



Co dinuclear catalyst for methyl methacrylate polymerization

Homa Parsaiyan¹, Gholam Hossein Zohuri^{1*}, Navid Ramezani¹

¹ Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, P.O. Box 91775, Mashhad, Iran

*zohuri@um.ac.ir

Abstract

Effect of polymerization parameters including cocatalyst concentration, polymerization time, and temperature on the behavior of a dinuclear α -diimine Co (II)-based catalyst was investigated. There was an optimum activity at (66.875 g (PMMA)/mmol Co. h) [Al]/[Co]= 1000:1 molar ratio, using a modified methylaluminoxane (MMAO) at 40 °C and 2 h. Also, spherical polymer particles was obtained at reaction temperature of 40 °C.

Keywords: dinuclear catalyst, late transition metal, polymerization, polymethyl methacrylate.

Introduction

As a powerful protocol for the preparation of common polymers, such as polyolefins, polyesters, and polycarbonates, late transition metal catalyzed polymerization can be carried out by controlling the reaction conditions or developing dynamic catalytic systems that use external stimuli to influence the performance of the active sites, resulting in well-defined polymeric materials. Based on the literature, catalyst structure along with the polymerization parameters led to the production of amorphous to semi-crystalline polymers. In regard to catalyst architecture, multinuclearity, as well as the ligand steric and electronic effects, are important in the catalyst behavior [1]. In addition, the monomer length in regard to the agostic interaction is important as well as the distance between the active centers [2]. To optimize the polymerization parameters, reactions were carried out at different conditions. The behavior of the complexes was evaluated using three parameters of [Al]/[Co] molar ratio, polymerization temperature, and polymerization time in order to obtain optimum reaction conditions. Effect of the parameters on the catalyst activity and microstructure of polymers was investigated.

Experimental

The ligand and corresponding catalyst were prepared according to our recent work [3]. The bulk polymerization of methyl methacrylate (MMA) monomer (purified prior to use) was carried out in a round bottom flask containing 10 ml toluene (solution polymerization) which was conducted under Schleck system. Afterward, the cocatalyst and catalyst were introduced to the flask, respectively. The polymethyl methacrylate (PMMA) was precipitated and purified by acidic methanol.

Results and discussion

Polymerization of MMA

With increased [Al]/[Co] molar ratio (MMAO as cocatalyst) the catalytic activity leads to the highest productivity at the optimum value of [Al]/[Co]= 1000:1 molar ratio (Table 1), due to reaching the highest concentration of active centers [4]. Catalyst activity at [Al]/[Co] molar ratios higher than the optimal ratio decreases, which may be attributed to the formation of inactive species at higher concentrations of the cocatalyst. The trend observed for the catalytic activity could be attributed to the formation of the deactivated form of the complex and the increase of reverse reaction rate that led to lower activity and more chain transfers from the cobalt species to aluminum and chain termination at the high molar ratios of [Al]/[Co] and, subsequently decreasing the polymer molecular weights [5]. The polymerization activity was increased with increasing polymerization temperature (from 30 to 40 °C) and temperature above 40 °C reduced catalyst activity gradually, which can be due to the deactivation of active catalytic sites (chemical agent) and also reduction of monomer solubility (an effective physical factor) in the reaction media [6]. Polymerization was carried out at different polymerization times (from 2 to 24 h) (Table 1). As the data showed, in the initial times of the polymerization (2 h), the activity of the catalyst increased and reached the optimum value of 66.875 g (PMMA)/mmol Co. h (at 40 °C and [Al]/[Co]=1000:1 molar ratio), however, the catalyst activity declined with increasing of the reaction time (up to 24 h) which studied. There is a possibility of thermal deactivation of active centers, with polymerization time [7].



Table 1. Result of MMA polymerization using the dinuclear catalyst.

Run	[Al]/[Co]	Temperature (°C)	Time (h)	Yield (g)	Activity g PMMA/mmol Co. h
1	500	30	24	0.11	1.16
2	1000	30	24	0.24	2.58
3	1000	40	24	0.28	2.93
4	1000	40	12	0.30	6.38
5	1000	40	6	0.45	19.0
6	1000	40	2	0.53	66.87
7	1000	50	24	0.18	1.90
8	1000	60	24	0.16	1.71
9	1500	30	24	0.14	1.56
10	2500	30	24	0.09	1.0

Polymerization conditions: MMAO as cocatalyst, catalyst: 4×10^{-3} mmol, 10 ml toluene as solvent.

Morphological study

Scanning electron microscope images of catalyst particles (Fig. 1) and also polymer samples were investigated in the different polymerization conditions (Fig. 2). As can be seen, the morphology of the samples prepared by this catalyst (at 30 °C) was similar to the morphology of the catalyst particles. A spherical polymer particles was obtained with using reaction at 40 °C (Fig. 2d).

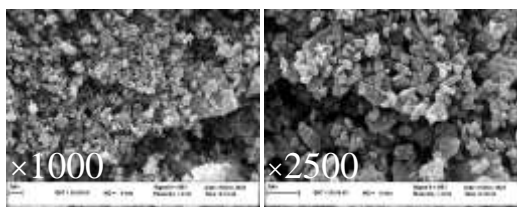


Fig. 1. The SEM image of the catalyst.

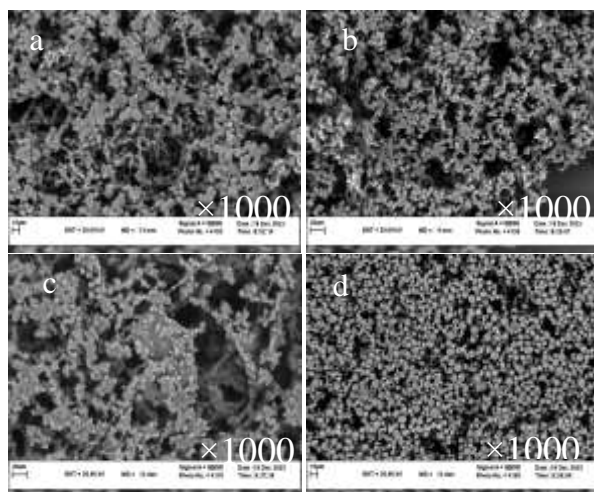


Fig. 2. SEM images of the PMMA produced in different polymerization condition: a (30 °C, 24 h), b (60 °C, 24 h), c (40 °C, 24 h), and d (40 °C, 2 h).

Conclusions

In order to achieve optimal conditions for performance of the catalyst, polymerization was carried out under different conditions of temperature and time. The study of polymerization showed that the reaction behavior of methyl methacrylate at temperature of 40 °C molar ratio of [Al]/[Co]= 1000:1 and duration of 2 h, give the highest catalyst activity. The dinuclear α -diimine Co (II)-based catalyst showed a suitable activity (66.875 g (PMMA)/mmol Co. h) in the polymerization of methyl methacrylate. The polymerization conditions had a significant effect on the catalyst activities. According to Table 1, with the increase in temperature, the activation energy is provided for the reaction, the optimum temperature dimension is 40 °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. Effect of polymerization temperature and time on the catalyst behavior confirmed the fact that polymerization temperature can enhance the catalyst performance by increasing the kinetic energy of molecules which facilitates the transfer of the monomer to the catalytic active centers and increasing alkylation reaction of metal centers (up to 40 °C).

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