PERGAMON

European Polymer Journal 35 (1999) 1037–1042

EUROPEAN
POLYMER
JOURNAL

Polymerization of styrene with calixarene–neodymium complex using alkylmagnesium as cocatalyst

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Received 10 March 1998; accepted 23 June 1998

Abstract

A new highly active coordination catalyst system, based on calixarene–neodymium complex using di-*n*-butyl magnesium as a cocatalyst and hexamethyl phosphoramide (HMPA) as an additive, for polymerization of styrene was developed for the first time. The catalytic activity of this new catalyst is $0.50–1.0 \times 10^3$ Kg PSt/mol Nd h with a molecular weight range of $6–12 \times 10^4$ in solution polymerization and 1.3×10^3 Kg PSt/mol Nd h with a molecular weight of 22×10^4 in bulk polymerization under the following conditions: $[Nd] = 2.0 \times 10^{-4}$ mol/l, Mg/Nd = 100, HMPA/Mg = 1, $T = 70°C$, time = 4 h. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Calixarene is a new class of macrocyclic compounds having the ability to form complexes with metal ions as well as with organic molecules so that it has attracted increasing interest [1–3]. Although a large number of calixarene–metal complexes have been prepared, few of them are applied to catalyze chemical reactions [4]. The study on their property of catalyzing polymerization is even less and up to now, there is only one example in which no modified calix[*n*]arene ($n = 4$, 6 and 8) titanium complexes, with MAO as cocatalyst, are used for the polymerization of ethylene and styrene [5].

The coordination polymerization of styrene is always an interesting subject because better materials such as syndiotactic polystyrene may be synthesized by this method. Although many catalyst systems for polymerization of styrene are based on transition metals, some examples using rare-earth as coordination catalysts are also given [6–8]. Recently, we have reported [8] that rare-earth phosphonate and di-*n*-butylmagnesium is a highly active catalyst system for polymerization of styrene in the presence of hexamethyl phosphoramide (HMPA). In order to further investigate this kind of catalyst system, calixarene is chosen as a ligand of rare-earth metals to form a new catalyst system for polymerization of styrene. As a preliminary result, we report for the first time that calix[4]arene–neodymium complex is a highly active coordination catalyst for polymerization of styrene using di-*n*-butyl magnesium as a cocatalyst in the presence of HMPA.

2. Experimental

2.1. Materials

Styrene(St) was chemical reagent grade and was purified by distilling under reduced pressure after dried over anhydrous calcium chloride for at least one day. HMPA was refluxed over calcium hydride and distilled through a Vigreux column in a vacuum. Other reagents and solvents were purified by conventional methods. Triethylaluminum was a commercial product from Roth Chemical Co. Anhydrous neodymium chloride was prepared by reflux hydration in thionyl chloride. A solution of di-*n*-butylmagnesium in toluene

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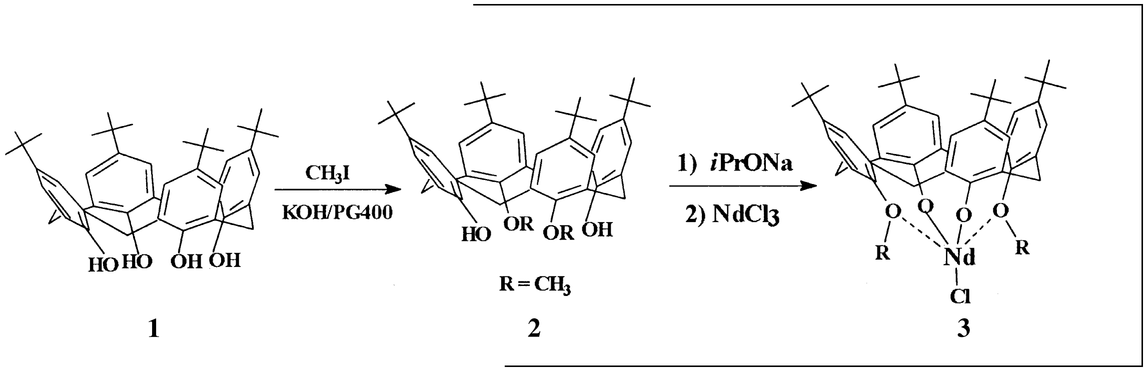
PII: S0014-3057(98)00184-0

was prepared by the method described in the literature [9] using triethylaluminum as a solvating agent. Magnesium and aluminum were analyzed by EDTA titration.

*2.1.1. Preparation of calixarene-neodymium complex, 5, 11, 17, 23-tetra-*tert*-butyl-25,27-chloroneodymiumdioxy-26,28-dimethoxycalix[4]arene* **3** *(see below)*

The reaction and procedure is as follows:



All the operations were carried out under dried nitrogen. *i*-Propanol (40 ml) and sodium (0.138 g, 6 mmol) were added to a solution of **2** (2.00 g, 2.96 mmol) in benzene (40 ml). The reaction mixture was refluxed until the sodium had completely disappeared and continued to reflux for another 0.5 h. After the solution was cooled to room temperature, anhydrous neodymium chloride (0.780 g, 3.10 mmol) was added under stirring and the mixture was refluxed for 2 h. Then the solvent was evaporated and the residual *i*-propanol was removed as thoroughly as possible in vacuum at about 100°C. The solid was dissolved in benzene (80 ml) and refluxed for 6 h. The reaction mixture was left overnight at room temperature. The cleared solution was separated and concentrated to about 5 ml to which *n*-hexane (50 ml) was added which yielded a blue precipitate [1.80 g, (73.2%)]. Microanalysis for $C_{46}H_{58}O_4ClNd$: calculated Nd, 16.88, actual Nd, 16.52 (neodymium was measured by EDTA titration).

2.1.2. Preparation of calixarene **1***, see literature [10]*

2.1.3. Preparation of calixarene **2**

To a solution of **1** (28.8 g, 44.4 mmol) in chloroform (350 ml) was added KOH (15.6 g, 276 mmol) in water (350 ml), polyglycol 400 (120 ml) and methyl iodide (75.6 g, 536 mmol). The mixture was stirred at room temperature until **1** disappeared (about 24 h; monitored by TLC, chloroform/petroleum ether 2/3). Upon acidification with hydrochloric acid, the organic phase was separated and the water layer was extracted once with chloroform. The combined organic phase was washed with water three times, dried over anhydrous sodium sulfate and evaporated to dryness. Methanol was added to the residue and the resultant precipitate was collected by filtration. After recrystallization from chloroform–methanol, white crystals (23.6 g) were obtained; yield 79.4%. ^{1}H–NMR spectra and m.p. is in accord with that prepared by other method [11].

2.2. Polymerization procedure

All the operations were carried out under dried nitrogen. Polymerization was carried out in a bottle which was heated under a vacuum of about 5 mmHg and then purged with nitrogen at least three times before use. Alkylmagnesium (0.50 mmol) and HMPA (0.50 mmol) were added to **3** (43 mg, 0.05 mol) in a bottle dried as above and the obtained solution was diluted to 10 ml with toluene to get a catalyst solution with Mg/Nd = 10 and HMPA/Mg = 1.

A certain amount of catalyst solution was introduced into a dried bottle and the additional alkylmagnesium and HMPA were added to the solution according to the required Mg/Nd and HMPA/Mg molar ratio. Then toluene and styrene were added and the polymerization was carried out at a certain temperature. The polystyrene was precipitated with ethanol containing 10% volume of hydrochloric acid, separated by decantation, washed with water, soaked in ethanol for more than 6 h, and finally dried in vacuum at 50°C.

2.3. Measurements

^{13}C–NMR spectra were measured on a JEOL-JNM FX-90 spectrometer in $CDCl_3$. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer. The intrinsic viscosity of the polymer was measured by an Ubblohde-type viscometer at 30°C in benzene. The viscosity–average molecular weight (*Mv*) was calculated according to the following equation [12]:

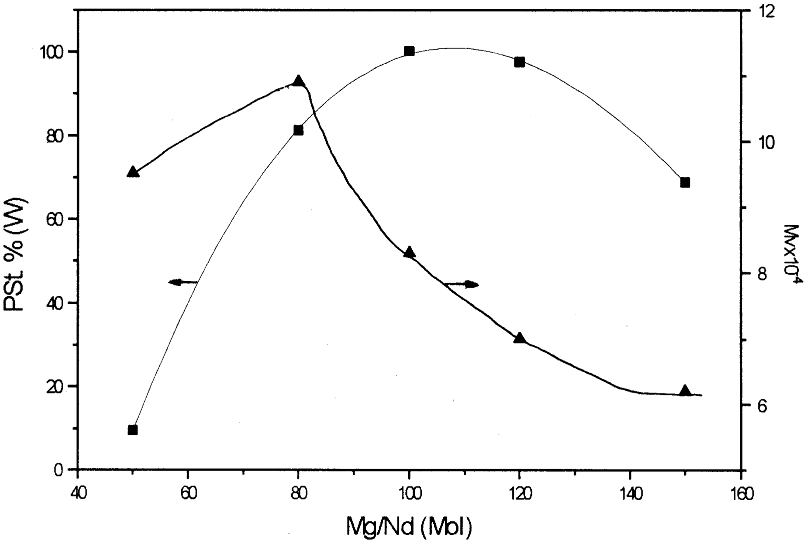


Fig. 1. Effect of Mg/Nd ratio on styrene polymerization. Conditions: [Nd] = 2.0 × 10^{-4} mol/l, HMPA/Mg = 1, T = 70°C, time = 4 h, [St] = 4.28 mol/l.

$$[\eta](\mathrm{dl/g}) = 0.75 \times 10^{-4} Mv^{0.783}.$$

GPC was measured on a Waters GPC-208 instrument at 30°C using THF as eluent.

3. Results and discussion

As shown in Fig. 1, the polymerization of styrene is greatly influenced by the Mg/Nd molar ratio. The conversion increases with increasing Mg/Nd molar ratio from 50 to 100 and then decreases from 100 to 150. At a Mg/Nd molar ratio of 100, the conversion reaches the maximum. The change of molecular weight is basically similar to that of conversion as the Mg/Nd ratio increases, but the highest molecular weight is at a Mg/Nd molar ratio of 80.

Fig. 2 illustrates the effect of catalyst concentration on the polymerization of styrene. The optimum conversion is at [Nd] = 2.0 × 10^{-4} mol/l at which the catalytic activity of calixarene–neodymium complex **3** is 0.56 × 10^{3} kg PSt/mol Nd h with a molecular weight of 10 × 10^{4}. The molecular weight increases with increasing catalyst concentration within the range of

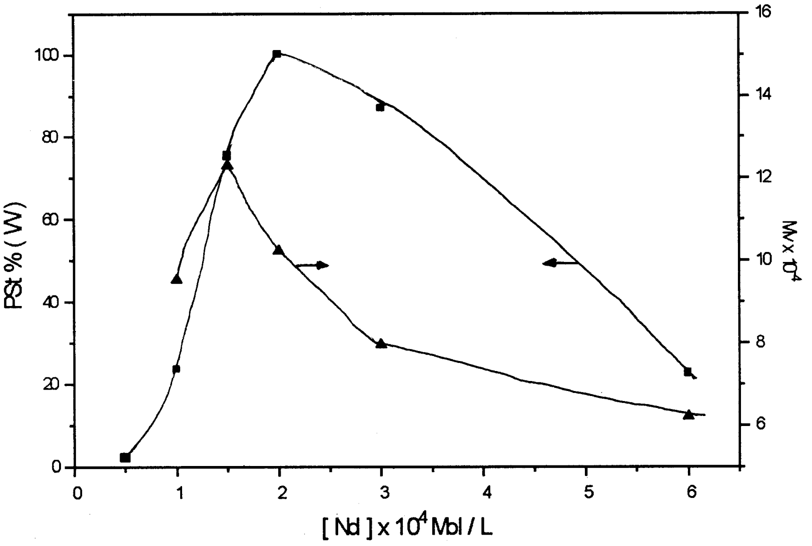


Fig. 2. Effect of catalyst concentration on polymerization. Conditions: Mg/Nd = 100, the other conditions are the same as in Fig. 1.

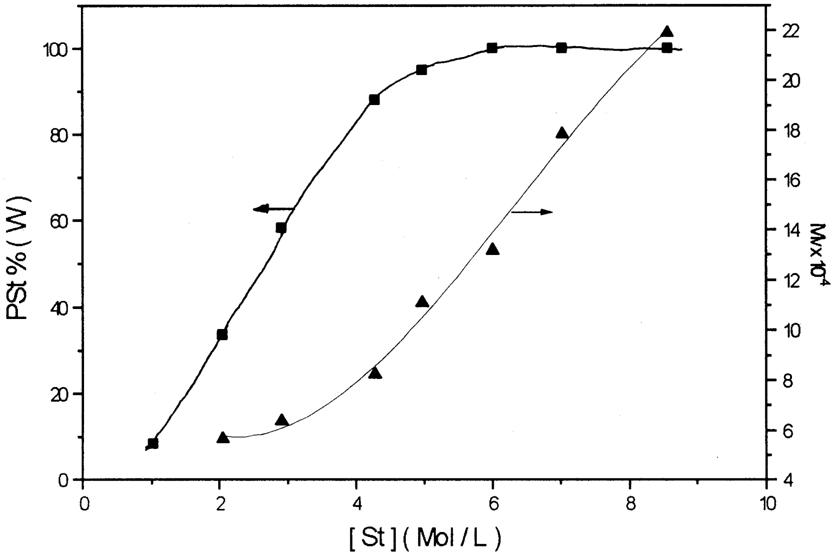


Fig. 3. Effect of styrene concentration on polymerization. Conditions: Mg/Nd = 100, time = 3.5 h, the other conditions are the same as in Fig. 1.

1–1.5 × 10^{-4} mol/l and then decreases within the range of 1.5–6 × 10^{-4} mol/l. When no calixarene–neodymium complex is added, only 9.43% of styrene is converted into polymer under the same conditions.

Increase of the styrene monomer concentration is always beneficial for increasing both the conversion and the molecular weight (see Fig. 3). When the polymerization is carried out in bulk, the catalytic activity is 1.3 × 10^3 Kg PSt/mol Nd h and the molecular weight is 22 × 10^4.

Effects of additives on polymerization are shown in Fig. 4 and Table 1. Although all the tested additives possess electron-donating atoms, only HMPA has a promotive role in polymerization. Especially for DMF and DMSO, which have a polarity and strong exothermic phenomenon when mixed with di-*n*-butylmagnesium, just like HMPA, no accelerative role is observed (see Table 1). It is probable that DMF and DMSO react, not simply complex, with dibutylmagnesium to produce new compounds which don't promote the polymerization. For HMPA, the promotive role reaches the maximum only at HMPA/Mg = 1. It is known [13] that the dissociation of dibutylmagnesium will increase a little when the dibutylmagnesium is dissolved in HMPA so that the added HMPA will make it easier for the butyl group to coordinate with neodymium which is favorable for polymerization. However, the HMPA which is more than that required by HMPA/Mg = 1 will directly coordinate with neodymium and be harmful to polymerization.

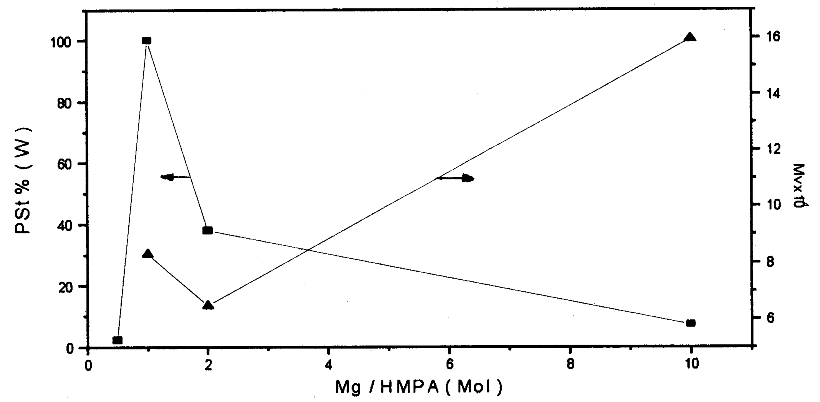


Fig. 4. Effect of HMPA/Mg molar ratio on polymerization. Conditions: Mg/Nd = 100, time = 24 h (4 h with Mg/HMPA = 1), the other conditions are the same as in Fig. 1.

Table 1
Effect of the additives on polymerization[a]

Additive	Additive/Mg	Time (h)	Conversion(W%)
DMF	1	4	Trace
DMSO	1	4	Trace
THF	1	4	2.80
TEA	1	4	Trace
HMPA	1	4	100

[a]Conditions: Mg/Nd = 100, the other conditions are the same as in Fig. 1.

The influence of reaction duration on polymerization is expressed in Fig. 5. It is found that the yield of polystyrene increases slowly with time over a period of less than 2 h, and then increases rapidly within 2.5–3.5 h and reaches 100% at 4 h. The polymerization has an acceleration effect in the second stage which was also observed previously [8]. One of reasons that the acceleration effect appeared is probably due to the heat of reaction which is not easily transfered after the reaction solution becomes viscous.

Since the added inhibitor 264 or $FeCl_3$ (both are 0.1% by weight of styrene), which is able to trap free radicals [6], doesn't inhibit or delay the polymerization and only 9.43% of the polymer is yielded in the case of no neodymium, the polymerization isn't induced by free radicals or anions. The probable mechanism of the polymerization is an anionic coordination to neodymium.

Reaction temperature has a great effect on polymerization. In Table 2, the polymerization rate increases but the molecular weight decreases when the temperature is raised from r.t. to 90°C.

Table 2
Effect of temperature on polymerization[a]

T (°C)	Time (h)	Conversion (w%)	$Mv \times 10^{-4}$
R.t.	48	69.8	22.1
50	13	99.9	12.5
70	4	100	8.30
90	3	100	5.99

[a]Conditions: Mg/Nd = 100, the other conditions are the same as in Fig. 1.

4. Characterization of polystyrene

The GPC trace of polystyrene prepared at Mg/Nd = 100 in Fig. 1 shows a single peak with $Mw/Mn = 2.51$. The ^{13}C–NMR and IR spectra are similar to that reported in Ref. [8].

5. Conclusions

The catalyst system, based on calixarene–neodymium complex using di-*n*-butyl magnesium as a cocatalyst and hexamethyl phosphoramide (HMPA) as an additive, is highly active for polymerization of styrene. The catalytic activity of this new catalyst is 0.50–1.0×10^3 Kg PSt/mol Nd h with a molecular weight range of 6–12×10^4 in solution polymerization and

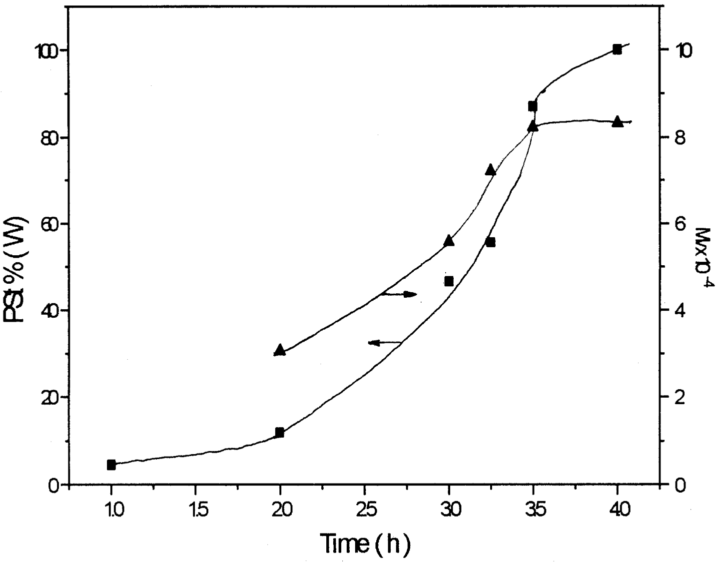


Fig. 5. Effect of time on polymerization. Conditions: Mg/Nd = 100, the other conditions are the same as in Fig. 1.

1.3×10^3 Kg PSt/mol Nd h with molecular weight of 22×10^4 in bulk polymerization under the following conditions: $[\mathrm{Nd}] = 2.0 \times 10^{-4}$ mol/l, Mg/Nd = 100, HMPA/Mg = 1, $T = 70$°C, time = 4 h. The polymerization of styrene with catalyst **3** having other *R* groups instead of the methoxyl group is under investigation.

Acknowledgements

Dr Yan-Song Zheng greatly acknowledges the Postdoctoral Science Foundation of China for financial support.

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