

Polymerization of Methyl Methacrylate with Nickel α -Diimine Catalysts: Effect of the Methyl Position in the Ligand

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Abstract: In the solution polymerizations of methyl methacrylate with (α -diimine)nickel(II)/methylaluminoxane (MAO), we observed effects of the position of two methyl substituents in the ligand on both the activities of the catalysts and the polymer microstructure. α -Diimine nickel(II) catalysts gave syndiotactic-rich poly(methyl methacrylate) with high molecular weight and narrow molecular weight distribution.

Keywords: late transition metals, methyl methacrylate, ligand structure variation, microstructure.

Introduction

Coordinative homo- and copolymerization of functional monomers is one of challenging topics, because simple coordination of the functional group to the metal may block monomer access to vacant coordination sites. Incorporation of functional groups into a nonpolar polymer is important to control over the physical properties such as toughness, adhesion, barrier properties, surface properties, miscibility with other polymers, and rheological properties.¹

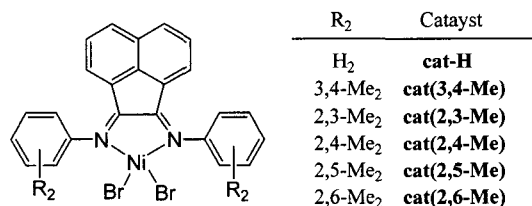
Zirconocenes² and lanthanocenes³ active for olefin polymerization have been known to carry out the polymerization of methyl methacrylate (MMA) though a group transfer polymerization mechanism. Ni(acac)₂ catalyst was also found to be an effective catalyst for the aspecific polymerization of MMA in the presence of methylaluminoxane (MAO).^{4,5}

Brookhart and co-workers recently reported palladium version of diimine complexes that were close to constituting true copolymerizations of ethylene and methyl acrylate.^{6,7} Chien and coworkers studied Brookharts nickel diimine complexes as catalysts for the copolymerization of olefin and trimethylaluminum protected polar monomers.⁸ Not only these reports, but many other reports suggest that late transition metal catalysts be characterized by reduced oxophilicity and thus more functional group tolerant. In this sense, they might be used as a catalyst for the polymerization of polar monomers such as MMA. However, there have been few reports on the late transition metal catalyzed

homopolymerization of MMA.

Recently, we demonstrated that late transition metal complexes such as (α -diimine)nickel(II), (pyridyl bis-imine) iron(II) and (pyridyl bis-imine)cobalt(II) could polymerize MMA in combination with methylaluminoxane (MAO) to give syndio-rich poly(methyl methacrylate) (PMMA).⁹ As a continuation of this study, we report here the effect of ligand structure variation of (α -diimine)nickel(II) complexes on the catalytic activity and the polymer microstructure. The Ni(II) precatalysts employed were prepared by changing the position of dimethyl substituents in the aryl ring (Scheme I). It is well known that protective bulk of the ortho substituents above and below the metal center is critical to achieve high molecular weight polymer in olefin polymerizations.⁷

Scheme I



Experimental

Materials. All reactions were performed under a purified nitrogen atmosphere using standard glove box and Schlenk techniques. MMA (Aldrich) was washed twice with aqueous sodium hydroxide (5 wt%) and twice with water, followed by drying over MgSO₄ and distillation over CaH₂ under N₂ atmosphere at reduced pressure. MAO was obtained from

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Aldrich as a 10 wt% total Al solution in toluene. Literature procedures¹⁰ were used to synthesize α -diimine nickel compounds shown in Scheme 1.

Polymerization of MMA. Solution polymerizations of MMA were carried out in a Schlenk tube (50 mL) connected with a vacuum system. In a typical procedure, 13.9 μ mol of precatalyst (MAO/precatalyst = 500 mol/mol) was dissolved in 10 mL of toluene. The polymerization started by adding 10 mL of MMA and MAO to the solution in this order. The reaction mixture was stirred at 30 °C for 1 hr. Bulk polymerizations and solution polymerizations to a high conversion degree over 10% were difficult to control due to an exothermic reaction and a stirring problem. The resulting solution was poured into acidified methanol (300 mL of a 5% v/v solution of HCl). The polymer was then isolated by filtration and washed with methanol before drying overnight at 40 °C. Polymer yield was determined by gravimetry.

Characterization of Polymers. The molecular weights of PMMA were determined by gel permeation chromatography (GPC) using a Waters M515 series system in dimethylformamide (DMF) at 25 °C as calibrated with polystyrene standards. The triad tacticity of PMMA was determined by using ¹H-NMR spectra recorded on a Varian Unity Plus 300 (300 MHz) spectrometer in CDCl₃ at 25 °C using tetramethylsilane as the internal reference.

Results and Discussion

The easily varied steric and electronic properties of the

α -diimine ligands are an important feature of the nickel α -diimine catalyst systems.⁷ Using a simple condensation of a diketone with 2 equiv of an alkyl- or arylamine, the backbone and aryl substituents are readily varied, enabling the preparation of arrays of ligands with independent control over the steric and electronic effects at the metal center. In the ethylene polymerizations, increased steric bulk of the diimine ligand aryl substituents of the nickel α -diimine catalyst leads to high polymer (\bar{M}_w = 30,000 to > 1,000,000) of the various microstructures from crystalline to amorphous, highly branched one.⁷ However, reduction in the steric bulk of the *ortho* substituents of the *N*-aryl ring leads to the production of linear α -olefins instead of high molecular weight polymer due to the increased chain transfer rates.

In order to study on the effect of the steric bulk of the *ortho* substituents of the *N*-aryl ring on the MMA polymerization, we prepared an array of nickel α -diimine catalyst by changing the position of dimethyl substituents of the aryl ring. Table I shows the results of the solution polymerizations of MMA by using various catalysts in combination with MAO. The **cat-H** containing no substituents in the aryl rings showed the highest activity in an hour of polymerization. The polymerization time was controlled to an hour for the easiness of agitation. The activity decreases in order of **cat-H** > **cat(3,4-Me)** > **cat(2,3-Me)** > **cat(2,4-Me)** > **cat(2,5-Me)**. It is surprising to note that **cat(2,6-Me)**, which shows very high activity in the ethylene polymerization up to 11 kg mmol⁻¹h⁻¹bar⁻¹,⁷ shows only negligible activity. High molecular weight polymer is produced by using Al(*i*-Bu)₃ as a

Table I. Solution Polymerization Results for MMA Using (α -diimine)nickel(II) Catalysts. Polymerization Conditions: [MMA] = 9.35×10^{-2} mol/L; [Cat.] = 1.39×10^{-5} mol/L; [MAO]/[Ni] = 500 (mole ratio); Toluene = 10 mL; Polymerization Temperature = 30 °C

Entry	Catalyst	Time (hr)	Yield (%) ^a	M_n ($\times 10^{-5}$) ^b	M_w/M_n ^b	Triad fractions ^c (%)		
						<i>mm</i>	<i>mr</i>	<i>rr</i>
1	cat-H	1	10.6	1.30	1.40	3.93	15.92	80.15
2	cat(3,4-Me)	1	8.86	2.54	1.71	4.65	18.06	77.29
3	cat(2,3-Me)	1	5.46	1.42	1.34	4.85	17.62	77.53
4	cat(2,4-Me)	1	5.03	1.38	1.34	3.55	14.90	81.55
5	cat(2,5-Me)	1	4.93	1.16	1.35	4.58	15.94	79.47
6 ^d	cat(2,6-Me)	1	nil	-	-	-	-	-
7	cat(2,4-Me)	1/3	1.02	1.65	1.47	6.35	17.89	75.76
8	cat(2,4-Me)	2/3	3.51	1.67	1.42	5.74	19.91	74.35
9	cat(2,4-Me)	1.5	5.93	1.32	1.38	4.93	18.54	76.53
10	cat(2,4-Me)	2	7.87	1.33	1.41	5.67	18.62	75.71
11	cat(2,4-Me)	3	7.90	1.50	1.41	5.99	18.42	75.60
12 ^e	cat-H	20	4.89	2.27	1.26	3.60	30.79	65.62

^aYield defined a mass of dry polymer recovered/mass of monomer used. ^bDetermined by GPC.

^cMeasured by ¹H-NMR spectra; from low to high field in the spectra (δ = 1.3–0.5 ppm). ^dNegligible activity at conditions of the present study.

^ePolymerization conditions are the same as Entry No. 1 except [Al(*i*-Bu)₃]/[Ni] = 100 (mole ratio).

cocatalyst instead of MAO (Entry No. 12 in Table I), even if the activity is relatively lower.

As indicated in Table I, the molecular weights of all polymers are very high (say, $\bar{M}_n = 250,000$ for **cat(2,3-Me)**); however, no clear trends can be found according to the position of substituents. Even the PMMA produced by **cat-H** shows very high molecular weight ($\bar{M}_n = 130,000$). These results suggest that increase of steric bulk of the *ortho* substituents of the *N*-aryl ring is not a necessary condition to achieve high molecular weight PMMA. Unlike ethylene polymerizations using the same catalysts, chain transfer in the MMA polymerization is quite slow relative to chain propagation, and thus, high molecular weight polymer is produced. As a result, the chain transfer processes proposed for the ethylene polymerization^{10a,11} are not appropriate to apply MMA polymerization. In MMA polymerization, the functional groups themselves may provide alternative mechanisms that facilitate propagation through intermediates unique to their structures. For example, the formation of a metal enolate species that is capable of rearranging from the oxygen-bound enolate to another carbon-metal-bonded intermediates.⁶

The data in Table I show that all catalysts produce PMMAs with narrow polydispersity index (PDI). The PDI values are narrow compared to other late transition metal catalysts such as Ni(acac)₂/MAO,^{12,13} and neutral Pd(II) and Ni(II) acetylacetonate.¹⁴ In order to check the degree of control attainable using (α -diimine)nickel(II)/MAO systems, we chose **cat(2,4-Me)** precatalyst that gives PMMA of narrow PDI and performed independent polymerizations by changing the time from 20 min to 3 hrs (see Table I). Both activity and molecular weight are not linearly increased, demonstrating that the narrow PDI is not induced by living character of the catalyst system. Group-transfer polymerization mechanisms originally proposed for the MMA polymerizations by zirconocenes² and lanthanocenes³ may be a factor to give narrow PDI with high molecular weight; however, further studies are needed to clarify the propagation and chain transfer mechanisms. If it is true and only mechanism, it should show living character.

The microstructure of PMMA was investigated by using ¹H-NMR.^{2,4,15} As summarized in Table I, all catalysts produce predominantly syndiotactic PMMA. The variation of dimethyl substituents of the aryl ring has little influence on the syndiotacticity (as *rr* triad) of PMMA. Using Al(*i*-Bu)₃ as a cocatalyst results in the decrease of syndiotacticity (see Entry No. 1 and 12). Triad tests may be a good clue to differentiate between enantiomeric site control and chain-end control.¹⁷ In the former case, 2(*mm*)/*mr* should equal one, and in the latter, 4(*rr*)(*mm*)/(*mr*)² is theoretically unity. All catalysts of the present study yield polymers that cannot be described exactly as having been formed under a specific control mechanism, enantiomeric site control or chain-end control.^{9,17}

Conclusions

All (α -diimine)nickel(II) catalysts prepared by changing two methyl substituents position of the aryl ring gave syndiotactic-rich PMMA. Increase of steric bulk of the *ortho* substituents of the *N*-aryl ring was not a necessary condition to achieve high activity and high molecular weight PMMA. All catalysts produced PMMA of narrow PDI (< 1.5), which was not caused living chains.

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