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Polymerization of methyl methacrylate by iron(II) pyridinebisimine complexes

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Abstract

Fe(II) pyridinebisimine complexes activated with trialkylaluminium or modified methylaluminoxane (MMAO) as catalysts were employed for the polymerization of methyl methacrylate. Polymer yields, activities and polymer molecular weights as well as molecular weight distributions can be controlled over a wide range by the variation of the structures of the Fe(II) pyridinebisimine complexes and the reaction parameters such as Al/Fe molar ratio, monomer/catalyst molar ratio, monomer concentration, reaction temperature and time applied to the polymerization of methyl methacrylate. Under optimum condition, the catalytic activity of Fe(II) complex is of up to 74.5 kg_{polym}/mol_{Fe} h.

Keywords: Ziegler–Natta polymerization; Catalysts; Methyl methacrylate

1. Introduction

It is well-known that early transition metal Ziegler–Natta type complexes are used extensively for the polymerization of olefins, but they are usually unable to promote the polymerization of common polar vinyl monomers such as acrylics. However, some earlier researches indicated that Groups V–X transition metal can promote some polar monomers to polymerize in the presence of trialkylaluminium compounds [1–11]. Recently, different nickel complexes in combined with methylaluminoxane (MAO) or modified methylaluminoxane (MMAO) have been investigated to use as the catalysts for the polymerization of methacrylate [12–19]. Nickel acetylacetonate, nickellocene, half-nickellocene and nickel (II) salicyldimnato complexes activated with MAO or MMAO all exhibited good catalytic activity for the polymerization of methacrylate. In contrast, only a few high active iron catalysts for the polymerization of polar vinyl monomers have been reported [9,10].

Recently, the groups of Brookhart and Gibson reported that iron pyridinebisimine complexes activated with MAO display excellent catalytic activity for the polymerization of ethylene [20–23]. In this contribution, we report iron pyridinebisimine complexes activated with organoaluminium compounds for the polymerization of methyl methylacrylate in homogeneous phase yielding syndiotatic-rich polymers.

2. Experimental

2.1. Materials

All the manipulations were performed with standard Schlenk techniques under a N_2 atmosphere. Toluene was distilled from Na/benzophenone ketyl. Methyl methacrylate (MMA), Butyl methacrylate (BMA), and *tert*-butyl methacrylate (*t*-BMA) were dried over CaH_2 for 3 days and distilled under a N_2 atmosphere. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. Dialkylaluminium chloride or alkylaluminium dichloride, triethylaluminium (TEA) and Tri-iso-butylaluminium (TiBA) were purchased from Aldrich. The pyridinebisimine complexes (Scheme 1) were prepared in good yields according to a published procedure by Brookhart and co-workers [20].

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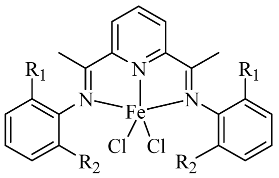

1a: $R_1 = R_2 = i$-Pr

1b: $R_1 = R_2 =$ Me

Scheme 1.

2.2. Measurements

Weight-average molecular weights ($\bar{M}_w$) as well as molecular weight distribution ($\bar{M}_w/\bar{M}_n$) of the polymers were determined by a Water 410 fitted with polystyrene–divinylbenzene columns (two Shodex KD 806 M and 802) and a Shodex RI-71 refractive index detector in tetrahydrofuran. The triad tacticity of the polymer was determined by using the area ratios of the splitting α-methyl protons in the ^{1}H NMR spectra recorded on a Varian Unity-300 NMR spectrometer in $CDCl_3$ at 25 °C.

2.3. Typical polymerization procedure

Ten milliliters of a fresh catalyst solution (toluene, 10 μmol catalyst), 2 g of MMA and 2 ml of toluene were added under an inert gas atmosphere into a Schlenk flask with a mechanical stirrer. The reaction was started by addition of 1 ml of MMAO solution (0.5 mmol MMAO in toluene) at 30 °C. The total reaction volume was 15 ml, unless otherwise stated. After 24 h, the reaction mixture was poured into 100 ml of acidic ethanol (ethanol/$HCl_{conc.} = 50/1$). The polymer was isolated by filtration, washed with methanol, and dried under vacuum at 40 °C for 24 h.

3. Results and discussion

Preliminary experiments indicated that the single-component iron pyridinebisimine complexes themselves were completely inert to MMA. Then, we used organoaluminium compounds as cocatalysts. Lenz and co-workers reported that alkylalumoxane alone was capable of polymerizing MMA [24], but we found that MMAO itself, like other organoaluminium compounds exhibited a low catalytic activity for the polymerization of MMA (Table 1).

Castro and co-workers just reported that iron pyridinebisimine complexes activated with methylaluminoxane (MAO) are capable of promoting the polymerization of *t*-BMA [25]. However, we found that MMAO alone displayed a high catalytic activity for the polymerization of BMA and *t*-BMA (entries 6 and 7 in Table 1). Hence, our research was focused on the investigation of the polymerization of methyl methacrylate. In the presence of dialkylaluminium chloride or alkylaluminium dichloride, the iron pyridinebisimine complexes showed only low catalytic activity towards MMA polymerization. The highest yield of PMMA was lower than 20%. However, the iron pyridinebisimine complexes, like nickel acetylacetonate, nickellocene, half-nickellocene and nickel salicyldimnato complexes, exhibited good catalytic activities in the presence of MMAO under moderate conditions. Furthermore, they showed higher catalytic activities when trialkylaluminium was used as cocatalyst, while nickel complexes display only low catalytic activity in the presence of trialkylaluminium.

Polymer yields, catalytic activities and molecular weights as well as tacticities were depended significantly on reaction parameters applied to the polymerization of MMA like the case of nickel-based catalysts.

As shown in Figs. 1 and 2, variation of the molar ratio of organoaluminium/Fe complex, which is expressed here as Al/Fe ratio, showed considerable effects on the polymerization of MMA. Polymer yields increase first and then decrease with the increase of the Al/Fe ratio. In the case of catalyst **1a**, the highest yields of PMMAs were obtained when the Al/Fe ratios were about 200, 50, and 100, respectively for MMAO, TEA, and TiBA. The results of MMA polymerization in optimum Al/Fe ratios are summarized in Table 2.

Among the three cocatalysts, **1a** activated with MMAO displayed low catalytic activity for the polymerization of MMA, and produced atactic PMMA with a narrow molecular weight distribution, while **1a** activated with trialkylaluminium showed higher catalytic activity, and produced syndiotactic-rich and greater mass PMMA with a slight broad molecular weight distribution. **1a** activated with TiBA exhibited the highest catalytic activity, and the property of PMMA obtained was comparable with that of PMMA obtained by **1a**/TEA.

Kim and colleagues just reported the polymerizations of

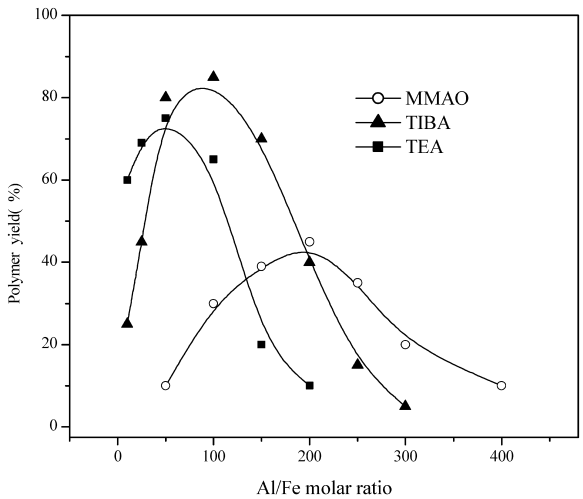

Fig. 1. Plot of PMMA yields versus the molar ratio of Al/Fe. **1a** (10 μmol), $V_{total} = 15$ ml, polymerization reaction at 30 °C for 24 h.

Table 1
Polymerization of methacrylates promoted by organoaluminium compounds (2 g methacrylate, $V_{total} = 15$ ml, polymerization reaction at 30 °C for 24 h)

Entry	Methacrylate	Al compounds	Methacrylate/Al (molar ratio)	Polymethacrylate (g)	Yield (%)
1	MMA	MMAO	10[a]	0.05	2.5
2	MMA	TEA	40[b]	0.10	5.0
3	MMA	TiBA	20[c]	0.10	5.0
4	MMA	$Al(i\text{-}Bu)_2Cl$	10	0.08	4.0
5	MMA	$Al(i\text{-}Bu)Cl_2$	10	0.07	3.5
6	BMA	MMAO	10	1.5	75
7	*t*-BMA	MMAO	40	1.6	80

[a] The molar ratio of MMA/Al is the same as that in entry 1 of Table 2.
[b] The molar ratio of MMA/Al is the same as that in entry 2 of Table 2.
[c] The molar ratio of MMA/Al is the same as that in entry 3 of Table 2.

Table 2
The effect of Al/Fe molar ratio on the polymerization of MMA

Entry	Catalyst	Cocatalyst	Galvinoxyl[a] (μmol)	Molar ratio of Al/Fe	Polymer (g)	Yield (%)	Activity (kg_{pol}/mol_{Fe} h)	$\bar{M}_w$ (10^3) (GPC)	$\bar{M}_w/\bar{M}_n$ (GPC)	Tacticity (^{1}H NMR)		
										rr	*mr*	*mm*
1	**1a**	MMAO	No	200	0.90	45	37.5	17.2	2.13	55	33	12
2	**1a**	TEA	No	50	1.50	75	62.5	34.8	2.51	69	29	2
3	**1a**	TiBA	No	100	1.70	85	70.8	22.3	2.48	54	32	14
4	**1b**	MMAO	No	150	0.80	40	33.3	18.7	1.97	67	31	2
5	**1b**	TEA	No	100	0.82	40	29.2	27.5	2.13	66	31	3
6	**1b**	TiBA	No	50	0.72	35	33.3	35.1	2.38	66	31	3
7	**1a**	MMAO	50	200	0.88	44	36.7	17.4	2.15	68	30	2
8	**1a**	TEA	50	50	1.46	73	60.8	34.5	2.48	69	28	3
9	**1a**	TiBA	50	100	1.68	84	70.0	22.5	2.51	68	29	3

10 μmol Fe complexes, 2 g MMA, $V_{total} = 15$ ml, polymerization reaction at 30 °C for 24 h.
[a] A inhibitor of radically initiated polymerization.

MMA promoted by iron and cobalt pyridinebisimine complexes or nickel diimine complexes activated with MAO [26]. However, they did not succeed in polymerizing MMA by iron pyridinebisimine complexes because the polymerizations were carried out under poor conditions (molar ratio of Al/Fe = 500). In our experiments, PMMA yields were also very low when the molar ratio was more than 400.

As shown in Fig. 3, the syndiotactic degree of PMMA by **1a** decreased, and the isotactic degree increased with the increase in Al/Fe ratio when MMAO was used as cocatalyst. In contrast, the tatacticity of PMMA was independent of the

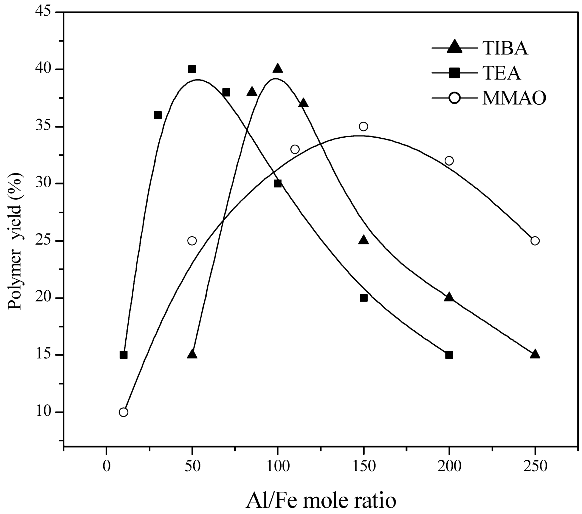

Fig. 2. Plot of PMMA yields versus the molar ratio of Al/Fe. **1b** (10 μmol), $V_{total} = 15$ ml, polymerization reaction at 30 °C for 24 h.

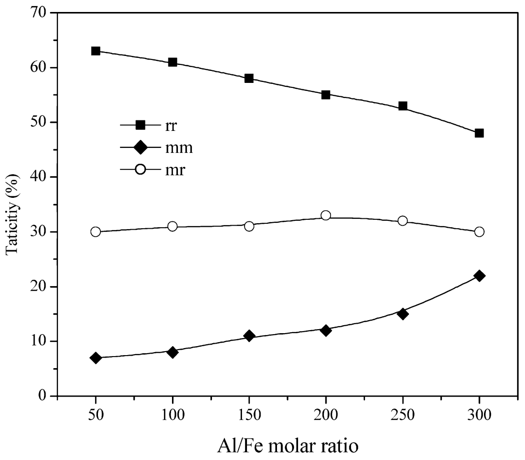

Fig. 3. Plot of PMMA tacticity versus the molar ratio of Al/Fe. Cocatalyst: MMAO, 10 μmol **1a**, $V_{total} = 15$ ml, polymerization reaction at 30 °C for 24 h.

Al/Fe ratio when TEA or TiBA was used as cocatalyst. However, the tatacticity of PBMA was independent of the Al/Fe ratio irrespective of the cocatalyst used.

The data in Table 1 indicate clearly that **1a** is a better catalyst for the polymerization of MMA than **1b**, and **1a**/TiBA is the best catalytic system for MMA polymerization. Then, investigation of the reaction parameters was focused on **1a**/TiBA system, and reaction time was fixed to 24 h according to the results shown in Fig. 4.

The reaction temperature considerably affects polymer yields and catalytic activities. With the increase in the reaction temperature, polymer yields increase first and then decrease, and the highest yield of PMMA (90%) was obtained at about 35 °C, as shown in Fig. 5. For syndiotatic degree, a great decrease was observed in the temperature range of 15–50 °C.

The concentration of MMA has a considerable effect on the polymerization reaction of MMA. The catalytic activities and polymer yields first increase, and then decrease with increase in the concentration of MMA. The highest yield (85%) and the highest activity (74.5 kg_{pol}/mol_{Fe} h) were obtained when monomer concentration was ca. 1.3 mol/l.

MMA/Fe molar ratio significantly influences polymer yields and catalytic activities as shown in Fig. 6. An increase in the MMA/Fe mole ratio caused an increase first and then a decrease in polymer yields and catalytic activities. The highest yield of PMMA (85%) and the highest catalytic activity (70.8 kg_{pol}/mol_{Fe} h) were obtained when MMA/Fe mole ratio come to 2000/1.

To gain a deep insight into the polymerization mechanism, polymerization experiments were repeated under the same conditions as in entries 7–9 (Table 2), but in the presence of galvinoxyl as radically initiated polymerization inhibitors, polymer yield and catalyst activity remained substantially the same (entries 1–3). This suggests that the polymerization of MMA promoted by iron pyridinebisimine complexes activated with organoaluminum may not be a radical polymerization, but could be an anionic coordination polymerization (via the enolate formation).

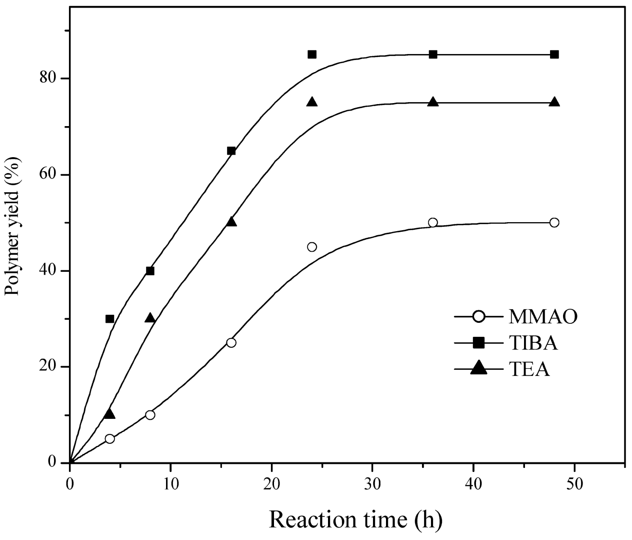

Fig. 4. Plot of yields of PMMA versus reaction time. **1a** (10 μmol), V_{total} = 15 ml, polymerization reaction at 30 °C.

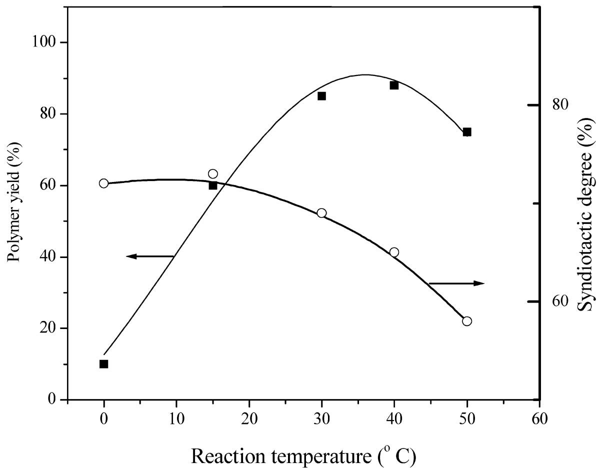

Fig. 5. Plot of PMMA yields and syndiotactic degree versus reaction temperature. **1a** (10 μmol), cocatalyst: TiBA, [Al]/[Fe] = 100/1, [MMA]/[Fe] = 2000, V_{total} = 15 ml, polymerization reaction for 24 h.

4. Conclusion

The iron(II) pyridinebisimine complexes activated with organoaluminium compounds display high catalytic activities for the polymerization of MMA, producing syndiotatic-rich PMMA with a narrow molecular weight distributions under mild conditions. The polymer yields, catalytic activities, the tacticity and the molecular weights as well as the molecular weight distributions of polymethacrylates

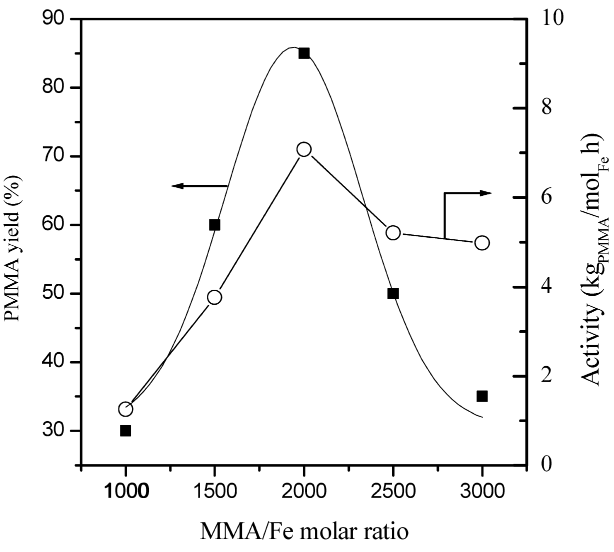

Fig. 6. Plot of PMMA yields and **1a** catalytic activity versus MMA/Fe molar ratio. **1a** (10 μmol), 2.0 g MMA, cocatalyst: TiBA, [Al]/[Fe] = 100/1, V_{total} = 15 ml, polymerization reaction at 30 °C for 24 h.

can be controlled by variation of the reaction parameters, the structure of the catalyst and cocatalyst. **1a**/TiBA is a promising catalytic system for the polymerization of MMA. The high yields of PMMA (85%) can easily be obtained under mild conditions.

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