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Synthesis of UHMW-PE by a Highly Active Homogeneous System: η^5-$(C_5H_5)_2Ti(\eta^1$-$OC(O)C_6H_5)_2$/MAO

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Summary

The complex η^5-$(C_5H_5)_2Ti(\eta^1$-$OC(O)C_6H_5)_2$ was synthesized and activated with MAO for ethylene polymerization. The resultant polymer is UHMW-PE with a viscosimetric molecular weight of Mv = 6.8 x 10^6 to 0.7 x 10^6 g/mol dependent on the temperature of the reaction. The effects of the Al/Ti molar ratio and temperature of the reaction on the catalytic activity and polymer properties were studied.

Introduction

UHMWPE is a linear polyethylene resin of industrial interest due to its exceptional toughness and also a combination of physical and mechanical properties: low coefficient of friction, high impact strength, low moisture adsorption, high chemical resistance and no known toxicity effects [1]. Its weight-average molecular weight of 4.0 x 10^6 is approximately ten times greater than high-density high molecular weight polyethylene (HDPE) resins [2]. As no conventional processing techniques are suitable for it, the standard pelletization is skipped and the material is available in its nascent morphology [1,3].

UHMWPE is currently manufactured, for commercial purposes, at moderate pressures and temperatures, by traditional Ziegler methods using titanium halides, titanium esters with aluminium alkyl co-catalysts, and by the Phillips method, using a chromium oxide catalyst [1b, 4]. High activity metallocene catalysts for UHMWPE synthesis are rare or not reported in the scientific literature. Recently, in the patent literature a double-bridged bisindenyl metal complex was reported to afford polyethylene with molecular weight between 5.0x10^5 to 1.0x10^7 g/mol upon activation with a suitable co-catalyst [5].

The generation of UHMWPE from metallocene catalysts might be expected to afford polymer with narrow molecular weight distribution (MWD $\leq$ 2), a feature characteristic of metallocene catalysed polymerization. This new material, UHMWPE-m (ultra-high molecular weight PE-metallocene) may have novel properties, and be suitable for new technological applications.

In our group, to obtain different reactivity and to achieve an active species resistant to electron-donating poisons, an exchange of halogen ligands for alkoxide, amide, carboxylate, etc., groups has been investigated. It has been found that by using the complex $Cp_2Ti(O_2CPh)_2$, activated with MAO, a very active catalytic system for UHMWPE-m synthesis is obtained.

In this work we describe the synthesis of UHMWPE-m by using $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}O_2CC_6H_5)_2$/MAO and the effect of the temperature of reaction and aluminium molar ratio on activity and polymer properties.

Experimental

General

All experiments were carried out under high purity nitrogen atmosphere (Praxair 99,97%) using standard Schlenk techniques. Solvents were distilled from Na/benzophenone and stored over molecular sieves (4Å). Benzoic acid (Aldrich) was recrystallized and dried under vacuum before use. Ethylene (Matheson 99,70 %) was passed through columns of molecular sieves prior to use. Cp_2TiCl_2 (Aldrich) and MAO, provided by Albemarle Corporation as 10 wt.-% solution in toluene, were used without further purification.

IR spectra were recorded using a FTIR Nicolet Nexus 470. NMR spectra were recorded on a Bruker spectrometer operating at 400 MHz, for ^1H and at 100 MHz for ^{13}C using $CDCl_3$ as solvent. The chemical shifts are reported in ppm referred to the signal of residual $CHCl_3$ for ^1H and to the signal of $CDCl_3$ for ^{13}C, both relative to tetramethylsilane (TMS). The titanium content was determined by means of colorimetry using a Perkin –Elmer Lambda 3 spectrometer [6].

$(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}O_2CC_6H_5)_2$ was synthesized according to the procedure reported in the literature [7]. Product characterisation, ^1H NMR (400 MHz,): δ (ppm) 6.59 (s, 10 H, CH of Cp), 7.48 (t, 4 H, J=7.3 Hz, CH of C_6H_5), 7.61 (t, 2 H, J= 6.3 Hz, CH of C_6H_5), 8.13 (d, 4 H, J_{ab} = 6.3 Hz, J_{bc}= 1.1 Hz, CH of C_6H_5). ^{13}C NMR (100 Hz): δ (ppm) $CDCl_3$): δ 120.2 (CH of Cp), 128.5 (CH_{meta} of C_6H_5), 129.3 (CH_{para} of C_6H_5), 130.2 (CH_{ortho} of C_6H_5), 133.8 (Cq of C_6H_5), 171.9 (C of COO^-). IR (KBr, Cm^{-1}): 3150, 2976-2830, ν_{asym} (COO) 1695, 1490, ν_{sym} (COO) 1371, 1288, 1161, 933, 719.

Polymerizations

A 500 ml Büchi stainless steel autoclave with mechanical stirrer and equipped with an external jacket for the circulation of water from a thermostatic bath to regulate internal temperature was dried and evacuated under vacuum and back-flushed with nitrogen several times. The reactor was then filled with 200 ml of freshly distilled toluene and the appropriate amount of MAO required for a given Al/Ti ratio. This mixture was stirred for 10 min to allow it to reach the desired temperature. 2 μmols of $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}O_2CC_6H_5)_2$ in toluene was added and stirring continued for 5 min, nitrogen was then evacuated and reactor saturated with ethylene at a pressure of 5 bar to start the polymerization. The temperature was kept within ± .01 °C. Polymerization temperatures tested were in the range of -25 °C to 60 °C. After 10 minutes, the ethylene supply was stopped and the polymerization mixture was quenched with acidic methanol (1% HCl). The polymers were isolated by filtration, washed with methanol and dried at 70 °C under vacuum until constant weight was obtained. Differential scanning calorimetric (DSC) measurements were performed using a

Rheometric Scientific DSC model QC & Plus. Samples were melted at 180 °C with a heating rate of 10 °C /min under nitrogen flow and kept at that temperature for 10 min. The thermograms were obtained by reheating the samples at rate of 10 °C/ min. The molecular weight was determined by intrinsic viscosity measurements using a PVS1 Lauda automatic viscometer.

Results and discussion

Ethylene Polymerisation Activity

Figure 1 shows the catalytic activity in ethylene polymerization as a function of the Al/Ti molar ratio for the system $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}O_2CC_6H_5)_2$/MAO, at –5°C . The maximum catalytic activity was obtained at an Al/Ti molar ratio of 3000. Low Al/Ti molar ratios are insufficient for total conversion to the active species due to the strong electron-donating interaction of the benzoate

Ligand impeding both the abstraction of carboxylate groups and subsequent methylation to generate the active species $[Cp_2TiMe]^+$. High Al/Ti ratios are also necessary to eliminate catalyst poisons present in the polymerization medium. As a result high Al/Ti ratio molar (3000 and above) are necessary to get the optimum performance in terms of catalyst activity, as shown in Figure 2. There is no apparent effect on activity at Al/Ti molar ratios greater than 3000, where a reversible deactivation of active centers due the coordination of the oxygen atoms of MAO to the complex cation or a deactivation process due to formation of inactive $Zr\text{-}CH_2\text{-}Al$ by the evolution of methane, as shown by Kaminsky et al. [8], may be expected [9].

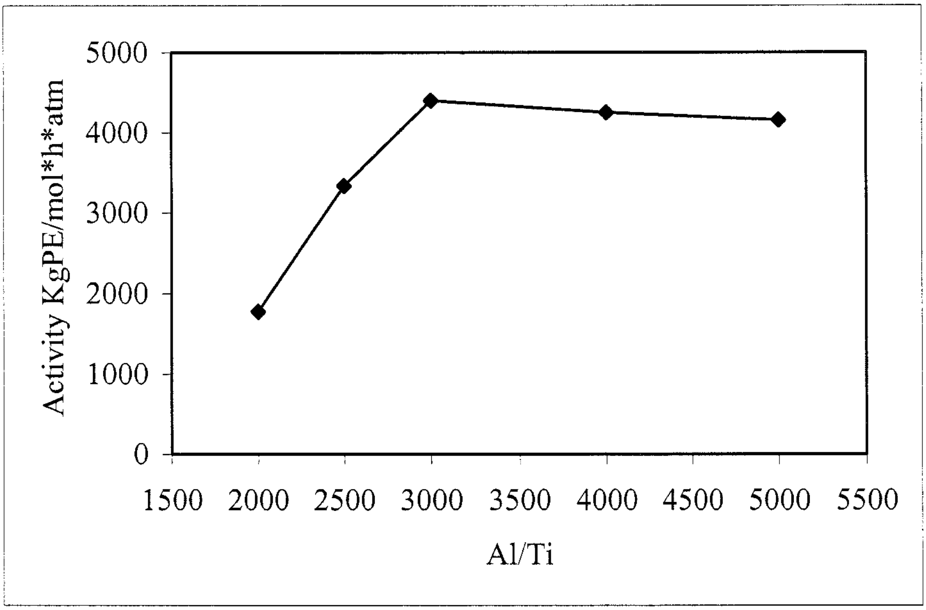

Figure 1. Plot of activity of $\eta^5\text{-}(C_5H_5)_2Ti(\eta^1\text{-}OC(O)C_6H_5)_2$/MAO versus Al/Ti molar ratio

The influence of polymerization temperature on activity and polymer molecular weight is displayed in figure 2. As can be seen, a strong effect of the polymerization temperature on the activity was found. The optimum activity was reached at -5 °C. Contrary to what was expected, higher temperatures resulted in a dramatic reduction in overall productivities. This may result from decreasing ethylene solubility at higher temperature in combination with a deactivation process due to the poor thermal stability of the cationic methyl complex [10].

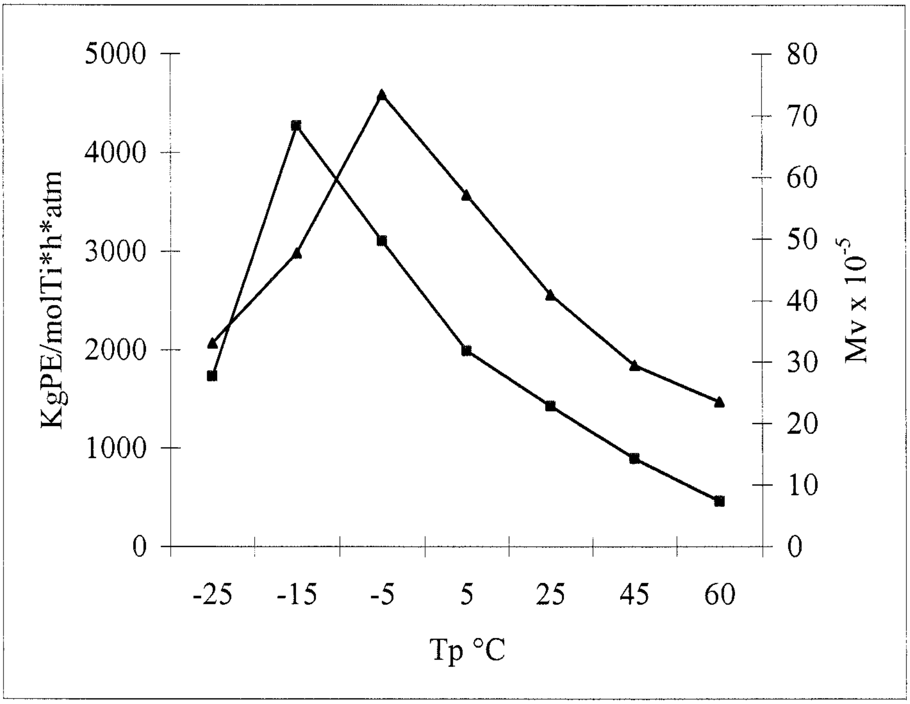

Figure 2. Plot of activity (▲) and molecular weight (■) versus polymerization temperature (Tp) for η^5-$(C_5H_5)_2Ti(\eta^1$-$O_2CC_6H_5)_2$/MAO

In the low temperature range, the activity increases with increasing Tp (from –25 °C to –5 °C). This may be reasonably attributed to the increase in the rate of insertion with temperature or a stronger interaction of $PhCO_2^-$ with the metal center at low temperature.

Active species

The active species is presumed to be the classic cationic species Cp_2TiMe^+. As this is derived from η^5-$(C_5H_5)_2Ti(\eta^1$-$O_2CC_6H_5)_2$, it is reasonable that the carboxylate ligands stripped during the formation of the active species could still be in close proximity to the catalyst, leading to a stabilization of the propagating species. Quian et al., [11] have previously proposed a similar stabilizing effect toward the active species of surrounding alkoxyl ligands stripped during the formation of an active species in syndiotactic styrene polymerization.

The π-donor capacity of carboxylate groups as Lewis bases can lead to a very strong interaction between the oxygen and the electron deficient aluminium atoms of MAO. This kind of interaction has been seen in the coordination of
[-Al(CH3)O-] units of the cocatalyt to methoxy groups of an unabridged metallocene bis(2,4-dimethyl-7-methoxyindenyl) zirconium dichloride recently reported by Yasin et al. [12].
Thus, the formation of $[Cp_2Ti^+Me]^-MAO\cdot O_2CC_6H_5$ involves the abstraction of carboxylate groups and the alkylation by MAO. The species $Cp_2Ti(Me)O_2CC_6H_5$ could be alkylated by MAO or trimethylaluminum (TMA), since MAO is always contaminated with some amount of TMA. Alternatively, MAO can abstract Me^- from Cp_2TiMe_2 or $^-OC(O)C_6H_5$ from $Cp_2Ti(Me)O_2CC_6H_5$; both pathways would lead to the formation of $[Cp_2Ti^+Me]^-MAO\cdot O_2CC_6H_5$.

Molecular Weight

The molecular weight of the polymer obtained also depended upon the temperature of reaction (figure 2). At temperatures between –15 °C and 5 °C ultra-high molecular weight polyethylene (Mv = 6.8×10^6 to 3.2×10^6 g/mol) was obtained.
The synthesis of UHMWPE by $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}O_2CC_6H_5)_2$/MAO can be explained as a result of a stabilizing effect on the active species to favor the propagation step over termination. A competition between the termination and the propagation steps determines the molecular weight of the polymer. The charge of the cationic metallic species type $[Cp_2Ti^+Me]^-MAO\cdot O_2CC_6H_5$ is dispersed and stabilized by the oxygen atoms of the carboxylate groups surrounding the active species; a substantial reduction of the Lewis acidity of the central metal atom results, reducing the rate of β-H chain transfer and favoring the propagation step. Additionally, a more stable active species is afforded by increasing the electron density on the metal center.
The molecular weight of the polymer decreased from 6.8×10^6 g/mol at –15 °C to 0.7×10^6 g/mol at 60 °C. Increased dissociation of the ion pair would be expected as the temperature increases, increasing the Lewis acidity of the metallic center. Consequently, higher temperature increases the rate of β-H chain transfer over the propagation rate to afford lower molecular weight polymer. On the other hand, at lower temperatures (–25 °C), the rate of insertion and propagation decrease. This affects not only the molecular weight but also the productivity as described previously.

Thermal properties

The melting temperature and the fusion enthalpies of the polymers were measured by DSC in the nascent state and melt-crystallized UHMWPE (Table 1). As is generally found nascent UHMPE displayed higher melting temperature and crystallinity than melt-crystallized samples of the same polymer. In the nascent state Tm were in the range of 139-140 °C while ΔH_f were between 30 and 60 Kcal/g corresponding to a crystallinity range of 50 to 80 % (with the exception of entry 3) which are close to the melting properties of a chain-extended PE crystal [13].

Table 1. Thermal properties of UHMWPE-m

Entry	T_P (°C)	T_{m1} (°C)	ΔH_{f1} (Kcal/g)	%X	T_{m2} (°C)	ΔH_{f2} (Kcal/g)	%X	M_v*10^{-6} (g/mol)
1	-25	140.5	50.1	72.6	136.2	32.0	46.4	2.8
2	-15	140.9	45.8	66.4	133.04	25.1	36.3	6.8
3	-5	132.6	29.7	43.0	133.23	32.4	46.9	5.0
4	5	133.6	33.2	48.1	133.40	35.0	50.7	3.2
5	25	138.7	36.1	52.3	133.09	20.3	29.4	2.3
6	45	138.9	43.4	62.9	134.70	33.4	48.3	1.4
7	60	138.2	60.5	87.7	134.70	38.3	55.5	0.7

T_{m1} : Melting temperature of polymers in nascent state
T_{m2}: Melting temperature of polymers recrystallized
M_v: Viscosimetric molecular weight
$\Delta H_{f(i)}$: Fusion enthalpy
%X: Crystallinity percent

UHMWPE obtained from Ziegler catalysts grow from this surface because the active species are located on the catalyst particle, consequently, the nascent morphology is conditioned by the local synthesis environment, which determines both the formation of molecule and their crystallization, and the reaction temperature as described by Loos et al. [3]. However, in a single-site catalyst a better dispersion of active species (depending on catalyst concentration) occurs, thus the chains will be much less entangled. Decreases in Tm of about 6 °C between melt crystallized and nascent polymer obtained from our catalytic system are consistent with a much lower degree of entanglement. It is unlikely that this results from a considerable structural reorganization during the DSC heating scan. Crystallinity values around of 50 % in melt-crystallized samples indicate a low degree of branching of PE. Finally, no correlation between Al/Ti molar ratio and temperature on the melting properties of the polymer were found.

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