

Nanofibers of polyethylene produced by SBA-15 supported zirconium catalyst [N-(3-*tert*-butylsalicylidene)-4'-allyloxylanilinato]₂Zr(IV)Cl₂

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Abstract

Ethylene polymerization was carried out with the zirconium catalyst bis[N-(3-*tert*-butylsalicylidene)-4'-allyloxylanilinato] zirconium(IV) dichloride supported on SBA-15, which had a uniform hexagonal array of linear channels, with MAO (methylalumoxane) as the cocatalyst. Both the molecular weight and melting point of the obtained polymers were much higher, compared with the polyethylene produced by its homogeneous counterpart. This observation indicates that the mesoporous zeolite SBA-15 can effectively control the direction and dimension of the growth of polymers in the process of polymerization, yielding polymers with improved properties. Nanofibrous polyethylene was also obtained under polymerization conditions with the use of this supported catalyst.

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Keywords: SBA-15 zeolite; Zirconium catalyst; Heterogeneous catalysis; Ethylene polymerization; Nanofibrous polyethylene

1. Introduction

The synthesis of polymers with improved properties and controlled morphology is of great interest to both academia and industry. So far, most polymers have been produced by organometallic catalysts in the process of olefin polymerization [1–3]. These homogeneous catalysts, such as metallocene [4,5] and post-metallocene [6,7], have very high catalytic activity; however, the lack of control over the morphology of polymers limits their application. One way to solve this problem is to immobilize these catalysts on suitable supports [8,9]. Immobilization of homogeneous catalysts for olefin polymerization is accomplished by the process of supporting the transition-metal complexes and MAO on the surface of inorganic solids or polymers, causing the contributing part to be adsorbed. Since the supports can effectively control the structure and morphology of polymers through polymerization [10], the properties of the obtained polymers can be greatly improved. First used in the 1990s,

mesoporous zeolite with a parallel hexagonal channel structure is becoming a promising support for catalyst immobilization [11–13]. The geometrical constraints of the parallel hexagonal channel structure affect the pattern of monomer insertion and the chain growth process, which offer a way to control the polymer chain structure and morphology in olefin polymerization [14,15]. Moreover, since the mesoporous zeolite has a nanoscale pore diameter, nanofibrous polymers can be obtained by olefin polymerization. A good example is provided by the work of Aida et al. [16], who produced the crystalline nanofibers of polyethylene with MSF-supported Cp₂TiCl₂ catalyst in the “extrusion polymerization.”

In this work, we used SBA-15 as the support. As a mesoporous zeolite, SBA-15 has a lot of particular characteristics, such as large surface area, narrow pore distribution, long pore diameter, large pore volume, and high mechanical intensity sustained by a thick wall [17], so it is a very ideal support for homogeneous catalysts. Our group has reported the support of post-metallocene catalysts such as diimine nickel complex [18] and pyridine bisimine iron complex [19] on SBA-15, with some satisfying results. To develop this aspect of our research, we synthesized the zirconium catalyst bis[N-(3-*tert*-butylsalicylidene)-4'-allyloxylanilinato] zirconium(IV) dichloride supported on SBA-15, which had a uniform hexagonal array of linear channels, with MAO (methylalumoxane) as the cocatalyst. Both the molecular weight and melting point of the obtained polymers were much higher, compared with the polyethylene produced by its homogeneous counterpart. This observation indicates that the mesoporous zeolite SBA-15 can effectively control the direction and dimension of the growth of polymers in the process of polymerization, yielding polymers with improved properties. Nanofibrous polyethylene was also obtained under polymerization conditions with the use of this supported catalyst.

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nium(IV) dichloride (Fig. 1) with very high catalytic activity, introduced it into the supported system, and characterized the property of polyethylene produced by the supported catalysts in the process of ethylene polymerization.

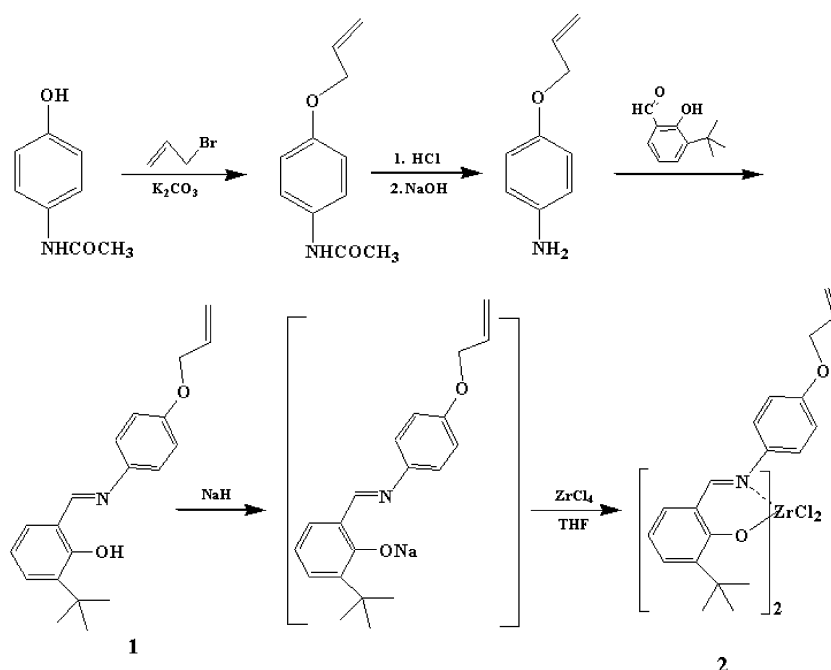
2. Experimental

2.1. Synthesis

All manipulations were performed under an argon atmosphere with standard Schlenk techniques. 3-*Tert*-butylsalicylaldehyde was prepared according to a method described in the literature [20]. 4-Acetamidophenol, ZrCl_4 , and co-catalyst MAO (1.7 M in toluene) were purchased from the Acros and Witco Corporations, respectively; other reagents were analytical-grade reagents. Solvents were dried with anhydrous calcium dichloride or a 4-Å molecular sieve for several days, then refluxed with appropriate drying reagents (sodium/benzophenone for toluene, diethyl ether, hexane, THF, and CaH_2 for dichloromethane) and distilled under argon before use. As stated in Ref. [17], the synthesis of mesoporous zeolite SBA-15 included the use of triblock copolymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123, BASF) as the template and tetraethoxysilane (TEOS, 98%; Acros) as the source of silica.

2.2. Catalyst preparation

2.2.1. Preparation of homogenous catalyst bis[*N*-(3-*tert*-butylsalicylidene)-4'-allyloxylanilinato] zirconium(IV) dichloride (**2**) (Scheme 1)



Scheme 1. Synthesis of complex **2**.

2.2.1.1. *Synthesis of the ligand N*-(3-*tert*-butylsalicylidene)-4'-allyloxylanilinato (**1**) 4-Acetamidophenol (0.1 mol, 15.1 g), allyl bromine (0.11 mol, 13.3 g), and potassium carbonate (0.25 mol, 34.6 g) were suspended in dried acetone, and the solution was refluxed for 24 h. After the solvent was cooled to room temperature, it was removed to give 13.1 g (69%) of 4-allyloxylacetanilide. ($^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 2.12 (3H, s, acetyl), 4.49 (2H, d, CH_2), 5.26 (1H, d, $=\text{CH}_{\text{cis}}$), 5.40 (1H, d, $=\text{CH}_{\text{trans}}$), 6.02 (1H, m, $-\text{CH}=\text{}$), 6.83 (2H, d, phenyl), 7.36 (2H, d, phenyl), 7.58 (1H, s, $-\text{NHCO}-$).

To a solution of 4-allyloxylacetanilide (68 mmol, 13 g) in ethanol was added 136 mmol of hydrochloric acid (12 M, 11.3 ml), and the reaction mixture was refluxed for 6 h. After removal of solvent, the mixture was poured into NaOH solution and extracted with diethyl ether. The diethyl ether extract was dried over Na_2SO_4 and then concentrated to leave crude product. 4-Allyloxylaniline (7.6 g, 75%) was purified by distillation under vacuum. ($^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 3.32 (2H, s, NH_2), 4.43 (2H, d, CH_2), 5.24 (1H, d, $=\text{CH}_{\text{cis}}$), 5.38 (1H, d, $=\text{CH}_{\text{trans}}$), 6.01 (1H, m, $-\text{CH}=\text{}$), 6.59 (2H, d, phenyl), 6.73 (2H, d, phenyl).

A solution of 4-allyloxylaniline (2.25 g, 15.1 mmol) in ethanol was added to a 3-Å molecular sieve (2 g) and 3-*tert*-butylsalicylaldehyde (2.39 g, 13.4 mmol) in ethanol drop by drop; then the reaction mixture was stirred for 24 h at room temperature. After filtration, ethyl acetate was used to wash the molecular sieve. The combined organic phases were evaporated in vacuo to give a crude product, which was purified by column chromatography on silica gel with hexane/ethyl acetate (10:1) as eluent to give the ligand **1** (3.4 g) as a pale yellow oil in 82% yield. ($^1\text{H-NMR}$

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