Scandium-Catalyzed Syndiospecific Copolymerization of Styrene with Isoprene

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The syndiospecific polymerization of styrene was first achieved more than two decades ago by use of homogeneous titanium catalysts. The resulting syndiotactic polystyrene (sPS) possesses many promising properties suitable for a large number of applications in industry, such as high melting point (ca. 270 °C), high crystallinity, high modulus of elasticity, low dielectric constant, and excellent resistance to heat and chemicals.[1] A drawback that has limited the application scope of sPS, however, is its brittleness. To improve the toughness of sPS, the syndiospecific copolymerization of styrene with conjugated dienes was considered to be a useful method, because the residual C−C double bonds derived from the diene monomers in the resulting copolymers could be further functionalized or hydrogenated to afford the corresponding sPS-containing functionalized or saturated copolymers. Despite extensive studies in this area, however, the diene monomers utilized so far for the stereospecific copolymerization of styrene were limited almost to butadiene and the catalysts reported were limited solely to titanium-based catalysts.[2,3] Although styrene−isoprene copolymers could show properties different from those of the styrene−butadiene analogues, the syndiospecific copolymerization of styrene with isoprene has hardly been explored.[4] In particular, diblock (AB type) or triblock (ABA type) styrene−isoprene copolymers with well-defined syndiotactic polystyrene blocks have not been reported previously. This is mainly due to the lack of appropriate (living) catalysts suitable for such copolymerizations. The search for new catalyst systems for the copolymerization of styrene with conjugated dienes, in particular for the syndiospecific copolymerization of styrene with isoprene, is therefore of obvious interest and importance.

During our recent studies on rare earth metal polymerization catalysts,[5,6] we found that the cationic half-sandwich scandium alkyl species generated from the dialkyl precursors such as $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ can serve as an excellent catalyst system for the syndiospecific polymerization of styrene and syndiospecific copolymerization of styrene with ethylene.[6a] We report here that such a cationic half-sandwich scandium alkyl species can also serve as a novel catalyst for the syndiospecific copolymerization of styrene with isoprene to give a new family of styrene−isoprene copolymers which possess well-defined syndiotactic styrene−styrene blocks.

In the presence of $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (**1**) and 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in toluene at room temperature, the polymerization of styrene took place rapidly in a living, syndiospecific fashion (Table 1, runs 1 and 2).[7] As the monomer/catalyst ratio was raised, a linear increase in the molecular weight of the resulting polymers was observed and the narrow molecular weight distribution remained almost unchanged (M_w/M_n = 1.26∼1.28) despite the poor solubility of the sPS products.[8] This catalyst system also showed high activity and excellent livingness for the polymerization of isoprene to give polyisoprenes with mixed 1,4- and 3,4-microstructures (Table 1, runs 3 and 4).[7] In consistence with the excellent livingness of this catalyst for the polymerization of both styrene and isoprene, the sequential polymerization of styrene and isoprene afforded selectively the corresponding diblock copolymers with a perfect syndiotactic polystyrene block (Table 1, runs 5 and 7). Addition of styrene to a completed isoprene polymerization system gave the similar diblock copolymers (Table 1, runs 6 and 8). Moreover, when the monomer/catalyst ratio was doubled in these copolymerization reactions, the molecular weights of the resulting copolymers were almost doubled (Table 1, runs 5−8). These results suggest that the present copolymerization of styrene and isoprene is also a living process, and the lengths of both the sPS block and polyisoprene (PI) block in the copolymers could be controlled easily by changing the monomer feeds. In agreement with these observations, a sequential polymerization of styrene, isoprene, and styrene yielded an ABA-type triblock copolymer with two syndiotactic polystyrene blocks connected by one polyisoprene block (Figure 1 and Table 1, run 9). These copolymers were all insoluble in THF at room temperature, but soluble in chlorobenzene at high temperatures (>100 °C). The copolymers showed melting points at ∼267−270 °C originating from the sPS blocks and glass transition temperatures at −35 to −37 °C and 100 °C originating from the PI blocks and sPS blocks, respectively. The ^{13}C NMR spectra of the copolymers showed a sharp singlet for the *ipso*-Ph carbon atoms at 145.67 ppm, demonstrating the excellent syndiotacticity of the PS blocks (*rrrr* > 99%) (Figure 2a).[1a,6a] The PI blocks possess mixed 1,4- and 3,4-microstructures, as shown by the ^1H and ^{13}C NMR spectra.

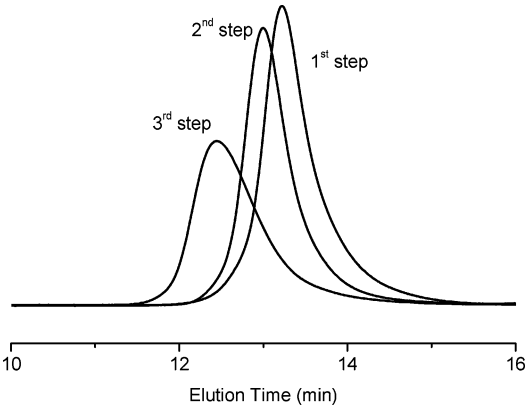

Figure 1. GPC profiles of sequential styrene−isoprene−styrene (ABA type) triblock copolymerizaiton (Table 1, run 9). First step, styrene (2.5 mmol), 15 min; second step, isoprene (2.5 mmol), 240 min; and third step, styrene (2.5 mmol), 15 min.

When the copolymerization was carried out in the presence of both styrene and isoprene in toluene, the corresponding multiblock copolymers containing sPS blocks with narrow molecular weight distributions (M_w/M_n = 1.17−1.29) were obtained (Table 2, runs 1−5). The styrene content in the

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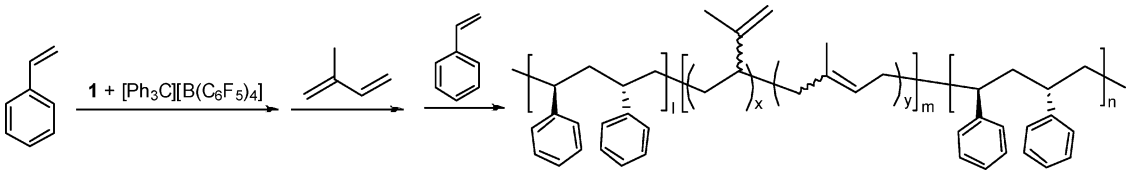
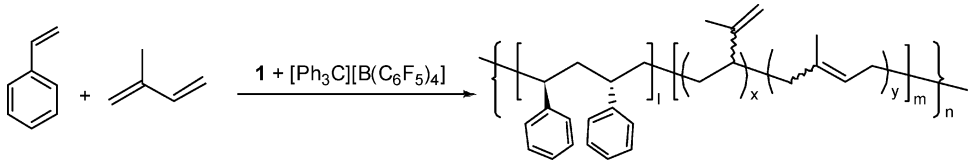
Table 1. Sequential Styrene (St)-Isoprene (Ip) Diblock and St-Ip-St Triblock Copolymerizaitons Catalyzed by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (1)/$[Ph_3C][B(C_6F_5)_4]$[a]



run	St/Ip/St[b] (first/second/third)	time (min)[c] (first/second/third)	yield[d] (%)	St content[e] (%)	Ip content[e] 1,4 (%)	Ip content[e] 3,4 (%)	M_n[f] × 10^{-4}	M_w/M_n[f]	$T_m(T_g)$[g] (°C)
1	125/0/0	15/0/0	100	100			1.7	1.28	270(100)
2	250/0/0	15/0/0	100	100			3.5	1.26	270(100)
3	0/200/0	0/240/0	100	0	34	66	1.8[h]	1.07[h]	(−36)
4	0/250/0	0/240/0	99	0	36	64	2.3[h]	1.05[h]	(−36)
5	125/125/0	15/240/0	98	51	16	33	3.2	1.28	268(−35, 100)
6[i]	125/125/0	240/15/0	98	48	13	39	3.7	1.23	n.d.[j]
7	250/250/0	15/240/0	96	53	14	33	6.2	1.31	270(−37, 100)
8[i]	250/250/0	240/15/0	94	51	11	38	8.7	1.45	n.d.[j]
9[k]	250/250/250	15/240/15	92	71	8	21	12.6	1.36	267(−36, 100)

[a] Polymerization conditions: Sc, 10 μmol; [Sc]/[B] = 1/1 (mol/mol); toluene + isopr ene + styrene = 30 mL; 25 °C. [b] Molar ratio to Sc. [c] Sequential polymerization time. Styrene was added first followed by isoprene unless otherwise noted. [d] Weight of the polymer obtained/weight of the monomer used. [e] Determined by ^{1}H NMR and ^{13}C NMR spectra. [f] Determined by GPC in 1,2-dichlorobenzene at 145 °C against polystyrene standard unless otherwise noted. [g] Determined by DSC. [h] Determined by GPC in THF at 45 °C. [i] Isoprene was added first followed by styrene. [j] Not determined. [k] Sequential styrene−isoprene−styrene triblock copolymerization.

Table 2. Random Copolymerization of Styrene (St) and Isoprene (Ip) Catalyzed by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (1) /$[Ph_3C][B(C_6F_5)_4]$[a]



run	St (mmol)	Ip (mmol)	t (h)	yield (g)	activity[b]	St content[c] (%)	Ip content[c] 1,4 (%)	Ip content[c] 3,4 (%)	M_n[d] × 10^{-4}	M_w/M_n[d]	T_m[e] (°C)
1	15	7.3	2	0.40	10	35	37	28	3.40	1.17	189
2	21	7.3	2	0.50	12	57	24	19	3.92	1.16	210
3	37	7.3	2	0.74	18	74	15	14	6.14	1.29	223
4	21	21	2	0.58	14	10	46	44	6.32	1.21	n.o.[f]
5	21	63	2	0.66	16	2	48	50	6.71	1.20	n.o.[f]
6[g]	21	7.3	0.25	2.68	510	76	6	18	19.5	2.14	241

[a] Polymerization conditions: Sc, 21 μmol; [Sc]/[B] = 1/1 (mol/mol); toluene + isopr ene + styrene = 30 mL; 25 °C, unless otherwise noted. [b] Given in kg of polymer/(mol Sc·h). [c] The styrene and isoprene contents were estimated from ^{1}H NMR and ^{13}C NMR spectra. [d] Determined by GPC in 1,2−dichlorobenzene at 145 °C against polystyrene standard. [e] Determined by DSC. [f] Not observed. [g] Bulk (solvent-free) polymerization.

copolymers could be adjusted in a wide range (2−74 mol %) by changing the styrene/isoprene feed ratio. More remarkably, the copolymerization could be carried out in bulk with a much higher efficiency, although the molecular weight distribution of the resulting copolymer became slightly broader ($(M_w/M_n$ = 2.14, Table 2, run 6). Homopolyisoprene or atactic polystyrene was not found in these reactions, as confirmed by solvent extraction experiments. The monomer reactivity ratios of $r_{styrene}$ = 2.47 and $r_{isoprene}$ = 21.6 were obtained by use of the Fineman−Ross method, which suggests that the formation of styrene−styrene sequences (blocks) is preferred in the present styrene−isoprene copolymerization.

The ^{13}C NMR spectrum of a copolymer with a styrene content of 74 mol % (Table 2, run 3) is shown in Figure 2b, which exhibited strong singlets at 145.67 ppm (*ipso*-Ph), 44.13 ppm ($S_{\alpha\alpha}$), and 40.77 ppm ($T_{\beta\beta}$), suggesting that this polymer contains syndiotactic polystyrene blocks. Both 1,4-insertion and 3,4-insertion units of isoprene were detected in the resulting copolymers by ^{1}H NMR and ^{13}C NMR analyses. The melting temperatures (T_m) of the multiblock copolymers given in Table 2 are generally lower than those of homopolystyrene and the di- or triblock copolymers shown in Table 1 and linearly increased with increasing styrene content. When the styrene content was below 10 mol %, a melting point was not observed. GPC/FT-IR analyses revealed that the styrene units are uniformly distributed in all the copolymers, suggesting that the copolymers do not contain homopolymers.

In summary, by use of a cationic half-sandwich scandium alkyl catalyst, the syndiospecific living copolymerization of styrene with isoprene has been achieved for the first time, which afforded a new family of styrene−isoprene copolymers that possess stereoregular syndiotactic styrene−styrene blocks and were difficult to be prepared previously, such as AB type styrene−isoprene diblcok copolymers, ABA type styrene−isoprene−styrene triblock copolymers, and multiblock styrene−isoprene copolymers. Further studies on the copolymerization of styrene with other conjugated dienes and on the functionalization and properties of the resulting copolymers are in progress.[9]

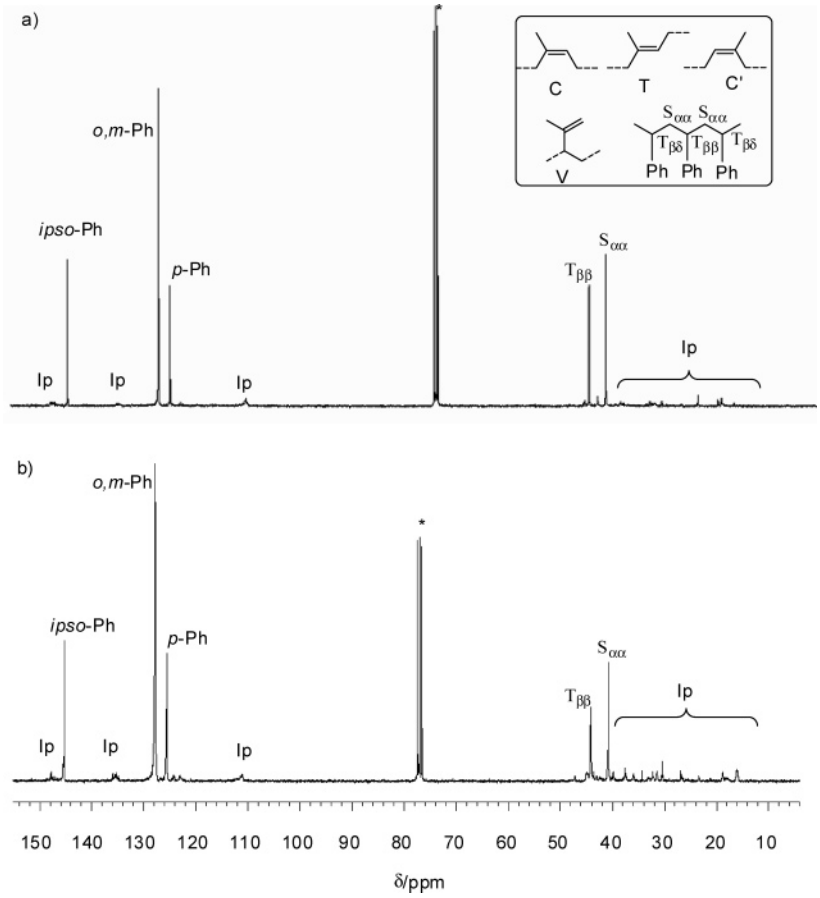


Figure 2. ^{13}C NMR spectra of (a) a styrene−isoprene−styrene triblock copolymer in 1,1,2,2-$C_2D_2Cl_4$ at 110 °C (St content = 71 mol %, Table 1, run 9) and (b) a styrene−isoprene random multiblock copolymer in $CDCl_3$ at 60 °C (St content = 74 mol %, Table 2, run 3).

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Supporting Information Available: Experimental details, NMR spectra, and GPC and DSC profiles of representative polymer products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) See Supporting Information for more details.

(8) The molecular weight distribution of the polymers depended to some extent on the concentrations of the catalyst and monomer. A dilute solution tends to give a narrower molecular weigh distribution.

(9) Preliminary studies showed that butadiene could also be copolymerized with styrene in a similar fashion. Details will be described in a forthcoming full paper.

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