Cocatalyst-Originated Aluminum Residues in Fibrous, Very High Molar Mass Polyethylene

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ABSTRACT: In this work, fibrous very high molar mass polyethylene was prepared by Cp_2TiCl_2, which was supported on methylaluminoxane (MAO) pretreated mesoporous silica fiber. After the polymerization, an "ordinary" washing procedure was not sufficient to remove the aluminum residues of the cocatalyst MAO from the polymerization product. When hydrochloric acid was used in the termination of the polymerization, the aluminum existed as $[Al(H_2O)_6]Cl_3$, the presence of which causes additional signals to DSC and XRD grams of the polyethylene. These signals have previously been interpreted to be attributed to the extended chain crystal structure of the polyethylene. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1812–1815, 2004

Key words: metallocene catalysts; supports; polyethylene (PE); methylaluminoxane; impurities

INTRODUCTION

Metallocene catalysts have an important part in the production of polyolefins. As a result, much research has been done on development of various metallocenes, with which different kinds of polymers can be tailored. In addition to the metallocene, a cocatalyst is often needed in the polymerization process to activate the metallocene. These cocatalysts are usually aluminum compounds, of which one of the most effective and common is methylaluminoxane (MAO). At the end of the polymerization the catalyst is destroyed to terminate the process, and the polymer is washed to remove the catalyst and cocatalyst residues. At this point the polymer is supposed to be pure enough for the characterization of its physical and chemical properties. When the polymer is in a powder or small granular form, the washing is more effective and the amount of impurities (i.e., remnants of catalyst and cocatalyst) is negligible. However, if the polymerization product forms a single lump in the reactor, it may be considerably harder to wash. If not enough care is taken to wash the polymer, the amount of impurities may easily be significant in the polymer's mass, which should be considered in the characterization of the product. The impurities not only alter the mass of the polymer sample but also may cause additional signals, for example, in DSC grams and X-ray diffractograms.

These signals may be—and have been—erroneously interpreted to be ascribed to the polymer.

We report here of significant amounts of aluminum residues in fibrous, very high molar mass polyethylene, produced with methylaluminoxane activated Cp_2TiCl_2, which was supported on mesoporous silica fiber. When hydrochloric acid is used in the termination of the polymerization or washing of the polyethylene, the aluminum is present as hexaaquaaluminum(3+)trichloride $[Al(H_2O)_6]Cl_3$, of which XRD and DSC signals were previously interpreted by Aida et al.[1] to be attributed to the extended chain crystal structure of the polyethylene.

EXPERIMENTAL

Materials

Toluene (Riedel-de Haën, Seelze, Germany) was dried over 4-Å molecular sieves and distilled using benzophenone and Na under nitrogen atmosphere. Titanocene dichloride (Strem Chemicals, Newburyport, MA) and methylaluminoxane (10% in toluene; Witco Chemical Corpo, Middlebury, CT) were used as received. Hexadecyltrimethylammoniumbromide and tetraethylorthosilicate were purchased from Aldrich (Milwaukee, WI) and used as received.

Catalyst preparation

Mesoporous MCM-41 silica fiber was used as the catalyst support and was synthesized in a couette flow reactor following the procedure of Lin and coworkers.[2] Surface area of the support material was about 1200 m^2/g and average pore size 28 Å. The silica fibers

were treated with an MAO solution (30 mmol of Al per 1 g of silica, shaken at 50°C for 16 h), washed with toluene, and dried in a vacuum at 50°C. After that Cp_2TiCl_2 was dissolved in toluene and impregnated on the MAO-pretreated silica fibers (with a titanocene concentration of about 300 μmol/g of silica, 50°C, 16 h). The catalyst was washed five times with toluene to remove nonbonded titanocene from the support and dried in a vacuum at 50°C. The resulting titanium loading on the support was usually 0.3–0.4 wt %.

Ethylene polymerization

The polyethylene samples were prepared using a 250 mL Büchi stainless steel reactor (Büchi Labortechnik AG, Flawil, Switzerland) with the following method: the catalyst (containing 3.0 μmol of Cp_2TiCl_2), MAO solution (Al/M = 1000), and 50 mL of toluene were packed in a stainless steel catalyst container in a nitrogen glove box. The solution was transferred into the evacuated reactor using a nitrogen overpressure and after 30 min of total activation at ambient temperature the polymerization was started by introducing a 5 bar pressure of ethylene and by starting the stirring (750 rpm). The partial pressure and temperature (25°C) were kept constant during the polymerization, which lasted for 30 min. The reaction was terminated by venting the ethylene and by adding ethanol. The product was stirred in acidic (HCl) ethanol solution for 3–4 h, filtered, washed with ethanol, and dried at room temperature.

Characterization

Nitrogen adsorption (ASAP 2010 Micromeritics, GmbH, Mönchengladbach, Germany) was used to determine the BET surface area and pore size of the silica fiber. The titanium loading on the supported catalyst was determined by atomic absorption spectrophotometry (AAS). An LEO 1550 scanning electron microscope (SEM) was used to evaluate the morphology of the freeze-dried polyethylene. The nominal molar masses were determined by measurement of the dilute solution viscosity.[3] In the solution 0.2 wt % of antioxidant BHT was used. Calculations were based on Mark–Houwink constants $K = 62 \times 10^{-3}$ mL g^{-1} and a = 0.700. Differential scanning calorimetry (DSC) measurements were performed on a Mettler-Toledo (Zürich, Switzerland) DSC821e calorimeter using a scanning rate of 10 K/min. The powder X-ray diffraction data were collected with a Bruker (Darmstadt, Germany) AXS D8 Advance diffractometer equipped with Göbel Mirror optics and Soller slits. Data collections were carried out at 298 K using Cu–K$_\alpha$ radiation (λ = 1.54060 Å). The data collection 2θ range was 10–50°. The single-crystal X-ray diffraction data were collected with a Nonius KappaCCD diffractometer (Bruker Nonius B.V., Delft, The Netherlands) using Mo–K$_\alpha$ radiation (λ = 0.71073 Å). Single crystals were mounted in an inert oil to the cold gas stream (163 K) of the diffractometer.

RESULTS AND DISCUSSION

The length of the silica fibers was 0.2–2 mm and thickness 30–300 μm depending on the synthesis conditions. Because the outer surface area of the fibers is negligible compared to the total surface area, it is reasonable to assume that most of the metallocene existed inside the silica fibers. This is supported by the fact that the BET surface area, pore volume, and average pore diameter of the silica decreased substantially during the catalyst immobilization.

The yield of the polymerization product was about 0.7–0.9 g. The polyethylene was fibrous and mostly entangled around the stirring rod of the reactor, forming a single lump (Fig. 1). Molecular weight (M_v) of the products was 2,000,000–2,300,000 g/mol.

In nearly all of the DSC first-melting curves of the polymerization products, a second endotherm could be seen, in addition to the melting endotherm of polyethylene. It appeared either as a high-temperature shoulder to the melting endotherm of the polyethylene, or as a separate signal in the temperature range of 160–220°C (Fig. 2). The larger the size of the endotherm, the higher was its temperature. This additional endotherm was observed only in the first heating, after which some loss of sample weight was observed.

When the polymerization products were measured by a powder X-ray diffractometer, several additional reflections to the ordinary (110) and (200) reflections of polyethylene around 21.7 and 24.2° (2θ), respectively, were detected (Fig. 3). The 2θ values of the additional reflections in Figure 3 are 14.9, 17.2, 22.9, 26.1, 27.0, 27.4, and 30.2°. Similar XRD reflections and an additional shoulder in the DSC melting curve were previously reported by Aida et al.,[1] who interpreted them to result from a phase transition of an extended chain crystal structure (ECC) of the polyethylene. Indeed, if the PE has an ECC structure or, if the PE sample is constrained, a phase transition from an orthorhombic to a hexagonal phase and the melting of the hexagonal phase is observed as an endothermic shoulder or a peak in the DSC melting curve, so the interpretation of Aida et al. is justified.[4,5] The ECC structure, however, was not the true reason for those signals, as presented in this study.

One of our polyethylene samples "sweated" a light yellow liquid a few weeks after the polymerization and, as the liquid droplets evaporated, clear crystals were left on the surface of the polymer. The crystals were measured with a single-crystal X-ray diffractometer, which proved them to be hexaaquaaluminum(3+)trichloride (crystal system: trigonal, space group $R\bar{3}c$ (no. 167), unit
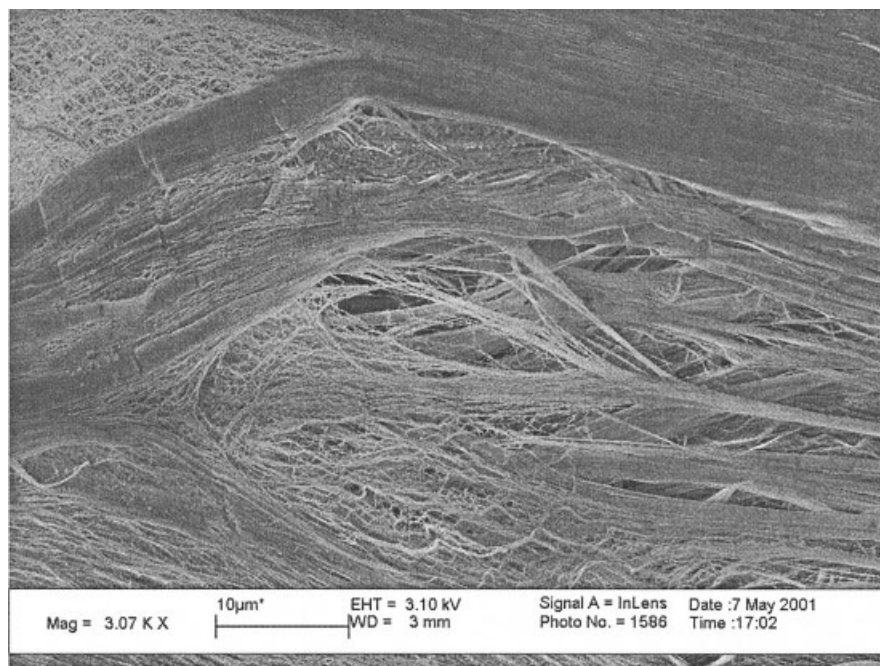
Figure 1   SEM micrograph of the polyethylene surface, revealing it to consist of 20- to 60-nm thick PE fibers.

cell: $a = 11.814(2)$, $c = 11.781(2)$. The X-ray structure was previously published.[6]). Also the water-soluble evaporation residue of the washing solutions of the polyethylenes was $[Al(H_2O)_6]Cl_3$. The simulated powder pattern of $[Al(H_2O)_6]Cl_3$, created from the single-crystal diffraction pattern, corresponded to the additional reflections in the polyethylene powder X-ray diffractogram (Fig. 3). The DSC heating curve of the $[Al(H_2O)_6]Cl_3$ crystals had only a single endotherm at 230°C, attributed to decomposition of the hexaaquaaluminum complex. From these observations it is obvious that the polymerization products contained $[Al(H_2O)_6]Cl_3$.

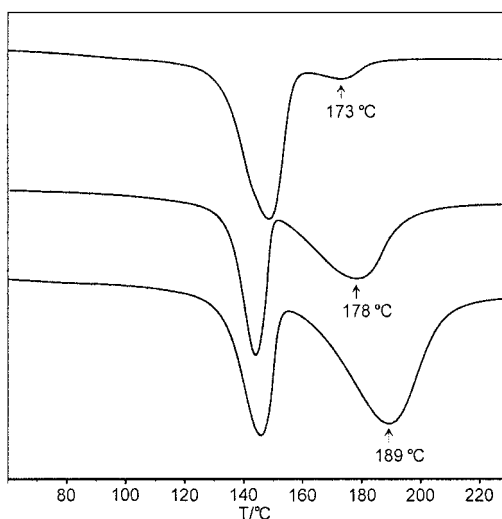The amount of aluminum in the polyethylenes was analyzed by burning the samples in air, dissolving the residues in HCl and HF, and by measuring the solu-
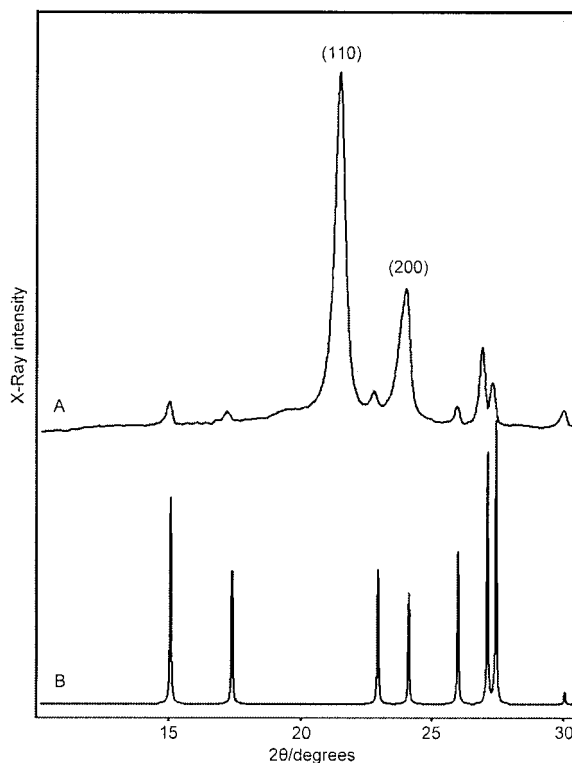

Figure 2   DSC first-melting curves of polyethylene samples containing different amounts of $[Al(H_2O)_6]Cl_3$.

Figure 3   Powder X-ray diffractogram of (A) polyethylene that contains $[Al(H_2O)_6]Cl_3$ and (B) simulated powder pattern of $[Al(H_2O)_6]Cl_3$.

tions by AAS. The samples contained 0.6–6.5 wt % of aluminum, the amount generally correlating with the size of the additional endotherm in the DSC melting curve. An aluminum amount of 6.5 wt % corresponds to 58 wt % of $[Al(H_2O)_6]Cl_3$ so, if all of the aluminum existed as the hexaaqua complex, over half of the polymerization product was something other than the polymer itself! In these cases the polyethylene already looked slightly glassy. The formation of $[Al(H_2O)_6]Cl_3$, however, requires washing of the polymer with hydrochloric acid. If only ethanol is used in the termination of the polymerization, aluminum ethoxides or some other aluminum compounds are formed.[7] The presence of these compounds is not detected by DSC or XRD, so other means of aluminum analysis are required.

What is the reason for the high aluminum content of these polyethylene samples after a "normal" washing procedure? An explanation could be the proposed extrusion polymerization mechanism[1] caused by the hexagonally ordered, tubular mesopores of the silica support. As a result, the polyethylene chains extruding from the pores are more oriented than those obtained with homogeneous polymerization (or heterogeneous polymerization using ordinary silica) and thus form more densely packed PE, which is harder to wash. The effect of heterogeneous catalyst on the aluminum content of PE is supported by the fact that, although in homogeneous polymerizations Cp_2TiCl_2 also yielded polyethylene with an M_v value of over 2,000,000 g/mol and the PE was wrapped around the stirring rod of the reactor, the amount of residual aluminum was in those cases only 0.1–0.5 wt %. In all cases washing with an acidic solvent enhanced the removal of aluminum residues compared to nonacidic solvent.

CONCLUSIONS

The additional endotherm in the DSC melting curve and the extra reflections in the powder X-ray diffractogram of the polyethylene are explained by the presence of $[Al(H_2O)_6]Cl_3$, residual from the cocatalyst and formed during the washing of the polymer with an acidic (HCl) solvent. Because the aluminum residues are hard to remove from dense and fibrous high molar mass polyethylene, care must be taken to obtain pure products and to avoid erroneous conclusions. Washing the polymerization products with an acidic solvent increases the removal of the residual aluminum but, on the other hand, turns the remaining aluminum into $[Al(H_2O)_6]Cl_3$, thus increasing the mass of the impurity. The impurities complicate the determination of the molar mass, heat of fusion in DSC, and all other calculations, where the mass of the polymer sample is required, so repeated washings with prolonged times and acidic solvent are required to ensure the purity of the densely packed polymer sample.

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