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

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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.
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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 avail-

able, 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

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binary systems. Interesting results were observed with the well-defined trinuclear complex $Nd_3(\mu_3\text{-}OtBu)_2(\mu_2\text{-}OtBu)_3(\mu\text{-}OtBu)_4(THF)_2$ and the monomeric precursor $(2,6\text{-}tBu_2\text{-}4\text{-}MeC_6H_2O)_3Nd(THF)$, 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. $Ce(OtBu)_4(THF)_x$ (**1**) and $Ce_3(OtBu)_{10}O$ (**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.
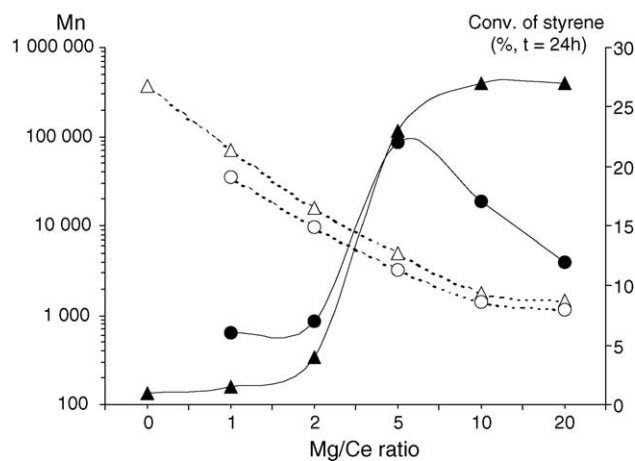[f] Multimodal distribution.

Fig. 1. Influence of the BEM/Ce ratio on the polymerization at 25 °C ($\triangle$ and $\blacktriangle$ refer to **1**; $\bigcirc$ and $\bullet$ refer to **2**; dashed lines and symbols refer to M_n values, solid lines and symbols refer to conversions).

initiation of styrene is negligible, complexes **1** and **2** lead to quite similar results in terms of activity and molecular masses, suggesting they are equivalent precursors of the same active species. With both systems, significant styrene conversions (>20%) were obtained only for BEM/Ce ratios ≥ 5. These results contrast with the results of our previous studies devoted to binary systems based on neodymocene [1] and neodymium alkoxides [2] precursors, for which high activities were observed for BEM/Nd ratios as low as one. In the present system, increasing the BEM/Ce ratio above a value of 5 did not increase the polymerization yield, but resulted in a monotonous decrease in the polymer molecular weight (Fig. 1). SEC analyses of the materials recovered under such conditions showed monomodal distributions of oligomers ($M_n = 650$–7400 g mol^{-1}) with relatively large

molar mass distribution ($M_w/M_n = 1.3$–2.5). Obviously, dialkylmagnesiums participate to a chain transfer reaction, as we previously observed with related binary polymerization systems [1,2]. To identify the terminus groups of the oligomers chains, the oligostyrenes were characterized by MALDI-TOF mass spectrometry [7]. As shown in Fig. 2, the two major sets of peaks correspond to oligostyrene chains cationized by Ag$^+$ with either an ethyl or a *n*-butyl end group derived from BEM and a H termination chain end from methanol during the work-up procedure using acidic methanol. Also, a lower intensity series of peaks was found to correspond to chains with H both as head group and end group [8]. These results are consistent with our previous observations in the case of styrene polymerization promoted by neodymocene/dialkylmagnesium systems [1e] and confirm that BEM acts as a transfer agent. The chain transfer efficiency factor with respect to the two alkylmagnesium groups, as evaluated from the experimental and calculated M_n values, ranges from 0.3 to 0.8 at room temperature [9]. However, as detailed below, two different polymerization/chain transfer mechanisms can be operative in this system.

2.2. Mechanistic investigations

It is well known that styrene can polymerize according different pathways, i.e. anionic, cationic, radical, and coordination/insertion routes. With the present systems, the two latter routes can be envisioned to account for the production of oligomers (Scheme 1). Both routes imply a preliminary transmetallation step between the cerium *tert*-butoxide precursor and dialkylmagnesium reagent to generate a Ce(IV)-alkyl intermediate (1), as we previously demonstrated for neodymium alkoxide precursors [2b,f]. At this stage, styrene may coordinate onto the Ce center and
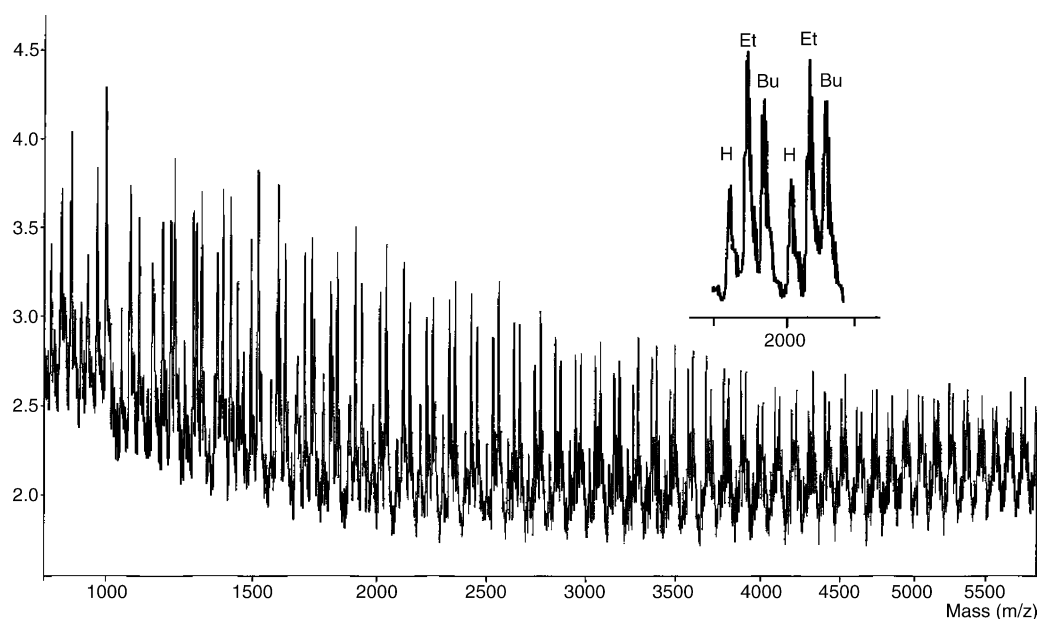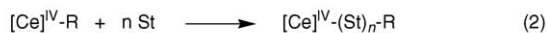

Fig. 2. MALDI-TOF mass spectrum (reflector mode) of oligostyrenes produced from the **2**–BEM system ($T = 105$ °C, Mg/Ce = 10).
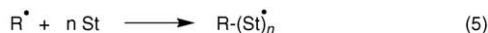
Preliminary transmetallation
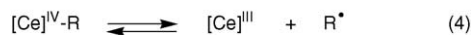
$$[Ce]^{IV}\text{-}OtBu + MgR_2 \longrightarrow [Ce]^{IV}\text{-}R + RMgOtBu \quad (1)$$

Coordination pathway

$$[Ce]^{IV}\text{-}R + n\,St \longrightarrow [Ce]^{IV}\text{-}(St)_n\text{-}R \quad (2)$$

$$[Ce]^{IV}\text{-}(St)_n\text{-}R + R'MgR \rightleftharpoons [Ce]^{IV}\text{-}R' + R\text{-}(St)_n\text{-}MgR \quad (3)$$

Radical pathway

$$[Ce]^{IV}\text{-}R \rightleftharpoons [Ce]^{III} + R^\bullet \quad (4)$$

$$R^\bullet + n\,St \longrightarrow R\text{-}(St)_n^\bullet \quad (5)$$

$$R\text{-}(St)_n^\bullet + R'MgR \rightleftharpoons R\text{-}(St)_n\text{-}MgR + R'^\bullet \quad (6)$$

Scheme 1. Possible polymerization mechanisms.

insert in the Ce–C bond, constituting the regular propagation step (2); in this mechanism, transfer would proceed via transmetallation between the growing polystyryl-cerium and dialkyl(oligostyryl)magnesium species (3) [1d].

A completely different polymerization mechanism can also be envisioned. Due to the versatility of the Ce(IV)/Ce(III) redox system, one can anticipate homolytic cleavage of the Ce(IV)–R bond to generate a Ce(III) species and a free alkyl radical (4), which should rapidly in turn initiate radical polymerization of styrene (5) (vide infra) [10]. Under such conditions, transfer would proceed via exchange of oligostyryl and alkyl radicals between cerium and magnesium species (6). Effective chain transfer between growing polystyryl radicals and organometallic compounds such as AlR$_3$, AlR$_2$H, InR$_3$, ZnR$_2$, or CdR$_2$, has been reported as early as in the 1960s [11]. We have evidenced similar chain transfer reactions in the presence of dialkylmagnesiumsms that most likely imply the reversible homolytic cleavage of Mg–C bonds [1e]. Note that, as outlined in Scheme 1, the exchange between dialkylmagnesium species and oligostyryl radicals is expected to release alkyl (Bu, Et) radicals, which should in turn initiate new oligostyryl chains. This is consistent with the aforementioned observation by MALDI-TOF-MS of Bu and Et end-groups in oligostyrenes.

It is noteworthy that in the latter hypothesis of a redox process (4), Ce(III) *tert*-butoxide species are co-produced. The latter can further undergo in situ transmetallation with excess dialkylmagnesium (similar to (1)), to generate Ce(III)-alkyl species that may also promote coordination/insertion polymerization of styrene (2).

To explore the relative contribution of these two fundamentally different routes, several experiments were conducted. First, it was observed that oligomerizations conducted with combinations of BEM and the trivalent precursor "Ce(O*t*Bu)$_3$" (**3**) [12] (BEM–**3** = 10:1) gave oligostyrenes with comparable molecular masses and polydispersities than from **1** or **2**; however, the polymerization yields were always much lower (about the half) (Table 1, entries 15 and 16). Because Ce(III)-alkyl species are stable [13], i.e. not prone
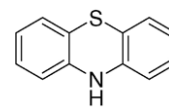

Fig. 3. Phenothiazine.

to homolytic cleavage and generation of free radicals, the oligomers produced under these conditions are assumed to arise solely from a coordination/insertion pathway. Thus, the latter route may account for at least part of the oligomers recovered from the systems based on **1** or **2** in association with BEM.

A possible, *indirect* way to evaluate the contribution of free radical pathways in transition-metal catalyzed processes consists in investigating the influence of radical inhibitors [14]. This approach is often complicated by the choice of a pertinent inhibitor; to be valid, the agent must inhibit selectively radical pathways without affecting other routes. This is obviously a difficult task with the present systems that contain highly reactive dialkylmagnesium and possibly alkyl-cerium species. We selected phenothiazine (Fig. 3) [15] for such investigations and some representative results are reported in Table 1 (entries 17–19). In the presence of 1 equiv. of phenothiazine versus Ce the polymerization was not inhibited but the polymer yields were ca. 50% decreased, both at room temperature and 105 °C (compare entries 9/17 and 13/18). At high temperature, with a larger amount of phenothiazine [16], the polymerization was even more affected and led to the formation of a mixture of oligomers and polymers with a multimodal distribution and a very broad dispersity (entry 19). These results suggest that part of the oligomers recovered from the systems based on **1** or **2** in association with BEM may derive from radical polymerization initiated by radicals generated from the metal precursors.

2.3. ESR investigations

To support the aforementioned generation of free radicals from Ce(IV) *tert*-butoxide–BEM combinations and the possible contribution of radical pathways to the polymerization of styrene promoted by these binary systems, ESR analyses were undertaken. The ESR signal in the solid state of a reaction mixture immediately frozen (77 K) after addition of styrene to a 1:10 mixture of **2** and BEM is shown in Fig. 4. The typical strong axial ESR signal centered at a g value of 2.008 with an axial $g_\parallel$ value of 2.019 indicates the presence of (an) organic centered radical(s) [17]. Although no quantification was attempted, the good signal-to-noise ratio suggests the formation of radicals in significant amounts.

Such experiments evidence that free organic radicals are indeed generated from these binary systems; however, no information on the radical(s) structure can be derived at this stage. To get a better insight in the nature of the radical(s) formed, spin trapping experiments using DMPO (5,5′-dimethyl-pyrroline *N*-oxide) as spin trap agent were
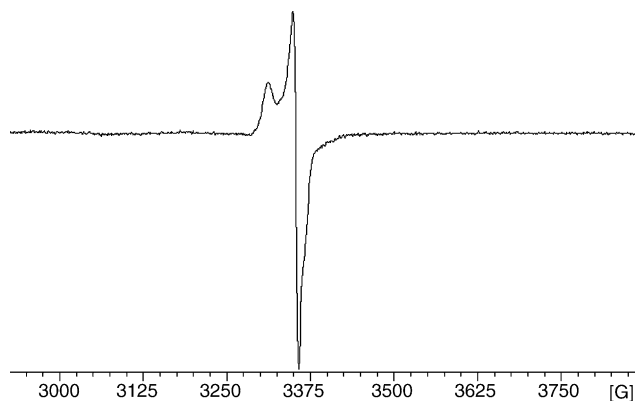
Fig. 4. ESR spectrum of a **2**–BEM–styrene (1:10:100) mixture recorded at 77 K. The microwave power, amplitude modulation and receiver gain were 10 mW, 1 G and 8×10^3, respectively.

Fig. 6. Room temperature ESR spectrum of DMPO-trapped radicals in the **2**–BEM (1:10) system. Microwave power, amplitude modulation and receiver gain were 10 mW, 0.8 G and 4×10^3, respectively. DMPO concentration = 32 mM.

performed [18,19]. The spectrum displayed in Fig. 5 shows the signals of the DMPO-trapped radicals formed during the polymerization of styrene initiated by the **2**–BEM (1:10) system. Three low-intensity lines with a hyperfine splitting constant $a_N = 14.3$ G are observed. As independently confirmed by an experiment using only **2** and DMPO (i.e. in the absence of BEM), this signal results from the direct reaction of DMPO with the Ce(IV) oxidant agent. More significantly, the ESR spectrum features six major lines with hyperfine splitting constants $a_N = 14.3$ G and $a_H = 20.75$ G. These values are consistent with Bu$^\bullet$ and/or Ph-CH(R)$^\bullet$ DMPO-trapped species [20,21]. Due to the close similarity of those two radicals, the hyperfine splitting constants are, however, not conclusive to attribute them unambiguously to either one or both of these species [19].

In fact, the ESR spectrum of DMPO-trapped species from the **2**–BEM (1:10) system in the absence of styrene (Fig. 6) features the same six-line signal with hyperfine splitting constants of $a_N = 14.3$ G and $a_H = 20.75$ G and three-line signal with an hyperfine splitting constant $a_N = 14.3$ G, as those observed in the presence of styrene (Fig. 4); as judged from the relative intensity of the ESR signals, the formation of
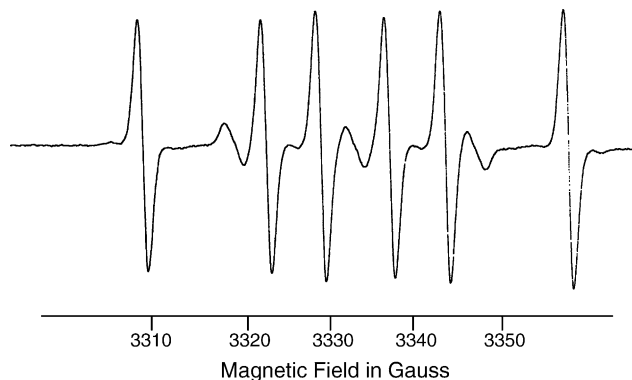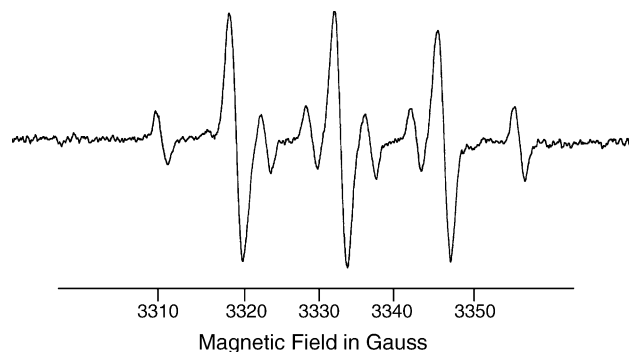
DMPO oxidized species is more important under these conditions. In this system where no styrene is present, the six-line signal can be only attributed to Bu$^\bullet$ species. Nonetheless, a very similar six-line signal with two hyperfine splitting constants of $a_N = 14.2$ G and $a_H = 20.65$ G is also measured from a styrene solution containing solely AIBN (azoisobutyronitrile) as initiating agent (Fig. 7); in these conditions, it is well known that (oligo)styryl radicals are generated.

2.4. Discussion

The formation of alkyl radicals from Ce(IV) *tert*-butoxide/dialkylmagnesium combinations can be accounted for by the elementary steps described in Scheme 1. In this reasonable hypothesis, alkyl-Ce(IV) species, first in situ produced from a transmetallation process (Eq. (1)), undergo homolytic cleavage of the Ce−C bond to liberate free alkyl radicals and Ce(III) species (Eq. (4)). An interesting question at this point is whether the latter homolytic cleavage step is reversible or not, i.e. do the systems described in this study

Fig. 5. Room temperature ESR spectrum of DMPO-trapped radicals in the **2**–BEM–styrene (1:10:100) system. Microwave power, amplitude modulation and receiver gain were 10 mW, 0.8 G and 4×10^3, respectively. DMPO concentration = 32 mM.
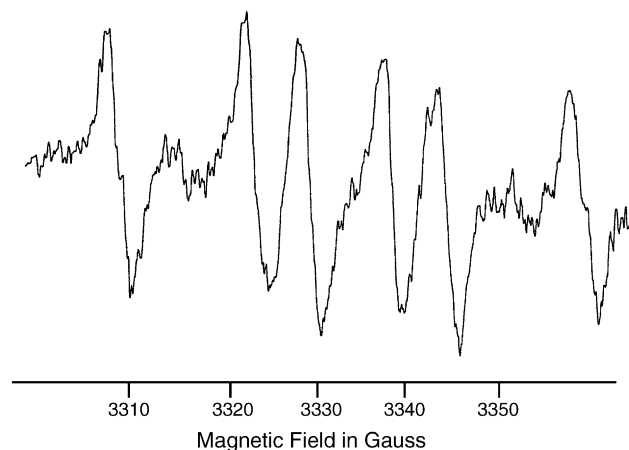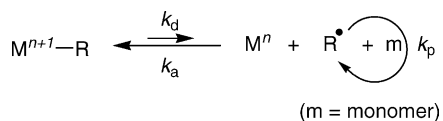

Fig. 7. Room temperature ESR spectrum of DMPO-trapped radicals in the AIBN–styrene (1:1000, w/w) system. Microwave power, amplitude modulation and receiver gain were 10 mW, 0.8 G and 4×10^3, respectively. DMPO concentration = 32 mM.

$$M^{n+1}-R \quad \underset{k_a}{\overset{k_d}{\rightleftharpoons}} \quad M^n \; + \; R^{\bullet} \; (+ \; m) \; k_p$$

$$(m = monomer)$$

Scheme 2.

belong or not to stable free radical polymerization (SFRP) systems. The concept of SFRP mediated by transition metals implies the fast reversible equilibrium between a dormant species (M–R) and the reactive radical ($R^{\bullet}$), via a thermal dissociation-combination mechanism (Scheme 2) [22]. Transition metal mediated SFRP is typically represented by Co [23], Mo [24], Fe [25], Te [26] and more recently Ti [27]. In these systems, bimolecular radical termination reactions are virtually suppressed and the polymerizations are well controlled "pseudo-living", resulting in narrow molecular weight distributions and number average molecular weights that linearly increase with conversion. The degree of control offered by the binary Ce–Mg combinations discussed in this study is clearly much lower than that achieved with the aforementioned transition-metal systems [23–27]. However, it must be noted that this may be the result of a concomitant contribution of a coordinative mechanism, a possibility which is unlikely with those other metal systems that are assumed to generate only radical active species. Detailed studies are therefore necessary to assess independently the reversibility of the dissociation step at the origin of the formation of radicals (Scheme 1, Eq. (4)).

3. Conclusions

We have shown that combinations of a Ce(IV) *tert*-butoxide and a dialkylmagnesium are effective systems for styrene polymerization. As such, the polymerization can be carried out at temperatures where thermal initiation of styrene is negligible. Although the activities are moderate, the polymerizations show a certain degree of control. The formation of organic free radicals from these binary systems at room temperature has been evidenced by ESR. This suggests that in situ produced alkyl-Ce(IV) species undergo homolytic bond cleavage to liberate free radicals, which in turn may initiate polymerization of styrene. Part of the polymers recovered in these polymerizations may therefore originate from a radical pathway. This hypothesis is supported by the decrease of the polymer yields when a radical inhibitor is introduced during polymerization. Since complete inhibition is not observed in this case, a regular coordination/insertion mechanism involving in situ generated Ce(III)- and/or Ce(IV)-alkyl species cannot be discarded as a parallel contribution to the polymerization of styrene.

An interesting feature in this study is the observation of effective transfer of growing polystyryl chains to magnesium. This chain transfer takes place under smooth conditions (room temperature), similar to those used for polymeriza-

tions mediated with combinations of a dialkylmagnesium and redox-inactive lanthanides (Y, La, Nd) [1,2]. Our results show that a single dialkylmagnesium reagent can act simultaneously as an effective transfer agent (in addition to its role of activator) towards two active polymerization species (viz. alkyl-metal and radical) that operate under completely different mechanisms.

4. Experimental

4.1. General

All operations were carried out under nitrogen or argon using Schlenk techniques or a high performance glove box. Solvents (toluene, THF) were freshly distilled from sodium–potassium amalgam under argon and degassed prior to use. *n*-Butylethylmagnesium (BEM, 20 wt.% in heptane, Texas alkyl) and *n,s*-dibutylmagnesium (1.0 M in heptane, Aldrich) were used as received. Styrene (99%, Aldrich) was distilled over CaH_2, stored at $-20\,^{\circ}C$ under argon, and degassed prior to use. Cerium(IV) *tert*-butoxides **1** and **2** were synthesized according to the reported procedure [4]. The trivalent precursor $Ce(OtBu)_3$ (**3**) was prepared by salt metathesis between $CeCl_3$ (99.9%, Strem) and 3 equiv. of sublimed NaOtBu in THF.

4.2. Styrene polymerization

In a typical procedure (Table 1, entry 8), a solution of complex **2** (0.039 g, 0.033 mmol) in toluene (2 mL) was transferred by cannula in a Schlenk flask containing BEM (0.275 g of a 20 wt.% solution in heptane, 0.50 mmol, 5 equiv. versus Ce). The reaction mixture was stirred for 15 min at room temperature, and freshly distilled styrene (11.5 mL, 100 mmol) was added. Magnetic stirring was maintained at the appropriate temperature ($25\,^{\circ}C$ or $105\,^{\circ}C$ with an oil bath) for a time period of 0.5–65 h, over which the color of the mixture changed from yellow to brown. The reaction was quenched by addition of 5% chlorhydric acid in methanol (50 mL), resulting in the precipitation of oligostyrenes and salts. Concentrated HCl (36 wt.%, 100 mL) was added to the mixture to dissolve magnesium salts and the organic phase was extracted with toluene ($3\times$ 100 mL). The organic phases were combined, dried over sodium sulfate, concentrated under vacuum and finally dried at $140\,^{\circ}C$ to leave oligostyrenes as white gummy solids.

4.3. SEC analysis

Molecular weights of oligomers/polymers were determined by gel permeation chromatography (SEC) at room temperature on a Waters apparatus equipped with two styragel columns, an autosampler Waters WISP 717, and a differential refractometer Shimadzu RID 6A. THF was used as eluent at a flow rate of $1.0\,mL\,min^{-1}$. Polystyrene

standards with a narrow distribution of molecular weight (M_w: 647–377,400) were used for molecular weight calibration.

4.4. MALDI-TOF-MS

MALDI-TOF-MS was performed on a Vision 2000 spectrometer (Finnigan MAT) equipped with a nitrogen laser operating at 337 nm and a viewing unit. The instrument was operated in either the reflector (5 kV acceleration) or linear (30 kV) mode. The spectra were recorded in the positive-ion mode. The samples were prepared by taking 2 µL of a THF solution of the polymer (10 mg PSt/mL) and adding this to 16 µL of 1,8-dihydroxy-9(10H)-anthracenone (dithranol, 10 mg/mL in THF) to which had been added 2 µL of CF_3SO_3Ag (2 mg/mL in THF). A 1-µL portion of this mixture was applied to the target and 50–100 single shot spectra were accumulated. The spectrometer was calibrated with an external mixture of angiotensin I, ACTH 18-39 and bovine insulin or PEG 1500.

4.5. ESR analysis

Electron spin resonance experiments were performed on a Varian E-109 (for spin trapping) and a Brüker ESP 300 (for low temperature) spectrometers operating at 9 GHz. The spectra were recorded at 100 kHz modulation field frequency, either at room temperature (294 K) or 77 K. Spin trapping experiments were performed using DMPO (5,5′-dimethyl-pyrroline N-oxide, 98%+, Sigma) freshly distilled prior to use. DMPO was added to the mixture to reach a final concentration of 32 mM. All samples for ESR analysis were prepared in the glove box.

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