Effect of reaction parameters on the polymerization of methyl methacrylate with nickel acetylacetonate/methylaluminoxane

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Summary

Polymerizations of methyl methacrylate (MMA) employing nickel acetylacetonate [$Ni(acac)_2$] as catalyst combined with methylaluminoxane (MAO) as cocatalyst were investigated. The main purpose of this work is concerned with the study of reaction parameters MMA polymerization. Temperature of polymerization, Al/Ni mole ratio, type of solvent, catalyst concentration and time dependence were examined. The influence of Lewis bases on the polymerization was also studied. The binary system $Ni(acac)_2$/MAO was the only one able to polymerize MMA at the conditions employed in this work. The cocatalytic activity of MAO was compared to those of common alkylaluminium compounds. The polymers were characterized by gel-permeation chromatography (GPC) and ^{13}C-NMR techniques.

Introduction

It is well-known that conventional Ziegler-Natta catalysts promote the polymerization of olefinic monomers but not the polar ones. The homogeneous catalytic systems based on metallocene and common alkylaluminium compounds do not polymerize olefins. Nevertheless, the use of methylaluminoxane (MAO) employed as co-catalyst with Group 4 metallocene-based compounds produces extremely active catalyst for olefins, giving entirely new families of homo- and copolymers (1). In addition, the stereoregularity of poly(α-olefins) obtained by these catalyst systems can be controlled by changing the structure of the metallocene compound. However, common polar vinyl monomers e.g., methyl methacrylate (MMA), cannot be polymerized by these catalyst systems.

Poly(methyl methacrylate) (PMMA) can be produced by different ways e.g., anionic polymerization, or group transfer polymerization (GTP), with well-controlled molecular weight and stereoregularity. Recently, cationic metallocene compounds of Group 4 have attracted attention due to their high activity and stereospecificity in olefin polymerization. It was also found that these compounds are able to promote stereospecific polymerization of MMA(2-5).

Recently, polymerization of MMA has been studied in anionic systems based on alkyllithium compounds or Grignard reagents. It is possible to obtain both isotactic and syndiotactic PMMA at very low temperatures (1). On the other hand, polymerization of MMA with MAO-containing homogeneous catalysts has received little attention, although some earlier works in regard to MMA polymerization with transition metals

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combined with trialkylaluminium compounds have reported the successful production of stereoregular polymers(6-9).

Otsu and Nishikawa have reported that the polymerization of MMA with transition metal compounds alone proceeds *via* radical mechanism at somewhat elevated temperatures e.g., 80°C(10,11). Endo and co-workers have found that catalyst systems based on acetylacetonate of transition metals combined with MAO [Mt(acac)$_x$/MAO] promote the polymerization of MMA under mild conditions(6,12).

The polymerization of MMA with these catalyst systems opens a new field of study and the production of different kinds of polymers e.g., homopolymers of polar vinyl monomers with different stereoregularities, copolymers of polar vinyl monomers with styrene or/and olefins. In fact, it is of great interest that a catalyst system promotes the copolymerization of ethylene (or propylene) with polar monomers like acrylates.

This work concerns preliminary results of the polymerization of MMA, using the catalytic system based on Ni(acac)$_2$ combined with MAO, and focuses the influence of polymerization parameters on this catalyst system.

Experimental part
Materials

Ni(acac)$_2$ (Toho Titanium Co.) was employed after recrystallization in toluene. Methylaluminoxane (MAO) was kindly donated by Witco GmbH and was employed without further purification as a solution in toluene (30% w/v). MMA was distilled over calcium hydride under nitrogen. All Lewis bases were dried over molecular sieve 3 Å at least for one day. Toluene was distilled over sodium/benzophenone under nitrogen. Methanol was purified by conventional method.

Polymerization procedure

Polymerizations of MMA were performed under a dry nitrogen atmosphere in a glass tube (Schlenk flask) equipped with a magnetic stirrer. The required amounts of reagents were transferred by a syringe under nitrogen. A typical polymerization process is as follows: A Schlenk tube was filled wiht toluene (freshly distilled), MAO in toluene solution (30% w/v), Ni(acac)$_2$ in toluene solution, 5 minutes of aging, MMA (freshly distilled), in this order, and the mixture was stirred for 24 h at 35°C. After polymerization, the charge was poured into a large amount of methanol containing a small amount of hydrochloric acid to precipitate the polymer formed and to kill the catalyst system. The resulting polymer was dried after filtration. Polymer yields were calculated from the weight of dry polymer.

Polymer characterization

The average molecular weight and molecular weight distribution were measured by GPC (Waters 600E) at room temperature using chloroform as solvent and calibrated with standard polystyrenes. The tacticity of PMMA was estimated by ^{13}C-NMR spectra measured with a Varian 300 spectrometer at room temperature in CDCl$_3$.

Results and discussion

Preliminarily, it was tried to polymerize MMA with Ni(acac)$_2$ alone as well as with MAO alone under the conditions discribed in the *Experimental*. It was noted that even after 24 hours at 35°C, no polymer was produced, indicating that no polymerization *via* free radical proceeds under these conditions. Srinvase and co-workers(13) reported that MMA polymerization proceeds in the presence of MAO under irradiation with UV light at 30°C. Since no polymer was formed with Ni(acac)$_2$ or MAO alone under our conditions, it may be said, that the binary catalyst system is necessary to promote the polymerization. It was observed that the reaction between the catalyst components (catalyst and cocatalyst) is instantaneous, changing the light green solution to dark brown after adding the cocatalyst. It was also noted that the color of the catalyst solution became lighter brown after introducing the monomer (MMA), probably due to the complex formed between catalyst and monomer. The polymerization was very fast and after 10 minutes large amount of gel was produced.

Typical results on the correlation between the polymerization yield and Al/Ni mole ratio are listed in Table 1. The catalyst activity increases markedly at first, followed by a gradual increase with an increase in the mole ratio of Al/Ni up to 500 and then remains constant. Figure 1 illustrates the conversion as a function of polymerization time. The polymer yield increased in proportion to the polymerization time, reaching a constant value (80% conversion) around 100 minutes. The results point out that the life time of the active species formed is very long. The polymerization of MMA promoted by Ni(acac)$_2$/MAO catalyst system produced white powdery polymers, having high molecular weights and quite broad molecular weight distributions at low MAO/Ni mole ratio (Run # 2). The polymer yield increased when the MAO/Ni mole ratio was higher, but the molecular weight distribution became broader.
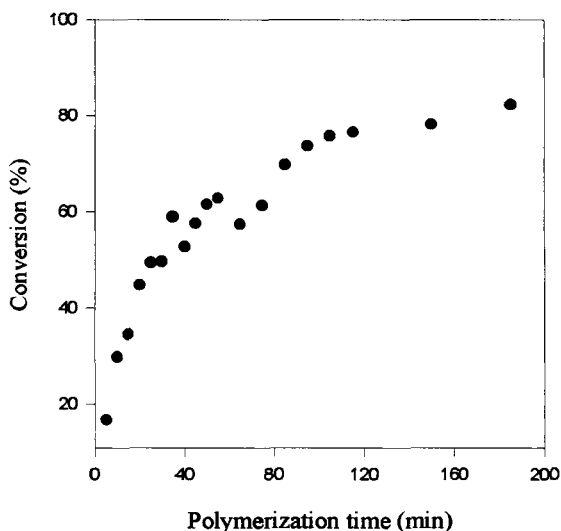
Table 1 - Influence of Al/Ni mole ratio on methyl methacrylate polymerization

Run #	Al/Ni mole ratio	Yield in %	Mn x 10^{-4}	M_w/M_n
1	50	16	n.d.	n.d
2	100	48	9.6	2.0
3	200	60	n.d	n.d
4	500	81	2.2	13.2
5	1000	84	n.d.	n.d

Polymerization conditions: time = 24 h; Ni amount = 0.03 mmol; temperature = 35 °C; volume of solvent = 10 mL; MMA/Ni mole ratio = 3140; cocatalyst = methylaluminoxane; n.d. = not determined

Table 2 shows the influence of the type of alkylaluminium as cocatalyst on the polymerization. Three types of alkylaluminiums were employed, namely triethylaluminium, triisobutylaluminium (Table 2) and methylaluminoxane (Table 1). Among the cocatalysts examined, MAO showed the highest catalytic activity although the polymerization mechanism is not clear.

Figure 1 - Polymer conversion as a function of polymerization time obtained with the Ni(acac)$_2$/MAO catalyst system

Polymerization time (min)

Polymerization conditions: Ni amount = 0.15 mmol; temperature = 35°C; volume of solvent = 250 ml; MMA/Ni mole ratio = 1570; Al/Ni mole ratio = 100; cocatalyst = methylaluminoxane.

Table 2 - Influence of cocatalyst type on methyl methacrylate polymerization

Run #	Type of cocatalyst	Al/Ni mole ratio	Yield (%)
6	Al(C$_2$H$_5$)$_3$	2.5	trace
7	Al(C$_2$H$_5$)$_3$	5.0	trace
8	Al(C$_2$H$_5$)$_3$	10.0	2
9	Al(C$_2$H$_5$)$_3$	20.0	5
10	Al(i-C$_4$H$_9$)$_3$	5.0	trace
11	Al(i-C$_4$H$_9$)$_3$	10.0	5
12	Al(i-C$_4$H$_9$)$_3$	20.0	11

Polymerization conditions: time = 24 h; Ni amount = 0.03 mmol; temperature = 35 °C; volume of solvent = 10 mL; MMA/Ni mole ratio = 1570; n.d. = not determined.

To check the role of solvent, solvents with different polarities were employed, namely toluene, iso-octane, tetrahydrofuran and dichloromethane. Table 3 shows the effect of the solvent type on yield. MMA polymerization in apolar solvent (toluene and iso-octane) produced higher amounts of polymer than that in polar solvent (tetrahydrofuran and dichloromethane). Thus, it is possible that the MMA polymerization with this catalyst system proceeds *via* a coordination mechanism.

Table 3 - Influence of solvent on methyl methacrylate polymerization

Run #	Type of solvent	Yield in %
13	toluene	49
14	iso-octane	42
15	tetrahydrofuran	21
16	dichloromethane	0

Polymerization conditions: time = 24 h; Ni amount = 0.03 mmol; temperature = 35 °C; volume of solvent = 20 mL; MMA/Ni mole ratio = 1570; Al/Ni mole ratio = 100; cocatalyst = methylaluminoxane.

The influence of the catalyst concentration on the polymerization of MMA was investigated and the results are listed in Table 4. The proportional increase of polymer yield when the catalyst concentration was decreased to 0.8×10^{-3} M is puzzling. It is possible that at high concentrations, catalyst sites were covered by a layer of PMMA gel, decreasing the rate of monomer diffusion.

Table 4 - Effect of catalyst concentration on methyl methacrylate polymerization

Run #	Catalyst concentration $\times 10^{-3}$ (M)	Yield in %
13	1.70	49
18	1.33	62
19	1.09	77
20	0.90	70
21	0.80	79
22	0.70	79

Polymerization conditions: time = 24 h; Ni amount = 0.03 mmol; temperature = 35 °C; volume of solvent = 20 mL; MMA/Ni mole ratio = 1570; Al/Ni mole ratio = 100; cocatalyst = methylaluminoxane.

The influence of temperature on the polymerization of MMA with the Ni(acac)$_2$/MAO catalyst system was examined and the results are shown in Table 5. The rate of polymerization was sensitive to temperature. The polymer yield increased with the increase in temperature from -41 to 75°C. This result indicated that the active sites of this catalyst system are thermally stable. These results are in opposition to what was observed by Endo and co-workers (12). Nevertheless, the relatively narrow molecular weight distributions did not depend significantly on temperature. High molecular weight was obtained when the polymerization was carried out at higher temperatures.

Table 5 - Effect of temperature on methyl methacrylate polymerization

Run #	Temperature (°C)	Yield in %	$M_n \times 10^{-4}$	M_w/M_n
23	-41[a]	6	2.1	1.6
24	5	17	n.d.	n.d.
2	35	48	9.6	2.0
26	75	45	27.8	1.7

Polymerization conditions: time = 24 h; Ni amount = 0.03 mmol; temperature = 35 °C; volume of solvent = 10 mL; MMA/Ni mole ratio = 3140; Al/Ni mole ratio = 100; cocatalyst = methylaluminoxane [a] Polymerization time = 8 h; n.d. = not determined

As it can be seen from Tables 6 and 7, Lewis bases strongly influence the catalyst behaviour and the polymer structure. The use of modifiers decreased the catalyst activity when the Lewis base/Ni mole ratio increased. Hence, it is possible that these compounds formed strong complexes with the catalyst system. In Table 6, it can also be seen that the average molecular weight decreased when the Lewis base was employed. These compounds broadened the molecular weight distribution and in some cases GPC analyses showed bimodal curves. ^{13}C-NMR analyses showed high syndiotactic contents (Runs # 31 and 33).

Table 6 - Effect of the type of Lewis base on methyl methacrylate polymerization

Run #	Type of Lewis base	Yield in %	$M_n \times 10^{-4}$	M_w/M_n	[a]mm (%)	[a]mr (%)	[a]rr (%)
2	-	48	9.6	2.0	23.4	65.0	11.6
28	DABO	25	n.d.	n.d.	n.d.	n.d.	n.d.
29	TBA	40	5.4	22	n.d.	n.d.	n.d.
30	DIBP	46	5.0	25	n.d.	n.d.	n.d.
31	TMP	45	8.7	18	0	31.0	69.0
32	EB	46	3.2	10	n.d.	n.d.	n.d.
33	DBE	44	3.3	36	4.0	9.0	87.0

Polymerization conditions: time = 24 h; Ni amount = 0.03 mmol; temperature = 35 °C; volume of solvent = 10 mL; MMA/Ni mole ratio = 3140; Al/Ni mole ratio = 100; cocatalyst = methylaluminoxane; Lewis base/Ni mole ratio = 1.0; DABO -1,4- diazabicyclo[2.2.2]octan ; TBA - tributylamine; DIBP - di-isobutyl phthalate; TMP - 2,2,6,6-tetramethylpiperidine; EB - ethyl benzoate; DBE - di-n-butyl ether; n.d.=not determined; [a]Tacticity determined by ^{13}C-NMR

Table 7 - Effect of the amount of Lewis base on methyl methacrylate polymerization

Run #	Lewis base (:B)	:B/Ni mole ratio	Yield in %
34	DABO	0.5	28
35	DABO	1.0	25
36	DABO	2.0	6
37	EB	0.5	48
38	EB	1.0	55
39	EB	2.0	31

Polymerization conditions: time = 24 h; Ni amount = 0.03 mmol; temperature = 35 °C; volume of solvent = 20 mL; MMA/Ni mole ratio = 1570; Al/Ni mole ratio = 100; cocatalyst = methylaluminoxane; DABO-1,4-diazabicyclo[2.2.2]octan; EB - ethyl benzoate.

The results described above have led to the following conclusions:
(1) $Ni(acac)_2$ can be markedly activated by methylaluminoxane for MMA polymerization;
(2) The polymerization of MMA with $Ni(acac)_2$/MAO catalyst system is better in apolar solvents;
(3) The rate of MMA polymerization with the $Ni(acac)_2$/MAO catalyst system is very fast;
(4) The behaviour of $Ni(acac)_2$/MAO changes by the addition of Lewis bases;
(5) The catalyst system produces syndiotactic PMMA in the presence of Lewis bases.
(6) The catalytic system studied polymerizes MMA *via* a coordination mechanism. Much more information is necessary to discuss the polymerization mechanism in detail. Meanwhile, further detailed study is in progress to investigate the copolymerization of MMA and styrene as well as the mechanism of polymerization, and the results will be published elsewhere.

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