Room-temperature polymerization of β-pinene by niobium and tantalum halides

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ABSTRACT

The easily accessible niobium pentahalides NbX_5 (X = F, **1a**; X = Cl, **1b**; X = Br, **1c**) and the tantalum TaF_5 (**2a**) were employed for the first time as effective catalysts for the synthesis of poly-β-pinene at room temperature. ^{1}H NMR analyses indicated that the produced β-pinene polymers were structurally identical to that formed by conventional cationic Lewis acid initiators. Niobium pentachloride gave low molecular weight (M_n = 1200-1600) polymer with high conversion degree. The effects of the main reaction parameters (i.e. solvent, temperature, catalyst concentration, time and eventual co-catalysts) on the $NbCl_5$-promoted polymerization were investigated. Polymerization quenching with methanol resulted in incorporation of a methoxy-end group into the polymer chain, thus suggesting a cationic mechanism. NMR investigations and analytical measurements outlined that the reactions of **1a,b** with limited amounts of β-pinene afforded Nb(V) ionic derivatives. On the other hand, NbI_5, $TaCl_5$, the carbamato-complexes $M(O_2CNEt_2)_5$ (M = Nb, Ta) and the mononuclear adducts NbX_5L [X = Cl, L = MeCN, Ph_2CO or $(NMe_2)_2CO$; X = F, L = EtOH] were not active in β-pinene polymerization.

Keywords: β-pinene; cationic polymerization; Lewis acids; niobium halides; tantalum halides.

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1. Introduction

β-Pinene is the most important distillation product of natural turpentine [1]. Its commercially available polymer (terpene resin) is used in a wide variety of industrial applications (e.g. adhesives and varnishes, bituminous materials, tackifying agents, additives in rubber [2,3]), because it exhibits a combination of desired and outstanding properties. For instance, high solubility in hydrocarbon solvents, compatibility with waxes and relatively high softening point (125-135 °C). Moreover the polymer is nontoxic and inert to common chemicals, that makes it suitable for the food packaging and the production of chewing gums [4]. Furthermore, due to the limited fossil resources, terpene resins, derived from renewable resources, have aroused increasing interest in both academic and industrial context as outstanding biomaterials.

A variety of polymerization techniques have been employed for the polymerization of β-pinene in recent years, i.e. the Ziegler-Natta type, the free-radical, the cationic and the radiation-induced cationic polymerization [4,5]. Lewis acid-promoted cationic polymerization represents the most efficient method in the commercial production of poly(β-pinene). The presence of two alkyl groups on the double bond determines rapid cationic polymerization of β-pinene with conventional or even living fashion [6]. The resulting polymers have alternating sequences of isobutylene and cyclohexene units (Fig. 1).

Fig. 1. near here

Different Lewis acids (AlCl$_3$, SnCl$_4$, ZnCl$_2$, ZrCl$_4$, BF$_3$ etc.) have been used for the polymerization of β-pinene [7, 8, 9, 10, 11, 12, 13,] and the results reported in the literature have been summarized in Table 1.

Table 1 near here

The catalytic conversion of β-pinene to polymer was studied with a number of Friedel-Crafts catalysts (Runs 4-13, Table 1) at fixed conditions. The results demonstrate that β-pinene polymerizes very fast and in a vigorous way after less than 1% of aluminum chloride is added; otherwise the conversion degree was much lower when SbCl$_3$ and ZnCl$_2$ were employed as catalysts. As far as aluminium alkyls are concerned, it has been observed that lower temperatures favour the global yield of the polymerization process using ethylaluminium dichloride [10], while an increase in the temperature of polymerization gave rise to resins of lower molecular weight, lower softening point, and darker color.

More recently, Zhou et al. [14] have stated that Keggin-type heteropolyacids (HPAs) are environmental friendly, have high Brønsted acidity and are efficient catalyst in the cationic polymerization of β-pinene.

Niobium and tantalum pentahalides are strong Lewis acids, easily available and biocompatible metal-based compounds [15] which are attaining increasing popularity as chemical reagents. In this contribution, we report a study on the polymerization reaction of β-pinene mediated by MX$_5$ (M = Nb or Ta; X = halide) [16] or their derivatives. We have found that NbCl$_5$ is an efficient catalyst leading to smooth and quantitative polymerization at room temperature. The effects of the reaction conditions, including the possible use of alkylaluminum co-catalysts, on the NbCl$_5$-mediated polymerization will be discussed.

2. Experimental

2.1. General

All manipulations of air and/or moisture sensitive compounds were performed under atmosphere of pre-purified Argon using standard Schlenk techniques. The reaction vessels were oven dried at 150 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. NbX_5 (X = F, **1a**; X = Cl, **1b**; X = I, **1d**) and TaX_5 (X = F, **2a**; X = Cl, **2b**) were commercial products (Strem) of the highest purity available, stored under argon atmosphere as received. $NbBr_5$ (**1c**) [17] $NbF_4(OPh)$ [18], $M(O_2CNEt_2)_5$ (M = Nb, Ta) [19], and NbX_5L (X = Cl, L = MeCN [20], Ph_2CO [21] or $(NMe_2)_2CO$ [22]; X = F, L = EtOH [23]) were prepared according to published procedures. Solvents were purchased from Sigma-Aldrich and distilled before use from appropriate drying agents. All the organic reactants and ethylaluminumdichloride (EADC; 25 wt.% in toluene), diethylaluminumchloride (DEAC; 25% w/w in toluene), methylaluminoxane (MAO; 10% w/w in toluene), trimethylaluminum (TMA; 2 M in toluene), triisobutylaluminum (TIBAL; 25% w/w in toluene) were used as received (Sigma-Aldrich) without further purification.

Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. NMR spectra were recorded on Bruker Avance DRX400 instrument equipped with probe BBFO broadband. Unless otherwise stated, NMR spectra were recorded at 298 K. The ^{1}H- and the ^{13}C spectra were assigned *via* DEPT experiments and ^{1}H,^{13}C correlation measured through gs-HSQC and gs-HMBC experiments [24]. The chemical shifts for ^{1}H and ^{13}C were referenced to the non-deuterated aliquot of the solvent; the chemical shifts for ^{19}F were referenced to $CFCl_3$; the chemical shifts for ^{93}Nb were referenced to $[NEt_4][NbCl_6]$. Molar conductivities (Λ_M) measurements were carried

out with Eutech Con 700 Instrument (cell constant = 1.0 cm^{-1}) at 298 K [25]. Carbon and hydrogen analyses were performed on Carlo Erba mod. 1106 instrument. The chloride content was determined by the Volhardt method [26] after exhaustive hydrolysis of the sample. The metal was analyzed as Nb_2O_5, obtained by hydrolysis of the sample followed by calcination in a platinum crucible. The Cl and Nb analyses were repeated twice in order to check for reproducibility.

The molecular weights and the molecular weight distributions of the polymer samples were measured with a gel permeation chromatograph (GPC) instrument, PL 220, at room temperature in $CHCl_3$ on μ-Styragel columns (106, 105, 104, 103, 500 Å) connected with a refractive-index detector with polystyrene as standard.

2.2. Polymerization of β-pinene

β- pinene polymerization experiments were carried out in a 50 mL Carius vessel under magnetic stirring and dry argon atmosphere. Carius vessel was covered with aluminum foil in order to avoid light. In a general procedure, the metal compound and the solvent (ca. 20 mL) were transferred into the Carius vessel in the order given. Then β-pinene (5 mL) was added. Immediate change of color of the solution from colorless to yellow was always observed. During all the polymerization experiments, the temperature of the reaction was controlled by a thermostated bath. The polymerization was quenched by pouring the reaction mixture into a large excess of methanol acidified with 5% aqueous HCl. Thus the white polymer was isolated by filtration, washed with methanol, dried in vacuum, weighed and characterized.

2.3. Synthesis, isolation and characterization of coordination compounds of NbX$_5$ (X = F, Cl) with β-pinene.

β-pinene (2.20 mmol) was added to NbF$_5$ (2.20 mmol) in pentane (20 mL). The mixture was stirred for 12 hours, then an ochre-yellow solid was isolated from a colourless solution. The solid was washed with pentane (2 x 10 mL) and dried under vacuo. Anal. Calcd. for C$_{10}$H$_{16}$F$_5$Nb: C, 37.05; H, 4.98; Nb, 28.66. Found: C, 35.88; H, 5.07; Nb, 28.97. IR (solid state): 2961w, 2931w, 2870w, 1526m, 1464m, 1368w-m, 1261m-s, 1091s, 1022s, 896m, 859m, 797vs cm^{-1}.

The reaction of β-pinene (2.35 mmol) with NbCl$_5$ (2.35 mmol) was performed analogously and afforded an ochre-yellow solid. Anal. Calcd. for C$_{10}$H$_{16}$Cl$_5$Nb: C, 29.55; H, 3.97; Nb, 22.86; Cl, 43.62. Found: C, 28.74; H, 3.75; Nb, 23.20; Cl, 42.64. IR (solid state): 2954w, 2925w, 2868w, 1587w-m, 1519m, 1462m-s, 1384w, 1366w-m, 1262w, 1101m, 872s, 814s, 779vs cm^{-1}.

Conductivity analysis: a mixture of NbX$_5$ (1.05 mmol) and CH$_2$Cl$_2$ (20 mL) was treated with β-pinene (1.05 mmol). Rapid dissolution of the solid into a dark-red solution was observed. $\Lambda_M = 1.7$ S·cm^2·mol^{-1} (X = F); $\Lambda_M = 2.1$ S·cm^2·mol^{-1} (X = Cl). Then additional two molar equivalents of β-pinene were added and the mixture was stirred for 15 minutes. $\Lambda_M = 2.0$ S·cm^2·mol^{-1} (X = F); $\Lambda_M = 3.0$ S·cm^2·mol^{-1} (X = Cl).

3. Results and Discussion

The results of β-pinene polymerization catalyzed by NbCl$_5$ are represented in Table 2. Preliminary experiments were carried out in the presence or in the absence of visible light (Runs 17 and 18, respectively), in order to exclude the possibility of light-induced radical polymerization. The fact that

similar conversion degrees and molecular weights were achieved in both conditions suggests that probably the polymerization reaction does not occur via radical pathway.

Table 2 near here

It was not possible to polymerize β- pinene in the absence of NbCl$_5$ (Run 19). Conversely, almost quantitative conversion of monomer to polymer was ascertained in the presence of NbCl$_5$ (Run 17).

We performed the β-pinene polymerization reaction by using NbCl$_5$ as catalyst under different experimental conditions, with the aim to see the influence of temperature, catalyst concentration, solvent, time, and co-catalyst.

In spite of the fact that the most favourable temperature range for the AlCl$_3$-directed β-pinene polymerization was reported to be $-50 \div -10$ °C (Table 1), the polymerization reaction with NbCl$_5$ was very slow at 0 °C (Run 20). Moreover a decrease of β-pinene conversion, as well as of polymer molecular weight, was ascertained at 50 °C (Run 21). These data suggest that the optimal performance of the catalyst can be achieved approximately at room temperature.

When toluene was replaced by chlorobenzene as reaction medium, a significant decrease of polymerization [from 98% to 4% in 5 hours (Run 22)] was observed, thus suggesting that solvents with higher dielectric constant have a negative effect on the rate of polymerization. The effect of the nature of the solvent in cationic polymerization is often difficult to predict: the solvent with higher dielectric constant gives more "free" carbocations, but may also increase the activation energy of propagation step, thus resulting in lower polymerization rates [27].

It was also observed that the molecular weight of poly(β-pinene) obtained by adopting a lower reaction time came almost unchanged (compare Runs 17 and 23). This indicates the short lifetime of the

propagating species. Remarkably, the increase of NbCl$_5$ concentration from 15 to 30 µmol sustained the monomer conversion degree and polymer molecular weight (compare Runs 17 and 24, Table 2).

In view of the fact that organoaluminum-based co-catalysts, e.g. MAO, TMA and TIBAL, generally play important roles in olefin polymerization [28], in terms of generation of active catalytic species, polymerization activity and molecular weight of polymers, we decided to test the polymerization reaction of β-pinene in the presence of aluminum co-catalysts. Besides, in the polymerization of β-pinene with nickel derivatives, it was ascertained that MAO helps to initiate the cationic polymerization forming an alkylated metal cation [29]. The obtained results (compare Run 17 with Run 25) inidicate that MAO did not influence conversion and polymer characteristics. On the other hand, the introduction of TMA and TIBAL provided negative effect both on the monomer conversion (compare Run 17 with Runs 26-27), while no effect was observed on the average molecular weight of the polymer. This means that the interaction of NbCl$_5$ with the co-catalysts presumably generates metal species which are less effective than NbCl$_5$ as β-pinene polymerization promoters. More in detail, the addition of TMA and TIBAL, which are strong reducing agents, could result in reduction of the niobium chloride to lower valent compounds [30]. It is worth mentioning that no catalytic activity was ascertained in the blank runs carried out by using Al-based compounds in the absence of NbCl$_5$ (Runs 28-30). The exceptions are represented by acid co-catalysts ethylaluminumdichloride (EADC) and diethylaluminumchloride (DEAC), which produced appreciable amounts of poly(β-pinene) with high monomer conversions (86 and 95% respectively, Runs 31,32). Notwithstanding the conversion values are lower than that obtained by using NbCl$_5$ only (98%). As expected, the use of combined NbCl$_5$/EADC or NbCL$_5$/DEAC (Runs 33, 34) resulted in enhancement of the conversion degree, while the polymer average molecular weight did not significantly change.

As far as niobium pentafluoride and pentabromide are concerned, we observed lower performances with respect to $NbCl_5$ (see Table 3, Runs 35,36), while NbI_5 was totally inactive. The result is not surprising for what concerns $NbBr_5$ and NbI_5, on account of the higher steric demand exerted by the heavier halide ligands with respect to the chloride. This steric effect may provide inertness to the niobium species resulting in progressively lower polymerization rates. Actually, we have recently reported that $NbBr_5$ derivatives are less active than analogous $NbCl_5$ derivatives in ethylene polymerization [31].

The low activity observed when using the strongly acidic NbF_5 could be a consequence of the tetranuclear structure of the former in comparison with the dinuclear structures of NbX_5 (X = Cl, Br, I) [16]. The possibility of a strong dependence of the polymerization activity from the nuclearity of the metal precursor prompted us to study the β-pinene polymerization reaction with mononuclear coordination compounds such as $NbF_5(EtOH)$ and $NbCl_5L$ (L = MeCN, Ph_2CO, $(NMe_2)_2CO$). However, these derivatives did not reveal good candidates as polymerization catalysts (see Table 3). In the same way, the substitution of one fluoride ligand with a phenoxy group, in the tetranuclear structure of NbF_5, did result in lower catalytic performance and lower molecular weight (compare Run 38 with Run 35) .

According to the general trend that niobium-based catalysts supply activities higher than those of their tantalum counterparts in ethylene polymerization [32], $TaCl_5$ did produce trace amounts of poly-β-pinene and TaF_5 was less efficient than NbF_5 (compare Run 17 with 44 and Run 35 with 43, respectively).

Table 3, near here

Finally, the carbamato complex $Nb(O_2CNEt_2)_5$, that is much more efficient than the parent compound $NbCl_5$ in ethylene polymerization [33, 34], was taken in consideration. No polymer was formed both in the presence and in the absence of co-catalyst (Runs 45 and 46, Table 3). This is in agreement with the

presumed cationic character of the β-pinene polymerization, which may be favoured by strong Lewis acids. Similar results were obtained when using $Ta(O_2CNEt_2)_5$ as catalyst (Runs 47 and 48, Table 3).

^{1}H NMR and IR analyses have outlined that the poly-β-pinene obtained with $NbCl_5$ as catalytic precursor is structurally identical to that formed by conventional cationic initiating systems [29].

The polymerization reaction was quenched by using a methanol/HCl solution. As a matter of fact, the ^{1}H NMR analysis of the polymeric material (Figure 2) pointed out that a methoxy group (resonance at 3.5 ppm) was present as the terminal group of the polymer chain. This is consequence of the formal addition of the $[MeO^-]$ ion to the terminal carbocation of the growing chain [29]. Analogously, the IR spectra of the poly-β-pinene samples showed two absorptions at 1160 to 836 cm^{-1} which have been assigned to C−O−C stretching vibrations related to the C−O−CH$_3$ group. The characteristics endo-olefinic band at 1666 cm^{-1} was also present.

Fig. 2 and Fig. 3. near here

In order to collect information about the possible mechanism involved in the polymerization of β-pinene mediated by Nb(V) pentahalides, we studied the 1:1 molar reactions of NbX_5 (X = F, Cl) with the monomer. In both cases, a solid product of empirical formula "NbX_5(β-pinene)" could be isolated by performing the reactions in pentane (see Experimental). According to conductivity measurements, the coordination compounds formed in the reactions of NbX_5 (X = F, Cl) with β-pinene are ionic, probably formed as result of some halide transfer. In fact, the values of molar conductivity fall in the range typical for ionic derivatives of MX_5 (M = Nb, Ta) [35]. The alkene molecules in "NbX_5(β-pinene)" are

probably coordinated by the [C=C] double bond to the metal centre, as suggested by IR and NMR spectroscopy. More in detail, the IR spectra displayed a medium-intensity band at ca. 1520 cm^{-1}, ascribable to a coordinated carbon-carbon double bond [36]. Moreover the ^{1}H NMR spectra recorded on the reaction mixtures NbX_5/β-pinene (molar ratio = 1) displayed broad resonances at low fields ascribable to protons bound to coordinated Csp^2-carbons [37]. Presumably "$NbCl_5$(β-pinene)" holds a lower nuclearity than "NbF_5(β-pinene)", see above. The ^{19}F NMR spectrum for NbF_5/β-pinene showed a broad resonance at *ca.* 160 ppm; low temperature NMR experiment was not helpful in freezing the presumably operative exchange process [23].

The isolation of possible ionic intermediate may explain the high efficiency of $NbCl_5$ as promoter of the polymerization of β-pinene, in view of the increased Lewis acidity on going from the neutral $NbCl_5$ to cationic derivatives.

3. Conclusion

The polymerization of β-pinene has been conveniently carried out at room temperature by employing $NbCl_5$ as catalyst, and the main reaction parameters (temperature, time, catalyst concentration, solvent) have been optimized. Other Nb(V) halides and TaF_5 are also effective as catalysts, although providing performances lower than that of $NbCl_5$. The presence of oxygen ligands in the coordination sphere of the metal centres appears to be detrimental to the polymer formation. The room temperature condition, associated with the substantial biocompatibility of niobium, is the most attracting feature which makes the use of $NbCl_5$ in β-pinene polymerization interesting by industrial point of view, compared to previously employed metal halides (e.g. $AlCl_3$).

According to spectroscopic and analytical studies, the polymerization by niobium halide probably proceeds via cationic mechanism on a niobium-containing cation.

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[36] The C=C bond stretching vibration of the uncoordinated β-pinene falls at 1642 cm^{-1} (liquid film).

[37] NbF$_5$ (0.640 mmol), CD$_2$Cl$_2$ (0.70 mmol) and β-pinene (0.640 mmol) were introduced into a NMR tube in the order given. Then the tube was sealed and shaken briefly in order to homogenize the content. NMR analyses on the dark red solution were recorded after 2 hours. ^{1}H NMR (CDCl$_3$): $\delta =$ 7.62, 7.06 (br), 2.9-0.8 ppm (br). ^{19}F NMR (CD$_2$Cl$_2$): $\delta =$ 158.8 ppm (Δ_v = 262 Hz). ^{19}F NMR (CD$_2$Cl$_2$, 211 K): $\delta =$ 158.8 ppm (Δ_v = 262 Hz). Analogous experiment was carried out by using NbCl$_5$ (0.760 mmol) and β-pinene (0.760 mmol). ^{1}H NMR (CDCl$_3$): $\delta =$ 7.24, 7.02 (br), 2.9-0.9 ppm (br).

Captions for Figures and Tables

Figure 1. Schematic representation of cationic polymerization of of β -pinene.

Figure 2. ^{1}H NMR of poly(β-pinene) obtained with NbCl$_5$ as catalytic precursor in Run 17.

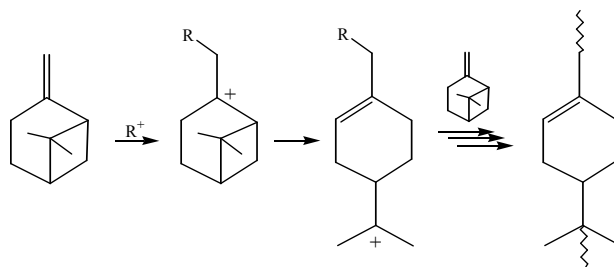**Figure 3.** FT-IR Spectra of poly(β-pinene) obtained with NbCl$_5$ as catalytic precursor in Run 17.

Table 1. Lewis acid catalyzed polymerization of β -pinene [7, 8, 9, 10] [a]

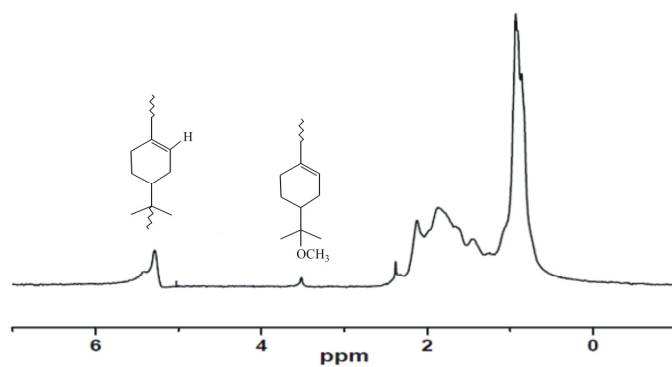**Table 2**. Polymerization of β -pinene in the presence of NbCl$_5$/alkylaluminium compounds [a]

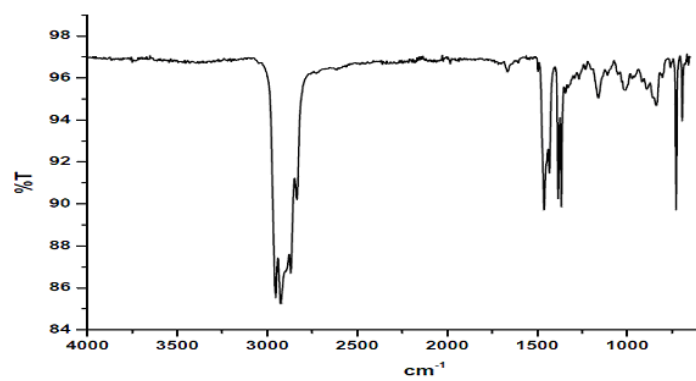**Table 3.** Polymerization of β -pinene catalyzed by Nb(V) and Ta(V) halides [a]

Figure 1

Figure 2

Figure 3

Table 1

Run	Catalyst [M]	β-pinene [M]	Time (min)	Temp. (°C)	Conversion (%)	M_n [b]	Ref.
1	$AlCl_3$ [0.4]	1.8	10	-40	100	4400	7
2	$AlCl_3/SbCl_3$ [0.2]	1.8	10	-40	100	3900	7
3	$AlCl_3$ [0.04] [c]	1.4	60	30	20	1890	8
4	$AlCl_3$ [0.05]	0.5	10	45	94	1500[c]	9
5	$AlCl_3.Et_2O$ [0.05]	0.5	10	45	76	1500 [c]	9
6	$AlBr_3$ [0.05]	0.5	10	45	93	1500 [c]	9
7	$ZrCl_4$ [0.05]	0.5	10	45	96	1500 [c]	9
8	BF_3 [0.05]	0.5	10	45	54	1500 [c]	9
9	$BF_3.Et_2O$ [0.05]	0.5	10	45	43	1500 [c]	9
10	$SnCl_4$ [0.05]	0.5	10	45	21	1500 [c]	9
11	$BiCl_3$ [0.05]	0.5	10	45	5	1500 [c]	9
12	$SnCl_3$ [0.05]	0.5	10	45	0.7	1500 [c]	9
13	$ZnCl_2$ [0.05]	0.5	10	45	0.5	1500 [c]	9
14	$C_2H_5AlCl_2$ [0.6]	4.4	120	10	90.3	2432	10
15	$C_2H_5AlCl_2$ [0.6]	4.4	120	20	90.2	1500	10
16	$C_2H_5AlCl_2$ [0.6]	4.4	120	50	90.4	1128	10

[a] Solvent: toluene.
[b] Determined by GPC, unless otherwise specified.
[c] Solvent: xylene.
[d] Average molecular weight obtained by cryoscopic methods

Table 2

Run	**1b** (μmol)	Co-catalyst	Al/Nb (mol/mol)	Temp. (°C)	Conversion (%)	M_n[b]	DPI[b]
17	15	-	-	R.T.	98	1442	3.4
18[c]	15	-	-	R.T.	97	1288	3.1
19	-	-	-	R.T.	0	-	-
20	15	-	-	0	18	1587	2.1
21	15	-	-	50	8	1125	2.3
22[d]	15	-	-	R.T.	4	n.d.[e]	-
23[f]	15	-	-	R.T.	67	1256	2.5
24	30	-	-	R.T.	97	1189	3.1
25	15	MAO	500	R.T.	98	1479	3.5
26	15	TMA	50	R.T.	10	1460	2.3
27	15	TIBAL	50	R.T.	66	1269	2.7
28	-	MAO[g]	-	R.T.	Trace	-	-
29	-	TMA[h]	-	R.T.	0	-	-
30	-	TIBAL[i]	-	R.T.	0	-	-
31	-	EADC[j]	-	R.T.	69	1379	2.8
32	-	DEAC[k]	-	R.T.	85	1242	2.7
33	15	EADC	50	R.T.	86	1201	3.4
34	15	DEAC	50	R.T.	95	1188	3.1

[a] Reaction Conditions: Toluene (20 mL), [β- pinene] = 1.2 M, reaction time 5h
[b] Determined by GPC.
[c] Absence of light.
[d] Solvent: chlorobenzene.
[e] Not determined
[f] Reaction time: 1 h
[g] MAO = 4.97 mL.
[h] TMA = 0.75 mL.
[i.] TIBAL = 0.41mL.
[j] EADC = 0.41 mL.
[k] DEAC = 0.40 mL.

Table 3

Run	Precursor	Conversion (%)	M_n[b]	PDI[b]
35	1a	85	720	4.1
36	1c	92	830	2.9
37	1d	0		
38	$NbF_4(OPh)$	42	610	3.1
39	$NbF_5(EtOH)$	0		
40	$NbCl_5(MeCN)$	Trace		
41	$NbCl_5(Ph_2CO)$	0		
42	$NbCl_5[(NMe_2)_2CO]$	0		
43	2a	77	750	2.9
44	2b	Trace		
45[c]	$Nb(O_2CNEt_2)_5$	0		
46[c,d]	$Nb(O_2CNEt_2)_5$	Trace		
47[c]	$Ta(O_2CNEt_2)_5$	0		
48[c,d]	$Ta(O_2CNEt_2)_5$	Trace		

[a] Reaction Conditions: Precursor: 15 μmol, [β- pinene] = 1.2 M, toluene (20 mL), t = 5 h, T = 25 °C.
[b] Determined by GPC.
[c] Precursor: 30 μmol.
[d] MAO was added as co-catalyst (Al/Nb = 500 mol/mol).