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Chain Growth Polymerization of Isoprene and Stereoselective Isoprene–Styrene Copolymerization Promoted by an *ansa*-Bis(indenyl)allyl–Yttrium Complex

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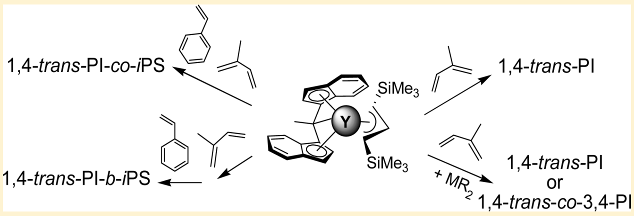
S *Supporting Information*



ABSTRACT: The ability of *rac*-[{Me$_2$C(Ind)$_2$}Y(1,3-(SiMe$_3$)$_2$-C$_3$H$_3$)] (Ind = 9-indenyl) (**1**) to catalyze isoprene polymerization, either as a single-site component or in combination with an alkyl–metal as a chain transfer agent (CTA) via coordinative chain transfer polymerization (CCTP), has been investigated. Complex **1** alone catalyzes the highly 1,4-*trans*-stereoselective polymerization of isoprene with moderate activity. The addition of ZnEt$_2$ provides an efficient catalytic system for the reversible CCTP of isoprene with retention of the 1,4-*trans* stereoselectivity. By contrast, in the presence of Mg(nBu)$_2$, with increasing amounts of CTA, the 1,4-*trans* specificity gradually decreases at the advantage of the 3,4-polymer. The copolymerization between isoprene and styrene has been also studied, resulting in the formation of materials with unprecedented architecture. Simultaneous copolymerization of isoprene and styrene with **1** provides copolymers with a wide range of compositions (χ_S = 0.30–0.98) and a stereospecific blocky distribution of the monomers in the copolymer chain. The reactivity ratios (average values: $r_{1,\mathrm{Ip}}$ = 2 and $r_{2,\mathrm{St}}$ = 18) determined by NMR spectroscopy confirmed the propensity to form multiblock materials. Microstructural ^{13}C NMR analysis showed the presence of stereoregular 1,4-*trans*-polyisoprene and isotactic polystyrene segments. The copolymerization via sequential monomer addition allowed the synthesis of well-defined 1,4-*trans*-polyisoprene-*block*-isotactic polystyrene, which contains two crystalline blocks. The authenticity of these new di- or multiblock copolymer materials was assessed by combined NMR, GPC, and DSC characterizations.

INTRODUCTION

The polymerization of 1,3-conjugated dienes is one of the most important industrial processes.[1] It affords efficient entries toward polymer materials with versatile properties and wide applications range, mainly depending on the microstructures generated during polymerization. In particular, isoprene is an attractive monomer and its stereospecific polymerization leads to polyisoprenes (PIs) with various microstructures (i.e., 1,4-*cis*,[2] 1,4-*trans*,[3] 3,4-*isotactic*,[2k,4] 3,4-*syndiotactic*,[3] 1,4-*cis*-*alt*-3,4[5]), which show quite different physical, thermal, and mechanical properties. Despite many catalysts having been developed for these processes, some of them showing high stereospecificity and a *living* character in the polymerization,[2m,3f] one of the intrinsic constraints is the single site nature of the polymerizations for which typically only one polymer chain can grow *per* active metal center. An attractive efficient alternative to living polymerization is the coordinative chain transfer polymerization (hereafter abbreviated CCTP; also referred to as Chain Growth Polymerization),[6] which involves the addition of several equivalents of main-group metal–alkyls (so-called chain transfer agents, CTAs) that act as surrogates of the metal chain growth sites. The heart of CCTP is the fast and reversible transfer of the growing polymer chain between the active metal propagating centers and the inactive (dormant) main-group metal–alkyls/polymeryls.

The concept of reversible CCTP has been introduced to the field of diene polymerization only recently and the stereoselective CCTP of diene in the presence of rare earth catalysts was mainly reported to be 1,4-*cis* stereospecific.[7] Living 1,4-*cis* stereoselective CCTP of isoprene was reported by Cui et al. using an aminophenyl-functionalized monocyclopentadienyl lanthanide bis(allyl)/AlR$_3$ catalytic system.[8] The 1,4-*trans* stereoselective CCTP of isoprene has been less explored, and as far as we are aware, only one example was reported by Visseaux et al. using the ternary catalytic system Cp*La(BH$_4$)$_2$(THF)$_2$/EtMg(nBu)/MR$_x$ (M = B, Zn, Al; R = Et, iBu; x = 2, 3).[9] Although the stereocontrol is maintained during the polymerization (1,4-*trans* ~ 97%), the latter ternary system showed modest catalytic efficiency and PIs with relatively broad polydispersities (M_w/M_n = 1.8–2.5) were obtained.

Conjugated dienes are attractive monomers not only when they are homopolymerized but also when copolymerized with

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Table 1. Isoprene Homopolymerization Promoted by *rac*-[{$Me_2C(Ind)_2$}Y(1,3-$(SiMe_3)_2C_3H_3$)] (1) Alone or in Combination with Different Chain Transfer Agents (CTA)[a]

entry	CTA	[Y]/[CTA]/[Ip]	temp [°C]	time [h]	conv [%]	$M_{n,theo}$ [$\times 10^3$][b]	$M_{n,GPC}$ [$\times 10^3$][c]	M_w/M_n[c]	1,4-*trans* [%][d]	3,4 [%][d]	PI/Y[e]	T_g [°C][f]
1		1:0:2800	25	17	6	11.4	29.4	1.7	91.5	8.5	0.4	−57.3
2		1:0:2800	40	17	20	38.2	47.8	1.6	87.9	12.1	0.7	−54.8
3		1:0:2800	60	17	42	80.2	77.3	1.6	87.2	12.8	0.9	−55.2
4		1:0:2800	60	24	60	114.4	98.0	1.9	87.0	13.0	1.0	−56.6
5	$Mg(nBu)_2$	1:5:2800	60	32	100	38.4	31.1	1.4	77.8	22.2	6	−57.2
6	$Mg(nBu)_2$	1:10:2800	60	32	100	19.0	14.6	1.4	66.5	33.5	12	−49.5
7	$Mg(nBu)_2$	1:20:2800	60	27	100	9.5	7.1	1.5	52.8	47.2	24	−43.2
8	$ZnEt_2$	0:5:2800	60	72	0							
9	$ZnEt_2$	1:2:2800	60	24	70	66.6	54.2	1.4	87.0	13.0	2.5	−54.1
10	$ZnEt_2$	1:5:2800	60	32	87	33.1	28.5	1.4	89.1	10.9	6	−55.6
11	$ZnEt_2$	1:10:2800	60	32	77	14.8	11.1	1.6	88.5	11.5	12	−53.2
12	$ZnEt_2$	1:20:2800	60	32	83	7.9	6.3	1.6	90.5	9.5	23	−52.2
13	$ZnEt_2$	1:70:2800	60	32	traces	nd[g]	nd	nd	nd	nd	nd	nd
14	$ZnEt_2$	1:10:5600	60	60	80	30.4	29.7	1.5	87.9	12.1	10	−54.6
15	$Al(iBu)_3$	1:10:2800	60	48	10	1.9	2.1	1.4	88.0	12.0	8.0	−53.5
16	$AlMe_3$	1:10:2800	60	48	traces	nd[g]	nd	nd	nd	nd	nd	nd

[a] Polymerization conditions: **1**: 40 μmol, bulk isoprene. [b] Number-average molecular weight (in g mol^{-1}) determined from $M_{n,theo}$ = [Ip]/[CTA or **1**] × conv × 68. [c] Number-average molecular weight (in g mol^{-1}) and molecular weight distributions determined by GPC in THF at 30 °C vs PS standards. [d] Composition determined by ^1H NMR spectroscopy from the integral value of the signals for the unsaturated hydrogen of 1,4-*trans* units over the sum of integrals for unsaturated hydrogens of 1,4-*trans* and 3,4-units: $[PI_{1,4}]/([PI_{1,4}] + 1/2[PI_{3,4}])$. [e] Number of PI chains per yttrium center. [f] Determined from the first heating cycle of DSC measurements run at 10 °C min^{-1}. [g] nd = not determined.

other monomers like ethylene[10,11] and styrene,[12−14] leading to materials of high interest from an industrial point of view. Styrene−butadiene copolymers are usually obtained via radical[12] or anionic[13] processes that do not allow precise regio- and stereocontrol. They can be also obtained via coordinative polymerization that can afford regio- and stereoregular copolymers.[14] Although styrene−isoprene copolymers can feature properties quite different from those of styrene−butadiene analogues, the stereospecific copolymerization of the former monomers has been hardly explored: 1,4-*trans*-polyisoprene-*co*-syndiotactic polystyrene (*trans*-PI-*co*-sPS)[15] and 1,4-*cis*-polyisoprene-*co*-syndiotactic polystyrene (*cis*-PI-*co*-sPS)[16] have been reported. Recently 1,4-*trans*-polyisoprene-*co*-atactic polystyrene has been prepared by Zinck and Visseaux et al. via chain growth copolymerization of both monomers.[17] To our knowledge, however, examples of stereoregular copolymers containing *isotactic* polystyrene fragments are known only for butadiene,[18] while *isotactic* polystyrene materials associated with 1,4-*trans*-PI remain elusive in the literature.

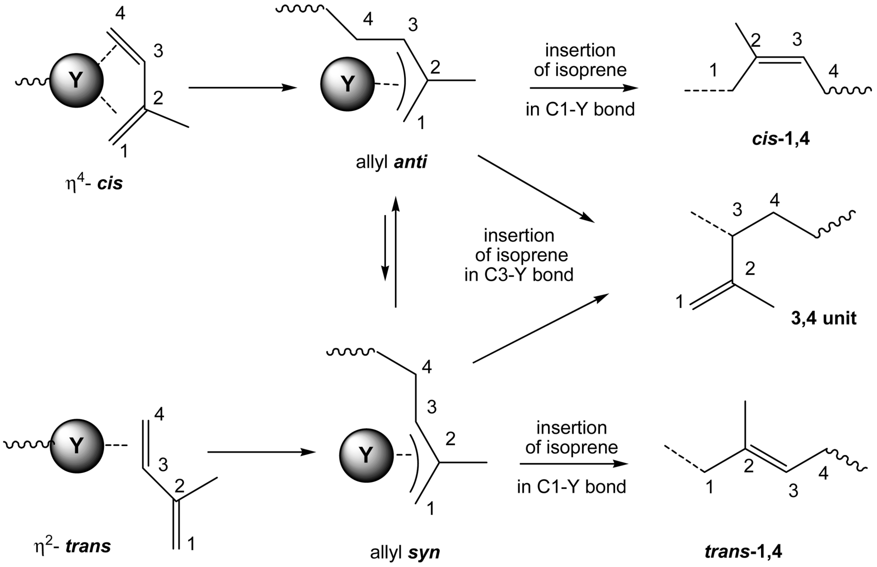
Herein we report the homopolymerization of isoprene with the *rac*-[{$Me_2C(Ind)_2$}Y(1,3-$(SiMe_3)_2C_3H_3$)] (**1**) complex (Ind = 9-indenyl)[19] acting as a single-site catalyst or combined with a metal−alkyl as CTA via CCTP. Also, compound **1**, which is an efficient initiator for the highly isospecific polymerization of styrene,[19] has been used as a single component catalyst for the simultaneous and sequential copolymerizations of isoprene and styrene. The obtained copolymers have unprecedented blocky and stereoregular architectures.

RESULTS AND DISCUSSION

Isoprene Homopolymerization. *rac*-[{$Me_2C(Ind)_2$}Y(1,3-$(SiMe_3)_2C_3H_3$)] (**1**) was evaluated as catalyst either alone or in combination with different chain transfer agents (CTAs, i.e., $Mg(nBu)_2$, $ZnEt_2$, $Al(iBu)_3$, or $AlMe_3$) in the homopolymerization of isoprene. Representative results are summarized in Table 1. As expected from previous studies on styrene homopolymerization,[19] compound **1** alone proved to be poorly active at room temperature; improved, although still moderate, reactivity was observed upon increasing the temperature up to 60 °C (entries 1−3, Table 1). The PIs obtained over the temperature range 25−60 °C showed a similar microstructure predominantly made of 1,4-*trans* units (87−92 mol %) with minor amounts of isolated 3,4-units (8−13 mol %) (entries 1−4, Table 1), as revealed by ^{13}C NMR spectroscopy. The absence in the ^{13}C NMR spectra of the obtained polymers of detectable signals at δ 23.6, 26.6, and 32.4 ppm, which are characteristic of 1,4-*cis* isoprene units,[20] indicated a high 1,4-*trans*-type stereospecificity of the title catalyst. In addition, those polymerizations led to highly regioregular polymers; in fact, no signals assignable to head-to head and tail-to-tail arrangements of monomer units[21] were observed in the ^{13}C NMR spectra.

The observed high regio- and stereoselectivity can be explained on the basis of the well-established mechanism for polymerization of conjugated dienes.[1] As depicted in Scheme 1, the two different η^4 or η^2 coordination modes of the monomer to the metal center lead to a η^3-coordinated allyl complex in *syn* or *anti* configuration, respectively. From these intermediates, 1,4-*cis*- and 1,4-*trans*-PI are respectively produced, while *syn*−*anti* isomerization of the π-allyl complex resulted in 3,4-units. Actually, the complete absence of 1,4-*cis* units in the polymer chain and the high 1,4-*trans* selectivity suggest that only η^2-*cis* coordination of isoprene is operative with the present catalyst system. GPC analysis of the polymer samples produced with **1** alone showed in all cases unimodal molecular weight distributions (M_w/M_n = 1.4−1.9), indicative of a single-site nature of the catalyst. A good

Scheme 1



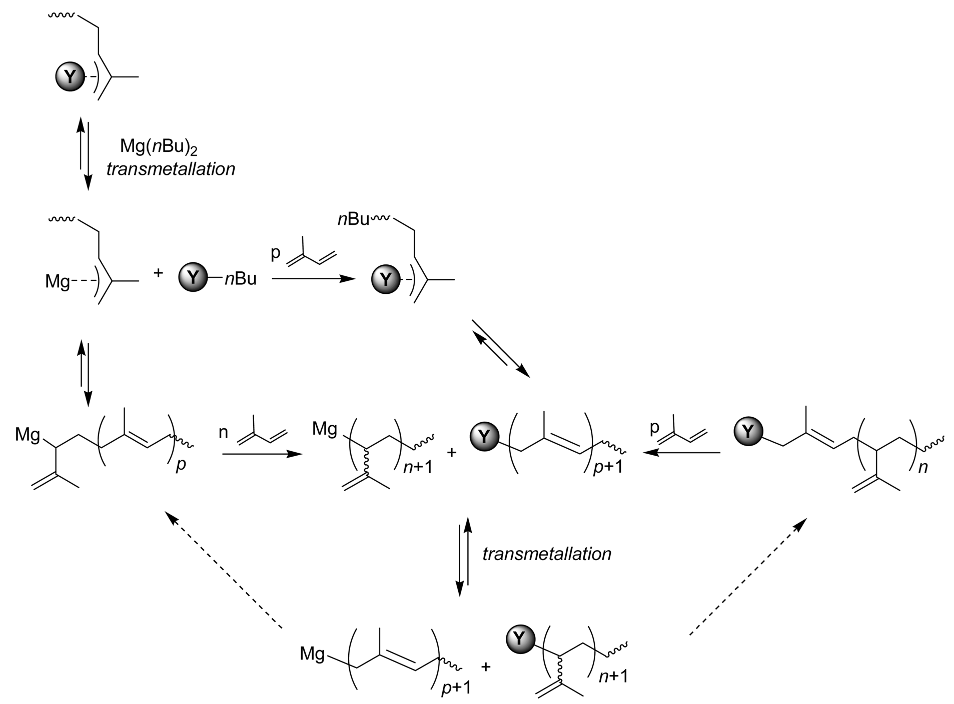
agreement between the experimental M_n values and the theoretical ones was noted, especially for the polymerizations performed at 60 °C where the initiation efficiency was close to 100%. The polymers were also characterized by DSC, revealing a glass transition temperature T_g in the range −57 to −55 °C consistent with a highly 1,4-*trans*-PI.[22] Low intensity melting transitions were also observed in the temperature range 37−56 °C, depending on the molecular weight and microstructure, also consistent with previously reported data.[11b,23] Only few examples of yttrium-based catalysts able to polymerize isoprene in a 1,4-*trans* fashion are reported in the literature.[23] So far, compound **1** is the first example of a single-component, single-site yttrium catalyst for the preparation of 1,4-*trans*-PI.

Isoprene Coordinative Chain Transfer Polymerization. It is well-known in the literature that the use of an alkyl−metal MR_n as CTA in polymerization does not alter [usually] the nature of the catalytically active species but allows for a fast and reversible intermolecular chain transfer of growing polymer chains, eventually leading to the formation of metal−[(polymeryl)-R]$_n$ species, considered as dormant species, where the polymeryl chains are selectively capped with R end-groups.[6] Recently, we have reported that the combination of complex **1** with di(*n*-butyl)magnesium ($Mg(nBu)_2$) provides an efficient binary system for the highly isoselective CCTP of styrene.[24]

The ability of catalyst **1** to operate CCTP of isoprene was assessed by polymerizing the monomer in the presence of different chain transfer agents, namely $Mg(nBu_2)$, $ZnEt_2$, $Al(iBu)_3$, and $AlMe_3$ (Table 1). In the presence of 5−20 equiv of CTA, the catalytic system **1**/$Mg(nBu)_2$ proved effective in CCTP of isoprene (runs 5−7). The fast and reversible transmetalation process operating between [Y]−polyisoprenyl species and Mg−polyisoprenyl ones was evidenced by (i) the unimodal, relatively narrow molecular weight distributions ($M_w/M_n = 1.6$), (ii) the good agreement between the calculated (on the basis of the [isoprene]-to-[$Mg(nBu)_2$] ratio) and the experimental molecular weights, (iii) the monotonously increasing number of PI chains generated per yttrium center with the number of $Mg(nBu)_2$ equivalents added, and (iv) the selective end-capping of PI chains by *n*-butyl groups. However, the addition of $Mg(nBu)_2$ in the reaction medium leads to a gradual modification of the 1,4-*trans* microstructure. As a matter of fact, the amount of 3,4-units in those PIs linear increased (from 13 to 47 mol %) by increasing the number of $Mg(nBu)_2$ equivalents (from 0 to 20, runs 4−7). In addition, DSC analysis of the PIs showed T_g values increasing from −57 to −43 °C, parallel to the increasing amounts of 3,4-units in the polymer. Interestingly, ^{13}C NMR analysis of the polymer sample containing an almost equal amount of 1,4-*trans* and 3,4- units (run 7, Table 1) revealed a blocky structure, with an average block length of 5 monomer units and a stereoirregular arrangement of the 3,4-blocks (see the Supporting Information).[25] The monodisperse GPC trace and the presence of a unique glass transition temperature confirms that the 3,4-units are inserted as small blocks into the 1,4-*trans* backbone and that the obtained materials are not blends of two homopolymers (1,4-*trans*-PI and 3,4-PI, respectively).

Dramatic changes in the regioselectivity of isoprene polymerization mediated by lanthanide complexes upon addition of an organometallic compound were already described in the literature.[23a] In particular, Hou et al. reported a remarkable switch from 3,4- to 1,4-*cis* stereoselective polymerization by adding $AlMe_3$ to yttrium amidinate catalysts which led to a stable heterobimetallic Y/Al species.[2k] On the other hand, Visseaux et al. reported the CCTP of isoprene promoted by borohydrido half-lanthanidocene and rare earth borohydrides, chlorides, and alkoxide in the presence of $EtMg(nBu)$ and noted a gradual modification of the selectivity upon the relative amount of the latter dialkylmagnesium component.[9,17b] The observed modification from 1,4-*trans* to 3,4- was ascribed to the ability of the Mg−alkyl/polyisoprenyl species to oligomerize isoprene in a 3,4-regioselective fashion,[2k,26] and the process was described as an efficient transmetalation of a growing polymer chain between two catalysts (La and Mg) with different regiospecificity.[9] In the present system associating complex **1** and $Mg(nBu)_2$, the Mg−polyisoprenyl species—eventually generated from transmetalation with Y-polyisoprenyl ones—cannot be also considered as dormant species and a likely mechanism for the CCTP

Scheme 2



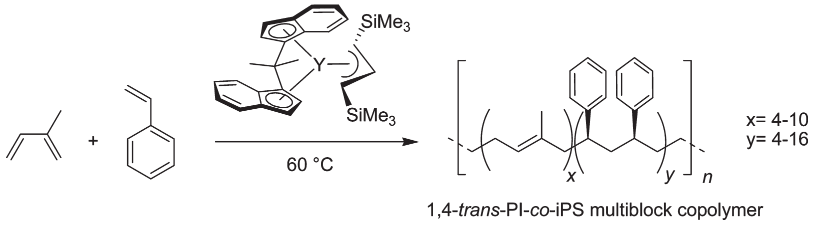
process is represented in Scheme 2. Thus, the polymerization of isoprene mediated by **1**/$Mg(nBu)_2$ occurs with a good transfer efficiency, but at the expense of the 1,4-*trans* selectivity.

Other chain transfer agents were then assessed with the idea to keep the high 1,4-*trans* stereoselectivity along the CCTP process. The use of aluminum—alkyls proved detrimental for the catalyst, inhibiting partially ($Al(iBu)_3$, run 15, Table 1) or completely ($AlMe_3$, run 16, Table 1) the polymerization activity. On the contrary, $ZnEt_2$ proved compatible and showed a transfer efficiency comparable to that of $Mg(nBu)_2$, with retention of the 1,4-*trans* stereospecificity. In fact, the microstructure of the PIs obtained with the **1**/ $ZnEt_2$ system was similar to that observed for PIs produced with catalyst **1** alone (88—90% of 1,4-*trans* units and 10—12% of 3,4-units, runs 9—14, Table 1). The good agreement between the calculated (on the basis of the [isoprene]-to-[$ZnEt_2$] ratio and conversion) and the experimental molecular weight and the presence of ethyl chain end groups in the ^{1}H and ^{13}C NMR spectra[27] of the polymers constituted convincing evidence of the effective chain transfer. In this case, the Zn—polyisoprenyl species eventually formed in the course of CCTP can be considered as dormant species, as generally accepted for this polymerization process. As far as we are aware, this is the first example of an Y-based/$ZnEt_2$ catalytic system for the 1,4-*trans*-stereoselective CCTP of isoprene. In comparison with other *trans*-stereoselective systems reported by Visseaux et al.,[9] this CCTP process is somewhat more controlled, as judged from the better correspondence between the expected molecular weights and the experimental ones and the narrower molecular weight distributions of the obtained PIs.

Isoprene—Styrene Copolymerization. The *ansa*-bis(indenyl) allyl yttrium complex **1** was found to be a unique single-site and single-component catalyst for the preparation of highly isotactic polystyrene with high activity in a broad range of molecular weights and distributions, under synthetically attractive conditions (solvent-free or high concentrations, 60—120 °C).[19] Theoretical and experimental investigations showed that the polymerization is highly regioselective and proceeds in a 2,1- mode via an enantiomorphic site control mechanism.[19b] The catalytic performances of the title catalyst in the homopolymerization of styrene and isoprene gave the possibility to explore the copolymerization of the two monomers. Several experiments by changing the composition of the initial monomer feed were carried out at 60 °C in heptane; representative results are reported in Table 2.

Albeit the copolymerization worked out in bulk, the addition of a solvent was necessary because of the high viscosity of the reaction medium. The obtained materials were characterized by NMR spectroscopy, GPC, and DSC. The GPC traces showed monomodal molecular weight distributions with PDI values of about 2, consistent with copolymers produced from a single-site catalyst. Increase of styrene in the feed resulted in copolymers with an expectedly higher molar fraction of styrene but also higher M_n values; for all samples, the observed composition, evaluated by ^{1}H NMR, systematically showed a styrene content higher than the one present in the initial feed, suggesting the preference of the catalyst to polymerize styrene (entries 1—4, Table 2). Thus, styrene—isoprene copolymers with a large range of composition (styrene molar fraction, $\chi_S = 0.30-0.98$) were obtained. Inspection of the $^{13}C\{^1H\}$ NMR spectra of those copolymers revealed that the chemo- and stereoselectivity of isoprene and the isoselectivity of styrene polymerization are retained by the catalyst when the two monomers are copolymerized (Figure 1, bottom). In all samples, the ^{13}C NMR signals for 1,4-*trans*-PI (δ 16.2, 26.9, 39.9 123.3, and 135.4 ppm) were clearly visible in contrast to signals for 1,4-*cis* isoprene units which were absent, while the amount of 3,4-units spanned in the 1,4-*trans* matrix (δ 18.8 31.4 32.4 37.6, and 47.4 ppm) remained constant (ca. 10% of the total isoprene molar fraction in the copolymer, χ_I). Moreover, the isotacticity of homopolystyrene

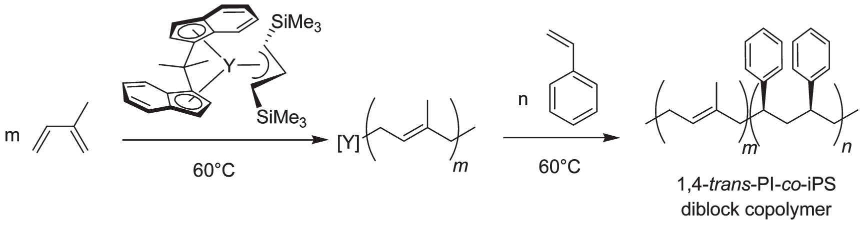
Table 2. Copolymerization of Isoprene and Styrene Mediated by Catalyst 1[a]



entry	feed (mol %)[b] Ip	feed (mol %)[b] St	time [h]	yield [g]	M_n[c] [×10^3]	M_w/M_n[c]	copolymer comp (mol %)[d] Ip 1,4-*trans*	copolymer comp (mol %)[d] Ip 3,4-units	copolymer comp (mol %)[d] St	[m^6] [%]	T_g [°C]	T_m [°C]
1	90	10	24	2.2	59.4	2.0	65.3	4.7	30.0	7	−33	51
2	75	25	18	2.2	60.2	2.1	46.9	4.9	48.2	43	63	139
3	50	50	8	3.4	77.7	2.0	26.0	2.2	71.8	67	72	205
4	25	75	2	3.8	73.2	2.2	2.0	0.0	98.0	98	94	214

[a] Polymerization conditions: **1**: 40 μmol; heptane = 4 mL; temp = 60 °C. [b] [Y]/([IP] + [St]) = 1:1000. [c] Number-average molecular weight in g mol^{-1} and polydispersity, as determined by GPC in THF at 30 °C vs PS standards. [d] Determined by ^{1}H NMR spectroscopy, from the integral value sum of the signals for unsaturated units of PI over the sum of integrals for aromatic hydrogens of isotactic block and unsaturated units of PI one: $([PI_{1,4}] + ([PI_{3,4}]/2))/([PI_{1,4}] + ([PI_{3,4}]/2)) + ([PS_{Ph}]/5)$.

Table 3. Sequential Copolymerization of Isoprene and Styrene Mediated by Catalyst 1[a]



entry	Ip[b] (equiv)	time [h]	St[b] (equiv)	time [min]	yield [g]	M_n[c] [× 10^3]	M_w/M_n[c]	copolymer comp[d] (mol %) Ip 1,4-*trans*	copolymer comp[d] (mol %) Ip 3,4-units	copolymer comp[d] (mol %) St	T_m [°C]
5	750	17	250	10	2.9	78.5	2.0	64.5	6.7	28.8	42, 212
6	500	15	500	30	2.3	80.6	2.2	42.3	4.2	53.5	37, 214
7	250	13	750	45	2.2	115.2	2.0	21.2	2.4	76.4	219

[a] Polymerization conditions: **1**: 40 μmol; heptane = 6 mL; temp = 60 °C. [b] Molar ratio to catalyst **1**. [c] Number-average molecular weight in g mol^{-1} and polydispersity, as determined by GPC in THF at 30 °C vs PS standards. [d] Determined from ^{1}H NMR spectroscopy, from the integral value of the signals for methyl groups of PI over the sum of integrals for methylene groups of iPS and methyl groups of PI = $([IP_{Me}/3])/([PI_{Me}]/3 + [PS_{CH2}]/2)$.

sequences (δ 146.5, 43.1, and 40.7 ppm), evaluated at the heptad level [m^6],[19] increased with increasing styrene contents in the copolymer (see the Supporting Information). The other minor signals observed at δ 30−38 ppm were assigned, according to the literature,[16] to Ip−St heterosequences at the diad level.

A rough estimation of the reactivity ratios, $r_1 = k_{II}/k_{IS}$ = 0.7−3.5 and $r_2 = k_{SS}/k_{SI}$ = 16−23 (k_{ij} is the rate constant for the addition of monomer M$_i$ to a growing chain ending with a M$_j$ monomer unit), was achieved from the monomer composition in the feed and in the resulting copolymers.[28] The reactivity ratio product, $r_1 \times r_2$ = 18−70, i.e., ≫1, is indicative of the preference of the catalyst to polymerize styrene and the formation of homosequences instead of alternated ones. The average monomer block length was evaluated by NMR using a diad copolymer composition.[29,30] Styrene block lengths (n_s) of 4−16 units were found in the copolymers with styrene molar fractions in the range χ_S= 0.30−0.72 (entries 1−3, Table 2). The corresponding block lengths for isoprene (n_I) in the decreased from 10 to 4, by decreasing the amount of isoprene in the copolymer χ_I = 0.70−0.28.

The thermal characterization of these new multiblock materials is consistent with the above microstructural analysis. The DSC profiles exhibit a single glass transition with a T_g value increasing from −33 to 67 °C as the styrene content in the copolymer increased in the range χ_S = 0.30−0.98. An increase of the melting temperature was also observed with a T_m of 51 °C for the richest copolymer in isoprene (χ_I = 0.70; entry 1, Table 2) to 205 °C for the copolymer with the highest amount of styrene (χ_S = 0.72; entry 3, Table 2), consistent with T_m values known for the corresponding homopolymers. Interestingly enough, the copolymer with an almost equimolar isoprene−styrene composition (χ_I = 0.52, χ_S = 0.48; entry 2, Table 2) showed a single melting transition with an intermediary T_m value of 139 °C. Hou et al. also reported a single T_m value (in the range 189−241 °C) for styrene-*co*-isoprene multiblock copolymers made of syndiotactic

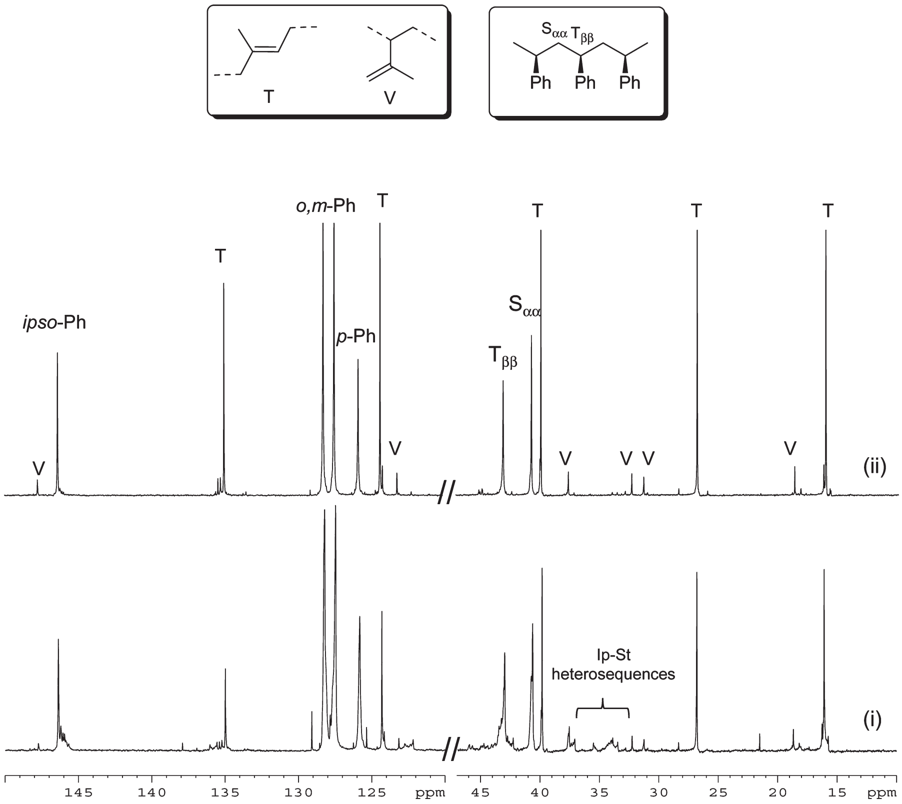


Figure 1. Details of $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K) spectra of isoprene−styrene copolymers obtained by (bottom) simultaneous (entry 3, Table 2) and (top) sequential (entry 6, Table 3) polymerization.

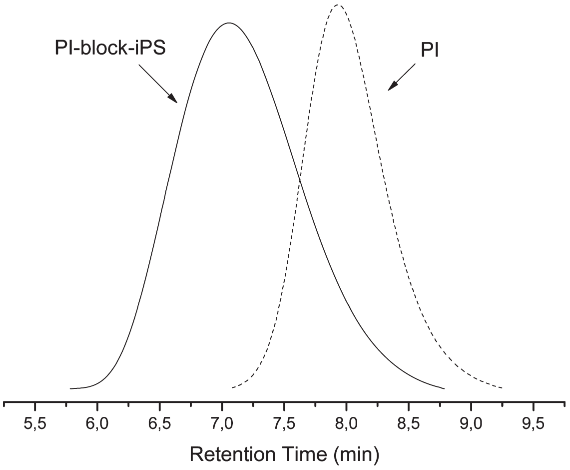


Figure 2. GPC traces of materials during a sequential isoprene−styrene copolymerization (entry 7, Table 3); dashed line: PI aliquot sampled before the addition of styrene (M_n = 16 000 g mol^{-1}, M_w/M_n = 1.6); solid line: the subsequent diblock copolymer PI-*b*-iPS.

PS and 1,4-*trans*-PI or 3,4-PI homosequences.[15b] On the other hand, Grassi et al. observed no melting temperature for styrene-*co*-isoprene multiblock copolymers made of sPS and 1,4-*cis*-PI homosequences, even in the samples having large contents of styrene.[16]

Although complex **1** is not a living catalyst for both isoprene and styrene polymerizations, the observed trend to form blocky materials in which the stereoselectivity of the catalyst vs the two monomers is retained, prompted us to explore the possibility to obtain unprecedented well-defined 1,4-*trans*-polyisoprene-*block*-isotactic polystyrene (1,4-*trans*-PI-*b*-iPS) copolymers. Sequential polymerizations were carried out at 60 °C, by leaving isoprene reacting the time necessary to reach complete monomer consumption before addition of styrene. Representative results are reported in Table 3.

Different copolymer samples were synthesized by changing the ratio between the two monomers in the feed, keeping constant the total monomers-to-catalyst ratio. Representative GPC traces of an aliquot of PI sampled from the reaction mixture before feeding with styrene and of the resulting diblock copolymer are shown in Figure 2. The shift of the traces that reflects the increase of the molecular weight and the monomodal molecular weight distribution with a value of 2, typical for a copolymer obtained from a single-site catalyst, are indicative of the formation of copolymer. The composition of the obtained diblock copolymers was determined by ^1H NMR spectra and found to reflect the composition in the monomers feed. The $^{13}C\{^1H\}$ NMR spectrum of the sample with an almost equimolar isoprene−styrene composition (χ_I = 0.465, χ_S = 0.535; entry 6, Table 3) is reported in Figure 1 (top) and shows the main signals for both highly iPS and 1,4-*trans*-PI blocks, together with less intense signals for isolated 3,4-isoprene units. Because of the high molecular weight of the formed copolymer, the signals for the isoprene−styrene junction between the two blocks were not detected. The thermal features of the resulting copolymers were investigated by means of DSC. The thermograms of the *trans*-PI-*b*-iPS copolymers revealed two glass transitions at T_g = −55 to −50 and 93−95 °C [sometimes difficulty detectable], as well as two endothermic peaks [observed in the first heating cycle] at

37–42 °C and 212–219 °C, indicative of the crystallinity of the 1,4-*trans*-PI and iPS blocks, respectively. This was observed in particular for the sample with an almost equimolar isoprene–styrene composition ($\chi_I = 0.465$, $\chi_S = 0.535$; entry 6, Table 3), in contrast to the aforementioned corresponding multiblock material ($\chi_I = 0.52$, $\chi_S = 0.48$; entry 2, Table 2) that featured a single T_m at an intermediary value of 139 °C. The observation of two melting transitions has been used previously to support the formation of iPS-*b*-1,4-*trans*-PBD by living stereospecific sequential copolymerization of styrene and butadiene using Okuda's dithiabisphenolate–titanium complexes.[18a]

CONCLUSION

The polymerization reactivity of *rac*-$\{Me_2C(Ind)_2\}Y(1,3\text{-}(SiMe_3)_2C_3H_3)$ (**1**) toward isoprene and isoprene–styrene mixtures has been investigated. The 1,4-*trans*-stereoselective polymerization of isoprene, with moderate activity, was observed. In combination with a chain transfer agent (CTA) such as $ZnEt_2$ or $Mg(nBu)_2$, **1** proved to be an efficient catalyst for the coordinative chain transfer polymerization (CCTP) of isoprene, leading to PIs with variable microstructures, ranging from highly 1,4-*trans*-PI to blocky 1,4-*trans*-*co*-3,4-PI, depending on the nature of the CTA.

Isoprene–styrene copolymers with a wide range of compositions (χ_S = 0.30–0.98) and the thus far unprecedented architecture 1,4-*trans*-PI-*co*-iPS were obtained via either sequential or simultaneous monomer copolymerization. The regio- and stereoselectivity of isoprene and the isotacticity of styrene polymerizations are indeed retained by catalyst **1** when the two monomers are copolymerized together. The estimated values of reactivity ratios, the ^{13}C NMR microstructural analysis and the DSC thermal characterization of the copolymers all indicate a blocky distribution of the two monomers in the copolymers prepared in a one-pot/one-step procedure. Well-defined 1,4-*trans*-PI-*b*-iPS diblock copolymers, prepared via sequential monomer addition, featured two crystalline blocks.

These results evidence the versatility of complex **1**, and further works will explore the potential of this catalyst system for stereospecific CCTP to prepare new materials with unprecedented molecular architectures.

EXPERIMENTAL SECTION

General Considerations. All manipulations of sensitive materials were carried out under an argon atmosphere using Schlenk or glovebox techniques. *rac*-$\{Me_2C(Ind)_2\}Y(1,3\text{-}(SiMe_3)_2C_3H_3)$ was synthesized according to the literature.[18] $Mg(nBu)_2$ (1.0 M solution in heptane, Aldrich), $ZnEt_2$ (1.0 M solution in hexanes, Acros), $Al(iBu)_3$ (neat, Aldrich), and $AlMe_3$ (1.0 M solution in heptane, Across) were used as received; the molarity of $Mg(nBu)_2$ solutions was regularly checked by titration with a solution of 2-butanol in toluene in the presence of phenantroline according to a literature protocol.[31] Isoprene (99%, Acros) and styrene (99%, Acros) were purified by distillation over calcium hydride under reduced pressure prior to use. Heptane was refluxed over sodium, distilled, and degassed thoroughly prior to use. The other solvents were used as received.

NMR spectra of the polymers were recorded on a AM-500 Bruker spectrometer at 298 K in $CDCl_3$ or $C_2D_2Cl_4$. A relaxation delay of 3 s was used during the acquisition to yield quantitative ^1H NMR spectra. The chemical shifts were referenced to hexamethyldisiloxane (HMDS) using the residual protio-solvent (^1H) or the carbon (^{13}C) resonance of the deuterated solvents. Molecular weights (M_n and M_w) and polydispersities (M_w/M_n) of polymers were determined by gel permeation chromatography (GPC) using a Polymer Laboratories PL-GPC 50 instrument equipped with a PLgel 5 Å MIXED-C column and a refractive index detector. The column was eluted with THF at 30 °C at 1 mL min^{-1} and was calibrated using 11 monodisperse PS standards (range of 580–380 000 g mol^{-1}). Differential scanning calorimetry (DSC) analyses were performed on a Setaram DSC 131 apparatus at a heating rate of 10 °C min^{-1} (unless otherwise stated), under a continuous flow of helium, using aluminum capsules. Melting temperatures were reported for the first heating cycle while glass transition temperatures were determined from the second cycle.

Polymerization of Isoprene. In a typical polymerization procedure, a 30 mL flask equipped with a magnetic stir bar was charged sequentially with **1** (21.7 mg, 40.0 μmol), isoprene (10.00 mL, 99.8 mmol) and, when required, the desired amount of chain transfer agent. The resulting yellow-orange solution was thermostated at 60 °C under vigorous stirring. After a given time period, the mixture was poured into acidified methanol (50 mL). When present, the polymers were recovered by filtration, washed with fresh methanol (20 mL), and dried at room temperature in a vacuum oven until constant weight.

Simultaneous Copolymerization of Isoprene and Styrene. In a typical polymerization procedure (Table 2, entry 2), a 50 mL flask equipped with a magnetic stir bar was charged sequentially with catalyst (21.7 mg, 40.0 μmol), isoprene (3 mL, 29.9 mmol), styrene (1.15 mL, 0.99 mmol), and heptane (4.0 mL). The resulting yellow-orange solution was thermostated at 60 °C under vigorous stirring. After a given time period, the mixture was poured into acidified methanol (60 mL). The polymers were recovered by filtration, washed with fresh methanol (20 mL) and dried at room temperature in a vacuum oven until constant weight.

Sequential Copolymerization of Isoprene and Styrene. In a typical polymerization procedure (Table 3, entry 6), a 50 mL flask equipped with a magnetic stir bar was charged sequentially with catalyst (21.7 mg, 40.0 μmol), isoprene (2.00 mL, 19.9 mmol), and heptane (2.0 mL). The resulting yellow-orange solution was thermostated at 60 °C under vigorous stirring. After a given time period (15 h), additional heptane (6.0 mL) and styrene (2.3 mL, 19.9 mmol) were added. After 1 h, the mixture was poured into acidified methanol (50 mL). The polymers were recovered by filtration, washed with fresh methanol (20 mL), and dried at room temperature in a vacuum oven until constant weight.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional NMR spectra; DSC and GPC analyses of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) The reactivity ratios were calculated by using the following equations: $r_1(1/f) = 2[\text{I—I}]/[\text{I—S}]$ and $r_2 f = 2[\text{S—S}]/[\text{S—I}]$, where f is the composition in the feed ($f = [\text{Ip}]/[\text{St}]$), and the mole fractions of the monomer diads I—I and S—S and of the heterodiads I—S in the copolymers were evaluated by integration of the appropriate ^{13}C NMR signals. For use of these equations in styrene—butadiene copolymerizations, see: (a) Ricciardi, R.; Napoli, M.; Longo, P. *J. Polym. Chem., Part A: Polym. Chem.* **2010**, *48*, 815 and refs 14b and 14c. For use of these equations in ε-caprolactone—lactide copolymerization, see: (b) Pappalardo, D.; Anunziata, L.; Pellecchia, C. *Macromolecules* **2009**, *42*, 5572.

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