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One-Step Block-Copolymerization of Ethylene with Styrene by C_5Me_5/ER-Ligated Samarium(II) Complexes (ER = OAr, SAr)

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The block copolymerization of two different monomers is an important method for creating new polymer materials and for modifying the properties of their homopolymers.[1] The most common method to achieve such copolymerization reactions is sequential living polymerization of the two monomers in two feeding steps.[1,2] Although a few examples of one-step block-copolymerization reactions are known, they are all limited to specially designed sophisticated systems,[3] most of which involve a polar monomer.

On the other hand, in view of the extensive uses of both polyethylene and polystyrene and the poor compatibility of these two polymers, the block copolymerization of ethylene with styrene is of particular importance and interest.[1] However, most of the studies on the copolymerization of ethylene and styrene have been focused on the synthesis of random or alternating ethylene−styrene copolymers,[4−6] while the block copolymerization of ethylene with styrene has been very scarcely explored.[7] Previous attempts to obtain a block ethylene−styrene copolymer by sequential polymerization of styrene and ethylene with group 4 metal-based catalysts yielded the homopolymers as major products (ca. 65 wt %),[7] due to the lack of "living" character in these reactions. The commercially available block ethylene−styrene copolymers are actually block copolymers of polystyrene/hydrogenated polybutadiene, which are prepared by sequential anionic living polymerization of styrene and butadiene followed by hydrogenation of the polybutadiene block,[1c,d,8] and in many cases still contain some unsaturated polybutadiene units. In this communication, we report a novel one-step block-copolymerization reaction of ethylene with styrene, which is promoted by a new type of C_5Me_5/ER-ligated samarium(II) complex (ER = OAr, SAr). As far as we are aware, this is the first example of one-step block copolymerization of ethylene with styrene as well as the first example of block-copolymerization of two different simple olefin monomers under their coexistence.

The C_5Me_5/ER-ligated Sm(II) complexes **1**−**3** (ER = $OC_6H_3{}^iPr_2$-2,6 (**1**), $OC_6H_2{}^tBu_2$-2,6-Me-4 (**2**), $SC_6H_2{}^iPr_3$-2,4,6 (**3**)) were easily obtained as green crystals in 85−90% yields by reactions of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of KER in THF (Scheme 1).[9] X-ray analyses have shown that all these complexes can be viewed as a "$(C_5Me_5)Sm(ER)$" complex coordinated by a neutral "C_5Me_5K" ligand.[10,11] In the case of **1** and **3**, a THF ligand is also coordinated to the central Sm atom apparently due to the smaller steric hindrance of their ER ligands (Scheme 1).

To assess the potential of this new type of heteroleptic Sm(II) complex as a catalytic system, their reactivity toward ethylene and styrene was examined (Table 1). The copolymerization reactions (runs 3−8, Table 1) were carried out in the presence of 0.05 mmol of a Sm(II) complex under 1 atm of ethylene with varying amounts of styrene using rigorously anhydrous/anaerobic procedures. Although the green Sm(II) complexes **1**−**3** are only slightly soluble in toluene, a homogeneous yellow solution was rapidly obtained upon reaction with styrene or ethylene in toluene, suggesting that rapid one-electron transfer from the Sm(II) species to the monomer occurred. The polymerization was stopped by addition of MeOH. The crude polymer products were first washed with THF at room temperature to remove homopolystyrene and then extracted with toluene at 100−108 °C to collect the copolymers. Since the homopolystyrene formed in the present reactions is atactic and very soluble in THF at room temperature while the homopolyethylene is insoluble in refluxing toluene (110 °C), the ethylene−styrene copolymers, which are soluble in hot toluene, can be easily separated from the homopolymers by the above extractions. Repeated extractions of the copolymers with THF did not cause any weight loss. The polymer products were characterized by NMR, GPC, and DSC.

As shown in Table 1, complex **1** is active for polymerization of both ethylene (run 1, Table 1) and styrene (run 2, Table 1). When the reaction was carried out in the presence of 3 mL of styrene under 1 atm of ethylene, an ethylene−styrene copolymer with a polystyrene content of 34 mol % was obtained together with a small amount of homopolystyrene (run 3, Table 1). When the feeding amount of styrene monomer was increased from 3 to 10 mL, the polystyrene content in the copolymers increased from 34 to 81 mol % (runs 3−6, Table 1), showing that the polystyrene content in the copolymers can be easily adjusted by changing the feeding amount of styrene monomer. The GPC curves of the copolymers all show a unimodal and narrow molecular-weight distribution ($M_w/M_n = 1.84−1.97$) with molecular weights (M_n) ranging from 1.31×10^5 to 1.59×10^5 (runs 3−6, Table 1). ^{13}C NMR analyses have revealed that these copolymers are block ethylene−styrene copolymers, in which the polystyrene unit possesses an atactic structure similar to that of the homopolystyrene obtained from the THF extracts.[12,13] Under similar conditions, complexes **2** and **3** also gave the corresponding block ethylene−styrene copolymers (runs 7 and 8, Table 1), although the activity of **2**, which bears the bulkier $OC_6H_2{}^tBu_2$-2,6-Me-4 ligand, is slightly lower than those of **1** and **3** (cf. runs 4, 7, and 8, Table 1).

To further confirm that the copolymer products do not contain homopolymers, an artificial mixture of homopolyethylene ($M_n = 5.7 \times 10^4$, $M_w/M_n = 1.11$), homopolystyrene ($M_n = 24.5 \times 10^4$, $M_w/M_n = 1.93$, obtained in run 2, Table 1), and a copolymer ($M_n = 15.1 \times 10^4$, $M_w/M_n = 1.92$, PS content = 68 mol %, obtained in run 5, Table 1) was extracted in the same way as the crude product was done (vide supra). Each of these three polymers was thus recovered quantitatively, which suggests that this copolymer does not contain homopolystyrenes with $M_n \leq 24.5 \times 10^4$ or homopolyethylenes with $M_n \geq 5.7 \times 10^4$.[14,15] Since the GPC curve

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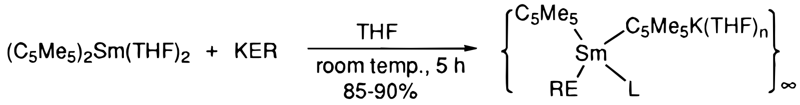
Scheme 1



1: $ER = OC_6H_3{}^iPr_2$-2,6, L = THF, n = 2

2: $ER = OC_6H_2{}^tBu_2$-2,6-Me-4, L = none, n = 2

3: $ER = SC_6H_2{}^iPr_3$-2,4,6, L = THF, n = 1

Table 1. Block Copolymerization of Ethylene and Styrene by Samarium(II) Complexes 1−3[a]

				yield/g						
run	cat.	amt of styrene/mL	rxn time/min	THF-sol (PS)[b]	tol-sol (<108 °C) (PES)[b]	tol-insol (108 °C) (PE)[b]	Ps cont/mol %[c]	M_n ($\times 10^{-4}$)[d]	M_w/M_n[d]	T_m/°C[e]
1	**1**	0	10			1.0		33.0	2.49	133.1
2	**1**	4[f]	30	3.64[g]				24.5	1.93	
3	**1**	3	30	0.46	2.14	trace	34	15.9	1.97	129.3
4	**1**	5	30	1.29	2.83	trace	48	14.6	1.82	120.0
5	**1**	7	30	1.37	2.94	trace	68	15.1	1.92	119.0
6	**1**	10	30	2.40	3.99	trace	81	13.1	1.84	115.1
7	**2**	5	30	0.10	1.60	trace	38	7.8	2.36	127.2
8	**3**	5	30	0.23	2.55	trace	37	10.7	2.01	n.d.[h]

[a] Conditions: a precatalyst, 0.05 mmol; ethylene, 1 atm; the total volume of styrene and toluene, 25 mL; room temperature, unless otherwise noted. [b] PS = polystyrene, PES = block ethylene−styrene copolymer, PE = polyethylene. [c] Polystyrene content in the copolymers determined by ^{13}C NMR in *o*-dichlorobenzene/$CDCl_2CDCl_2$ at 125 °C. [d] Determined at 135 °C against polystyrene standard by GPC. [e] Determined by DSC (second scan, 20−300 °C). [f] Reaction was carried out in the absence of ethylene. [g] Atactic polystyrene (100% conversion). [h] Not determined.

of the copolymer shows a unimodal narrow molecular-weight distribution ($M_w/M_n = 1.92$) and that of its mixture with the homopolystyrene ($M_n = 24.5 \times 10^4$) or the homopolyethylene ($M_n = 5.7 \times 10^4$) is bimodal, the content of homopolystyrenes with $M_n > 24.5 \times 10^4$ or homopolyethylenes with $M_n < 5.7 \times 10^4$ in this copolymer should also be negligible.[15] These results clearly demonstrate that the polymer products obtained from the toluene extracts are true block ethylene−styrene copolymers rather than mixtures of the homopolymers.

The selective formation of block ethylene−styrene copolymers in the present reactions are in sharp contrast with what was previously observed in group 4 metal-catalyzed reactions, in which random or alternating ethylene−styrene copolymers were always obtained under the coexistence of both monomers.[4,16] The present reactions are also in sharp contrast with those promoted by samarocene(II) complexes such as $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$, in which the maximum incorporation of styrene into polyethylene was only two molecules per chain due to the steric hindrance of the bulky bis(pentamethylcyclopentadienyl) ligand set $(C_5Me_5)_2$.[6a] None of $Sm(ER)_2$, C_5Me_5K, and KER were found to be active for the copolymerization of ethylene with styrene under the same conditions. These results strongly suggest that the heteroleptic "$(C_5Me_5)Sm(ER)$" unit in **1**−**3** plays a crucially important role in the present copolymerization reactions. It is well-known that the samarocene(II) complexes $(C_5Me_5)_2Sm(THF)_n$ (n = 0, 2) can reductively dimerize ethylene to produce the corresponding Sm(III) species $(C_5Me_5)_2Sm(CH_2CH_2)_2Sm(C_5Me_5)_2$, which is active for polymerization.[2c,6a] In the present systems, the similar Sm(III) species that are ligated by the heteroleptic C_5Me_5/ER ligands could be formed.[11,17] The more open ligand sphere provided by the the C_5Me_5/ER ligand set could explain why the present systems are more active than the corresponding metallocene complexes.

In summary, we have demonstrated that the C_5Me_5/ER-ligated Sm(II) complexes **1**−**3** can be used as excellent catalyst precursors for one-step block copolymerization of ethylene with styrene, which constitutes the first example of a catalytic system that efficiently produces block ethylene−styrene copolymers under the coexistence of both monomers. Further studies on the influences of the ancillary ligands and on the mechanistic aspects of the copolymerization reactions are under progress.[16]

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Supporting Information Available: A listing of atomic coordinates, thermal parameters, and bond distances and angles, solid structures for **1** and **3**, a typical procedure for copolymerization experiments, and the ^{13}C NMR spectra and GPC curves of representative polymer products (18 pages). Ordering and accessing information is given on any current masthead page.

References and Notes

(1) Block copolymers, which contain two or more long linear homopolymeric segments boned at terminal sites, generally have uniquely different chemical, physical, and mechanical properties compared to their random or alternating copolymeric analogues and particularly show a great emulsifying or compatibilizing effect in the blending of the corresponding homopolymers. For examples, see: (a) Bradford, E. B.; McKeever, L. D. In *Progress in Polymer Science*; Jenkins, A. D., Ed.; Pergamon Press: Oxford, U.K., 1971; Vol. 3, p 109. (b) Noshay, A.; McGrath, J. *Block Copolymers: Overview and Critical Survey*; Academic Press: Orlando, FL, 1977. (c) Fayt, R.; Jerome, R.; Tessie, P. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1269. (d) Cohen, R. E.; Cheng, P. L.; Kofinas, P.; Berney, C. V. *Macromolecules* **1990**, *23*, 324.

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Science; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 3, p 17. (c) Boffa, L. S.; Novak, B. M. *Tetrahedron* **1997**, *53*, 15367. (d) Yasuda, H.; Ihara, E. *Adv. Polym. Sci.* **1997**, *133*, 53. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1745.

(3) The previously reported one-step block-copolymerization reactions are all achieved by specially designed approaches, such as using a bifunctional initiator,[3a] adding an oxidant to change the polarity of the propagation center,[3b] or using two monomers that have very different polymerizabilities.[3c,d] (a) Mecerreyes, D.; Moineau, G.; Dubois, P.; Jerome, R.; Hedrick, J. L.; Hawker, C. J.; Malmstrom, E. E.; Trollsas, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1274. (b) Guo, H.-Q.; Kajiwara, A.; Morishima, Y.; Kamachi, M. *Macromolecules* **1996**, *29*, 2354. (c) Kuntz, I. *J. Polym. Sci.* **1961**, *54*, 569. (d) Azuma, N.; Sanda, F.; Tanaka, T.; Endo, T. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 1007 and references therein.

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(5) $Me_2Si(C_5Me_4)_2NdCH(SiMe_3)_2$ was reported to be capable of copolymerizing ethylene with styrene in the presence of $PhSiH_3$ to give a copolymer with $M_n = 3.3 \times 10^3$ and polystyrene content of 26 mol %. The structure of the copolymer was not described. See: Fu, P.-F.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 10747.

(6) In the case of samarocene complexes, the incorporation of styrene into a polymer unit seemed to be difficult. See: (a) Evans, W. J.; DeCoster, D. M.; Greaves, J. *Macromolecules* **1995**, *28*, 7929. (b) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219.

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(8) For examples, see: (a) Kishimoto, Y.; Morita, H. US. Pat. 4673414, 1984; *Chem. Abstr.* **1984**, 101, 211911q. (b) Teramoto, T.; Goshima, K.; Takeuchi, M. Eur. Pat. 339986, 1989; *Chem. Abstr.* **1990**, 112, 181159h. (c) Hattori, I.; Oshima, N. JP 02051503, 1990; *Chem. Abstr.* **1990**, 113, 79282b. (d) Hattori, I, Takashima, A.; Imamura, T. JP 02272004, 1990; *Chem. Abstr.* **1991**, 114, 144297x. (e) Molova, J.; Svoboda, P.; Reiss, J.; Miroslav, J. H. Czech Patent, CS 268208, 1990; *Chem. Abstr.* **1991**, 114, 172419g. (f) Chamberlain, L. R.; Gibler, C. J. US. Pat. 5039755, 1991; *Chem. Abstr.* **1991**, 115, 208933g.

(9) The synthesis and structure of **2** have been described previously. Complexes **1** and **3** were prepared in a similar way. See: Hou, Z.; Zhang, Y.; Yoshimura, T.; Wakatsuki, Y. *Organometallics* **1997**, *16*, 2963.

(10) Crystal data for **1**: $C_{44}H_{71}O_4KSm$, $F_w = 853.54$, monoclinic, space group $P2_1/n$ (No. 14), $a = 14.867(6)$ Å, $b = 18.269(2)$ Å, $c = 17.362(6)$ Å, $\beta = 103.190(7)°$, $V = 4591(2)$ Å^3, $Z = 4$, $D_c = 1.235$ g cm^{-3}, μ(Mo Kα) = 14.080 cm^{-1}, $R = 0.096$ ($R_w = 0.120$) for 4800 unique data with $I > 3\ \sigma(I)$ and 411 variables. Serious decay occurred during data collection. Anal. Calcd. for $C_{36}H_{55}O_2KSm$ (**1**-2THF): C, 60.96; H, 7.82. Found: C, 60.47; H, 7.94. **3**: $C_{43}H_{69}O_2SKSm$, $F_w = 839.59$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.139(6)$ Å, $b = 14.180(6)$ Å, $c = 17.465(5)$ Å, $\alpha = 105.79(3)$, $\beta = 93.83(3)$, $\gamma = 70.70(4)°$, $V = 2279(2)$ Å^3, $Z = 2$, $D_c = 1.224$ g cm^{-3}, μ(Mo Kα) = 14.643 cm^{-1}, $R = 0.0551$ ($R_w = 0.740$) for 7299 unique data with $I > 3\ \sigma(I)$ and 433 variables. Anal. Calcd. for $C_{39}H_{61}OSKSm$ (**3**-THF): C, 61.04; H, 8.01. Found: C, 60.83; H, 7.95.

(11) The "C_5Me_5K" ligand in the polymeric complexes **1**−**3** could be easily replaced by a strongly coordinative ligand such as HMPA (hexamethylphosphoric triamide) to give the corresponding HMPA-coordinated monomeric complexes $(C_5Me_5)Sm(ER)(HMPA)_2$. For an example, see ref 9.

(12) See Supporting Information for details.

(13) For NMR characterization of polystyrenes, see: K. Matsuzaki, T.; Uryu, T. Asakura. *NMR Spectroscopy and Stereoregularity of Polymers*; Japan Scientific Societies Press/S. Karger AG: Tokyo; 1996; pp 137−156.

(14) It has been found that the solubility of polyethylene decreases greatly as the molecular weight increases.

(15) Actually, atactic polystyrenes with $M_n > 24.5 \times 10^4$ are also soluble in THF at room temperature and therefore can be removed by the extraction with THF.

(16) The selective formation of block ethylene−styrene copolymers in the present systems strongly suggests that the reactivity of the propagation center of the polyethylene unit is critically different from that of the polystyrene unit, one being able to incorporate both ethylene and styrene, while the other being able to incorporate only the identical monomer. The nature of the metals and the ancillary ligands seems to be an important factor in determining the behavior of the propagation centers. In the present cases, we tentatively assume that the propagation center of the polystyrene unit has some extent of anionic character, which could not allow the insertion of ethylene monomer, and thus the copolymerization reaction might probably be initiated by polymerization of ethylene followed by incorporation of styrene. Further studies are under progress to confirm this hypothesis.

(17) Both the formation of a yellow solution at the beginning of the reactions and the narrow molecular weight distribution of the resulting polymers strongly suggested that the active species in the present polymerizations is a homogeneous Sm(III) species. For a C_5Me_5/OAr-supported Sm(III)−ketyl species, see: (a) Hou, Z.; Fujita, A.; Zhang, Y.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 754.

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