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Polymerization of a Styrene and Ethylene Mixture with a Trichloro(2,6-di-*tert*-butylphenoxy)titanium/Methylaluminoxane Catalyst System

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ABSTRACT: A homogeneous titanium halide catalyst containing one bulky phenoxy ligand was synthesized by the reaction of a lithium salt of 2,6-di-*tert*-butylphenol and $TiCl_4$. The complex was tested, with methylaluminoxane as cocatalyst, in the copolymerization of ethylene and styrene. The reaction product was not a copolymer but a mixture of polyethylene and atactic polystyrene. The formation of two fractions may indicate the presence of several active species in the catalyst or a different polymerization mechanism for the two monomers.

Introduction

Metallocene complexes of group 4 metals are the subject of continuing interest in the area of catalytic research.[1] These complexes can be activated with methylaluminoxane (MAO) to yield very high activity catalysts in the polymerization of olefins.[2] Active species in these catalyst systems are proposed to be cationic d^0 alkyl compounds, Cp_2MR^+ (M = Ti, Zr, Hf; R = alkyl).[3]

Little attention has been paid to metal alkoxide/MAO-type catalyst systems. It has been shown that Hf and Zr complexes with two or three bulky phenoxo ligands catalyze olefin polymerization,[4] and titanium tetrabutoxide in the presence of MAO produces syndiotactic polystyrene.[5] The Ti complex with a 2,2′-thiobis(6-*tert*-butyl-4-methylphenoxy) ligand has been reported to produce syndiotactic polystyrene and ethylene–styrene copolymers.[6]

Sterically demanding phenoxy ligands are well-known in chemistry.[7] The 2,6-dialkyl substitution of phenols in many cases prevents the formation of oxygen bridges, and the metal complexes with these ligands are usually monomeric.[8] The unsubstituted phenoxy ligands have a tendency to form oxygen bridges.[9] The alkyl substituents in the aromatic ring can undergo intramolecular CH bond activation and become a part of the ring system.[10] However, ring formation has not been observed in Ti halide phenoxy complexes, even at high temperatures.[11]

We replaced one Cl ligand in $TiCl_4$ with a bulky phenoxy ligand to obtain a Ti d^0 complex. The complex was activated with MAO and tested as a homogeneous catalyst for polymerization of styrene and copolymerization of styrene and ethylene.

Experimental Section

Materials. 2,6-Di-*tert*-butylphenol (>98%, Fluka Chemica) was purified by distillation under reduced pressure. Butyllithium was a 1.6 M solution in hexane (Merck), and metallic Na was pro analysis grade (Merck). The toluene used in catalyst synthesis was pro analysis grade (R.P. Normapur). Pentane was analytical grade (from Lab-Scan). Toluene, pentane, and diethyl ether were dried and purified by refluxing over $LiAlH_4$ and distilled under an argon atmosphere. The purity of $TiCl_4$ (from Aldrich) was 99.9%.

The cocatalyst was a 10 wt % solution of methylaluminoxane in toluene (Schering AG). Toluene used as a diluent was synthesis grade (from Merck), and ethylene was of grade 3.5 (Messer Griesheim). Toluene and ethylene were further purified before feeding to the reactor by passing them through columns containing molecular sieves, CuO and Al_2O_3. Styrene was synthesis grade (Fluka Chemika) and was purified by distillation in vacuum. It was stored under nitrogen at −25 °C.

Catalyst Synthesis. Because some of the reagents and products were air- and moisture-sensitive, all manipulations were carried out under an argon atmosphere using standard Schlenk techniques.

Synthesis of a Lithium Compound of 2,6-di-*tert*-butylphenol (LiOAr′). A total of 9.2 mL (0.01472 mol) of butyllithium (1.6 M solution in hexane) was added dropwise to a stirred toluene solution (30 mL) of 2,6-di-*tert*-butylphenol (3 g, 0.0145 mol) in an ice bath. Upon warming the mixture to room temperature, a white precipitate began to form. The mixture was stirred overnight, and the white compound was filtered and washed with pentane. The solvent was evaporated under vacuum to obtain the white product (2.2 g, 71%).

^1H NMR shifts of the Li salt of 2,6-di-*tert*-butylphenol (in DMSO, TMS = 0): 6.25 (d, 2H, C_6H_3), 5.57 (t, 1H, C_6H_3), 1.23 (s, 18H, $C[CH_3]$).

Synthesis of a Sodium Compound of 2,6-di-*tert*-butylphenol (NaOAr′). Preparation of sodium phenoxides in THF requires a lengthy refluxing of phenol and metallic sodium.[12] We found that the refluxing time could be shortened if the phenol was refluxed with sodium under reduced pressure without any solvent.

A total of 5 g of 2,6-di-*tert*-butylphenol (0.024 mol) and 0.4 g of metallic Na (0.017 mol) were placed in the Schlenk bottle connected to the vacuum distillation apparatus and heated. When sodium began to dissolve, a white precipitate rapidly began to form. Unreacted 2,6-di-*tert*-butylphenol was distilled off, while the reaction mixture was refluxed under vacuum. The reaction mixture was cooled to room temperature under an argon atmosphere, the white precipitate was dissolved in THF, and unreacted sodium was filtered out from the solution. Adding pentane to the solution precipitated a white sodium compound. It was washed with Et_2O and dried under vacuum. The NMR spectrum of the product showed it to be an ether solvate of NaOAr′ (2.2 g, 56%).

^1H NMR shifts of the Na salt of 2,6-di-*tert*-butylphenol (in DMSO, TMS = 0): 6.47 (d, 2H, C_6H_3), 5.46 (t, 1H, C_6H_3), 1.20 (s, 18H, $C[CH_3]$).

Synthesis of Trichloro(2,6-di-*tert*-butylphenoxy)titanium ($Ti(OArCl_3)$). Both LiOAr′ and NaOAr′ gave the same product in reaction with $TiCl_4$. A total of 0.52 mL (0.0047 mol)

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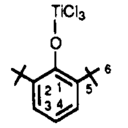
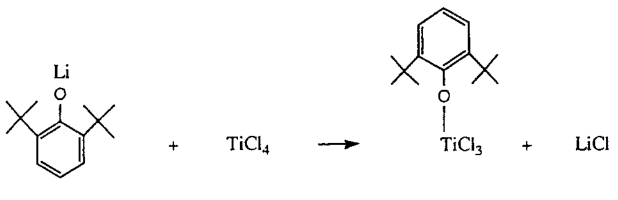
Table 1. NMR Shifts of the Titanium Complex

^1H,[a] ppm	^{13}C NMR,[a] ppm
7.15 (d, 2H)	150.17 (C1)
6.82 (t, 1H)	141.04 (C2)
1.45 (s, 18H)	126.22 (C3)
	121.93 (C4)
	39.95 (C5)
	32.25 (C6)



[a] In $CDCl_3$, TMS = 0.

Scheme 1



of $TiCl_4$ was added dropwise to a stirred toluene suspension of LiOAr′ (1 g, 0.0047 mol) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. Toluene was then evaporated under vacuum, and the resulting mixture of the Ti complex and LiCl was extracted with pentane. The extract was filtered through Celite to remove LiCl, and pentane was evaporated under vacuum. The product was a deep-red viscous liquid (1.1 g, 65%).

Ether peaks: 3.37 (q, 2H, CH_2Me), 0.96 (t, 3H, CH_2CH_3). The spectrum shows that there is one phenoxy group for two ether molecules in the Na compound. Sodium alkoxides are reported to have complicated structures with many Na atoms.[12] NMR shifts and IR spectral data of the Ti complex are given in Table 1.

Polymerizations. Polymerization reactions were performed in toluene in a 0.5-dm^3 reactor at 50 °C for 60 min. Toluene was charged under a nitrogen atmosphere into the evacuated autoclave at the polymerization temperature. The cocatalyst (MAO) was introduced into the reactor 1 min before addition of the catalyst. Immediately thereafter styrene was injected into the reactor and, after the temperature had stabilized, ethylene was fed at a required pressure. The partial pressure of ethylene was maintained constant with an electronic pressure control and a solenoid valve. The process was stopped by degassing the reactor, after which the organic layer was washed with a mixture of ethanol and diluted hydrochloric acid and water. Toluene and water were evaporated, and the product was dried under vacuum.

Characterization of the Polymer. The styrene content of the products was determined with a Nicolet 750 Magna FTIR spectrometer using melt-pressed thin films. The analysis was carried out using the 1494-cm^{-1} band for polystyrene and the 1473-cm^{-1} band for polyethylene, against polystyrene/polyethylene standards prepared by mixing polymers at different ratios.

The structure of the polymer was determined with a Varian 400 Unity NMR spectrometer. Molecular weight distributions were measured with a Waters high-temperature GPC instrument equipped with three mixed-bed columns with the exclusion limit for polystyrene 4×10^8. 1,2,4-Trichlorobenzene solvent was used at a flow rate of 1.0 cm^3/min. The columns were calibrated with low-density polyethylenes with broad molecular weight distributions. Melting points were measured with a Polymer Laboratories DSC analyzer at heating and cooling rates of 10 °C/min.

Results and Discussion

$Ti(OAr)Cl_3$ can be synthesized by reacting the lithium (or sodium) salt of 2,6-di-*tert*-butylphenol (LiOAr′) with $TiCl_4$ at a molar ratio of 1:1 (Scheme 1).

The lithium salts of di-*tert*-butylphenols are known as phenoxide transfer reagents, and they have been used in preparing corresponding phenoxy complexes of transition metals.[12] The crystal structures of the lithium salts that they are dimers and may also contain a solvent molecule (THF or ether).[13] In our case, based on ^1H NMR results LiOAr′ does not contain toluene.

Table 2. Results of the Polymerizations[a]

run	styrene, mol/L	activity, kg/(g cat·h)	Al/Ti	PE content, wt %	T_m, °C	$\bar{M}_w$
1	0.09	0.48	2000	2	138	394 000
2	0.17	0.47	2000	5	133	303 000
3	0.35	0.43	2000	10	133	318 000
4	0.87	0.20	2000	22	128	293 000
5	0.35	0.13	500		131	307 000
6	0.35	0.15	1000		134	342 000
7	0.35	0.54	2000		135	344 000
8	0.35	0.64	3000		133	308 000

[a] Polymerization conditions [Ti] = 11.1 μmol/L; $p(C_2H_4)$ = 6.0 bar; T = 50 °C; t = 30 min.

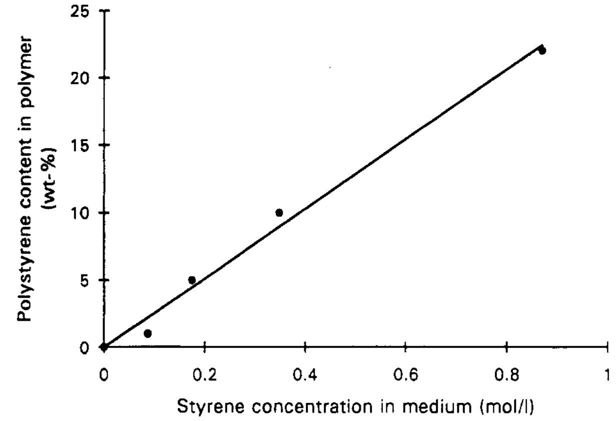


Figure 1. Relation between the styrene concentration in the medium and polystyrene content of the product. [Ti] = 11.1 μmol/L; $p(C_2H_4)$ = 6.0 bar; T = 50 °C; t = 30 min.

The reaction products of $TiCl_4$ and LiOAr′ (or NaOAr′) is a deep-red viscous liquid at room temperature, but it can be crystallized at low temperatures. The complex is air- and moisture-sensitive and soluble in hydrocarbon solvents. According to the ^1H-NMR spectrum, an intramolecular ring system is not formed.

The catalytic activity of $Ti(OAr)Cl_3$ with MAO was studied in copolymerization reactions of styrene and ethylene at 50 °C. Polymerization conditions and polymer properties are shown in Table 2. Polymerization reactions were carried out at different styrene concentrations (runs 1–4) and Al/Ti mole ratios (runs 5–8). Figure 1 illustrates the relation between the styrene concentration in the polymerization medium and the polystyrene content of the product.

The ^{13}C NMR spectrum of the product exhibited only two major resonances, at 30 ppm due to the methylene group in the aliphatic chain and a broad resonances at 41–45 ppm attributed to atactic polystyrene. The absence of other resonances indicates that the polymerization product is not a true copolymer but a mixture of atactic polystyrene and polyethylene. Atactic polystyrene was separated from polyethylene in the polymerization product by extracting for 7 h with boiling butanone. The insoluble fraction, polyethylene, was characterized by NMR.

Melting temperatures of the products were measured using a DSC analyzer at heating and cooling rates of 10 °C/min. Upon heating, the polymer showed only a single melting endotherm, but upon cooling two glass temperatures arising from polyethylene and atactic polystyrene were observed. The melting temperature of the polyethylene fractions decreased significantly with increasing the styrene concentration in the feed. Figure 2 shows the relation between the polystyrene content of the product and the melting point of the polyethylene fraction. The

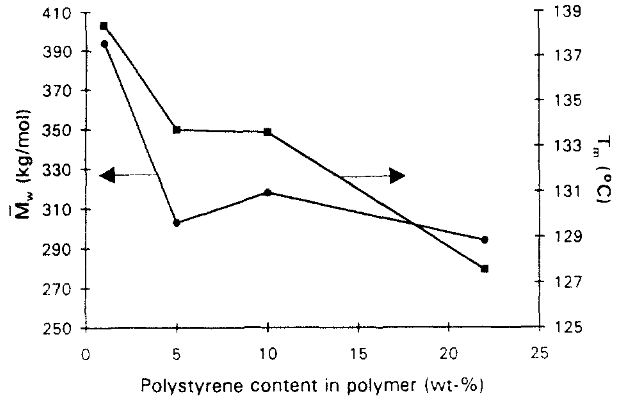


Figure 2. Relation between the polystyrene content of the product and the melting temperature and weight-average molecular weight of the polyethylene fraction.

polymer mixture with 2 wt % of polystyrene melts at 138 °C, whereas the mixture with a polystyrene content of 22 wt % has a melting point of 128 °C. Figure 2 also shows that the addition of styrene causes the weight-average molecular weight to drop from 394 000 to 294 000 for polymers 2 and 22 wt % of styrene, respectively. The decrease in the molecular weight may be due to chain transfer between polyethylene and styrene which terminates the chain growth. This may also cause a decrease in the melting point of the product.

As can be seen in Table 2 (runs 5–8), the activity of the catalyst in the polymerization increased sharply with the Al/Ti mole ratio when the ratio was below 2000 but remained more or less constant at higher ratios. The molecular weight of the product was not significantly affected by the different Al/Ti mole ratios.

Conclusions

The catalyst system trichloro(2,6-di-*tert*-butylphenoxy)titanium/MAO is active in ethylene polymerization and also produces atactic polystyrene, but it is not able to form an ethylene–styrene copolymer. The polymerization product is a mixture of polyethylene and atactic polystyrene, which are easily separated by extracting polystyrene with boiling butanone. The formation of two fractions may indicate the presence of several active species in the catalyst or different polymerization mechanisms for the two monomers.

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