **2**, the activity increases with temperature for the lowest temperatures and reaches a plateau around 20°C. Above 60°C, the activity decreases with temperature, probably due to thermal instability. These behaviors are quite different from the behavior described for ethylene polymerization. Indeed, in this last case, the PBICo complexes always exhibit a maximal activity around 40°C and lower activities for other temperatures. [14, 26, 27]

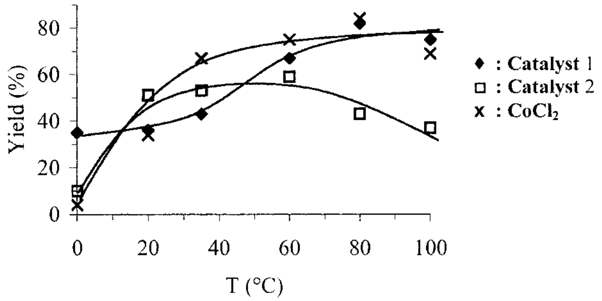


Figure 6. Evolution of the norbornene polymerization yield with polymerization temperature (Catalyst loading: 3.6 µmol; [NBE]=3 mol/L; [NBE]/[Co]=1500; [Al]/[Co]=500; $t_{Pol.}$=1 h; Solvent: Chlorobenzene).

Again, the molar masses were measured by SEC in chlorobenzene. With $CoCl_2$, the molar mass distribution is monomodal up to 80°C, with a decrease of the molar mass probably due to an increase of the transfer reactions with temperature. The shoulder appearing for temperatures higher than 80°C, is due to the polynorbornene generated by MAO alone. Indeed, at such elevated temperatures, MAO was shown to be able to polymerize NBE, with nevertheless lower yields than in the presence of a cobalt complex. Besides, the molar mass of the polynorbornenes obtained with MAO alone is exactly the same as the one of the shoulder obtained with $CoCl_2$/MAO (Figure 7). Moreover, the proportion of high molar mass polynorbornene is in good agreement with the polymerization yield observed with MAO alone. Thus, the presence of the shoulder may be attributed without any doubt to the polymerization of the monomer by MAO alone. Catalyst **2** gives monomodal molar mass distribution below 60°C and bimodal ones above 60°C. In this case, the high molar fraction is too important to be attributed to MAO. Again catalyst **1** yields bimodal molar mass distribution even at 20°C. The proportion of the high molar mass fraction increases with temperature. Concerning catalysts **1** and **2**, as the amount of high molar mass polymer chains is too important to be attributed to MAO alone, a partial decoordination of the ligand could be suggested to assume the presence of at least two kinds of active sites of different nature.

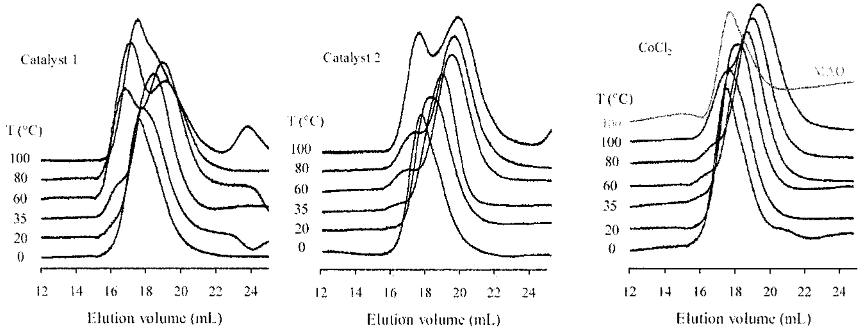


Figure 7. Evolution of polynorbornene molar masses with polymerization temperature for catalysts **1** and **2** and $CoCl_2$.

Kinetic study

Finally, the evolution of the polymerization yield with time was examined with 3 catalysts. Results are reported in Figure 8. The same behavior is observed for all the catalysts. Indeed, the yield increases linearly during the first hours and increases more slightly for longer reaction times. It should be noted that even after 48 h, the catalysts seem to be still active. Again, this behavior is quite different from that observed for the ethylene polymerization. Indeed, it is described in the literature that for such catalytic systems only 10% of the maximal activity remains after only 1h.[11, 26] In our case, one has to wait much longer to detect the same activity decay.

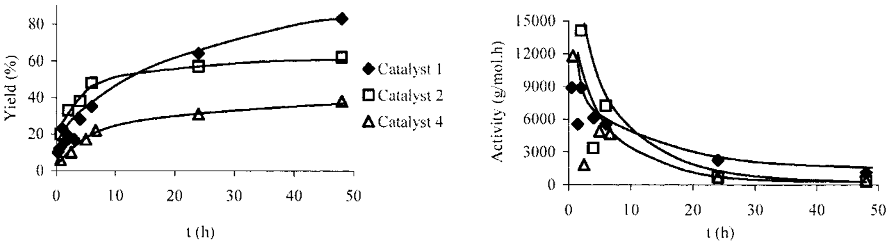


Figure 8. Evolution of the polymerization yield and activity with reaction time (Catalyst loading: 9 µmol; [NBE]=1 mol/L; [NBE]/[Co]=1500; [Al]/[Co]=400; $T_{Pol.}$=35 °C; Solvent: Chlorobenzene).

Concerning the molar masses, again polymers obtained with catalyst **1** exhibit bimodal molar mass distribution even for the lowest reaction times, the amount of the higher molar mass fraction increasing with polymerization time. For the other 2 complexes, longer reaction times have to be waited to see the appearance of a high molar mass fraction. Again, one can suggest the simultaneous existence of several kinds of active species, due to partial decoordination of the ligand.

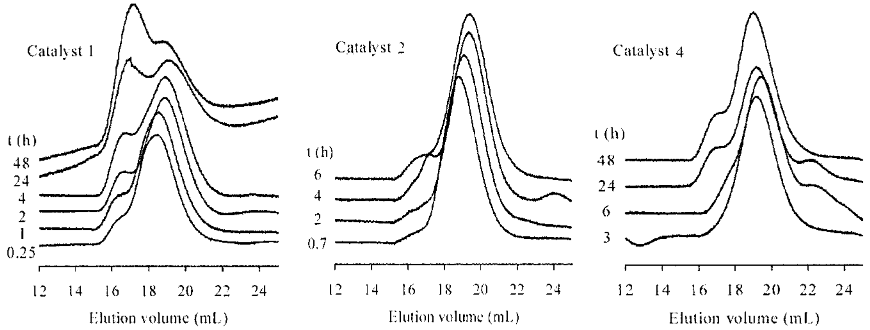


Figure 9. Evolution of polynorbornene molar masses with time for catalysts **1**, **2** and **4**.

Conclusion

The addition polymerization of norbornene was performed with 6 pyridine bis(imine) cobalt dichloride complexes, generally used for ethylene polymerization. In this study, norbornene was also polymerized for the first time with $CoCl_2$. The influence of several reactions parameters ([NBE], [Al]/[Co] ratio, polymerization temperature and time) was investigated. High molar mass polynorbornenes were obtained, exhibiting monomodal or bimodal molar mass distributions, depending on the ligand and the polymerization conditions. This behavior may be attributed to the coexistence of several active sites in the reaction medium. Moreover, the substituents on the pyridine bis(imine) ligand may influence the proportion of the different active species. Indeed, a *t*-butyl group (catalyst **1**) seems to favor the synthesis of high molar mass polynorbornene, whereas with a trifluoromethyl group (catalyst **2**) the synthesis of high molar mass polymer is disfavored. Besides, different behaviors were observed compared to ethylene polymerization. Indeed, the complexes revealed generally more robust versus temperature and less deactivation of the active species was detected with time.

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