Available online at www.sciencedirect.com

Journal of Molecular Catalysis A: Chemical 238 (2005) 207–214

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Binary cerium(IV) *tert*-butoxides-dialkylmagnesium systems: Radical versus coordinative polymerization of styrene

Yann Sarazin[a], Thomas Chenal[a], André Mortreux[a],
Hervé Vezin[b], Jean-François Carpentier[c,*]

[a] *Laboratoire de Catalyse de Lille, UMR 8010 CNRS-Université de Lille 1, ENSCL, BP 90108, 59652 Villeneuve d'Ascq Cedex, France*
[b] *Laboratoire de Chimie Organique Physique, UMR 8009 CNRS-Université de Lille 1, Villeneuve d'Ascq Cedex, France*
[c] *Laboratoire Organométalliques et Catalyse, UMR 6509 CNRS-Université de Rennes 1, 35042 Rennes Cedex, France*

Received 3 March 2005; received in revised form 9 May 2005; accepted 13 May 2005
Available online 1 July 2005

Abstract

Combinations of a dialkylmagnesium and a cerium *tert*-butoxide complex have been explored for styrene polymerization. Cerium(IV) precursors, equivalently $Ce(OtBu)_4(THF)_x$ (**1**) or $Ce_3(OtBu)_{10}O$ (**2**), when associated to 5 or more equivalents of *n*-butylethylmagnesium (BEM), oligomerize styrene in a controlled way with activities ranging from 10 to 1000 mol St mol Ce^{-1} h^{-1} at 25 and 105 °C, respectively. Effective chain transfer to BEM takes place in the course of polymerization, as evidenced by the decrease of the molecular weight of polystyrene with increasing amounts of BEM, eventually yielding Et and *n*-Bu end-capped oligostyrenes (identified by MALDI-TOF-MS) with $M_n = 650–7400\ g\ mol^{-1}$ and $M_w/M_n = 1.3–2.5$. ESR analyses established the formation of butyl and/or styryl radicals from these binary systems. The use of phenothiazine as a radical inhibitor did not inhibit completely the polymerization of styrene but significantly decreased the polymer yields. Therefore, the polymerization of styrene is proposed to arise from two different, concomitant pathways, which both enable effective transfer of growing polystyryl chains to dialkylmagnesium species: (i) radical polymerization initiated by free radicals generated from the redox-active metal precursors, as the major pathway, and (ii) coordination/insertion polymerization based on in situ produced Ce(III)- and/or Ce(IV)-alkyl species.

Keywords: Alkoxides; Cerium; ESR; Magnesium; Polymerization; Radical; Styrene

1. Introduction

We have thoroughly investigated over the past decade new versatile polymerization catalysts based on combinations of a lanthanide precursor and a dialkylmagnesium reagent [1,2]. Those binary systems enable the controlled polymerization of ethylene [1a–d, 1f, 2a–c], styrene [1e] and methyl methacrylate [2d], as well as the synthesis of original materials such as high molecular weight poly(ethylene-*b*-methyl methacrylate) [2b,c] and poly(butadiene-*b*-glycidyl methacrylate) [2e] diblock copolymers. Also, in situ alkylation of readily available, stable chlorolanthanidocene precursors by dialkylmagnesium reagents provides a useful method for the formation of long chain dialkylmagnesium derivatives, thanks to a rapid, reversible transfer of growing polymeryl chains from the lanthanide to magnesium center [1d]. For most of these systems and monomers, this reversible chain transfer proceeds solely via an anionic/coordinative transmetallation mechanism [1d]; however, in the specific case of styrene polymerization, an additional radical contribution, which implies the reversible homolytic cleavage of covalent Mg–C bonds, has been evidenced [1e].

More recently, because of the permanent search for new-generation polymerization catalysts, we have undertaken studies aimed at replacing chlorolanthanidocene precursors by simple homoleptic lanthanide alkoxides in those

---

[*] Corresponding author. Tel.: +33 223 235 950; fax: +33 223 236 939.
E-mail address: jean-francois.carpentier@univ-rennes1.fr (J.-F. Carpentier).

1381-1169/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2005.05.025

binary systems. Interesting results were observed with the well-defined trinuclear complex $Nd_3(\mu_3\text{-O}t\text{Bu})_2(\mu_2\text{-O}t\text{Bu})_3(\mu\text{-O}t\text{Bu})_4(THF)_2$ and the monomeric precursor $(2,6\text{-}t\text{Bu}_2\text{-}4\text{-MeC}_6H_2O)_3Nd(THF)$, which also enable reversible chain transfer to magnesium [2]. Possible intermediates including an alkyl-bis(aryloxide) neodymium species were intercepted from these precursors, supporting the common-sense hypothesis that alkyl-lanthanides are the active species in these anionic/coordinative polymerizations initiated by binary lanthanide–magnesium systems [2f]. We report here a study on styrene polymerization initiated by related cerium(IV) *tert*-butoxides/dialkylmagnesium combinations, which are potentially redox-active systems [3]. The results obtained in styrene polymerization, combined with an ESR study, suggest that radical species contribute significantly to styrene polymerization [3].

2. Results and discussion

Our previous work on lanthanide alkoxide polymerization catalyst precursors has highlighted the appropriateness of homoleptic *tert*-butoxide complexes [2]. Those alkoxides are generally highly soluble in organic solvents and readily prepared by salt elimination (metathesis) procedures from cheap sources. Evans and co-workers have synthesized and fully characterized a variety of cerium(IV) *tert*-butoxide complexes from cerium ammonium nitrate and sodium *tert*-butoxide [4]. Two of these complexes were selected for the present study, i.e. $Ce(\text{O}t\text{Bu})_4(THF)_x$ (**1**) and $Ce_3(\text{O}t\text{Bu})_{10}O$ (**2**). The mononuclear complex **1** turned out, however, to be quite unstable, rapidly decomposing under inert atmosphere at room temperature in solution and in the solid state (although more slowly) into the trinuclear oxo species **2**. Obtaining and maintaining of samples of **1** uncontaminated by **2** proved somewhat problematic.

2.1. Styrene polymerization

Styrene polymerization was investigated by combining **1** or **2** with *n*-butylethylmagnesium (BEM) in variable amounts [5]. Representative results are reported in Table 1. Controlled experiments showed that neither **1** and **2** nor BEM have activity for styrene polymerization when used alone in the temperature range 25–105 °C (only minor thermally self-initiated polymerization may take place at 105 °C; [1e]). This is in direct line with many previous reports, which have stated the inability of dialkylmagnesiums to initiate styrene polymerization [6]. On the other hand, the binary combinations allow smooth poly/oligomerization of bulk styrene at room temperature (entries 1–10, TOF = ca. 10 mol St mol Ce^{-1} h^{-1} over 24 h), and with better activity at 105 °C (entries 11–14, TOF = ca. 1000 mol St mol Ce^{-1} h^{-1} over 0.5 h). Though moderately active, the systems are productive over a long time period. Remarkably, the yields and molecular masses of polymers increase linearly with time (compare entries, 7/8 and 9/10), indicating a certain degree of control. At room temperature, where thermal

Table 1
Styrene polymerization promoted by cerium *tert*-butoxide/BEM combinations[a]

Entry	Complex	BEM/Ce	Temperature (°C)	Time (h)	PSt (%)	$M_{n,exp}$[b]	$M_{n,calc}$[c]	M_w/M_n[b]
1	**1**	0	25	24	1	366000	ns	2.8
2	**1**	2	25	24	4	15700	ns	3.2
3	**1**	5	25	24	23	7400	2400	2.5
4	**1**	10	25	24	27	1800	1400	1.32
5	**1**	20	25	24	27	1450	700	1.34
6	**2**	1	25	24	7	35200	3640	3.7
7	**2**	5	25	24	22	3200	2300	1.76
8	**2**	5	25	65	52	8530	5400	2.1
9	**2**	10	25	24	17	1400	900	1.66
10	**2**	10	25	60	42	2800	2200	1.94
11	**2**	2	105	0.5	2	38500	ns	3.3
12	**2**	5	105	0.5	50	2300	5200	1.97
13	**2**	10	105	0.5	51	850	2650	1.86
14	**2**	20	105	0.5	47	650	1200	1.56
15	**3**	10	25	24	11	1050	600	1.88
16	**3**	10	105	0.5	25	900	1150	1.98
17[d]	**2**	10	25	24	6[d]	800	300	3.0
18[d]	**2**	10	105	0.5	22[d]	950	1150	2.2
19[e]	**2**	10	105	0.5	10[e]	[f]	1050	[f]

[a] Reaction conditions: styrene 100 mmol (bulk); Ce 0.10 mmol.

[b] Determined by GPC using polystyrene standards.

[c] Calculated on the basis of transfer of **2** polymer chains per Mg center. ns refers to non-significant values, considering the poor yield and the resulting high uncertainty.

[d] Reactions conducted in the presence of 1 equiv. of phenothiazine per Ce.

[e] Reaction conducted in the presence of 10 equiv. of phenothiazine per Ce.

[f] Multimodal distribution.