

Polymerization of methyl methacrylate using late transition metal catalyst of [(1,4-phenylenebis(azaneylylidene)) bis(1-benzylinolin-2-one)] CoCl₂

Homa Parsaiyan¹, Gholamhossein Zohuri^{1,*}, Navid Ramezani¹

1. Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran.

Email address: zohuri@um.ac.ir

Abstract

Transition metal catalysts at the end of the periodic table have attracted a lot of attention for catalytic polymerizations in recent years, because in addition to the catalytic polymerization of non-polar olefins, they have been studied for polymerization of polar monomers such as methyl methacrylate (MMA), as well. In this project, a catalyst of [(1,4-phenylenebis(azaneylylidene)) bis(1-benzylinolin-2-one)] CoCl₂, (a dinuclear cobalt (II) catalyst (NCCL)) was synthesized based on phenoxy-imine ligand with 1,4-phenylenediamine bridge, a rigid bridge, for polymerization of MMA. The synthesis reactions were followed with TLC studies. Structures of both ligand and catalyst are studied using FTIR technique. Also, a synthesised modified methyl aluminoxan (MMAO) is used as a co-catalyst for the polymerization. The dinuclear cobalt (II) catalyst was suitable for catalytic polymerization which could be due to the presence of second metal center that give a sufficient activity for the polymerization of MMA. The optimum molar ratio of [Al]/[Co] for this catalyst is 1000:1. This reaction was investigated at ambient temperature (29±1°C) and the highest activity was 2.582 (g PMMA/mmol Co. h).

Keywords: Catalytic polymerization, Dinuclear cobalt catalyst, Transition metal catalysts, Polymethyl methacrylate.

Introduction and Methodology

1. Introduction

polymethyl methacrylate (PMMA) is an important member of the family of polyacrylates, which is used in the commercial and industrial sector due to its suitable properties, easy process and low price. As a transparent thermoplastic, this polymer is often a suitable substitute for glass. Various polymerization methods have been used to prepare PMMA, but among them, the coordination polymerization method is of great importance in order to better control its microstructure and process [1,2].

2. Material. toluene (99.5%) over CaH₂ and also was refluxed over Na and benzophenone, distilled, and stored over activated molecular sieves (4A/13X). Toluene (99.9%) was used for synthesis of ligand and polymerization, ethanol (99.5%) and n-hexane, were used for synthesis of the catalyst. MMA (98%) was supplied from Merck Chemical Company (Steinheim, Germany) and purified by distillation over activated molecular sieves (4A/13X) and then stored over the activated molecular sieves. MMAO was synthesized according to a literature procedure [3].

3. Synthesis of Legands and Catalysts
Synthesis of BNC1(N- benzyl isatin). To a stirred solution of isatin (5.9 mmol), K₂CO₃ (7.172 mmol) and KI (1.201 mmol) together with acetonitrile (15 mL) in a round bottom flask, under reflux, benzyl-chloride (1 mL) was added dropwise. The solution was stirred for further 4 hours. The product was dissolved in ethyl acetate and repeatedly extracted with hot water, and recrystallized using hot ethanol. In both steps of synthesis, the reaction progress and consumption of the reactant was checked using TLC technique. FTIR (KBr, cm⁻¹): 1331 cm⁻¹ (-C-N-), 1616 cm⁻¹ (-C=C-), 1728 cm⁻¹ (-C=O-), 3191 cm⁻¹ (-N-H-).
3.1.Synthesis of BNC2 [(1,4-phenylenebis(azaneylylidene))bis(1-benzylinolin-2-one)], the ligand. To a solution of the synthesized compound BNC1 (1.8 mmol) and toluene (15 mL) in a round-bottomed flask in the presence of glacial acetic acid (4 drops) a solution of 1,4-phenylenediamine (0.6 mmol) in toluene (10 mL) was added while stirring. Progress of the reaction was followed by TLC. The mixture was stirred for 24 h at room temperature. After the completion of the reaction, the precipitate obtained was separated and washed with Et₂O for several times and dried in a vacuum desiccator. FTIR (KBr, cm⁻¹): 1720 cm⁻¹ (C=O), 1603 cm⁻¹ (-C=C-), 1656 cm⁻¹ (-N=C-), 3427 cm⁻¹ (-N-H-).
3.2.synthesis of NCCL Catalyst. Procedure of the catalyst synthesis was conducted under atmosphere of argon gas using the using the standard Schlenk techniques. Into a solution of CoCl₂ (0.19 mmol) in ethanol (15 mL), a solution of the ligand BNC2 [(1,4phenylenebis(azaneylylidene))bis(1-benzylinolin-2-one)] (0.09 mmol) in ethanol (13 mL) was added dropwise. The mixture was stirred for further 24h at room temperature. The precipitat product was filtered and washed with n-hexane several times. The solid product was collected after its solvent evaporation. FTIR (KBr, cm⁻¹): the carbonyl signal was shifted (from 1728 to 1719 cm⁻¹), and the area under the peak has also decreased. The changes could be due to the coordination of the cobalt metal with the desired ligand structure.

4. Polymerization. The polymerization of MMA was carried out in a round-bottomed glass flask with two openings, equipped with a magnetic stirrer under argon gas atmosphere. The desired amount of toluene was introduced into the reactor and then monomer and MMAO were injected and continuously stirred for about 5 minutes. A solution of catalyst in toluene was added to the polymerization medium. After the end of polymerization, acidic methanol was used as an anti-solvent. The polymer was dried under reduced pressure and collected.

Results & Discussion

To investigate the effect of different concentrations of methyl aluminoxan on the catalyst behavior, methyl methacrylate polymerization was carried out using the NCCL catalyst. Modified methyl aluminoxan was used as cocatalyst. In order to achieve optimal conditions in terms of catalyst performance, the polymerization of methyl methacrylate was carried out in different cocatalyst (MMAO) concentrations. Initial investigation showed that the catalyst NCCL have sufficient activity at about ambient temperature (29±1°C). The maximum activity at the temperature was obtained in molar ratio of [Al]/[Co]: 1000:1, which was 2.582 (g PMMA/ mmol Co. h) in the studied range (Figure 1).

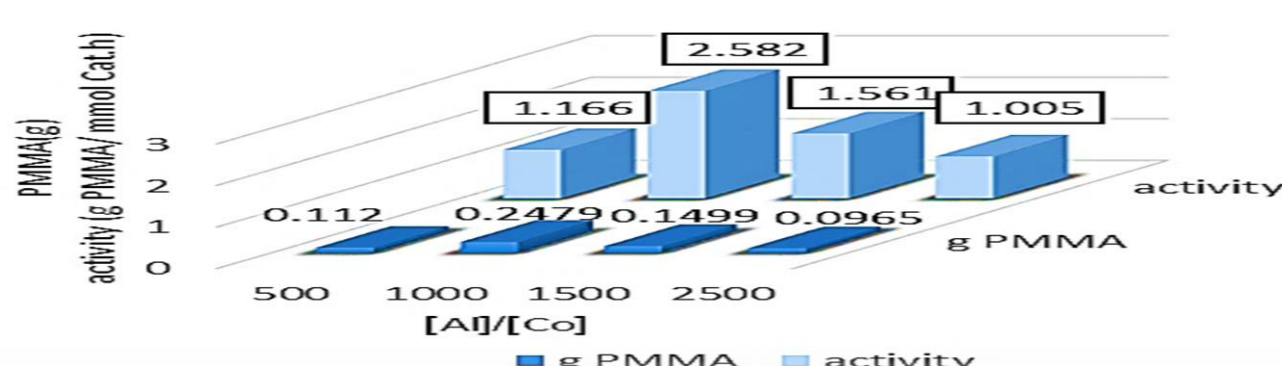


Figure 1. Clustered chart of NCCL; activity versus [Al]/[Co], polymerization condition as Table 1.

Table 1. Polymerization of methyl methacrylate using the NCCL catalyst.

Run	[Al]/[Co]	Yield (g)	Activity (g PMMA/ mmol Co. h)
1	500	0.1120	1.166
2	1000	0.2479	2.582
3	1500	0.1499	1.561
4	2500	0.0965	1.005

Polymerization condition: polymerization time=24 h, polymerization temperature=29±1°C, monomer MMA=10 mL, mmol NCCL= 4 ×10⁻³ mmol, Solvent for polymerization (10 mL) from toluene.

Conclusion

Synthesis, characterization and polymerization behaviors of a novel dinuclear (NCCL) Co (II) based catalyst for methyl methacrylate were presented. The optimum molar ratio of [Al]/[Co] for this catalyst was 1000:1. This reaction was investigated at about ambient temperature (29±1°C) and the highest activity was 2.582 (g PMMA/mmol Co. h). The dinuclear cobalt catalyst structure was suitable for the catalytic polymerization due to having the second metal center.

Selected References

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