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Half-sandwich samarium (III) diketiminate bromide as a catalyst for methyl methacrylate polymerization

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Abstract

Half-sandwich samarium(III) diketiminate bromide was successfully synthesized and was shown to be active in methyl methacrylate (MMA) polymerization. The effects of temperature, polymerization time and catalyst concentration were studied. Activities of ca. 18 kg of polymethacrylate (PMMA) per mol of samarium per hour were obtained under optimum conditions (0 °C and a MMA/catalyst molar ratio of 100/1), giving a polymer with a molar mass $M_n > 24{,}000$ g mol^{-1} and a molar mass distribution (M_w/M_n) < 1.4. After 1 h of polymerization, conversions of MMA as high as 96% were observed.

Keywords: Methyl methacrylate polymerization; Samarium(III) complex; Diketimino ligand

1. Introduction

Due to their commercial relevance, the preparation of polyolefins has attracted considerable industrial and academic interest. This involves the development of catalysts that present high catalytic activity and new polymerization methodologies that allow a precise control of the molar mass, molar mass distribution, stereoregularity and other aspects of the polymer architecture [1,2].

The basis of metal-mediated polymerization of methacrylates was laid at the beginning of the 1990s by Yasuda et al. [3,4], who carried out the polymerization of methyl methacrylate (MMA) with organolanthanide catalysts (Sm, Yb, etc.) containing two cyclopentadienyl ligands without any co-catalyst. The polymerization proceeds in a ‘living’ mode over a wide temperature range, giving polymers with good yields and narrow molar mass distributions. Moreover, the stereospecificity of the resultant poly(methyl methacrylate), PMMA, was highly syndiotactic. In a recent review, Hou and Wakatsuki [5] present progress on polymerization reactions with organolanthanide compounds, emphasizing complexes, which show high activity and selectivity.

A low lifetime of the catalyst is a typical problem of some organolanthanide systems; the steric and electronic properties of the ligand play, therefore, an essential role, modulating activity and selectivity of the catalyst and leading to systems with higher lifetimes. In this way, β-diketimines can be important auxiliary ligands, due to their tunable steric demands and their bulky structures [6]. Thus, we synthesized an organosamarium catalyst containing both cyclopentadienyl and diiminic ligands and studied its catalytic activity in methyl methacrylate polymerization. Yao et al. [7] synthesized a similar ytterbium complex, reducing it to the divalent form for the polymerization of methyl methacrylate. Detailed studies about the effects of the catalyst concentration, temperature and polymerization time were undertaken for a better comprehension of the catalyst behavior during the polymerization process.

2. Experimental

2.1. General considerations

The synthesis of the complex and the polymerization of methyl methacrylate (MMA, Aldrich) were carried out under a dry argon atmosphere, using standard Schlenk techniques. Tetrahydrofuran (THF, Tedia) and toluene (Merck) were

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freshly distilled from sodium benzophenone under argon prior to use. MMA was dried over anhydrous $CaCl_2$ for 2 days, over CaH_2 for another 2 days, and then vacuum-distilled into an ice-cooled flask containing CaH_2. Anhydrous samarium tribromide was prepared from the oxide (INB) as described in the literature [8].

2.2. Synthesis of bis(2,6-diisopropylphenylimino)-2,4-pentanedione (DIPPh-H)

The diketimine ligand was synthesized in a similar way as described in Ref. [9]. Acetylacetone (4 g, 40 mmol, Vetec) and ethanol (30 mL, 95% QM) were placed into a 125 mL flask fitted with a condenser. Under stirring, concentrated HCl (3.3 mL, 40 mmol, QM) was slowly added and, finally, 2,6-diisopropylaniline (15.1 g, 85 mmol, Aldrich) was added. The mixture was refluxed for 24 h. The white solid formed was filtered, washed with cold ethanol and dried under vacuum. In an erlenmeyer flask, this solid was magnetically stirred in a mixture containing 100 mL of saturated aqueous $NaHCO_3$ and 150 mL of dichloromethane for 2 h. The aqueous phase was discarded. The organic phase was dried with anhydrous Na_2SO_4, filtered and the solvent was evaporated under vacuum. ^1H NMR (300 MHz, C_6D_6) ppm: 1.13; 1.15; 1.19; 1.20 (dd, 12H, CH_3CHCH_3), 1.65 (s, 6H, CH_3), 3.32(m, 2H, CH_3CHCH_3), 4.89 (s, 1H, C=C tautomeric), 7.14–7.21 (m, 6H, aromatic), 12.48 (s, 1H, NH). Elemental Analysis calculated: C, 83.2%; H, 10.1%; N, 6.7%, found: C, 83.3%; H, 9.7%; N, 6.8%. Yield: 87%.

The lithium salt (DIPPh–Li) was obtained, as described in Ref. [10], by the reaction of one equivalent of the neutral ligand and one equivalent of butyl lithium (1.6 mol/L in hexane, Aldrich) in a Schlenk tube using THF as solvent. The solution was stirred for 2 h at room temperature and used directly for the synthesis of the complex.

2.3. Synthesis of the samarium(III) complex

Under a dry argon atmosphere, a solution of DIPPh-Li (1.0 mmol) in THF was slowly added to a suspension of anhydrous $SmBr_3$ (0.4 g, 1.0 mmol) in about 5 mL of THF at room temperature. After the $SmBr_3$ had reacted completely, butyl lithium (3.0 mL, 2 mmol, 1.6 mol/L in hexane, Aldrich) was added to the mixture, which was stirred for 2 h. Cyclopentadienyl sodium (2 mL, 1.0 mmol, 2.0 mol/L in THF, Aldrich) was then slowly added. The mixture was stirred at room temperature for two more hours, until a white precipitate of bromides was obtained. The crude product was isolated by evaporation of the solvent and purified by dissolving several times in THF and in toluene until no more impurities precipitated during dissolution, these being separated by centrifugation. The product was obtained by removal of the solvent under vacuum. The complex obtained was CpSm(DIPPh)Br·2THF (**3**): lanthanide analysis (% Sm) expected: 17.56% found: 17.65%; bromide analysis (% Br) expected: 9.32% found: 9.46%.

2.4. Polymerization of methyl methacrylate

The polymerization was carried out in a 50 mL Schlenk tube under a dry argon atmosphere, using 0.08–0.48 mmol of the catalyst in 1.0 mL of toluene followed by the addition of 5 mL of toluene and 2.0 mL (2.0 g, 21 mmol) of methyl methacrylate. The Schlenk tube was introduced into a thermostated bath. Temperatures between −15 and 25 °C were evaluated as well as times from 30 to 120 min. The polymerization was interrupted by introducing 5 mL of a solution of 5% HCl in ethanol. The polymer was then precipitated by addition of petroleum ether (200 mL), filtered and dried under vacuum.

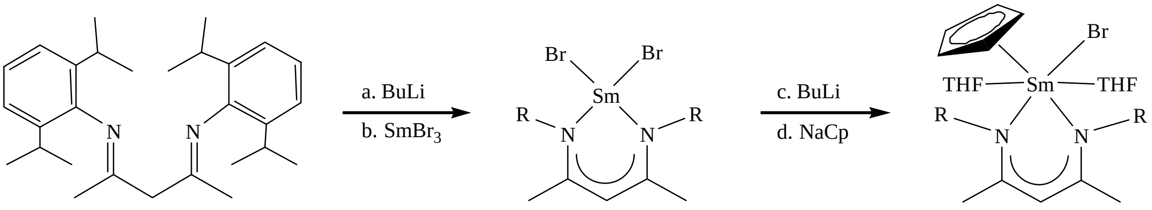
2.5. Characterization

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300P spectrometer at room temperature in $CDCl_3$. Molar mass distributions (M_w/M_n) were examined in a waters chromatograph 150-CV LC/GPC employing polystyrene as calibration standard. Elemental analyses were performed using a Perkin Elmer 2400C/H/N analyzer. The lanthanide analyses were performed using an axial atomic emission spectrometer Ciros^{CCD} from Spectro Co. The synthesis steps of the complex were monitored by UV/vis/NIR spectroscopy using a Perkin–Elmer Lambda-9 serie 1645 spectrometer with THF as solvent.

3. Results and discussion

3.1. Synthesis of the samarium(III) complex

The diketimine ligand synthesized as a pale-yellow solid was directly used in the synthesis of the samarium catalyst. All compounds used in the synthesis were soluble in THF or in toluene, but sensitive to air and moisture. The synthesis of the complex is shown in Eq. (1). A study using UV–vis spectroscopy was carried out during the synthesis in an attempt to examine the effect of ligand coordination at the metallic center. The spectra show that the neutral diketimine ligand **1** presents an absorption band at 390 nm, which after ionization is shifted to around 400 nm. By addition of the ionized diketimine ligand to the samarium bromide, complex **2** is formed, which has a maximum absorption at 391 nm. After addition of another equivalent of butyl lithium the absorption of the complex undergoes a strong batochromic shift to 456 nm. Addition of cyclopentadienyl sodium forms the final complex **3** which absorbs at 436 nm. This complex does not show any other absorptions, indicating that the ligands are coordinated to the metallic center. We have not yet been able to get suitable crystals of **3** for a single crystal X-ray structure, however, all analyses indicate that it is a hexacoordinated samarium complex with two associated THF, giving the formula CpSm(DIPPh)Br·2THF.



1 **2** **3** (1)

(R = 2,6-diisopropylphenyl)

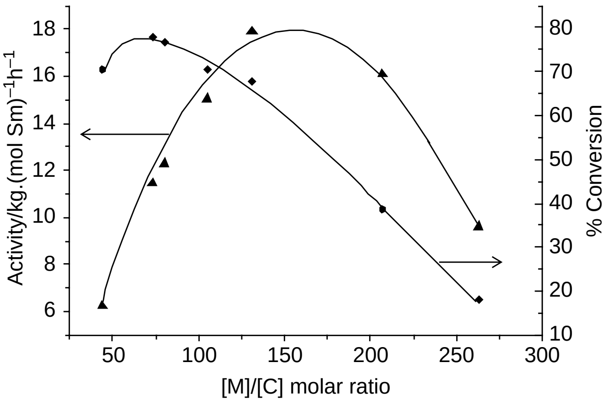


Fig. 1. Conversion (●) and activity (▲) as a function of the $[M]/[C]$ molar ratio (0 °C, 30 min).

3.2. Polymerization of methyl methacrylate

Polymerization results are presented in Fig. 1 and Table 1. With an increase of the monomer/catalyst molar ratio $[M]/[C]$ we observe that the activity first increases to a maximum of 17,900 g of polymer per mol of samarium per hour, obtained for a $[M]/[C]$ molar ratio of 131, and then decreases. The conversion reaches a maximum of 77.8% at a $[M]/[C]$ molar ratio of 73. The GPC curve is unimodal, indicating that no side-reactions occur under the reaction conditions studied. The molar mass of the polymer slightly increases with the $[M]/[C]$ molar ratio, reaching a maximum M_n of 25,200 g mol^{-1} for a $[M]/[C]$ molar ratio of 263. An inverse proportionality between molar mass and catalyst concentration was also observed by Yasuda et al. [4] who attributed this effect to the number of active sites present in the reaction mixture.

Table 1
Effect of the $[M/C]$ molar ratio on the polymerization of MMA

Entry	$[M]/[C]$[a]	Activity[b]	Conversion (%)	M_w[c]	M_n[c]	M_w/M_n	Tacticity		
							M_m%	mr%	rr%
1	44	6.2	70.6	24.0	19.5	1.23	43	49	8
2	73	11.4	77.8	28.1	21.5	1.31	46	52	2
3	80	12.3	76.6	32.5	23.8	1.36	46	54	0
4	105	15.0	70.4	34.2	24.9	1.38	59	41	0
5	131	17.9	67.6	32.1	23.6	1.36	58	42	0
6	207	16.1	38.6	32.9	24.0	1.37	65	29	6
7	263	9.6	18.0	34.2	25.2	1.36	67	33	0

Conditions: solvent: toluene (3 mL), 0 °C, 30 min.

[a] Monomer/catalyst molar ratio.

[b] kg (mol Sm)$^{-1}$ h^{-1}.

[c] Average molar mass in ($\times 10^{-3}$) g mol^{-1}.

Table 2
Temperature effects of the MMA polymerization

Temperature (°C)	Activity[a]	Conversion (%)	M_w[b]	M_n[b]	M_w/M_n	Tacticity		
						mm%	mr%	rr%
−15	5.9	28.2	46.5	31.0	1.50	61	33	6
0	12.7	60.8	32.4	23.7	1.37	63	37	0
10	8.0	38.2	24.4	18.8	1.30	63	32	5
25	6.9	32.8	17.8	14.7	1.21	60	33	7

Conditions: solvent: toluene (3 mL), 30 min, $[M]/[C]$ molar ratio = 104.

[a] kg (mol Sm)$^{-1}$ h^{-1}.

[b] Average molar mass in ($\times 10^{-3}$) g mol^{-1}.

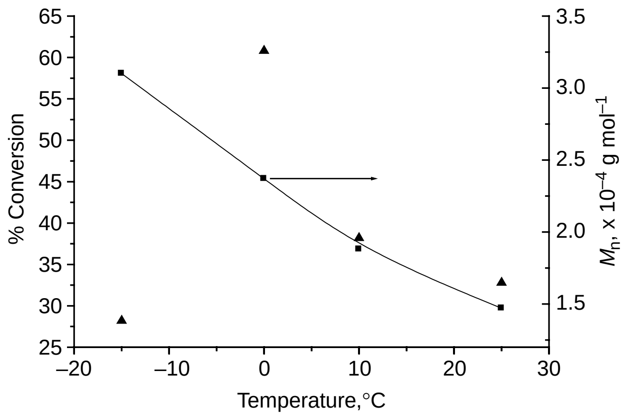


Fig. 2. Conversion (▲) and molar mass (■) as a function of temperature. ($[M]/[C]$ molar ratio of 104, 30 min).

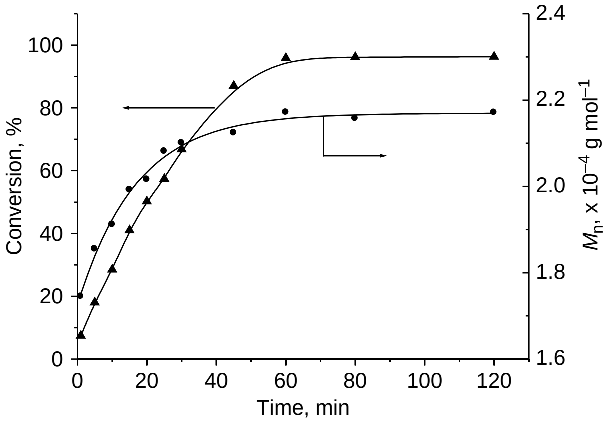


Fig. 3. Time-dependence of the MMA polymerization. ($[M]/[C]$ molar ratio of 104, 0 °C).

Under these reaction conditions not all samarium sites are active for polymerization. Considering a molar mass of 100 g mol^{-1} for the monomer and a $[M]/[C]$ molar ratio of 105, the expected M_n would be 10,500 g mol^{-1} if all samarium sites were active. However, the M_n found is 24,900 g mol^{-1}, showing that only 42% of the samarium sites are active. At lower $[M]/[C]$ molar ratios this percentage is even smaller.

The isotacticity of the polymer was low for $[M]/[C]$ molar ratios below 100, however, it reached values of 60% or more for $[M]/[C]$ molar ratios above 100. The tacticity and the molar mass of the polymer are strongly influenced by the amount of active sites. For higher $[M]/[C]$ molar ratios, coordination of the monomer at the active site is more rapid, thus reducing the possibility of an inversion of the active site and increasing the isotacticity of the polymer. Furthermore, a smaller number of active sites produces polymers with higher molar masses, showing the good stability of the active sites under the reaction conditions. Yao et al. [7], using a divalent DIPPh–ytterbium complex with a higher monomer/catalyst molar ratio, obtained polymers with a molar mass around 60,000 g mol^{-1}, however, with opposite tacticity (syndiotactic preference) and a wider molar mass distribution, M_w/M_n around 3.0, when compared to this study.

The effect of the polymerization temperature is shown in Table 2 and Fig. 2. Increasing the temperature, the catalytic activity gradually increases up to a maximum value at 0 °C and then decreases. The decrease in catalytic activity with higher temperatures is consistent with other lanthanide mediated MMA polymerizations [11]. Side reactions of the active sites are in constant competition with chain propagation, resulting in a loss of catalytic efficiency at higher temperatures. This behavior is intrinsically related to catalyst stability, since polymerization mechanisms of homogeneous Ziegler–Natta catalysts may involve cationic intermediates. Steric and electronic ligand effects that make cationic species more stable or unstable therefore affect the stability of the catalyst and lead to an increase or decrease of catalytic activity. Using temperatures around 0 °C the catalyst shows good stability giving conversions above 60% and producing a polymer with good molar mass and isotacticty. At -15 °C the catalyst activity is too low to give acceptable yields.

The time dependence of the MMA polymerization is shown in Fig. 3. The conversion increases during the first 60 min. After this time, chain termination processes predominate, leading to deactivation of the catalyst. The molar mass increases nearly linearly during the first 30 min, but then

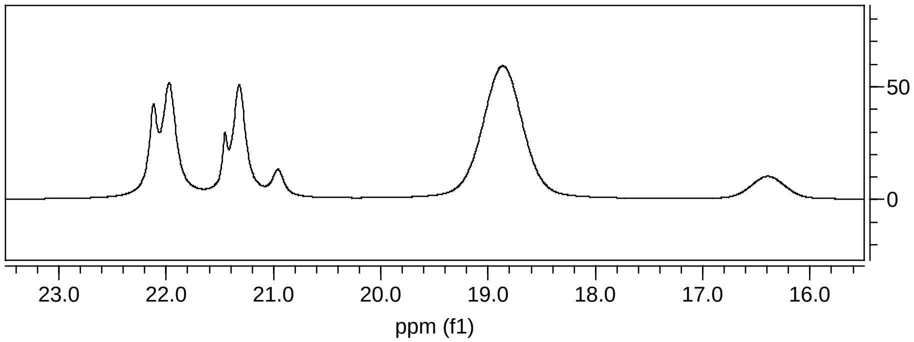


Fig. 4. ^{13}C NMR spectrum of the α-CH_3 region of a PMMA sample.

levels off, showing that after this time chain transfer processes occur. An excellent conversion of 96% was obtained after 60 min of polymerization, giving a polymer with a molar mass, M_n, of 21,700 g mol^{-1} and an isotacticity of 63%.

^{13}C NMR spectra were used to determine the tacticity of the PMMA. Fig. 4 shows a typical NMR spectrum, emphasizing the methyl region. As elucidated by Ferguson and Overnall [11], a distinct pattern occurs in the α-$^{13}CH_3$ region (15.5–23.3 ppm), which permits determination of the tacticity of the polymers The peak at 16.4 ppm corresponds to syndiotactic, the peak at 18.9 ppm corresponds to atactic and the group of well defined peaks between 20.9 and 22.4 ppm to isotactic PMMA. Integration of these peaks permits calculation of the tacticity of the polymers, which is certainly affected by the reaction conditions. Throughout the temperature range of −15–25 °C, similar tacticities are observed. This is strongly influenced by the $[M]/[C]$ molar ratio, giving an isotacticity of 67% for a $[M]/[C]$ molar ratio of 263 at 0 °C. This result clearly shows that the active sites are quite stable at high $[M]/[C]$ molar ratios, due to a fast coordination of the monomer to the samarium complex.

4. Conclusions

Half-sandwich samarium(III) diketiminate bromide **3** was successfully prepared and showed high activity for the polymerization of methyl methacrylate. The polymerization temperature and the $[M]/[C]$ molar ratio were found to be the main factors that influence catalyst efficiency. By careful choice of the optimum reaction conditions (0 °C, $[M]/[C]$ molar ratio of 100), a predominantly isotactic (mm of 63%) and moderately disperse ($M_w/M_n < 1.4$) polymer of good molar mass ($M_n > 25{,}000$ g mol^{-1}) was obtained.

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