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Bis(alkylphenylaminopyridinato) titanium dichlorides as ethylene polymerization catalysts

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Abstract

Four titanium complexes derived from 2-(2-ethylanilino)-, 2-(3,5-dimethylanilino)pyridine, 2-(4-*n*-butylanilino)- and 2-(2-*t*-butylanilino) pyridine were synthesized and characterized by spectroscopic methods. These complexes were used to catalyze the polymerization of ethylene in the presence of MAO as cocatalyst. The effect of the complex structures on the polymerization behavior was studied. All the alkylphenylaminopyridinato titanium complexes used in this study yielded higher molar masses than the unsubstituted bis(phenylaminopyridinato) titanium dichloride complex. Correspondingly, activities were lower and molar mass distributions were broader than those in the case of the unsubstituted bis(phenylaminopyridinato) titanium catalyst. The fluxional behavior of alkylphenylaminopyridinato titanium catalysts is probably the reason for the broad molar mass distributions. This might be due to the electron-donating effect from the alkyl substituent because the alkyl substituent enhances the active site isomerization rate.

Keywords: Aminopyridinato; Titanium; Polyethylene; Catalysis; Polymerization

1. Introduction

The development of the olefin polymerization catalysts forms one of the most impressive examples in organometallic chemistry. Usually, the catalytic properties of the organometallic complexes are highly dependent on the structure of the ligand framework around the metal centre [1–4]. As an alternative to the metallocenes, aminopyridinato complexes have gained interest in the field of catalysis of α-olefin polymerization [5,6]. Commonly, substituents include phenyl [7], aryl [8,9], silyl [10] and alkyl [11] groups. Scott et al. claimed that the alkyl substituents are better than trialkylsilyl substituents to control the stoichiometry and structure of aminopyridinato complexes [10,11]. The bis(*N*-adamantyl-2-aminopyridinato) zirconium dichloride used by them produced the activity of 20 kg mol^{-1} h^{-1} bar^{-1} in ethylene polymerization [11].

Our aim was to study the effect of alkyl group in the phenyl group of the bis(phenylaminopyridinato) titanium dichloride complexes on the catalytic activity in ethylene polymerization (Fig. 1). The alkyl substituents should increase the bulkiness of the phenyl group in the phenylaminopyridinato titanium catalyst and thus should affect the length of the polyethylene chain produced by the catalyst. We claim that in the case of alkyl substituents the propagation/elimination ratio would increase to produce a higher molar mass than with the unsubstituted phenylaminopyridinato titanium catalyst. Also, the activity should increase if the alkyl substituent does not prevent the coordination of ethylene. Furthermore, the less bulky catalysts should produce more branched polyethylene than the catalysts with the more sterically demanding ligand framework.

2. Experimental

2.1. Chemicals

Methylaluminoxane (30%) was acquired from Borealis Polymers. Toluene (Lab Scan, an analytical grade) was refluxed with sodium and distilled under argon. Polymerization-grade ethylene was purchased from AGA and used without further purification.

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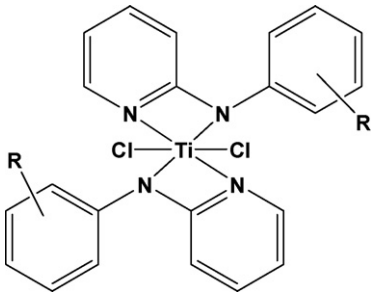

Fig. 1. Bis(alkylphenylaminopyridinato) titanium dichloride complexes: R = 2-Et; 2-*t*-Bu; 3,5-Me; 4-*n*-Bu.

2.2. Proligand preparation

2-Phenylaminopyridine is commercially available. The other proligands were synthesized from 2-chloropyridine and from the desired alkylaniline hydrochloride. Corresponding hydrochloride salt was made from the alkyl aniline and dried in a vacuum. 2-Chloropyridine and the alkylaniline hydrochloride were heated for 2 h at 180 °C. The resulting alkylaminopyridine hydrochloride was suspended to the sodium carbonate. The proligand was crystallized from a diethyl ether/heptane solution.

2.3. Proligand characterization

2.3.1. 2-[(2-Ethyl)phenylamino]pyridine [12]

^{1}H NMR ($CDCl_3$) δ: 1.21 (t, 3H), 2.65 (q, 2H), 6.41 (br s, 1H), 6.63 (d, 1H), 6.69 (d, 1H), 7.09–7.47 (m, 5H), 8.17 (d, 1H).

^{13}C NMR ($CDCl_3$) δ: 14.24, 24.43, 107.15, 114.45, 123.97, 124.93, 126.72, 129.25, 137.66, 137.85, 145.48, 148.51, 157.32.

2.3.2. 2-[(3,5-Dimethyl)phenylamino]pyridine

^{1}H NMR ($CDCl_3$) δ: 2.22 (s, 6H), 6.69 (t, 1H), 6.87 (s, 1H), 6.91 (s, 2H), 7.26 (br s, 1H), 7.43 (t, 1H), 8.18 (d, 1H).^{13}C NMR ($CDCl_3$) δ: 21.34, 108.01, 114.53, 118.26, 124.60, 137.56, 138.87, 140.42, 148.32, 156.41.

2.3.3. 2-[(4-n-Butyl)phenylamino]pyridine

^{1}H NMR ($CDCl_3$) δ: 0.93 (t, 3H), 1.36 (sept, 2H), 1.60 (sept, 2H), 2.58 (t, 2H), 6.67 (dd, 1H), 6.83 (d, 1H), 7.05 (br s, 1H), 7.18 (m, 4H), 7.44 (td, 1H), 8.17 (dd, 1H).^{13}C NMR ($CDCl_3$) δ: 13.93, 22.29, 33.70, 34.98, 107.63, 114.45, 121.04, 129.13, 137.57, 137.74, 137.95, 148.33, 156.59.

2.3.4. 2-[(2-t-Butyl)phenylamino]pyridine

^{1}H NMR ($CDCl_3$) δ: 1.42 (s, 9H), 6.32 (br s, 1H), 6.45 (d, 1H), 6.64 (dd, 1H), 6.73 (dd, 1H), 7.13–7.50 (4m, H), 8.16 (d, 1H).

^{13}C NMR ($CDCl_3$) δ: 30.56, 35.00, 106.98, 114.04, 125.85, 127.06, 127.23, 128.59, 137.59, 138.58, 145.69, 148.52, 158.12.

2.4. Pre-catalyst preparation

The general procedure for preparing bis(amidopyridinato) titanium complexes: The amidopyridine ligand was let to react with NaH (excess) in dry Et_2O (40 ml) at room temperature until no gas was evolved. The yellow ether solution of sodium amidopyridine was filtrated through the glass filter and then added dropwisely to the orange toluene solution of $TiCl_4$ (5 mmol in 40 ml) and stirred one hour at room temperature. The reaction mixture was filtrated through Kieselguhr and the solvent was evaporated under vacuum.

2.5. Pre-catalyst characterization

2.5.1. Bis[2-(2-Ethyl)phenylaminopyridinato]$TiCl_2$

^{1}H NMR ($CDCl_3$) δ: 1.11 (t, 6H), 2.39–2.63 (q, 4H), 5.93 (d, 2H), 6.12 (d, 2H) 6.68 (dd, 2H), 7.09–7.24 (m, 6H), 7.46 (t, 2H), 7.96 (br s, 2H).

^{13}C NMR ($CDCl_3$) δ: 14.64, 24.30, 104.86, 114.67, 121.67, 126.27, 126.81, 129.00, 139.16, 142.16, 144.31, 147.72, 167.09.

Anal. Calc. For $C_{26}H_{26}Cl_2N_4Ti$ C(60.84%), H(5.11), N(10.92%). Found C(59.94%), H(5.89), N(10.15%).

2.5.2. Bis[2-(3,5-dimethyl)phenylaminopyridinato]$TiCl_2$

^{1}H NMR ($CDCl_3$) δ: 2.22 (s, 12H), 6.51 (s, 2H), 6.59 (s, 4H), 6.83-6.94 (m, 4H), 7.49 (t, 2H), 7.89 (d, 2H).^{13}C NMR ($CDCl_3$) δ: 21.34, 105.26, 115.14, 119.08, 127.21, 138.40, 142.01, 142.24, 148.96, 168.90.

Anal. Calc. For $C_{26}H_{26}Cl_2N_4Ti$ C(60.84%), H(5.11), N(10.92%). Found C(60.24%), H(5.71), N(10.10%).

2.5.3. Bis[2-(4-n-Butyl)phenylaminopyridinato]$TiCl_2$

^{1}H NMR ($CDCl_3$) δ: 0.87 (t, 6H), 1.32 (sept, 4H), 1.54 (sept, 4H), 2.53 (t, 4H), 6.45 (dd, 2H), 6.48 (dd, 2H), 6.87–7.18 (m, 8H), 7.47 (t, 2H), 7.87 (br s, 2H).

^{13}C NMR ($CDCl_3$) δ: 13.95, 22.33, 33.63, 35.16, 104.95, 115.05, 121.13, 128.67, 140.22, 141.92, 142.15, 146.75, 165.84.

Anal. Calc. For $C_{30}H_{34}Cl_2N_4Ti$ C(63.28%), H(6.02), N(9.84%). Found C(62.51%), H(5.89), N(9.41%).

2.5.4. Bis[2-(2-t-Butyl)phenylaminopyridinato]$TiCl_2$

^{1}H NMR ($CDCl_3$) δ: 1.27 (s, 18H), 5.8 (dd, 2H), 6.41 (d, 2H), 6.69 (d, 2H), 7.05–7.26 (m, 6H), 7.43 (t, 2H), 7.89 (br s, 2H).

^{13}C NMR ($CDCl_3$) δ: 30.79, 35.12, 106.88, 115.23, 125.20, 126.68, 127.84, 128.13, 141.42, 141.95, 145.12, 151.60, 166.01.

Anal. Calc. For $C_{30}H_{34}Cl_2N_4Ti$ C(63.28%), H(6.02), N(9.84%). Found C(62.98%), H(6.44), N(9.51%).

2.6. Polymerization procedure

Toluene (250 ml) and the cocatalyst (MAO) were charged into the argon-purged reactor. Once the polymerization temperature had been reached, the vessel was pressurized with ethylene to the appropriate pressure. Introduction of the catalyst precursor solution (20 ml) into the reactor started the polymerization. After a desired polymerization time the reactor was depressurized and the contents of the vessel were poured into methanol acidified with a small amount of HCl. The solid polymer was filtered off, washed with methanol and dried under vacuum.

Table 1
Results of ethylene polymerizations promoted by complexes **1**–**5** with MAO[a]

Run	Cat.	Yield (g)	T_m[b] (°C)	Activity[c]	M_w (g mol^{-1})	M_w/M_n	X_c (%)[d]
1	2-EtPh (**1**)	0.27	136.8	27	630000	20.0	59
2	3,5-MePh (**2**)	0.47	136.1	47	390000	20.3	33
3	4-*n*-BuPh (**3**)	0.48	132.9	48	500000	26.6	22
4	2-*t*-BuPh (**4**)	0.30	135.2	30	390000	22.9	48
5	Ph (**5**)	0.80	135.9	80	250000	2.5	55

[a] Polymerization conditions: [Al]:[Ti] = 3000:1; n_{cat} = 20 μmol; t_p = 3600 s; T_p = 60 °C; P_p = 5 bar C_2H_4.
[b] Melting point determined by DSC. These values have been obtained from remelted samples at heating rate of 10 °C min^{-1}.
[c] Activity of catalyst in kg PE mol^{-1} Ti^{-1} h^{-1}.
[d] X_c (%): Crystallinity = $100(\Delta H_m/\Delta H_m^*)$; $\Delta H_m^* = 290$ J/g.

2.7. Polymer characterization

For the analysis of polymer molar masses and molar mass distributions a Waters 150C GPC chromatograph was used. 1,2,4-Trichlorobenzene was used as eluent at 145 °C and the calibration of the system was done with linear polystyrene standards. Melting temperatures of preheated and cooled samples were determined by differential scanning calorimetry using a PerkinElmer DSC-2 calorimeter. Heat of fusion was measured by DSC with a heating rate of 10 °C min^{-1} using a Mettler Toledo Star^e System. Crystallinity was calculated by using 290 J g^{-1} for the specific heat of fusion of polyethylene crystallites [13].

3. Results and discussion

The polymerization activities of the catalyst precursors **1**–**5** were studied in the ethylene polymerization. With MAO as a cocatalyst, catalysts **1**–**5** yielded polyethylene with moderate activity (Table 1).

The ethylene polymerization activity of alkylphenylaminopyridinates **1**–**4** decreased compared with phenylaminopyridinato **5**. This might be due to the electron-donating effect from the alkyl substituent. The longer the distance between the alkyl substituent and metal center the more active is the alkylphenylaminopyridinato titanium catalyst. This refers to the fact that the alkyl substituents at the 2 position of phenyl group of the phenylaminopyridinato ligand inhibit the coordination of the monomer to the metal centre, i.e. the steric factors affect the polymerization activity (Runs 1, 4 and 5).

All the present alkylphenylaminopyridinato titanium catalysts **1**–**4** produced higher molar masses than the phenylaminopyridinato titanium catalyst **5**. The alkyl substituent significantly enhances the active site isomerization rate. This might also be due to the electron-donating effect from the alkyl substituent. When the activity decreases the length of the polymer chain increases and its molar mass distribution broadens. Obviously, this is caused by the alkyl substituents preventing the β-elimination and thus by the increase in the propagation/elimination ratio. Furthermore, the electron donating alkyl substituents lead to an increase in the length of the polymer chain, i.e. they lower the ethylene insertion transition state [14].

Concluding from the crystallinities and the melting points of the polymers the 4-*n*-Bu-substituted phenylaminopyridinato titanium catalyst produced the most branched polyethylene in this study (Run 3). This conclusion is based on the information that melting points of polyethylenes decrease nearly linearly with the branching degree, i.e. one branch per 1000 carbon atoms in the chain reduces the melting point by approximately 1 C° [15]. This would mean that in the polyethylene produced by the catalyst **3** there are about 4 branches per 1000 carbon atoms more than in the polyethylene produced by the catalyst **1**. As in the case of the catalyst **3**, phenylaminopyridinato titanium catalyst **5** leaves the titanium centre open but it produced polyethylene which has the higher crystallinity and the melting point (Runs 3 and 5). In contrast, 2-ethylphenylaminopyridinato titanium catalyst **1** produced the most linear polyethylene in this study. The open titanium aminopyridinato catalyst structure (**5**) produced the more linear polyethylene than the catalyst (**4**).

The molar mass distributions of polyethylenes produced by alkylphenylaminopyridinato titanium catalysts **1**–**4** refer to the several existing active centres. On these kinds of co-ordination catalysts both mono- and dimeric titanium complex might appear as in the case of pyridyldiamines [16]. The catalytic cycle can also be complex because of possible other oxidation states of the titanium. In addition, it is known that amidopyridines form complexes with aluminum and hence the broadening of the observed molar mass distribution can be caused by the transfer of the amide to aluminum [17,18]. The most probable explanation for the broad molar mass distributions is, however, the rotation of the phenyl group of the phenylaminopyridinato titanium catalyst and thus several conformations can exist in solution. It is already known that in solution aminopyridinato titanium complexes have different configurations due to the weak pyridine nitrogen coordination to titanium centre [19,20]. The broad molecular weight distribution might also be due to the electron-donating effect from the alkyl substituent. The electron-donating effect from the alkyl substituent makes the Ti center more electron rich, thus significantly weakening the N···Ti coordination strength between the pyridine and the Ti center, therefore the rotation around the pyridine-amidonitrogen bond would be activated. This situation produces multiple Ti active sites with different coordination spheres, which makes polymer fractions with different molecular weights.

The broad ^{1}H NMR signals of the alkylphenylaminopyridinato titanium complexes refer to the fact that in solution rotation takes place around the amido titanium bond. Further-

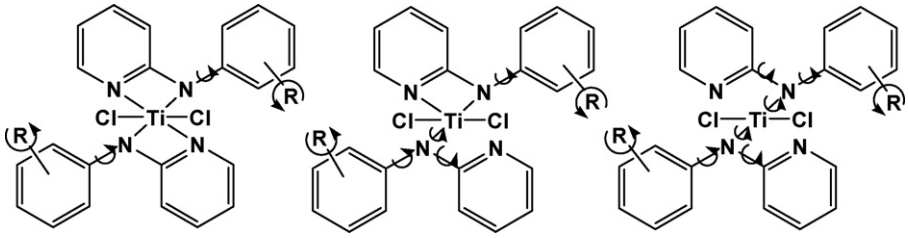

Fig. 2. Possible rotation modes of alkylphenylaminopyridinato titanium complexes in solution.

more, rotation around the pyridine-amidonitrogen bond and the aryl-amidonitrogen bond is possible (Fig. 2). In other words, the rotation rate of the alkylphenylaminopyridinato ligand changes in relation to the polymerization rate and thus the molar mass distribution broadens. In the case of *ansa*-aminopyridinato catalysts only the rotation of the pyridine part should be possible and thus the molar mass distribution should be narrower but no data has been reported [10,21].

The comparison of activities with the trialkylsilyl and adamantyl aminopyridinates is not simple because the values that have been experimentally determined depend on the used devices and their settings. The activation time or the lifetime of the catalyst is not often reported, the length of the polymer chain should be also a reliable indicator about catalyst behavior because the electronic effects have usually stronger influence on the molar mass than to the activity. In the case of trialkylsilyl and adamantyl aminopyridinato catalysts the published information about the molar masses of polymers is not available [10,11].

4. Conclusion

It is clear that the properties of polyethylene are related to the molecular structure of the alkylphenylaminopyridinato titanium catalyst used. The alkyl substitution of the phenyl group in the phenylaminopyridinato titanium complexes did not produce a better activity and narrow molar mass distribution compared with the phenylaminopyridinato titanium complex. This might be due to the electron-donating effect from the alkyl substituent.

The alkyl substituted phenylaminopyridinato titanium catalysts produced longer polyethylene chains than the unsubstituted reference titanium catalyst because bulky substituents reduced the probability of β-elimination and because the electron donating alkyl substituents lead to an increase in the length of the polymer chain. The alkyl substituent significantly enhanced the active site isomerization rate. This might also be due to the electron-donating effect from the alkyl substituent. When the concentration of the branches in the polyethylene decreases, the crystallinity and the melting point of the polyethylene increases and thus approaches the melting point of the known linear polyethylene and vice versa. The open titanium aminopyridinato catalyst centre does not necessarily produce polyethylene which has more branches.

Several rotation modes of the alkylphenylaminopyridinato titanium catalyst in solution are most probably responsible for the broad molar mass distribution due to the electron-donating effect from the alkyl substituent. A bridged phenylaminopyridinato titanium catalyst should be used to make the molar mass distribution narrow. On the other hand, the bridged aminopyridinato catalysts do not necessarily improve activity significantly according to known examples [10,11].

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