

Polymerization of methyl methacrylate by diphenylamido bis(methylcyclopentadienyl)ytterbium complex

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Methyl methacrylate (MMA) was effectively polymerized by diphenylamido bis(methylcyclopentadienyl)ytterbium complex $(\text{MeCp})_2\text{YbNPh}_2(\text{THF})$. The reaction can be carried out over a range of polymerization temperature from -40°C to 40°C and gives the polyMMA with high molecular weights. The initiation mechanism was demonstrated by diphenylamido-terminated methyl methacrylate oligomer.

Keywords Methyl methacrylate, polymerization, diphenylamido bis(methylcyclopentadienyl)ytterbium

Introduction

Poly(methyl methacrylate) is an important polymer with a wide range of uses in materials. Recently, the application of organolanthanide complexes in MMA polymerization has attracted a great deal of attention. In 1993, Yasuda *et al.* first reported that lanthanocene hydride and alkyl compounds are able to polymerize methyl methacrylate in a living fashion to afford the syndiotactic PMMA with high molecular weights and extremely narrow molecular weight distribution.¹ Marks *et al.* also reported the stereocontrol in the polymerization of MMA mediated by chiral organolanthanide metallocenes.² More recently, we found that diisopropylamido bis(methylcyclopentadienyl)lanthanoids³ and piperidino bis(methylcyclopentadienyl)lanthanoids⁴ are highly effective initiators for the polymerization of methyl methacrylate. However, the polymerization activity decreased dramatically with the increase of temperature because of some side reactions that inhibited the polymerization reaction. In order to understand further effect of the amido ligand on

the catalytic activity and to improve the catalytic behavior of lanthanocene amides, bulky amido complex $(\text{MeCp})_2\text{YbNPh}_2(\text{THF})$ was synthesized and its catalytic activity for the polymerization of MMA was studied. It was found that the lanthanocene amide complex with bulky NPh_2 ligand shows much higher catalytic activity at 40°C than the complexes containing $\text{N}(i\text{-Pr})_2$ and NC_5H_{10} ligands. Here we wish to report the preliminary results.

Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Toluene, THF and diethyl ether were dried over Na or sodium benzophenone ketyl and distilled before use. MMA was dried over calcium hydride powder for 4 days and stored over molecular sieves 0.3 nm under argon after distillation. Gel permeation chromatographic analyses were run on a Shimadzu GPC apparatus equipped with two Ultrastayragel linear columns in THF at 30°C . $^1\text{H-NMR}$ spectra were taken on a Unity Inova-400 apparatus in CDCl_3 .

Preparation of the complex $(\text{MeCp})_2\text{YbNPh}_2(\text{THF})$

To a solution of $(\text{MeCp})_2\text{YbCl}$ in THF (51.3 mL, 0.172 mol/L) was added 15.8 mL of a THF solution of NaNPh_2 (0.558 mol/L). The mixture was stirred for 1 h at 0°C and then for another 48 h at room temperature. After the THF was completely removed, the residue was

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extracted with diethyl ether to remove NaCl. The extracts were concentrated and cooled to -30°C for crystallization. Dark red crystals were formed. Yield: 3.83 g (76%). Anal: $\text{C}_{28}\text{H}_{32}\text{NOYb}$. Calcd: C, 58.84; H, 5.64; N, 2.45; Yb, 30.27. Found: C, 58.22; H, 5.36; N, 2.41; Yb, 30.53. ν_{max} (KBr): 3042m, 2970w, 2919w, 2873w, 1593s, 1508s, 1495s, 1455w, 1419m, 1311s, 1245m, 1173m, 1030m, 881m, 748s, 692s cm^{-1} . The crystal structure was identified by X-ray diffraction analysis to be monomer.

Polymerization of MMA

To a toluene solution (10 mL) of MMA (1 mL, 9.35 mmol) was added at once the toluene solution (1 mL) of $(\text{MeCp})_2\text{YbNPh}_2(\text{THF})$ (10.7 mg, 0.019 mmol) with vigorous magnetic stirring at the desired temperature. After the polymerization was held for 2 h, the viscous solution was poured into ethanol containing 2% HCl solution (100 mL) to induce the precipitation of the polymer. The polymer was washed with ethanol and dried in vacuum.

Oligomerization of MMA

To a toluene solution 20 mL of $(\text{MeCp})_2\text{YbNPh}_2(\text{THF})$ (0.115 g, 0.2 mmol) was added at once the toluene solution (3.4 mL) of MMA (2.0 mmol) with vigorous magnetic stirring at room temperature. After the solution had been stirred for 5 min, ethanol containing 2% HCl solution was added to terminate the reaction. After the solvent had been completely removed in vacuum, the remaining solid was extracted with toluene. When the toluene was removed for the second time, the oligomer was purified by reprecipitation from acetone to petroleum ether until the catalyst was completely removed.

Results and discussion

Table 1 summarized the results of MMA polymerization using ytterbium initiator $(\text{MeCp})_2\text{YbNPh}_2(\text{THF})$ at various temperatures and initiator concentrations. It can be seen from Table 1 that the title complex has good catalytic activity. The polymerization reaction can proceed at a wide range of temperature from -40°C to 40°C . The monomer conversion is all greater than 95%

at 0°C for 2 h even though the initiator concentration decreases from 0.2 to 0.07 mol%. The polymer obtained has high molecular weight. The number-average molecular weight of polyMMA exceeds 100,000.

In comparison with the results reported on the polymerization of MMA using less bulky amido complexes $(\text{MeCp})_2\text{LnN}(i\text{-Pr})_2(\text{THF})^3$ and $(\text{MeCp})_2\text{LnNC}_5\text{H}_{10} \cdot (\text{HNC}_5\text{H}_{10})^4$, the present complex shows much higher activity at the temperature as high as 40°C . For example, the monomer conversion still reaches to 80.3% (experiment 8) when the initiator concentration is as low as 0.07 mol%, while 45.2% (experiment 10) for $(\text{MeCp})_2\text{YbN}(i\text{-Pr})_2(\text{THF})$ under the same reaction conditions and only 30.3% for $(t\text{-BuCp})_2\text{YbNC}_5\text{H}_{10} \cdot (\text{THF})$ in the initiator concentration as high as 0.2 mol% (experiment 11). It means that inducing bulky amido group into the complexes is beneficial to inhibit the undesired side reactions. However, the phenomenon of conversion decreasing with increase of temperature was still observed. The conversion decreases from 96.4% (experiment 7) to 80.3% (experiment 8) when the polymerization temperature is elevated from 0°C to 40°C in the case of 0.07 mol% initiator concentration. The results indicated that the NPh_2 ligand could not completely inhibit the side reactions. It is expected that the catalytic activity is low below -40°C because the bulky amido ligand (NPh_2) makes it difficult to initiate the insertion of MMA for the steric hindrance. Further study is in progress on the relationship between the size of ligands around the central metal and the polymerization activity.

The coordination anionic mechanism¹ was proposed for the present polymerization (Fig. 1). In the initiation step, the amide attacks the CH_2 group of MMA to generate a transient $\text{Yb}-\text{O}-\text{C}(\text{OCH}_3)=\text{C}(\text{CH}_3)\text{CH}_2\text{NPh}_2$ species, and then the incoming MMA molecule may participate in a 1,4-addition to afford the eight membered ring intermediate. In the propagation step, another MMA molecule may attack the growing end and the coordinated ester group will be liberated. According to this initiation mechanism, the end of polymer chain should have NPh_2 group. This was confirmed by the ^1H NMR spectroscopy of methyl methacrylate oligomer obtained from the oligomerization of MMA at the room temperature in the case of 1:10 feed ratio (initiator to monomer). The signals due to $-\text{NPh}_2$ protons appear distinctly at δ 6.88, 6.95, 7.24 and indicate that methyl methacry-

late oligomer is terminated with NPh_2 group (see Fig . 2) .

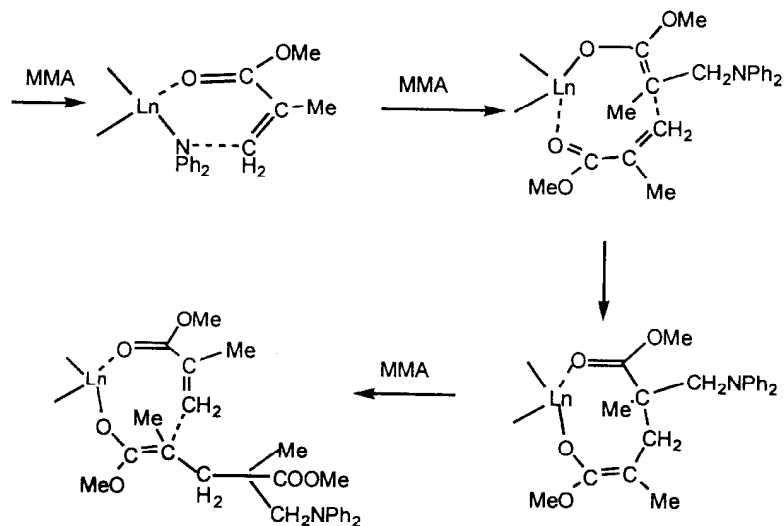


Fig. 1 Initiation mechanism for the present polymerization.

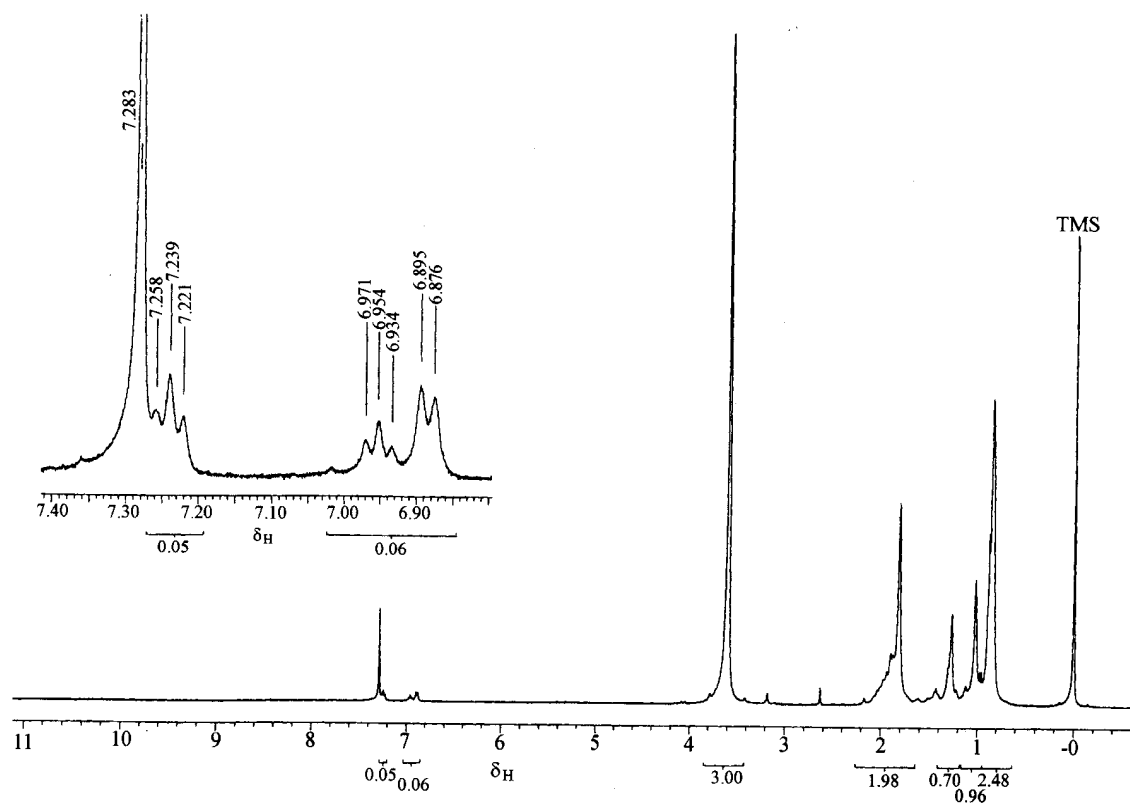


Fig. 2 ^1H NMR spectra of diphenylamido-terminated MMA oligomer (CDCl_3).

Table 1 Polymerization of MMA with $(\text{MeCp})_2\text{YbNPh}_2(\text{THF})$

No.	Catalyst concentration (mol%)	Temp. (°C)	Conversion (%)	$M_n \times 10^{-3}$	M_w/M_n
1	0.2	40	93.1	103	1.53
2	0.2	20	95.3	164	1.52
3	0.2	0	95	253	1.67
4	0.2	-40	65.2	1096	3.85
5	0.2	-78	0
6	0.1	0	95	330	2.4
7	0.07	0	96.4	420	1.88
8	0.07	40	80.3	219	1.48
9 ^a	0.07	0	96.2	478	1.27
10 ^a	0.07	40	45.2	---	---
11 ^b	0.2	40	30.3	---	---

Reaction condition: Solvent, toluene; Solvent/monomer = 10 V/V; Reaction time 2 h.

^a Catalyst: $(\text{MeCp})_2\text{YbN}(i\text{-Pr})_2(\text{THF})$. ^b Catalyst: $(t\text{-BuCp})_2\text{YbNC}_5\text{H}_{10}(\text{THF})$.

References

1. Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N., *Macromolecules*, **26**, 7134(1993).
2. Giardello, M.A.; Yamamoto, H.; Brard, L.; Marks, T. J., *J. Am. Chem. Soc.*, **117**, 3276(1995).
3. Mao, L.; Shen, Q., *J. Polym. Sci.: Part A: Polym. Chem.*, **36**, 1593(1998).
4. Mao, L.; Shen, Q.; Sun, J., *J. Organomet. Chem.*, **566**, 9(1998).

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