

A Novel Lanthanocene Catalyst System for the Polymerization of Methyl Methacrylate

$\text{Me}_2\text{Si}(\text{CpSiMe}_3)_2\text{NdCl}-n\text{-BuMgCl}^*$

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ABSTRACT: $\text{Me}_2\text{Si}(\text{CpSiMe}_3)_2\text{NdCl}$ activated by $n\text{-BuMgCl}$ at low molar ratio (1 : 1.2) was successfully used to polymerize methyl methacrylate (MMA) for the first time. Grignard reagent indicated better co-catalytic properties than alkyl aluminum. Effects of the catalyst concentration, polymerization time, temperature, and solvents were studied in bulk and solution polymerization respectively. The results showed that this catalyst system was very active for MMA polymerization in toluene at 40°C, producing PMMA with high molecular weight (53.5×10^4) and high conversion (100%). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2245–2250, 2001

Key words: lanthanocene catalyst; Grignard reagent; polymerization; methyl methacrylate

INTRODUCTION

Since the mid-1980s, polyolefins with all kinds of feasible microstructures, such as syndiotactic, isotactic, hemiisotactic, and stereoblock, have been synthesized by novel metallocene-based catalysts with methyl aluminoxane (MAO) or cationic borane.^{1–3} Most of them are being made in commercial quantities for their excellent properties. All the above-mentioned advances have also greatly stimulated research in polymerization of polar monomers.

It is well known that conventional Ziegler–Natta catalysts promote the polymerization of

olefins but not the polar ones. Methyl methacrylate (MMA), a common vinyl monomer, can be initiated in different methods such as free radical, anionic, coordination,⁴ group transfer polymerization,⁵ and atom transfer radical polymerization.⁶ Preliminarily, much attention was focused on anionic systems based on alkyl lithium compounds⁷ or Grignard reagents,⁸ due to the living and stereoregular features at very low polymerization temperature (–78°C). Coordinated lanthanide catalysts have also been developed for the polymerization of MMA after the studies of stereoregular polymerization of conjugated dienes⁹ and acetylene.¹⁰ $\text{Nd}(\text{P}_{204})_3\text{-Al}(\text{i-Bu})_3\text{-CCl}_4$,¹¹ $\text{Y}(\text{acac})_3\text{-Al}(\text{i-Bu})_3\text{-BuLi}$,¹² $\text{Nd}(\text{naph})_3\text{-BuLi}$,⁴ and $\text{Nd}(\text{O-iPr})_3\text{-Al}(\text{i-Bu})_3$ ¹³ could polymerize MMA with fairly good activity.

In 1992, S. Collins and co-workers¹⁴ reported that MMA could be efficiently polymerized using a two-component catalyst system comprised of $[\text{Cp}_2\text{ZrMe}(\text{THF})][\text{BPh}_4]$ and Cp_2ZrMe_2 at or below room temperature, providing partial syndiotacticity (ca. 80% r diads at 0°C) in high yield and with

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a narrow molecular weight distribution (MWD). Two possible mechanisms concerning the intermediacy of neutral enolate complexes were proposed after detail kinetic studies.

H. Yasuda and co-workers¹⁵ continually reported their elegant discoveries on neutral lanthanocene catalysts and their application in living homo- and copolymerization of methacrylate and acrylate. They obtained the desired 1 : 2 adduct of $[\text{SmH}(\text{C}_5\text{Me}_5)_2]$ with MMA as an orange crystal successfully.¹⁶ On the basis of X-ray structural data, Yasuda proposed a coordination anionic mechanism involving an eight-membered transition state for the initiation of polymerization of MMA by the organolanthanide catalysts.

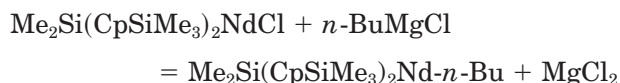
Isotactic PMMA has been achieved by using $\{\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)[\text{C}_5\text{H}_3-(1\text{S}), (2\text{S}), (5\text{R})\text{-neomenthyl}]\text{-LaR}\}$, as reported by T. J. Marks,¹⁷ but $\{\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)[\text{C}_5\text{H}_3-(1\text{S}), (2\text{S}), (5\text{R})\text{-menthyl}]\text{-LaR}\}$ has been effective to produce syndiotactic PMMA. A possible explanation for this difference is that the menthyl complex produces syndiotactic polymer via a cyclic eight-membered intermediate, while the neomenthyl complex produces isotactic PMMA via a nonlinear intermediate.

Novak et al.¹⁸ found that divalent lanthanocene complex possessed the ability to polymerize MMA by the formation of bimetallic bisinitiator, which was generated *in situ* by the addition of a one-electron reducing agent to a vinyl monomer.

Recently, K. Soga's group¹⁹ reported that isotactic PMMA could be synthesized using dialkyl zirconocene complexes, in combine with stoichiometric amount of activators such as $\text{B}(\text{C}_6\text{F}_5)_3$ in the presence of a large excess of diethylzinc.

The above-described research have opened an interesting new field of synthesizing novel polymer materials—for example, homopolymers of polar vinyl monomers with different microstructures, copolymers of olefin, or styrene with polar monomers.

However, most of these metallocene catalysts, especially lanthanocene hydrides and alkyls, are extremely sensitive to moisture and oxygen. They are also very trouble in synthesis and storage. $\text{Me}_2\text{Si}(\text{CpSiMe}_3)_2\text{NdCl}$, which is the precursor of the corresponding neodymocene alkyl or hydride, is somewhat stable. Thus it was selected to activate by common alkylating reagent, *n*-BuMgCl, and to initiate the polymerization of MMA.



In order to ensure the sufficient alkylation of neodymocene and scanning impurities, 20% excess of Grignard reagent was used in the polymerization system.

This paper concerned the polymerization behaviors of MMA catalyzed by the title catalyst and the structure analysis of PMMA produced.

EXPERIMENTAL

Materials

MMA was washed with diluted NaOH until it became colorless, dried over anhydrous MgSO_4 , then distilled over calcium hydride under reduced pressure and stored in a refrigerator. Toluene for the polymerization was refluxed over blue benzophenone-Na complex. $\text{Me}_2\text{Si}(\text{CpSiMe}_3)_2\text{NdCl}$ was prepared according to literature²⁰ and used as the mixture of racemic and mesomeric isomers.

Polymerization

Under Ar protection, $\text{Me}_2\text{Si}(\text{CpSiMe}_3)_2\text{NdCl}$ was dissolved in toluene, and then a stoichiometric amount of *n*-BuMgCl was added. The mixture was aged for half an hour with occasional shaking at 25°C.

The polymerization was performed in a 25 mL ampoule that was purged with dry nitrogen several times before use. Solvent, monomer, and catalyst solution were introduced into the ampoule sequentially. Then the ampoule was placed in a temperature-controlled oil bath for designated time. Polymerization was terminated by ethanol containing 5% hydrochloric acid, and the polymer precipitated was washed with ethanol several times and then dried at 50°C under vacuum.

Measurement

The molecular weight and molecular weight distribution of polymers were measured at 30°C by gel permeation chromatograph (Waters-150C), using tetrahydrofuran (THF) as solvent. The gas permeation chromatography (GPC) chromatogram was calibrated against standard polystyrene samples. The content of syndio-PMMA was determined by ¹H and ¹³C NMR spectra at room temperature on Varian Unity-400 NMR spectrometer using CDCl_3 as solvent.

RESULTS AND DISCUSSIONS

At first, we tried to polymerize MMA with single component neodymocene chloride and test the

Table I Polymerization Results of MMA with Different Catalysts and Cocatalysts^a

Catalyst	Cocatalyst	Temp. (°C)	MMA/Cat.	Time (h)	Yield (%)	M_w ($\times 10^4$)	MWD
Catalyst Nd	Al(<i>i</i> -Bu) ₃	40	500	4	32.2	10.7	2.18
Catalyst Nd	<i>n</i> -BuMgCl	40	500	4	100	53.5	1.65
Catalyst Y	—	80	1000	20	70.3	152	1.80

^a Polymerization condition: catalyst Nd for the title catalyst and catalyst Y for O(C₂H₄C₅H₃CH₃)₂YCl; Cocat./Cat. = 1.2 (molar ratio), toluene 1 mL, MMA 1 mL, except for catalyst Y (bulk).

probability of initiation. It was noted that even after 24 h at 40°C, only a little polymer was obtained, indicating that Me₂Si(CpSiMe₃)₂NdCl was not very active for polymerization as expected under this condition. Although O(C₂H₄-C₅H₃CH₃)₂LnCl (Ln = Y, Nd, Sm) were found to be able to initiate the polymerization of MMA, it proceeded at higher temperature (>60°C) and lasted for a longer polymerization time (about 20 h) to reach high conversion.²¹ A stoichiometric amount of *n*-BuMgCl can significantly promote the polymerization. The GPC spectra of PMMA catalyzed by the binary initiator in toluene solution indicated a narrow molecular weight distribution (MWD = 1.62 at 30°C and 1.60 at 60°C) in the range of polymerization temperature investigated. In contrast with the early work of K. Hatada,²² *n*-BuMgBr gave the syndiotactic PMMA in low yield (8.1%) with rather broad MWD as 13.4 in toluene at -78°C. As the alkyl group became bulkier, the isotacticity of the polymer increased greatly and the MWD became narrower.

Alkyl aluminum like Al(*i*-Bu)₃ was not a suitable cocatalyst for Me₂Si(CpSiMe₃)₂NdCl, only

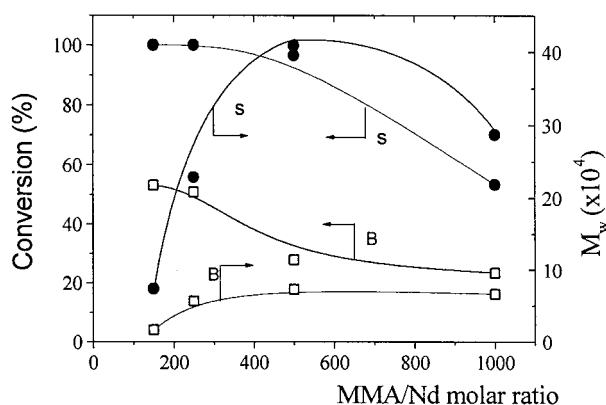


Figure 1 Effect of the MMA/Nd molar ratio. Polymerization condition: 4 h, 20°C, MMA 1 mL, toluene 1 mL. B: bulk polymerization; S: solution polymerization.

32.2% monomer converted into polymer under the same condition (see Table I).

Effect of the MMA/Nd molar ratio on the polymerization is shown in Figure 1. The amount of catalyst added affected both the conversion of monomer and the molecular weight of PMMA greatly in bulk and solution polymerization. The conversion increased monotonously to a plateau while the molecular weight of PMMA has a peak value at the molar ratio of MMA/Cat. = 500 nearby. In toluene solution, the catalyst exhibited much higher activity than in bulk system, giving PMMA with nearly perfect conversion and high molecular weight (40.8×10^4).

Figure 2 demonstrates the effect of polymerization time. Both the conversion of monomer and the molecular weight of PMMA increased with the prolongation of polymerization time. The polymerization in toluene proceeded so rapidly that the monomer consumed completely at the end of 4 h. As a comparison, the results of bulk polymerization system did not change remarkably within the time investigated probably due to the gel effect occurring with the increased viscosity.

Typical curves on the relation between the polymerization temperature and polymer yield are

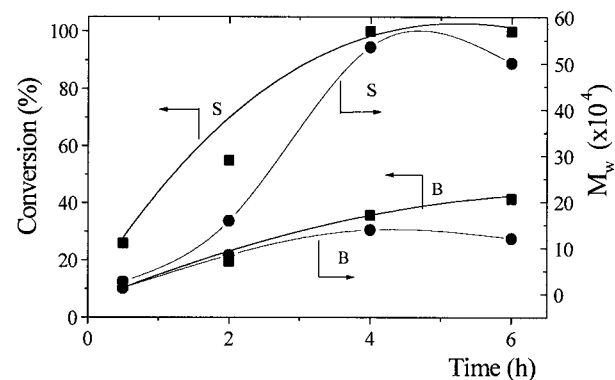


Figure 2 Effect of the polymerization time Polymn. Condition: MMA/Nd = 500 (molar ratio), 40°C, MMA 1 ml, toluene 1 ml B: bulk polymerization; S: solution polymerization

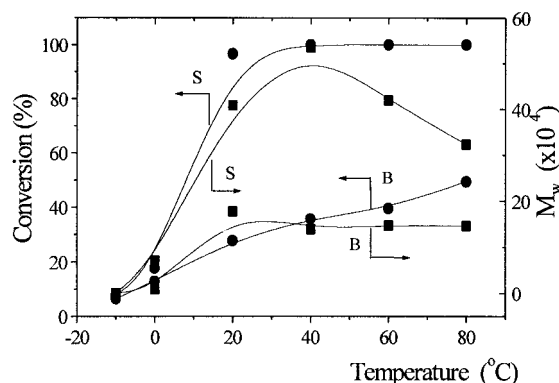


Figure 3 Effect of the polymerization temperature Polymn. Condition: MMA/Nd = 500 (molar ratio), 4 hrs, MMA 1 ml, toluene 1 ml B: bulk polymerization; S: solution polymerization

plotted in Figure 3. The polymerization rate was sensitive to temperature. The polymer yield increased rapidly with the rising of temperature from -10 to 20°C , while the molecular weight of PMMA reached a maximum value at 20 and 40°C in bulk and solution polymerization, respectively. Lanthanocene alkyls, as reported, are highly active to initiate the polymerization even at 0°C .¹⁵ For these reasons, the alkylating reaction between neodymocene chloride (Nd) and Grignard reagent might be expected to carry out during the polymerization. Chain transfer reaction became more frequently at higher temperature. These behaviors are quite in agreement with other lanthanide catalysts such as $\text{Ln}(\text{acac})_3\text{-}n\text{-BuMgCl}$.²³

As well known, the electron donor, the third component used in coordination polymerization, strongly influences the activity of Ziegler–Natta catalyst.²⁴ The addition of Lewis base decreased the yield of polymer when the Lewis base/catalyst molar ratio increased; however, it did help obtain higher molecular weight. It is possible that the

Table III Effect of Solvents on the Polymerization of MMA^a

Solvent	Petroleum Ether	THF	Toluene	Ethyl Acetate
ϵ	—	7.35	2.38	6.02
Yield (%)	56.7	20.2	96.6	<10
$M_w (\times 10^4)$	21.0	6.57	40.8	0.53

^a Polymerization condition: MMA/Nd = 500 (molar ratio), Nd/Mg = 1 : 1.2, 20°C , 4 h, solvent 1 mL, MMA 1 mL.

catalyst formed more stable active species with these electron donors, lowering the polymerization rate of methyl methacrylate. Different Lewis bases showed different effects on the polymerization (as listed in Table II).

Various solvents influence the polymerization remarkably due to their solubility and polarity. The results of MMA polymerization carried out in solution systems are listed in Table III. It is obvious that an aromatic hydrocarbon such as toluene is the best solvent for polymerization. That an aliphatic hydrocarbon precipitated the PMMA produced in the polymerization may explain the low yield. Polar solvents, such as ethyl acetate, inhibit the polymerization by the strong coordination interaction between neodymium and heteroatoms. Especially, the chain transfer probably presents in ethyl acetate solution, causing from the acidic $\alpha\text{-H}$ of carbonyl.²⁵

The ^{13}C NMR spectrum of a typical polymer is displayed in Figure 4 whereas the pentad distribution are listed in Table IV, both of which indicate that PMMA produced with $\text{Me}_2\text{Si}(\text{CpSiMe}_3)_2\text{-NdCl}$ and $n\text{-BuMgCl}$ is a syndio-rich atactic polymer. The microtacticity distributions of polymer were found to obey Bernoullian statistics, suggesting that the syndiospecific polymerization proceeds via a chain end-controlled mechanism.

Table II Effect of the Electron Donor on the Polymerization of MMA^a

	Yield (%)	$M_w (\times 10^4)$		Ratio	Yield (%)	$M_w (\times 10^4)$
—	96.6	40.8	CCl_4	0.5	62.7	50.2
CCl_4	51.3	78.7		1.0	51.3	78.7
EA	21.9	45.4		2.0	32.6	50.7
TEA	42.8	72.8	TEA	0.5	60.3	74.2
Pyridine	40.2	69.3		1.0	42.8	72.8
				2.0	26.5	66.3

^a Polymerization condition: [MMA]/cat = 500 (molar ratio), Nd/Mg = 1 : 1.2, 20°C , 4 h, solvent 1 mL, MMA 1 mL; the molar ratio of the electron donor added was 1.0 if not mentioned.

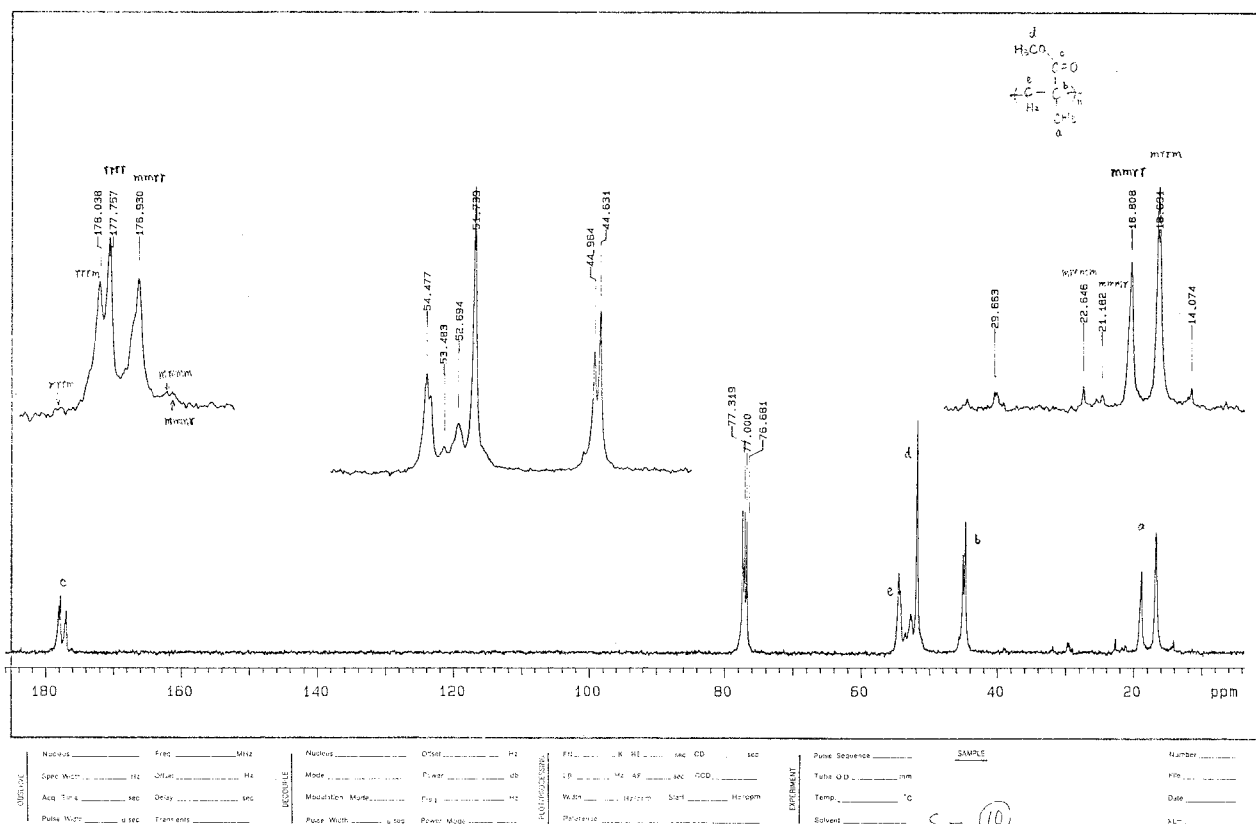


Figure 4 ^{13}C NMR spectrum of typical PMMA with the title catalyst. Polymerization condition: MMA/Cat. = 500 (molar ratio), Mg/Nd = 1.2, 40C, 4 hrs, toluene as solvent (the condition is also pointed out below Table IV).

Similar results have been reported with the lanthanocene and $\text{Cp}_2\text{ZrCH}_3(\text{THF})^+(\text{BPH}_4)^-$ / $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ catalysts.²⁶

CONCLUSION

Silicon-bridged neodymocene chloride, $\text{Me}_2\text{Si}(\text{CpSiMe}_3)_2\text{NdCl}$, combined with *n*-BuMgCl was

first applied in the polymerization of methyl methacrylate. The results showed that $\text{Me}_2\text{Si}(\text{CpSiMe}_3)_2\text{NdCl}$ catalytic system was very active in toluene at low temperature, producing PMMA with high molecular weight and high conversion. Addition of some electron donor was favor to obtain higher molecular weight polymer (78.7×10^4). ^{13}C NMR spectrum indicated that the polymer was syndio-rich atactic. The polymeriza-

Table IV Observed and Calculated Steric Pentad Distribution of PMMA^a

Pentad Fraction (%)	Triad Test ^d										Triad Test ^d	
	m m m m	m m m	r m m r	m m r m	r m r m	m m r r	r m r r	m r r m	r r r m	r r r r	$4[\text{rr}][\text{mm}]/[\text{mr}]^2$	$2[\text{rr}]/[\text{mr}]$
Observed ^b	0.0	0.0	2.2	7.3		23.0		6.0	19.5	42.0	1.12	4.2
Calculated ^c	0.1	1.1	2.4	5.9		25.0		2.4	20.2	42.8		4.7

^a Polymerization condition: MMA/Nd = 500, 40°C, 4 h, solvent 1 mL, MMA 1 mL.

^b Observed from carbonyl absorption in ^{13}C NMR spectra.

^c Calculated from the Bernoullian equation with $p = 0.81$ (40°C) for atactic PMMA.

^d $4[\text{mm}][\text{rr}]/[\text{mr}]^2 = 1$ for a chain end-controlled mechanism; $2[\text{rr}]/[\text{mr}] = 1$ for a site-controlled mechanism.

tion maybe proceeded via a chain end-controlled mechanism.

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