

# Novel polymerization and copolymerization of ethylene, styrene, and/or butadiene by new organolanthanide-based catalysts\*

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*Abstract:* Replacement of one of the two C<sub>5</sub>Me<sub>5</sub> ligands in the samarocene(II) complex (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(THF)<sub>2</sub> with a monodentate anionic ligand (e.g., OAr, SAR, or NR<sup>1</sup>R<sup>2</sup>) gives a unique catalytic system, which can not only polymerize styrene and ethylene, but also copolymerize them into block styrene–ethylene copolymers under the presence of both monomers. On the other hand, addition of an appropriate cocatalyst such as MMAO or AlR<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] to the samarocene complex (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(THF)<sub>2</sub> or (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(μ-Me)<sub>2</sub>AlMe<sub>2</sub> affords a novel catalytic system for stereospecific 1,4-*cis* living polymerization of butadiene and copolymerization of butadiene with styrene.

## INTRODUCTION

In the past two decades, extensive studies on lanthanide complexes bearing two substituted or unsubstituted cyclopentadienyl ligands have been carried out, and a variety of such lanthanide metallocene complexes have been synthesized and structurally characterized [1–3]. Particularly, divalent samarium metallocene complexes of the type of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm(THF)<sub>n</sub> (n = 0–2) and trivalent lanthanide metallocene alkyl or hydride complexes of the type of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>LnR (R = H or alkyl) have received much interest as homogeneous catalysts or precatalysts for various useful transformations including polymerization/copolymerization of olefins and polar monomers [4]. Recently, there has been an impetus toward the search for new lanthanide systems to extend the lanthanide chemistry beyond the traditional realm of metallocene complexes. Among the most successful approaches are the use of the mixed C<sub>5</sub>Me<sub>5</sub>/ER ligands in place of the two C<sub>5</sub>Me<sub>5</sub> ligands (ER = a monodentate anionic ligand) [5–10] and the combination of a lanthanide metallocene complex with an appropriate cocatalyst [11]. This manuscript is intended to provide an overview of our progress in this area and to show how effectively the reactivity of a lanthanide complex can be modified by changing the steric and electronic environment around the metal center.

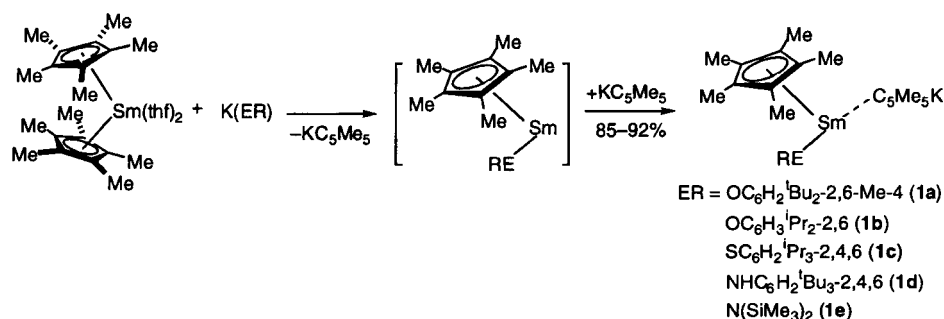
## POLYMERIZATION AND BLOCK-COPOLYMERIZATION OF ETHYLENE AND STYRENE BY C<sub>5</sub>Me<sub>5</sub>/ER-LIGATED Sm(II) COMPLEXES

Previous studies have shown that lanthanide metallocene-based catalytic systems are usually inactive for polymerization of styrene [12–14], although they are active for polymerization of ethylene and polar monomers. For example, the reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Sm with an excess of styrene in toluene yielded a stable bimetallic complex that was inert toward styrene owing to steric hindrance [12]. In an attempt to solve this problem, we have examined a series of samarium(II) complexes bearing mixed C<sub>5</sub>Me<sub>5</sub>/ER

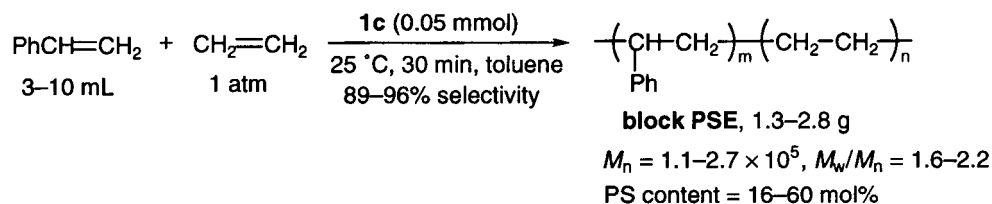
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ligands (ER = a monodentate anionic ligand). Generally, lanthanide(II) complexes with mixed ancillary ligands are difficult to isolate owing to easy ligand redistribution to give a mixture of the corresponding homoleptic complexes. We found that when “C<sub>5</sub>Me<sub>5</sub>K” was used as an additional stabilization ligand, the C<sub>5</sub>Me<sub>5</sub>/ER-ligated Sm(II) complexes could be easily isolated (Scheme 1) [15]. This type of complex showed high activity not only for the polymerization of ethylene but also for the polymerization of styrene [6,7], as a result of dissociation of the neutral “C<sub>5</sub>Me<sub>5</sub>K” ligand from the lanthanide metal center to yield a sterically unsaturated, C<sub>5</sub>Me<sub>5</sub>/ER-supported Sm(II) species. Moreover, since the ER ligand is less sterically demanding and less electron donating than the C<sub>5</sub>Me<sub>5</sub> ligand [16], the mixed C<sub>5</sub>Me<sub>5</sub>/ER ligand system provides a sterically and electronically unique environment for the central metal ion, which could distinguish styrene from ethylene in reactivity under their coexistence. Thus, in the presence of both monomers the copolymerization of styrene with ethylene by **1a–c** resulted in formation of *block* (rather than random) styrene–ethylene copolymers (**PSE**), a unique reaction which has never been reported for any other catalytic systems (Scheme 2) [7,17]. These reactions are not only of great fundamental interest, but could also be of practical usefulness as a convenient route to a new class of important polymer materials. In the present copolymerization reactions, homopolystyrene (**PS**) was also formed as a byproduct, while homopolyethylene was not observed. The selectivity for the copolymerization reaction was dependent on the ER ligands and the feeding amount of styrene monomer. Among these complexes, the thiolate complex **1c** showed the highest selectivity, which could reach up to as high as 96%. As the feeding amount of styrene monomer was raised under 1 atm of ethylene, the selectivity for styrene–ethylene copolymers generally decreased owing to increased formation of homopolystyrene. The polystyrene content in the copolymers, however, increased almost linearly as the feeding amount of styrene was raised [7,17].

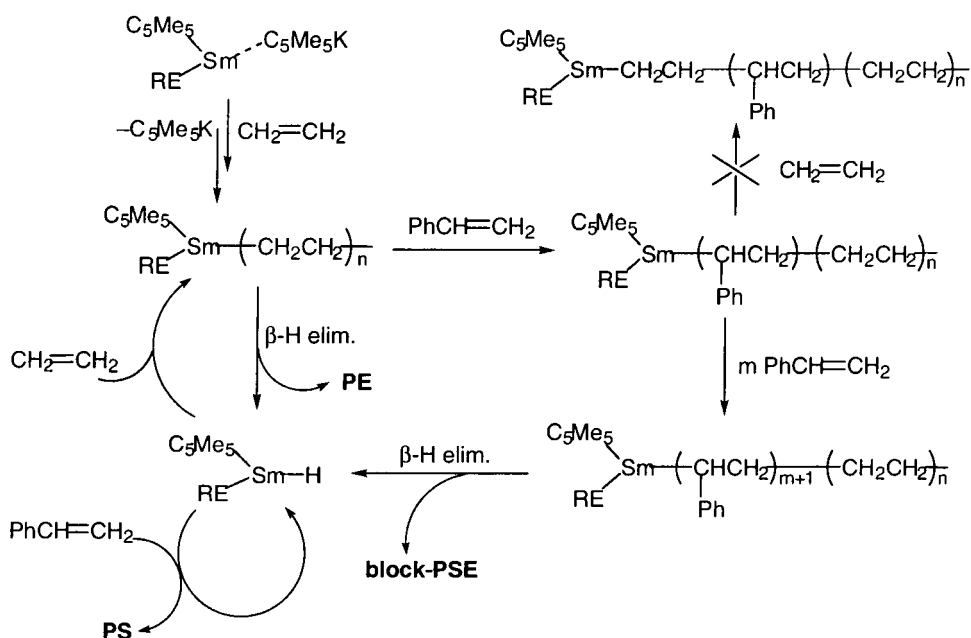


Scheme 1

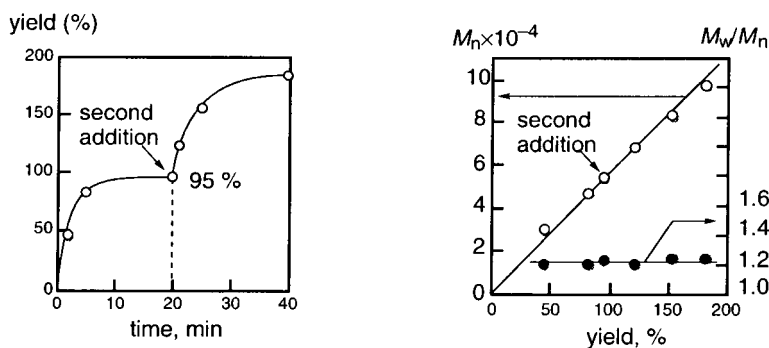
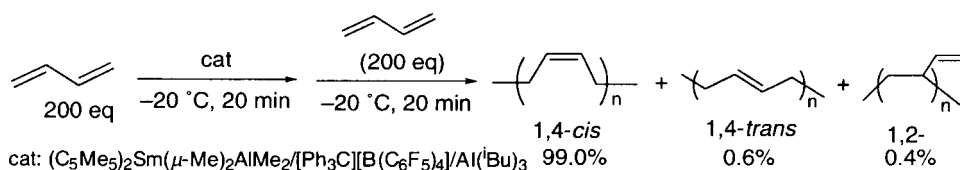


Scheme 2

Sequential polymerization reactions of styrene with ethylene showed that insertion of ethylene into the propagation site of a polystyrene unit did not occur, while incorporation of styrene into a polyethylene unit was possible [17]. These results suggest that the copolymerization reaction may begin with polymerization of ethylene followed by successive incorporation of styrene. The catalytic species in the present systems is thought to be a C<sub>5</sub>Me<sub>5</sub>/ER-supported Sm(III) hydride species generated through a β-H elimination process. A possible mechanism for the copolymerization of ethylene with styrene is shown in Scheme 3.



Scheme 3

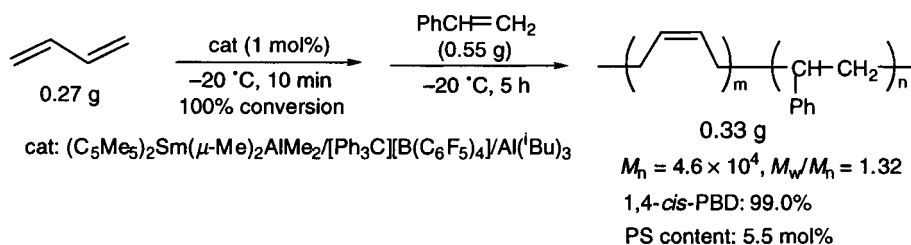


Scheme 4

### STEREOSPECIFIC 1,4-CIS LIVING POLYMERIZATION OF BUTADIENE AND COPOLYMERIZATION OF BUTADIENE WITH STYRENE BY SAMAROCENE-BASED CATALYSTS

It has been well known that the reactions of lanthanide metallocene complexes such as  $(C_5Me_5)_2Sm(THF)_2$  or  $[(C_5Me_5)_2Sm(\mu-H)]_2$  with an excess of butadiene yielded the corresponding  $\pi$ -allyl complexes which were not active for polymerization of butadiene [18]. We found that when the

samarocene(II) complex  $(C_5Me_5)_2Sm(THF)_2$  was treated with methylaluminoxane containing isobutylaluminoxane (MMAO) or  $Al(tBu)_3/[Ph_3C][B(C_6F_5)_4]$ , it showed extremely high activity for the polymerization of butadiene, yielding polybutadienes with very high 1,4-*cis* microstructures (up to 98.8%), high molecular weights ( $M_n = 10^5 \sim 10^6$ ), and narrow-molecular-weight distributions ( $M_w/M_n < 2$ ) [11]. Further studies have shown that an excellent “living” system for the stereospecific 1,4-*cis* polymerization of butadiene could be obtained by the combination of  $(C_5Me_5)_2Sm(\mu-Me)_2AlMe_2$  with  $Al(tBu)_3/[Ph_3C][B(C_6F_5)_4]$  (Scheme 4). This “living” system was also active toward styrene, which upon sequential reaction with butadiene and styrene, afforded block butadiene–styrene copolymers containing a polybutadiene unit with extremely high 1,4-*cis* microstructures (Scheme 5) [19]. When the copolymerization reactions were carried out in the presence of both butadiene and styrene, random butadiene–styrene copolymers with high 1,4-*cis* polybutadiene microstructures were obtained. Further studies are under progress to clarify the mechanistic aspects of these novel reactions.



Scheme 5

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