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Polymerization Catalyst\([(\text{BDI})\text{ZnN}(\text{TMS})_2]\) Synthesis

Guangyao Gao, Chris Schaller
Abstract

The goal of this project was to synthesize [[BDI]ZnN(TMS)₂], a catalyst for a ring-opening trans-esterification polymerization reactions. The BDI ligand was synthesized from the reaction of 2,6-diisopropylaniline and 2,4-pentanedione; four trials resulted in an average yield of 12.5%.

The ligand formation was confirmed by the appearance of peaks at 3.481 ppm in the 1H NMR spectrum, indicating the —CH₂ group. After recrystallization from methanol, the zinc complex was formed by treating Zn[N(TMS)₂] with BDI, resulting in a yield of 38.5%.
Introduction
Polymer chemistry is a type of reactions deal with structures and synthesis of polymers. An important area in modern chemistry. Because of the wide usage of polymers it is really important to examine the synthesis of them.

Polymerization reactions always have an initiator to start the reaction, before multiple monomers add to form a polymer chain. A typical example is a ring opening polymerization of ε-caprolactone (CL), l-lactide (LA), etc. Common catalysts are very slow to in these reactions.

In this project, the idea was to try a faster catalyst. A faster catalyst [(BDI)ZnN(TMS)$_2$] was reported in literature. There will be multiple steps to synthesize the catalyst [(BDI)ZnN(TMS)$_2$]. The BDI ligand was synthesized from the reaction of 2,6-diisopropylaniline and 2,4-pentanedione. Then the BDI ligand will be formed to [(BDI)ZnN(TMS)$_2$]. After the synthesis, testing the efficiency is also really important for the project.
Reflex HCl
3 days, 85 °C

Toluene
6 days 80 °C

2-propanol
6 hrs, 20 °C
Experimental synthesis \{(BDI)\text{ZnN(TMS)}2\}

it will use concentrated HCl, 2,4-pentanedione, 2,6-diisopropylaniline, methylene chloride and general solvent methanol and ethanol. This is a reflux reaction, so a hot plate is needed.

- HCl (0.4 mL, 4.8 mmol) is added to a solution of 0.5 ml, 4.9 mmol 2,4-pentanedione and 1.96 g, 11 mmol 2,6-diisopropylaniline in about 20 ml ethanol.
- set up the heat plate and the equipment for reflux reaction and stir for 3 days.
- After 3 days the product is concentrated to brown solid. Dissolve the solid in about 10 ml methylene chloride.
- Evaporate the solvent and recrystallize the solid from methanol. The white solid product will be collected.
- A glove box and vacuo are needed. (BDI)H, toluene and zinc bis(trimethylsilyl)amide.
- zinc bis(trimethylsilyl)amide in 1.36 ml toluene is added to a solution of 0.83 g (BDI) in 4.05 ml toluene.
- Set up the heat plate at 80 °C and stir for 6 days.

The proton NMR is provided below.

First step:

1H NMR CDCl$_3$ 7.119 (6H, arH), 4.856 (s, 1H), 3.133 (s, 4H, CHMe$_2$), 1.746 (s, 6H, Me), 1.271 (d, 12H, CHMeMe$'$), 1.113 (d, 12H,CHMeMe$'$).

Second step:

1H NMR CDCl$_3$ 7.143 (6H, m, ArH), 4.852 (1H, s, CH), 3.120 (4H, m, CH), 1.704 (6H, s, Me), 1.211 (12H, d, CHMeMe), 1.117 (12H, d, CHMeMe), 0.049 (18H, s, SiCH$_3$).
Result and discussion

The result for the experiment is pretty successful. Because it is a synthesis experiment, the only important point is to get the right product. According to the NMR, there are peaks at around 0 ppm which insist that I have CH$_3$----Si bond. Which means the reaction was successful.

Comparing the literature, even the color is different, but all the NMR peaks matched well. This means the experiment is successful for it is the product that it should obtain.
Concerns and un-expectations

- Low yield during the first reaction
- Different solution color according to the literature
The future plan?

Keep running the reaction and get the catalyst. Run LA polymerization to test the effectiveness.
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