

Study of temperature and polymerization kinetics using a dinuclear cobalt catalyst for polymerization of methyl methacrylate

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

Polymerization of methyl methacrylate was investigated with a catalytic system (a dinuclear cobalt (II) catalyst based on phenoxyimine ligand [(1,4-phenylenebis(azaneylylidene)) bis(1-benzylolin-2-one)] with 1,4-phenylenediamine bridge). Methylaluminoxane (MMAO) was used as a co-catalyst with a molar ratio of [Al]/[Co]=1000:1. Effect of temperature (29±1 up to 60±1 °C) and polymerization time (2 up to 24 h) on the polymerization behavior were studied. The highest activity was obtained at 40±1°C at the early polymerization time (66.87 g PMMA/mmol Co. h).

Keywords: Dinuclear cobalt catalyst, Catalytic polymerization, Phenoxyimine ligand, Polymethyl methacrylate.

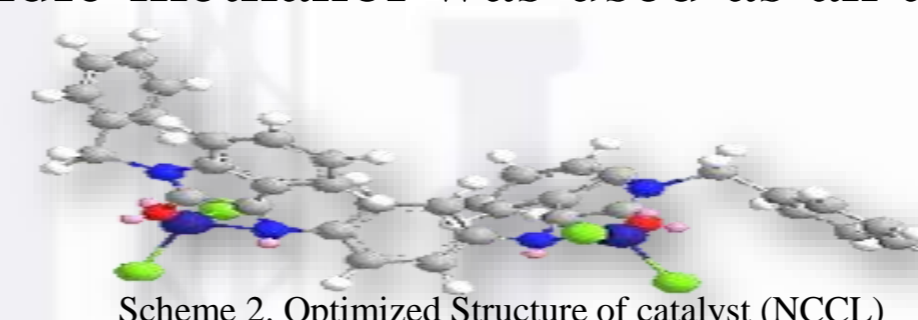
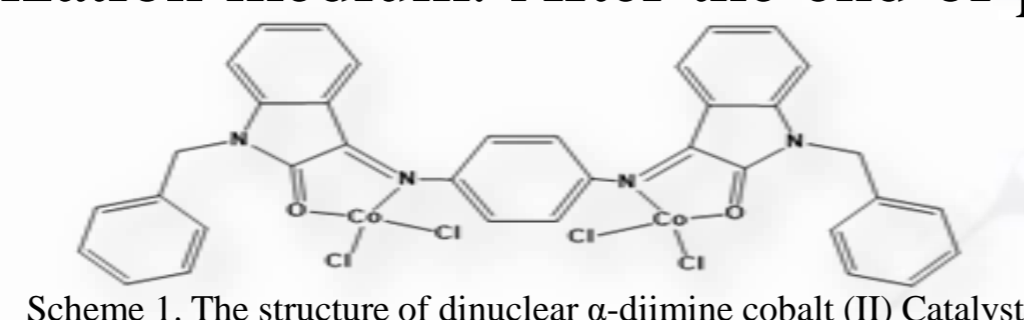
Introduction and Methodology

1. Introduction

Transition metal catalysts at the end of the periodic table have attracted a lot of attention in recent years, because in addition to The polymerization of non-polar olefins has been studied for the polymerization of polar monomers such as methyl methacrylate (MMA). Polar groups have very important properties, such as: adhesion, solubility, toughness, impermeable properties, colorability and They can be printed [1-3].

2. Material. All manipulations of air and/or water sensitive compounds were conducted under argon or nitrogen atmosphere using the standard Schlenk techniques. Toluene (99.5%) was purified over sodium/benzophen-one. Toluene (99.9%) was used as polymerization media. Triisobutyl aluminum (93% TiBA) was used to prepare the modified methylaluminoxane (MMAO) co-catalyst. MMA monomer before use Distilled and purified by molecular sieve (4A/13X).

3. Polymerization. All stages of the MMA polymerization reaction were carried out using the binuclear catalyst with the presented structure (Figure 1& 2) under argon gas atmosphere. Polymerization was carried out in a round-bottomed glass flask with two openings and equipped with a magnetic stirrer. 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 final polymer was dried under reduced pressure and collected.



Results & Discussion

1. Effect of Polymerization Conditions

Due to the high catalytic activity of the catalyst NCCL, further studies have been focused on this catalyst. The effect of polymerization temperature and kinetics study of polymerization on the catalyst behavior (Table 1) confirmed the fact that polymerization temperature can enhance the catalyst performance through increasing in the kinetic energy of molecules which facilitates transfer of the monomer to the catalytic active centers and increasing alkylation reaction of metal centers (until 40±1°C). Polymerization temperature higher than 40±1°C can cause irreversible deactivation of the active centers (chemical effect) and the reducing of solubility of monomer in solvent as a physical function to reduce activity of the catalyst. Polymerization of methyl methacrylate in higher temperatures meanwhile (50±1 and 60±1°C) yielded polymer PMMA. Furthermore, the highest polymerization activity was obtained after 2 h of polymerization. After ward, degradation and deactivation of active centers and encapsulation of the centers by the polymer chain to the metal which inhibit of insertion of monomer can cause to decreasing in catalyst activity.

2. FT-IR analysis

As infrared spectrum of polymers illustrate in Figure 4, The bands in the range of 2843-2961 cm⁻¹ was attributed to the CH stretching vibration. The was CH bending vibrations for methyl group of MMA at 1450-1486 cm⁻¹. Also, band at 1360-1389 cm⁻¹ was attributed to CH bending vibration of methylene in MMA. The peaks at 1274, 1244, 1149, and 991 cm⁻¹ were assigned to CO stretching of MMA. The absorbance of band at 1732 cm⁻¹ was corresponded to the carbonyl group of MMA.

Table 1. Polymerization of Methyl Methacrylate Using the Catalyst NCCL

Run	Time (h)	Temperature (°C)	Yield (g)	Activity (g PMMA/mmol Co. h)
1	24	29±1	0.2479	2.582
2	24	40±1	0.2818	2.935
3	24	50±1	0.1833	1.909
4	24	60±1	0.1643	1.711
5	2	40±1	0.5350	66.875
6	6	40±1	0.4560	19
7	12	40±1	0.3064	6.383

Polymerization condition: [Al]/[Co]= 1000:1; monomer MMA 10 mL, mmol NCCL= 4 × 10⁻³ mmol, solvent for polymerization (10 mL) from toluene.

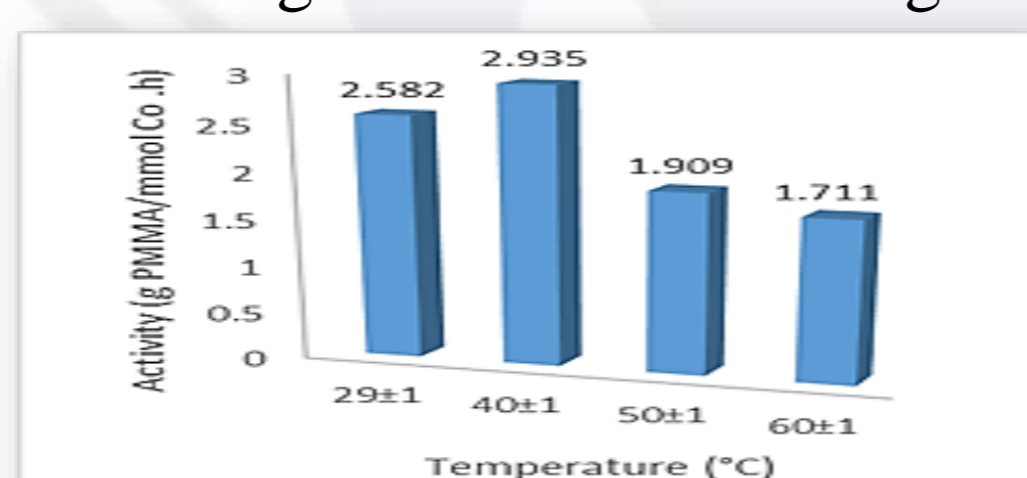


Figure 1: Clustered chart of NCCL activity versus [Al]/[Co], polymerization condition: monomer MMA 10 mL, solvent for polymerization (10 mL) from toluene, polymerization time 24 h, mmol NCCL= 4 × 10⁻³ mmol.

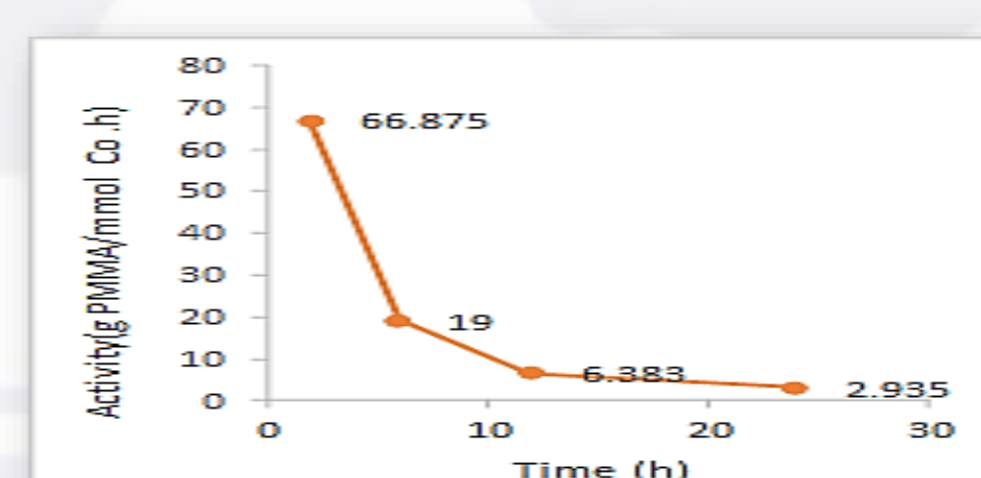


Figure 2: Scatter chart of NCCL activity versus [Al]/[Co], polymerization condition: monomer MMA 10 mL, solvent for polymerization (10 mL) from toluene, polymerization time 24 h, mmol NCCL= 4 × 10⁻³ mmol.

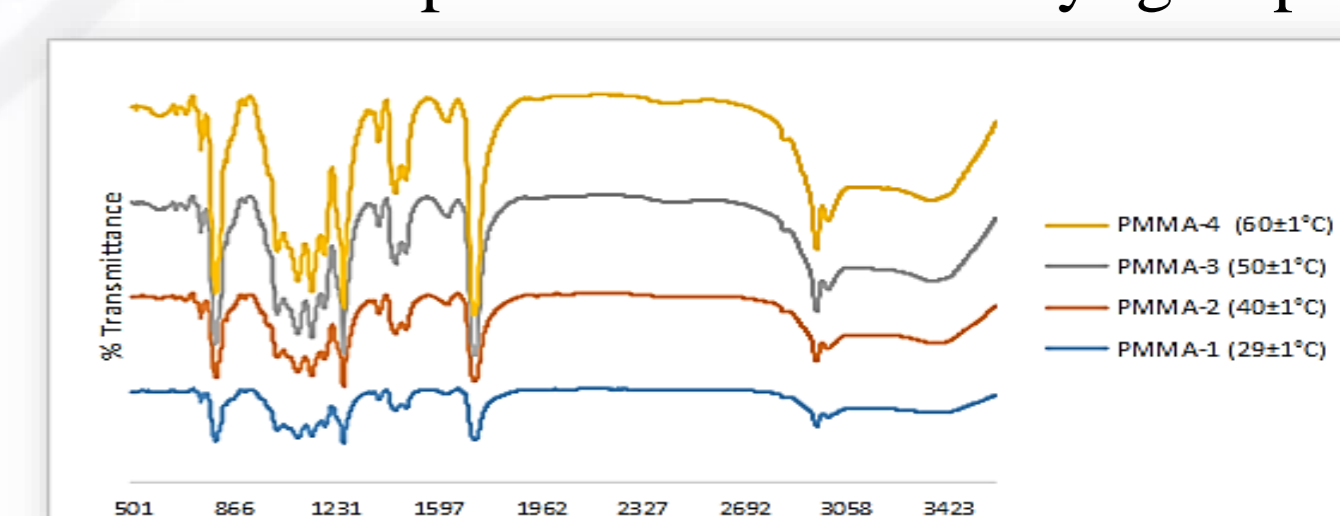


Figure 3: FTIR spectra of the resulted PMMA using the NCCL catalysts.

Conclusion

In order to achieve optimal conditions for the performance of the catalyst, polymerization was carried out under different conditions of temperature and time. The study of polymerization kinetics showed that the polymerization behavior of methyl methacrylate at temperature of 40±1°C and molar ratio of [Al]/[Co]:1000:1 and duration of 2 hours, the highest catalyst activity and maximum product was obtained. The two-centered cobalt complex based on phenoxyimine ligand showed a suitable activity (66.87 g PMMA/mmol Co. h) in the polymerization of methyl methacrylate. The polymerization conditions had a significant effect on the catalyst activities. According to figure 1, with the increase in temperature, the activation energy is provided for the reaction, the optimum temperature dimension is 40±1°C, with the increase in temperature, the possibility of destroying the active centers of the catalyst increases, the solubility of the monomer decreases, as a result, the activity decreases. These polymerization conditions ([Al]/[Co]: 1000:1, polymerization temperature 40±1°C, polymerization time 2 h) is relatively low for this type of polymerization, which is one of the advantages of this catalyst.

Selected References

1. Khoshsefat, M., Ma, Y., & Sun, W. H. (2021). Multinuclear late transition metal catalysts for olefin polymerization. *Coordination Chemistry Reviews*, 434, 213788.
2. Khoshsefat, M., Dechal, A., Ahmadjo, S., Mortazavi, S. M. M., Zohuri, G., & Soares, J. B. (2019). Cooperative effect through different bridges in nickel catalysts for polymerization of ethylene. *Applied Organometallic Chemistry*, 33(6), e4929.

3. مولوی، ح.، ظهوری، غ.، زاهد احمد، ز.، "سنتز کاتالیست دو هسته‌ای کبالت بر پایه لیگاند فنوکسی-ایمین برای پلیمریزاسیون متیل متاکریلات"، چهارمین کنگره ملی شیمی و نانو شیمی از پژوهش‌ها توسعه ملی، تهران، ایران، 1400.