

Note

POLYMERIZATION OF METHYL METHACRYLATE WITH ORGANOLANTHANIDES AS SINGLE-COMPONENT CATALYSTS*

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Abstract It was first found that $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$ and $\text{Ind}_2\text{LnN}(\text{i-Pr})_2$ ($\text{Ln} = \text{Y}, \text{Yb}$) exhibit extremely high catalytic activity in the polymerization of methyl methacrylate. The reactions can be carried out over a quite broad range of polymerization temperatures from -30 to 50°C . PMMA with high molecular weight (7.8×10^5) and high isotacticity (94%) can be obtained by using $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$, and narrow molecular weight distribution ($M_w/M_n < 1.5$) can be obtained by using $\text{Ind}_2\text{LnN}(\text{i-Pr})_2$ ($\text{Ln} = \text{Y}, \text{Yb}$).

Keywords Organolanthanide, MMA, Polymerization

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is an important polymer in materials and surface coating industries. Since 1950s, a large number of papers have been published on the synthesis and characterization of stereoregular PMMA^[1-6]. The application of organometallic compounds in the polymerization of PMMA has attracted much attention, and many new effective initiators have been explored^[1-5]. Recently, Yasuda *et al.* reported the fact that lanthanocene hydride and alkyl compounds can polymerize methyl methacrylate in a living fashion to afford a syndiotactic PMMA with high molecular weight and extremely narrow molecular weight distribution^[7]. In the meantime Collins and Ward discovered that a cationic zirconocene compound $\text{Cp}_2\text{Zr}(\text{CH}_3)(\text{THF})^+\text{BPh}_4^-$ promotes the syndiospecific polymerization of MMA in the presence of neutral zirconocene ($\text{Cp}_2\text{Zr}(\text{CH}_3)_2$), and a substoichiometric mixture of $[\text{n-Bu}_3\text{NH}][\text{BPh}_4]$ and *rac*- or (*S*)-(+)- $\text{Et}(\text{H}_4\text{Ind})_2\text{Zr}(\text{CH}_3)_2$ gives isotactic PMMA in a polar solvent like CH_2Cl_2 ^[8]. More recently, Marks *et al.* also described the stereocontrol in the polymerization of MMA mediated by chiral organolanthide metallocenes^[9]. In this article, we found that $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$, $\text{Ind}_2\text{LnN}(\text{i-Pr})_2$ ($\text{Ln} = \text{Y}, \text{Yb}$) exhibit extremely high catalytic activity in the polymerization of MMA.

EXPERIMENTAL

Monomer and Solvent

Methyl methacrylate (MMA) was distilled over calcium hydride powder and stored over molecule sieves under argon. Toluene, THF and other solvents (analytical grade) were dried and freed from oxygen by refluxing over Na/K alloy and distilled under argon before use.

MMA Polymerizations

All polymerization reactions were performed under dry argon. A typical example is given as follows. To a

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toluene solution (10 mL) of MMA (20 mmol, 2.13 mL) was added at once a toluene solution (2 mL) of $\text{Ind}_2\text{LnN}(i\text{-Pr})_2$ (0.04 mmol, 0.02 mol/L) with vigorous magnetic stirring at the desired temperature. After the polymerization had proceeded for a given time, the viscous solution was poured into ethanol containing 5% HCl solution (50 mL) to precipitate the polymer. The resulting polymer was washed for three times with ethanol and dried under vacuum at 50 °C.

Measurements

The intrinsic viscosity of PMMA was determined in chloroform at 25 °C using a viscometer and the molecular weight of PMMA was calculated from the following formula:

$$[\eta] = 4.8 \times 10^{-5} M_v^{0.8} (\text{CHCl}_3, 25^\circ\text{C})$$

NMR spectra were taken on a Unity-400 apparatus in CDCl_3 . Gel permeation chromatographic analyses were run on a Waters-410 instrument in THF at 25 °C. The molecular weights were calculated and calibrated by standard polystyrene.

RESULTS AND DISCUSSION

Table 1 summarizes the results of MMA polymerizations using catalyst $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$ at various temperatures and catalyst concentrations. It can be seen from Table 1 that the polymerization gives high conversion (100%) at -25 °C for 4 h. When the temperature decreases from -25 to -78 °C or increases from -25 to 50 °C, the catalytic activity and molecular weight of PMMA decline. When the catalyst concentration decreases from 0.2 to 0.1 mol%, the conversion decreases but molecular weight increases. Table 1 also shows that the isotacticity is very high (> 90%) over a quite broad range of temperatures from -25 to 25 °C.

Table 1. Polymerization of MMA with $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$

Polymerization temperature (°C)	[MMA]/[Cat]	Conversion (%) (reaction time, h)	$M_v (\times 10^{-4})$	Tacticity (%)		
				<i>mm</i>	<i>mr</i>	<i>rr</i>
-78	500	24(4)	26.5	—	—	—
-25	500	100(4)	59.8	94.8	2.7	2.5
0	500	64(2)	54.2	94.2	3.0	2.8
25	500	62(2)	48.5	93.1	3.5	3.4
50	500	51(2)	39.4	—	—	—
0	1000	13(4)	78.3	—	—	—

Polymerization condition: solvent = toluene; solvent/[MMA] = 4 (vol/vol)

The influence of $\text{Ind}_2\text{LnN}(i\text{-Pr})_2$ (Ln = Y, Yb) on the polymerization activity has also been investigated. The results are shown in Table 2 and 3. Both yttrium and ytterbium exhibit excellent activity for the MMA polymerization. It can be seen from Table 2 and 3 that the molecular weight, polydispersity and isotacticity of the polymers change with temperature. Polymers with high isotacticity (74%) and narrow polydispersity ($M_w/M_n = 1.18$) can be obtained by using $\text{Ind}_2\text{YbN}(i\text{-Pr})_2$ at -30 °C.

Table 2. Polymerization of MMA with $\text{Ind}_2\text{YN}(i\text{-Pr})_2$

Polymerization temperature (°C)	[MMA]/[Cat]	Conversion (%)	$M_n (\times 10^{-3})$	M_w/M_n	Tacticity (%)		
					<i>mm</i>	<i>mr</i>	<i>rr</i>
-30	500	87	17.2	1.32	57	24	19
0	500	94	14.2	1.49	51	31	18
25	500	92	13.6	1.52	50	34	16
50	500	92	13.1	1.71	49	36	15
0	300	96	11.4	1.58	—	—	—
0	1000	83	21.2	1.34	—	—	—

Polymerization condition: solvent = toluene; *t* = 24 h; solvent/[MMA] = 5 (vol/vol)

Table 3. Polymerization of MMA with $\text{Ind}_2\text{YbN}(\text{i-Pr})_2$

Polymerization temperature (°C)	[MMA]/[Cat]	Conversion (%)	$M_n \times (10^{-3})$	M_w/M_n	Tacticity (%)		
					<i>mm</i>	<i>mr</i>	<i>rr</i>
-30	500	64	19.7	1.18	74	15	11
0	500	87	14.5	1.29	61	27	12
25	500	88	13.4	1.35	58	30	12
50	500	82	11.7	1.51	56	34	10
0	300	90	10.2	1.43	—	—	—
0	1000	83	18.9	1.21	—	—	—

Polymerization condition: solvent = toluene; $t = 24$ h; solvent/[MMA] = 5 (vol/vol)

CONCLUSIONS

It has been found that $\text{Ind}_2\text{Y}(\mu\text{-Et})_2\text{AlEt}_2$, $\text{Ind}_2\text{LnN}(\text{i-Pr})_2$ ($\text{Ln} = \text{Y}, \text{Yb}$) complexes are able to act as new kinds of highly effective initiators for polymerization of MMA over quite a broad range of temperatures from -30 to 50 °C. The influence of the temperature on polymerization activity of PMMA has been investigated.

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