Homopolymerization of methyl methacrylate by Ni(II)(salophen) Complex

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Abstract. A new Ni(II)(salophen) complex (C1) was used to polymerize MMA in the presence of methyl aluminoxane (MAO). It shows better activity in MMA polymerization up to $10^5$ (g·mol$^{-1}$Ni·h$^{-1}$), higher molecular weight and narrower molecular weight distribution. The products are syndiotactic PMMA with better mechanical properties.

1. Introduction

There are two kinds of classic catalysts in late metal catalyst, Brookhart catalyst and Grubbs catalyst. Since 1990s professor Brookhart and his group reported a series of new cationic Pd(II) and Ni(II) α-diamine catalysts for the polymerization of ethylene[1, 2], late metal catalyst comes to play an important role in catalyzing olefin polymerization. The most attractive feature of these catalysts is that their steric and electronic properties can be modified by the judicious introduction of diverse substituents, but it showed lower activity in catalyzing ethylene. Otherwise in 1998, Grubbs and his group reported a Pd (II) catalyst with big steric (N^O) ligand were synthesized and it catalyzed ethylene polymerization with high activity[3, 4]. On the other side, multi-metal complex have been studied in the past decade [5, 6], it was found that these catalysts with different substituents performed high activity or high molecular weights. In this paper, we would like to report homopolymerization of methyl methacrylate by Ni(II)(salophen) complex in the presence of methylaluminoxane (MAO). A good activity in MMA polymerization up to $10^5$ (g·mol$^{-1}$Ni·h$^{-1}$), high molecular weight and narrow molecular weight distribution were obtained.

2. Materials

All air- and moisture-sensitive compounds were handled under an atmosphere of dried and purified argon using standard Schlenk techniques. Dichloromethane and diethyl were distilled under an argon atmosphere from sodium/benzophenone prior to use. MAO (10 wt. % in toluene, containing ca. 30% AlMe$_3$) was purchased from ALBEMARLE CORPORATION and used as received. Methyl methacrylate(MMA) was purified as styrene according to the literature[7].

3. Characterization

Nuclear magnetic resonance (NMR) analysis of multi-imine ligand and PMMA was performed on a Varian Unity 400 MHz spectrometer at room temperature, using CDCl$_3$ as solvent.$^1$H NMR spectra were referenced to solvent peaks. Gel permeation chromatography (GPC) measurements were performed in THF at 35°C on Waters 1515GPC. Infrared spectra (IR) were recorded on a Shimadzu IRPrestige-21 Fourier Transform Infrared spectrophotometer; the sample was ground with KBr and pressed into thin wafers.
4. Result and Discussion

4.1. Polymerization of PMMA

The results of MMA polymerization with Ni complex $\text{C1}$ was shown in Table 1.

| Entry | $T$ (°C) | Al/Ni | $t$ (min) | Conversion | $10^4 \text{Activity}$ (g·mol$^{-1}$ Ni·h$^{-1}$) | $10^5 \text{Mn}$ | PDI |
|-------|---------|-------|-----------|------------|---------------------------------|----------------|-----|
| 1     | 25      | 800   | 60        | 2.30       | 5.83                            | 5.29           | 3.68|
| 2$^b$ | 25      | 800   | 60        | 1.88       | 5.52                            | 2.17           | 1.22|
| 3     | 25      | 1000  | 30        | 2.10       | 10.6                            | 2.53           | 2.96|
| 4     | 25      | 1000  | 60        | 5.02       | 12.8                            | 1.99           | 1.13|
| 5     | 50      | 1000  | 30        | 18.6       | 93.6                            | 3.50           | 1.92|

Conditions: m(catalyst)=0.001 g. co-catalyst: MAO, [MMA] = 4.19 mol/L.

a. Molecular weights of the polymers were determined by GPC (using a universal calibration) in THF at 35°C.
b. solvent = toluene.

In Table 1, comparing 1 with 2, activity is higher in CH$_2$Cl$_2$ than toluene. Comparing 1 with 3, when decreasing polymerize time, catalyst activity, molecular and PDI decreased. In entry 1 and 4, activity increased with increasing the mole ratio of Al/Ni because of the active centers increasing. Comparing 3 with 5, activity increased with temperature increasing. Activity is up to $9.36 \times 10^5$ (g·mol$^{-1}$ Ni·h$^{-1}$) under 50°C. In addition, C1 showed narrower PDI and higher molecular weight.

4.2. Characterization of PMMA

Figure 1. The $^1$H NMR spectrums of PMMA synthesized by catalyst C1

According to Fig.1, it shows three peaks corresponding to -OCH$_3$(a), CH$_3$(b) and CH$_2$(c) appear at 3.60 ppm, 1.81 ppm, and 0.85-1.25 ppm. Position esplit into three peaks because of having three kinds of space three-dimensional configurations: a tactic, is tactic and syndiotactic structures. And the
mainly proportion of syndiotactic PMMA is up to 56.61%.

5. **Summary**
Homopolymerization of methyl methacrylate by a new Ni(II)(salophen) complex C1 under different polymerization conditions were investigated including the molar ratio of Al/Ni, temperature and time. The results show that catalytic activity increases with the molar ratio of Al/Ni and temperature increasing, and decreased with time increasing. It showed better activity in MMA polymerization up to \(10^5\) (g·mol\(^{-1}\)Ni·h\(^{-1}\)), high molecular weight and narrow molecular weight distribution. The mainly products are syndiotactic PMMA with better mechanical properties, and the proportion is up to 56.61%.

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