**Block Copolymerization**

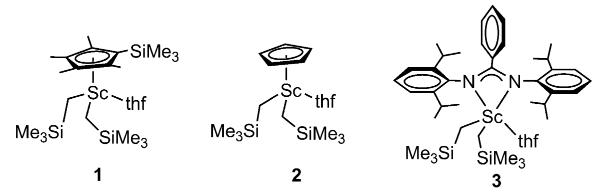
DOI: 10.1002/anie.201104011

# Chain-Shuttling Polymerization at Two Different Scandium Sites: Regio- and Stereospecific “One-Pot” Block Copolymerization of Styrene, Isoprene, and Butadiene**

*Li Pan, Kunyu Zhang, Masayoshi Nishiura, and Zhaomin Hou**

The development of new generations of polymerization catalysts and technology for efficient, selective synthesis of novel polymer materials having well-controlled microstructures and desired properties has been a long-standing research subject of both academic and industrial scientists. In this endeavor, exploring the potential of untapped elements is an important strategy. Recently, the chain-shuttling copolymerization of two different monomers by two Group 4 metal catalysts that show different monomer selectivities has emerged as a powerful technology for the preparation of olefin block copolymers with different segments.[1] In contrast, the potential of rare-earth catalysts in such chain-shuttling copolymerization has remained unexplored to date.[2,3] Moreover, the success of chain-shuttling copolymerization reported to date has been limited mostly to the copolymerization of ethylene and propylene (or 1-hexene), while the chain-shuttling copolymerization of styrene and a conjugated diene such as isoprene or butadiene has not been reported.

We report herein the first example of chain-shuttling copolymerization of styrene, isoprene, and butadiene by two different scandium catalysts. In the presence of scandium catalyst **1** (Scheme 1), which shows high activity and high selectivity for the syndiotactic polymerization of styrene but low activity and low selectivity for isoprene,[4a–c] and scandium catalyst **2**, which shows high activity and high *cis*-1,4-selectivity for the polymerization of isoprene[4c] but low activity and low selectivity for styrene, together with a chain-shuttling agent, the copolymerization of styrene and isoprene has been achieved regio- and stereoselectively at each monomer, affording for the first time block copolymers with perfect syndiotactic polystyrene (*s*PS) and highly regulated *cis*-1,4-polyisoprene (PIP) blocks. In a similar manner, the terpolymerization of styrene, isoprene, and butadiene has also been achieved for the first time to give terpolymers containing perfect *s*PS, highly regulated *cis*-1,4-PIP and highly regulated *cis*-1,4-PBD blocks. By replacement of the catalyst **2** with a catalyst **3**,[4d] which showed high 3,4-selectivity for the polymerization of isoprene in the chain-shuttling polymerization of styrene and isoprene, novel styrene–isoprene block copolymers with *s*PS and 3,4-PIP blocks have been obtained for the first time.



***Scheme 1.*** Scandium catalysts of different activities and selectivities. **1**: High activity and high syndiospecific selectivity for styrene polymerization but low activity and low selectivity for isoprene polymerization. **2**: High activity and high *cis*-1,4-selectivty for isoprene or butadiene polymerization but low activity and low selectivity for styrene polymerization. **3**: High activity and high 3,4-selectivity for isoprene polymerization but low activity for styrene polymerization.

Some representative results of the polymerization and copolymerization of styrene and isoprene by three different Sc catalysts **1**, **2**, and **3** (Scheme 1) under various conditions are summarized in Table 1. As reported, the half-sandwich scandium dialkyl complex **1** bearing the sterically demanding $C_5Me_4SiMe_3$ ligand in combination with $[Ph_3C][B(C_6F_5)_4]$ showed high activity and high syndiospecific selectivity ($rrrr >$ 99 %) for the polymerization of styrene (Table 1, run 1),[4a] but low activity and poor regio- and stereoselectivity for the polymerization of isoprene (Table 1, run 4).[4b,c] The smaller $C_5H_5$-bound Sc analogue **2** exhibited much lower activity and no stereoselectivity for the polymerization of styrene (Table 1, run 2) but showed high activity and high *cis*-1,4-selectivity (97 %) for the polymerization of isoprene (Table 1, run 5) under the same conditions.[4c] In the presence of both **1** and **2** without a chain-shuttling agent, the copolymerization of styrene and isoprene gave a polymer mixture of *cis*-1,4-PIP homopolymer and a styrene–isoprene copolymer containing mainly *s*PS blocks with mixed 1,4-/3,4-PIP units, as confirmed by solvent extraction (Table 1, run 7). In sharp contrast, when five equivalents (per Sc center) of $i\mathrm{Bu}_3\mathrm{Al}$ (TIBA) were added to the above reaction system, the copolymerization of styrene and isoprene took place selectively and rapidly to give the block copolymer containing perfect *s*PS ($rrrr > 99$ %) and highly regulated *cis*-1,4-PIP (97 % selectivity) blocks with high molecular weight ($M_n = 109.4\ \mathrm{kg\,mol^{-1}}$) and narrow molecular-weight distribution ($M_w/M_n = 1.43$, Table 1, run 8). When the amount of TIBA was increased from five equiv-

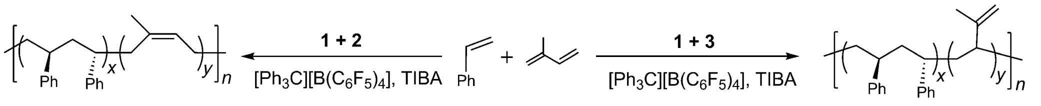
---

[*] L. Pan, Dr. K. Zhang, Dr. M. Nishiura, Prof. Dr. Z. Hou
Organometallic Chemistry Laboratory and
Advanced Catalyst Research Team
RIKEN Advanced Science Institute
2-1 Hirosawa, Wako, Saitama 351-0198 (Japan)
E-mail: houz@riken.jp

[**] This work was supported by a Grant-in-Aid for Scientific Research (S) (No. 21225004) from Japan Society for the Promotion of Science.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201104011.

***Table 1:*** Chain-shuttling copolymerization of styrene and isoprene by two different scandium catalysts.[a]



| Run | Cat. | St/IP[b] | TIBA/ [Sc][c] | $t$ [min] | Conv. [%] | $M_n$[d] [kg mol$^{-1}$] | $M_w/M_n$[d] | sPS [%] | PIP [%] | Microstructure of PIP[e] | | | $T_m$[f] [°C] | $T_g$[f] [°C] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | *cis*-1,4- | *trans*-1,4- | 3,4- | | |
| 1 | **1** | 500/0 | 0 | 1 | 100 | 154.5 | 1.24 | > 99 | – | – | – | – | 272 | 95 |
| 2 | **2** | 500/0 | 0 | 60 | 59 | 5.8 | 1.34 | –[g] | – | – | – | – | – | 90 |
| 3 | **3** | 500/0 | 0 | 60 | < 1 | – | – | – | – | – | – | – | – | – |
| 4 | **1** | 0/500 | 0 | 60 | 27 | 24.5 | 1.31 | – | 100 | 5 | 54 | 41 | – | −38 |
| 5 | **2** | 0/500 | 0 | 5 | 100 | 86.7 | 2.15 | – | 100 | 97 | 0 | 3 | – | −61 |
| 6 | **3** | 0/500 | 0 | 5 | 100 | 63.3 | 1.71 | – | 100 | 1 | < 1 | 98 | – | 40 |
| 7 | **1**+**2** | 250/250 | 0 | 20 | 35,[h] 92[i] | 39.8[j] | 1.40 | 92 | 8 | 4 | 50 | 46 | 261 | – |
| | | | | | | 82.4[k] | 1.90 | – | > 99 | 98 | 0 | 2 | – | −57 |
| 8 | **1**+**2** | 250/250 | 5 | 10 | 100 | 109.4 | 1.43 | 50 | 50 | 97 | 0 | 3 | 272 | −59 |
| 9 | **1**+**2** | 250/250 | 10 | 10 | 100 | 71.5 | 1.52 | 50 | 50 | 98 | 0 | 2 | 270 | −59 |
| 10 | **1**+**2** | 250/250 | 20 | 10 | 100 | 46.2 | 1.79 | 50 | 50 | 98 | 0 | 2 | 268 | −60 |
| 11 | **1**+**2** | 500/500 | 20 | 60 | 100 | 96.7 | 1.75 | 50 | 50 | 98 | 0 | 2 | 267 | −59 |
| 12 | **1**+**2** | 1000/1000 | 20 | 120 | 100 | 194.3 | 1.67 | 50 | 50 | 98 | 0 | 2 | 268 | −59 |
| 13 | **1**+**2** | 500/250 | 10 | 10 | 100 | 126.1 | 1.78 | 67 | 33 | 97 | 0 | 3 | 270 | −60 |
| 14 | **1**+**2** | 250/500 | 10 | 10 | 100 | 87.2 | 1.54 | 34 | 66 | 97 | 0 | 3 | 267 | −60 |
| 15 | **1**+**2** | 125/125 | 20 | 10 | 100 | 27.8 | 1.66 | 50 | 50 | 98 | 0 | 2 | 268 | −59 |
| 16 | | 2nd 125/125[l] | 20 | 30 | 100 | 40.7 | 1.78 | 50 | 50 | 98 | 0 | 2 | 268 | −59 |
| 17 | | 3rd 125/125[l] | 20 | 30 | 100 | 52.6 | 1.89 | 50 | 50 | 98 | 0 | 2 | 268 | −59 |
| 18 | | 4th 125/125[l] | 20 | 60 | 100 | 65.2 | 1.94 | 50 | 50 | 98 | 0 | 2 | 268 | −59 |
| 19 | **1**+**3** | 250/250 | 0 | 60 | 100 | 70.4[j] | 1.60 | 77 | 23 | 16 | 32 | 52 | 254 | 6 |
| | | | | | | 75.1[k] | 1.41 | 21[m] | 79 | 9 | 8 | 83 | – | 26 |
| 20 | **1**+**3** | 250/250 | 5 | 10 | 100 | 67.2 | 1.79 | 50 | 50 | 10 | 2 | 88 | 263 | 22 |
| 21 | **1**+**3** | 250/250 | 10 | 10 | 100 | 26.5 | 1.68 | 50 | 50 | 8 | 2 | 90 | 262 | 35 |

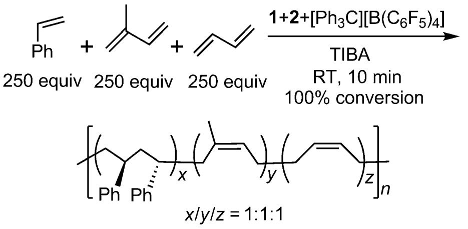
[a] Conditions: catalyst feed: [**1**] = [**2**] = [**3**] = 20 μmol, $[Ph_3C][B(C_6F_5)_4]/[Sc] = 1$, toluene $V = 40$ mL, 25 °C. [b] Molar ratio of monomer to total catalyst feed [Sc]. [c] Molar ratio of tri(isobutyl)aluminum (TIBA) to total catalyst used. [d] Determined by GPC against PS standards in *o*-dichlorobenzene at 140 °C or in THF at 40 °C. [e] Molar ratio determined by $^{13}C$ NMR spectroscopy in 1,1,2,2-tetrachloroethane. [f] Measured by differential scanning calorimetry. [g] Atactic polystyrene. [h] Conversion of styrene. [i] Conversion of isoprene. [j] THF-insoluble portion. [k] THF-soluble portion. [l] Sequential addition of 125 equiv styrene and 125 equiv of isoprene to run 15. [m] *a*PS.

alents to 10 and 20 equivalents, the molecular weight of the resulting copolymers decreased significantly, but the molecular-weight distribution remained rather narrow and the syndiospecific selectivity for styrene (> 99 %) and *cis*-1,4-selectivity for isoprene (98 %) remained constantly high (Table 1, runs 9 and 10). In the presence of 20 equivalents TIBA, the increase of the monomer/catalyst ratio resulted in an almost linear increase of the molecular weight of the copolymer products, while the molecular-weight distribution and the selectivity for either styrene or isoprene remained almost unchanged (Table 1, runs 10–12). The styrene/isoprene content in the resulting copolymers could be easily changed simply by changing the styrene/isoprene feed ratio (Table 1, runs 13 and 14). Sequential additions (four steps) of a 125/125 mixture of styrene and isoprene to the chain-shuttling copolymerization catalyst system afforded the copolymer products with increased molecular weights ($M_n$ from 27.8 to 65.2 kg mol$^{-1}$) and almost constant molecular-weight distributions ($M_w/M_n = 1.66$–1.94) as well as consistently high syndiospecific selectivity for styrene (> 99 %) and *cis*-1,4-selectivity for isoprene (98 %, Table 1, runs 15–18), suggesting that the chain-shuttling reactions in the present polymerization system are highly reversible and efficient. The resulting styrene–isoprene copolymers showed melting points around 270 °C originating from the *s*PS blocks[4a,b,5] and glass transition temperatures ($T_g$) at approximately −60 °C originating from the *cis*-1,4-PIP blocks[4d,6] (Table 1, runs 8–18).

To further confirm the composition of the copolymer products obtained in chain-shuttling copolymerization, solvent (THF) extraction of the crude polymer product obtained in Table 1, run 9 was carried out. The THF-soluble portion (32 wt %) showed a *s*PS content of 18 mol % and a *cis*-1,4-PIP content of 82 mol % with $M_n = 68.2$ kg mol$^{-1}$ and $M_w/M_n = 1.45$. The THF-insoluble portion (68 wt %) showed *s*PS content of 72 mol %, *cis*-1,4-PIP content of 28 mol %, $M_n = 74.2$ kg mol$^{-1}$, and $M_w/M_n = 1.61$. These results suggest that this crude polymer product contains predominantly *s*PS–*cis*-1,4-PIP block copolymers rather than a mixture of homopolymers.

The present chain-shuttling copolymerization of styrene and isoprene constitutes the first efficient protocol for the preparation of styrene–isoprene copolymers having perfect *s*PS and highly regulated *cis*-1,4-PIP blocks. *s*PS is a well-known semicrystalline polymer which possesses many useful properties, such as high modulus of elasticity and excellent resistance to heat and chemicals,[5] while *cis*-1,4-PIP is a major component of natural rubber and can serve as an excellent elastomer.[6] Although styrene–isoprene copolymers with both *s*PS and highly regulated *cis*-1,4-PIP blocks are of much interest, such highly stereoregulated copolymers are difficult to prepare and have not been reported to date.[4b]

The scandium amidinate complex **3**, similar to its known yttrium analogue,[4d] showed high activity for the 3,4-polymerization of isoprene (selectivity 98 %, Table 1, run 6) but very poor activity for the polymerization of styrene (Table 1, run 3). In the presence of **1** and **3** without a chain-shuttling agent, the copolymerization of styrene and isoprene afforded a crude copolymer product containing PS and PIP sequences. Solvent extraction experiments revealed that the THF-soluble portion (44 wt %) contained blocks rich in 3,4-PIP (79 mol %, 83 % 3,4-selectivity) and atactic PS units (21 mol %), while the THF-insoluble portion (56 wt %) possessed *s*PS blocks (77 mol %) and mixed 1,4-/3,4-PIP units (23 mol; Table 1, run 19). In contrast, in the presence of TIBA, the copolymerization of styrene and isoprene took place selectively and more rapidly to give the corresponding block copolymers containing perfect *s*PS (*rrrr* > 99 %) and 3,4-PIP (ca. 90 %) blocks (Table 1, runs 20 and 21). The resulting copolymers showed $T_g$ around room temperature (22–35 °C) originating from the 3,4-PIP blocks,[4d,7] in addition to melting points at approximately 263 °C originating from the *s*PS blocks (Table 1, runs 20 and 21). This is the first example of styrene–isoprene copolymerization with high syndiospecific selectivity for styrene and high 3,4-selectivity for isoprene.

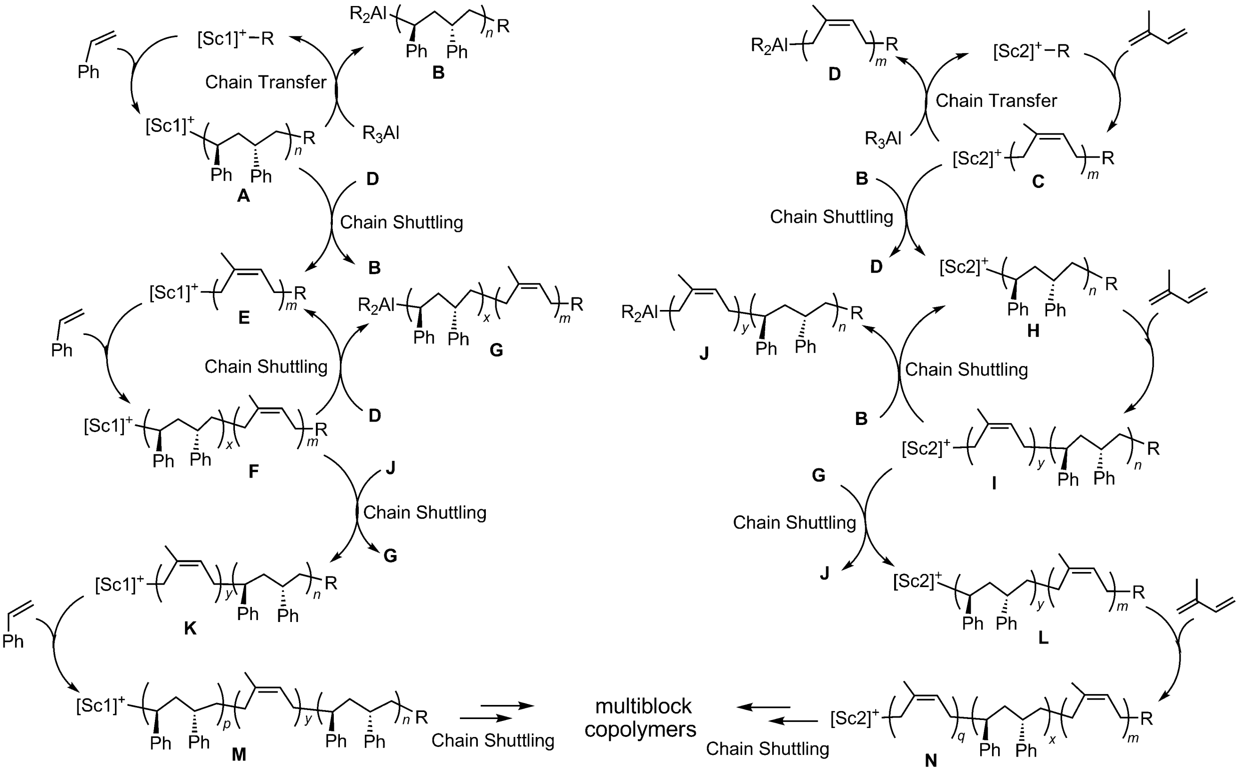


*s*PS > 99%, *cis*-1,4-PIP > 97 mol%, *cis*-1,4-PBD > 97 mol%
5 equiv TIBA: $M_w$ = 166.8 kg mol$^{-1}$, $M_w/M_n$ = 1.38, $T_m$ = 267 °C, $T_g$ = –77 °C
10 equiv TIBA: $M_w$ = 94.4 kg mol$^{-1}$, $M_w/M_n$ = 1.50, $T_m$ = 266 °C, $T_g$ = –76 °C

***Scheme 2.*** Scandium-catalyzed regio- and stereospecific terpolymerization of styrene, isoprene, and butadiene in the presence of a chain-shuttling agent (TIBA).

By use of the combination of **1** and **2** with TIBA as a chain-shuttling agent, the terpolymerization of styrene, isoprene, and butadiene has also been achieved to give rapidly and selectively novel block copolymers containing *s*PS (*rrrr* > 99 %), *cis*-1,4-PIP (selectivity > 97 %), and *cis*-1,4-PBD (selectivity > 97 %) blocks for the first time (Scheme 2). Such highly stereoregulated *s*PS–*cis*-1,4-PIP–*cis*-1,4-PBD copolymers should be of particular interest in comparison with the nonstereoregular styrene–isoprene–butadiene polymers (SIBR) prepared by conventional anionic polymerization.[8,9]

A possible scenario for the copolymerization of styrene and isoprene by the catalyst combination **1** + **2** in the presence of TIBA is shown in Scheme 3. Chain growth of styrene at the active site [Sc1]$^+$–R generated from **1** and [Ph$_3$C][B(C$_6$F$_5$)$_4$] should give a scandium active species bearing a *s*PS block such as **A**,[4a,b] which after transmetallation with TIBA (R$_3$Al,



***Scheme 3.*** A possible chain-shuttling mechanism for the formation of multiblock *s*PS–*cis*-1,4-PIP copolymers by the combination of catalysts **1** and **2**. [Sc1] denotes an active species generated from **1**, which shows high activity and syndiospecific selectivity for styrene polymerization. [Sc2] denotes an active species generated from **2**, which shows high activity and *cis*-1,4-selectivity for isoprene polymerization. The polymer species containing aluminum end groups, such as **B**, **D**, **G**, and **J**, could undergo reversible transmetallation with scandium active species, thus leading to efficient chain shuttling.

chain transfer) would afford *s*PS having an R$_2$Al-functionalized end group (**B**). Analogously, the R$_2$Al-functionalized *cis*-1,4-PIP species **D** could be generated by IP chain propagation at the [Sc2]$^+$ site formed from **2** and [Ph$_3$C][B(C$_6$F$_5$)$_4$][4c] and subsequent transmetallation between the resulting [Sc2]−PIP species **C** and R$_3$Al. If transmetallation between the [Sc1]−*s*PS species **A** and the Al−PIP species **D** or between the [Sc2]−*cis*-1,4-PIP species **C** and the Al−*s*PS species **B** takes place, the [Sc1]−*cis*-1,4-PIP species **E** or the [Sc2]−*s*PS species **H** would be formed, respectively (chain shuttling). Continuous styrene insertion into **E** could give the [Sc1]−*s*PS–*cis*-1,4-PIP species **F**, which on transmetallation with the Al−PIP species **D** would afford the Al-functionalized *s*PS–*cis*-1,4-PIP diblock copolymer **G**. Analogously, the R$_2$Al−*cis*-1,4-PIP-*s*PS diblock copolymer **J** could be formed by isoprene insertion into **H** followed by transmetallation between the resultant [Sc2]−*cis*-1,4-PIP–*s*PS species **I** and the Al−*s*PS species **B**. The repeated chain-shuttling polymerization should give multiblock styrene–isoprene copolymers with stereoregulated *s*PS and *cis*-1,4-PIP blocks (Scheme 3). The chain-shuttling terpolymerization of styrene, isoprene, and butadiene by **1** + **2** to give copolymers containing *s*PS, *cis*-1,4-PIP, and *cis*-1,4-PBD blocks and the copolymerization of styrene and isoprene by **1** + **3** to yield copolymers with *s*PS and 3,4-PIP blocks could take place in an analogous fashion.

In summary, by use of two scandium catalysts such as **1** and **2** or **1** and **3**, which show different monomer selectivity and stereoselectivity, with TIBA as a chain-shuttling agent, the regio- and stereospecific copolymerization of styrene, isoprene, and butadiene has been achieved for the first time to afford a novel family of copolymer materials composed of highly stereoregulated *s*PS, *cis*-1,4-PIP, and *cis*-1,4-PBD blocks or copolymers containing *s*PS and 3,4-PIP blocks. This work demonstrates for the first time that rare-earth-catalyzed chain-shuttling copolymerization of styrene and conjugated dienes can constitute a unique protocol for efficient synthesis of novel polymer materials that are difficult to obtain by other means. Further studies on the chain-shuttling copolymerization of other monomers by rare-earth-based catalysts are in progress.

Received: June 11, 2011
Revised: August 15, 2011

**Keywords:** block copolymers · chain shuttling · copolymerization · scandium · syndiotactic polystyrene

---

[1] Selected examples: a) D. Arriola, E. Carnahan, P. Hustad, R. Kuhlman, T. Wenzel, *Science* **2006**, *312*, 714–719; b) V. Gibson, *Science* **2006**, *312*, 703–704; c) M. Zintl, B. Rieger, *Angew. Chem.* **2007**, *119*, 337–339; *Angew. Chem. Int. Ed.* **2007**, *46*, 333–335; d) P. Chum, K. Swogger, *Prog. Polym. Sci.* **2008**, *33*, 797–819; e) P. Hustad, *Science* **2009**, *325*, 704–705; f) L. Sita, *Angew. Chem.* **2009**, *121*, 2500–2508; *Angew. Chem. Int. Ed.* **2009**, *48*, 2464–2472; g) Z. Guan, *Chem. Asian J.* **2010**, *5*, 1058–1070.

[2] A recent review on rare-earth polymerization catalysts: M. Nishiura, Z. Hou, *Nat. Chem.* **2010**, *2*, 257–268.

[3] For chain-transfer polymerization catalyzed by rare-earth complexes with main-group-metal alkyl compounds as chain-transfer agents, see: a) W. Kretschmer, A. Meetsma, B. Hessen, T. Schmalz, S. Qayyum, R. Kempe, *Chem. Eur. J.* **2006**, *12*, 8969–8978; b) P. Zinck, A. Valente, A. Mortreux, A. Organome, *Polymer* **2007**, *48*, 4609–4614; c) A. Valente, P. Zinck, A. Mortreux, M. Visseaux, *Macromol. Rapid Commun.* **2009**, *30*, 528–531; d) P. Zinck, F. Bonnet, A. Mortreux, *Prog. Polym. Sci.* **2009**, *34*, 369–392; e) P. Zinck, A. Valente, F. Bonnet, A. Violante, A. Mortreux, M. Visseaux, S. Ilinca, R. Duchateau, P. Roussel, *J. Polym. Sci. Part A* **2010**, *48*, 802–814; f) Z. Jian, D. Cui, Z. Hou, X. Li, *Chem. Commun.* **2010**, *46*, 3022–3024; g) C. Fan, C. Bai, H. Cai, Q. Dai, X. Zhang, F. Wang, *J. Polym. Sci. Part A* **2010**, *48*, 4768–4774; h) A. Valente, P. Zinck, A. Mortreux, M. Visseaux, *J. Polym. Sci. A* **2011**, *49*, 1615–1620.

[4] a) Y. Luo, J. Baldamus, Z. Hou, *J. Am. Chem. Soc.* **2004**, *126*, 13910–13911; b) H. Zhang, Y. Luo, Z. Hou, *Macromolecules* **2008**, *41*, 1064–1066; c) X. Li, M. Nishiura, L. Hu, K. Mori, Z. Hou, *J. Am. Chem. Soc.* **2009**, *131*, 13870–13882; d) L. Zhang, M. Nishiura, M. Yuki, Y. Luo, Z. Hou, *Angew. Chem.* **2008**, *120*, 2682–2685; *Angew. Chem. Int. Ed.* **2008**, *47*, 2642–2645.

[5] For copolymers containing syndiospecific polystyrene, see: a) H. Ban, Y. Tsunogae, T. Shiono, *J. Polym. Sci. Part A* **2005**, *43*, 1188–1195; b) Z. Hou, Y. Luo, X. Li, *J. Organomet. Chem.* **2006**, *691*, 3114–3121; c) H. Zhang, D. Byun, K. Nomura, *Dalton Trans.* **2007**, 1802–1806; d) A. Rodrigues, E. Kirillov, C. Lehmann, T. Roisnel, B. Vuillemin, A. Razavi, J. Carpentier, *Chem. Eur. J.* **2007**, *13*, 5548–5565; e) A. Rodrigues, E. Kirillov, B. Vuillemin, A. Razavi, J. Carpentier, *Polymer* **2008**, *49*, 2039–2045; f) Z. Jian, S. Tang, D. Cui, *Chem. Eur. J.* **2010**, *16*, 14007–14015; g) L. Pan, K. Zhang, M. Nishiura, Z. Hou, *Macromolecules* **2010**, *43*, 9591–9593; h) F. Guo, M. Nishiura, H. Koshino, Z. Hou, *Macromolecules* **2011**, *44*, 2400–2403; i) F. Guo, M. Nishiura, H. Koshino, Z. Hou, *Macromolecules* **2011**, *44*, 6335–6344. See also Refs. [4a,b].

[6] Examples of *cis*-1,4-polymerization of isoprene: a) A. Fischbach, M. Klimpel, M. Widenmeyer, E. Herdtweck, W. Scherer, R. Anwander, *Angew. Chem.* **2004**, *116*, 2284–2289; *Angew. Chem. Int. Ed.* **2004**, *43*, 2234–2239; b) L. Zhang, T. Suzuki, Y. Luo, M. Nishiura, Z. Hou, *Angew. Chem.* **2007**, *119*, 1941–1945; *Angew. Chem. Int. Ed.* **2007**, *46*, 1909–1913; c) M. Zimmermann, N. Froystein, A. Fischbach, P. Sirsch, H. Dietrich, K. Tornroos, E. Herdtweck, R. Anwander, *Chem. Eur. J.* **2007**, *13*, 8784–8800; d) W. Gao, D. Cui, *J. Am. Chem. Soc.* **2008**, *130*, 4984–4991; e) Y. Yang, Q. Wang, D. Cui, *J. Polym. Sci. Part A* **2008**, *46*, 5251–5262; f) Y. Yang, K. Lv, L. Wang, Y. Wang, D. Cui, *Chem. Commun.* **2010**, *46*, 6150–6152; g) K. Lv, D. Cui, *Organometallics* **2010**, *29*, 2987–2993; h) D. Li, S. Li, D. Cui, X. Zhang, *Organometallics* **2010**, *29*, 2186–2193; i) Y. Luo, S. Fan, J. Yang, J. Fang, P. Xu, *Dalton Trans.* **2011**, *40*, 3053–3059. See also Refs. [3e,4c,d].

[7] Examples of 3,4-polymerization of isoprene: a) G. Ricci, M. Battistella, L. Porri, *Macromolecules* **2001**, *34*, 5766–5769; b) C. Bazzini, A. Giarrusso, L. Porri, *Macromol. Rapid Commun.* **2002**, *23*, 922–927; c) Y. Nakayama, Y. Baba, H. Yasuda, K. Kawakita, N. Ueyama, *Macromolecules* **2003**, *36*, 7953–7958; d) C. Bazzini, A. Giarrusso, L. Porri, B. Pirozzi, R. Napolitano, *Polymer* **2004**, *45*, 2871–2875; e) L. Zhang, Y. Luo, Z. Hou, *J. Am. Chem. Soc.* **2005**, *127*, 14562–14563; f) B. Wang, D. Cui, K. Lv, *Macromolecules* **2008**, *41*, 1983–1988; g) G. Ricci, G. Leone, A. Boglis, A. Bossia, L. Zetta, *Macromolecules* **2009**, *42*, 9263–9267; h) G. Du, Y. Wei, L. Ai, Y. Chen, Q. Xu, X. Liu, S. Zhang, Z. Hou, X. Li, *Organometallics* **2011**, *30*, 160–170. See also Refs. [4c,d].

[8] A. Halasa, *Rubber Chem. Technol.* **1997**, *70*, 295–308.

[9] Note added in proof: A report on the Lu-catalyzed terpolymerization of styrene, isoprene, and butadiene (with *cis*-1,4-PIP $<$ 80%) recently appeared, see Z. Jian, S. Tang, D. Cui, *Macromolecules* **2011**, *44*, 7675–7681.