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Highly Regio- and Stereoselective Terpolymerization of Styrene, Isoprene and Butadiene with Lutetium-Based Coordination Catalyst

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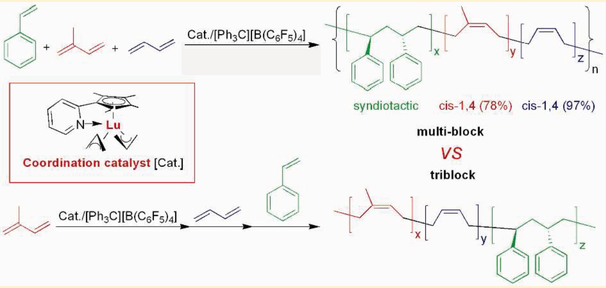
Supporting Information

ABSTRACT: By using the cationic lutetium allyl species $(C_5Me_4-C_5H_4N)Lu(\eta^3\text{-}C_3H_5)_2$ (**1**)/$[Ph_3C][B(C_6F_5)_4]$, the copolymerization of isoprene (IP) with styrene (St) could be achieved in a full range of monomer feed ratios (10 mol %−90 mol %). The ^{13}C NMR and DSC analyses, and the competitive polymerization ratios (r_{St} = 3.1 *vs* r_{IP} = 23.9) clearly revealed that the obtained IP−St copolymers were multiblocked microstructure with high *cis*-1,4-polyisoprene (PIP) units (80%) and crystalline syndiotactic polystyrene (sPS) sequences, which was in contrast to the copolymerization behavior of butadiene (BD) and St with the same system that afforded only diblock copolymer. Strikingly, the terpolymerization of St with IP and BD via coordination mechansim was realized for the first time with high conversions (74−85%) and high activities (111−144 kg $(mol_{Lu}\,h)^{-1}$). The ^{13}C NMR spectroscopic analysis indicated that the resultant terpolymers were composed of perfect sPS blocks, high *cis*-1,4-PIP units (77.7%) and almost pure *cis*-1,4-polybutadiene (PBD) sequences (97.5%) arranged in multiblocked mode. The insertion rate of styrene monomer in the terpolymer could be tuned swiftly by changing its feed ratio. DSC curves suggested that these multiblock terpolymers had continuously variable but single T_g and (or) T_m values, which was different from the triblock IP−BD−St terpolymer having two distinct T_g values (−105 and −57 °C) and one high T_m value (265 °C). Such novel terpolymers could not be accessed by any other methods known to date.



INTRODUCTION

With the human society moving into the twenty-first century, the burden of source shortage and environment pollution becomes more and more heavier. Therefore, low-carbon release, environmental benigness, and energy saving have become effective strategies for the sustainable development of the international economy. In particular, for the rubber industry, many modifications have been implemented in recent years to make the motor vehicles more energy efficient, among which the green tire first proposed by Michelin in the 1990s is most promising, as it features safety, long service life, low fuel consumption, and environmental protection due to its excellent properties: low rolling resistance and good wear resistance (correlated with flexibility of macromolecular chains of a rubber) and a strong wet grip (corresponding to the rigidity of macromolecular chains of a rubber). Henceforth, many efforts have been devoted to explore high-performance rubbers such as high *cis*-1,4 regulated polydiene rubbers, natural rubber (NR) and styrene−butadiene rubber (SBR), *etc.*, to satisfy the integral property requirements of the green tire.[1,2] Hitherto, however, there is no escaping acceptance of the sad facts: on the basis of the available general purpose rubbers, it is not possible to fulfill simultaneously all the requirements for green tire; while improvement of one property seems possible only at sacrifice of the others, which is called "devil triangle".[2] To balance the "devil triangle", physical blending BR and NR and SBR has also been attempted[3a,b] to give a macroscopically homogeneous polymer blend that unfortunately exists serious microphase separation, which usually does not benefit for exerting the synergetic effects[4] of the three individual rubbers.

A terpolymer of styrene−isoprene−butadiene (SIBR), namely integral rubber, introduced by Nordsiek in 1984,[2] integrates chemically the excellent properties of SBR, BR and NR together, anticipated to serve as one of the most suitable high-performance rubber potentially applied in the green tire owing to its random macromolecular chain structure: the highly *cis*-1,4 regulated polybutadiene segments are flexible providing necessary elasticity and excellent abrasion resistance and low rolling resistance; while the *cis*-1,4-polyisoprene units having the same microstructure as that of NR give outstanding low temperature performance

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and processability and low hysteresis; the rigid polystyrene sequences afford excellent skid resistance and braking behavior.[2,3,5] To date the synthesis of SIBR can be achieved only by anionic terpolymerization of styrene (St), isoprene (IP) and butadiene (BD) with alkyllithium initiators.[3a] Since the carboanion of initiator has a very open configuration, which offers similar probability of *cis*-1,4 and *trans*-1,4 and 1,2- (or 3,4-) addition of the monomers and therefore leads to uncontrolled regio- and stereoselective copolymers. In particular, as the relative polymerization activity of these monomers follows a trend of BD > IP ≫ St,[3a] the anionic terpolymerization usually affords a diblock copolymer of PBD-*b*-(PIP-*co*-PS) or (PBD-*co*-PIP)-*b*-PS. Since the control of monomer sequence distribution in polymers is an important subject. In order to reduce the difference among the monomer activities to obtain random terpolymer with tunable composition and controllable monomer sequence distribution, some methods are usually adopted: addition of an electron donor to the polymerization system to interrupt the aggregation of alkyllithium active species, addition of a chain transfer agent, varing the polarity of the solvent, or raising the polymerization temperature.[6] Nevertheless, this will arouse the 1,2- or 3,4- or *trans*-1,4- regularity more higher in the polydiene sequences of the resultant SIBR and the formation of gel, which reduce flexibility of the molecular chains and hurt the physical properties of SIBR such as rolling resistance and traction.[3a]

On the other hand, the coordination catalysts especially those based on rare-earth metals have superiority on control of regio- and stereomicrostructure of polymers, some of which have been extensively investigated for the (co)polymerizations of 1,3 conjugated dienes such as BD and IP with high activity and excellent *cis*-1,4 selectivity (up to 99%).[7] Noteworthy is that most of the above-mentioned excellent catalysts show low or even no activity toward styrene polymerization. Fortunately some transition metal and other rare-earth metal based coordination catalysts have been abundantly reported to easily catalyze the copolymerizations of St−BD[8] and St−IP[9] to prepare high impact PS resin or high strength rubbers, although they provided enriched *cis*-1,4 or *trans*-1,4 or 3,4- regio-selectivities in the polydiene units. To date, however, neither of such a large number of coordination catalysts was reported to expand to the scope of the St−IP−BD terpolymerization due to the differences of St and IP and BD in activity and structure. Therefore, the terpolymerization of St with IP and BD via coordination mechanism is a challenging but promising project.

During our recent studies on linked-half-sandwich rare-earth metal coordination catalysts,[10] we found that a cationic pyridyl−cyclopentadienyl lutetium allyl species generated from (C_5Me_4−C_5H_4N)Lu(η^3-C_3H_5)$_2$(**1**)/[Ph_3C][$B(C_6F_5)_4$] displayed the dual catalysis on both *cis*-1,4 selective polymerization of BD and syndiospecific polymerization of St, which provided PBD-*b*-PS diblock copolymer no matter if it was by sequential polymerization or "one-pot" polymerization.[10a] Herein, we report that, by using this cationic lutetium allyl species, the copolymerization of IP with St can be achieved to give either multiblock or diblock IP−St copolymers with *cis*-1,4-PIP units and crystalline syndiotactic polystyrene (sPS) sequences. Strikingly, this cationic species has been also used for the terpolymerization of St with IP and BD for the first time. The resultant terpolymers have well-defined architectures that combine the sPS blocks, high *cis*-1,4 PIP units and almost pure *cis*-1,4 PBD sequences. This represents the first St−IP−BD terpolymerization achieved by coordination catalyst, and in particular, with excellent control over the regio- and stereoregularity as well as the composition.

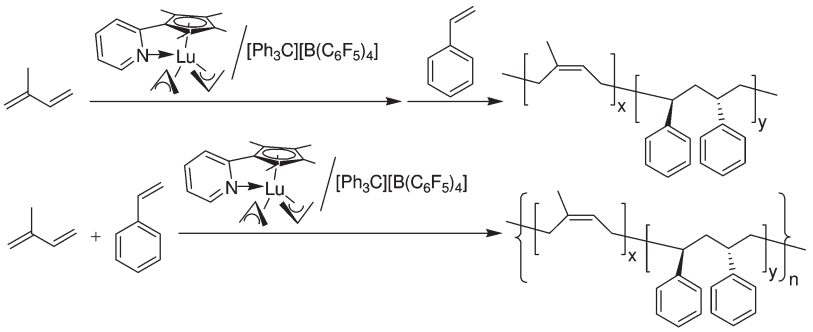
RESULTS AND DISCUSSION

Homopolymerization of Isoprene and Copolymerization of Isoprene with Styrene. In the presence of **1**/[Ph_3C]-[$B(C_6F_5)_4$] in toluene at 20 °C, the polymerization of IP took place rapidly (Table 1, runs 1−4). With the increase of the monomer-to-catalyst ratio, the molecular weight of the resulting polymer increased linearly and the molecular weight distribution remained within a narrow range (M_w/M_n = 1.05−1.10), suggesting a livingness mode of the polymerization. In comparison with the BD and St polymerization results reported recently,[10a] we came to conclude that the activity of the three monomers followed the order of BD > St > IP, in consistence with that established by Ti-based catalyst systems.[9b,f] Furthermore, the ^{13}C NMR and DSC analyses of the obtained PIP revealed a prevailing *cis*-1,4 microstructure (80.8%) identified by giving strong resonances at 23.37, 26.29, and 32.09 ppm,[11] and a T_g at −53 °C, respectively.

Taking the benefit of the excellent livingness of the polymerization of IP with this catalytic system, the sequential addition of St to the system afforded the corresponding IP−St diblock copolymer selectively (Table 1, run 5). GPC curve of the copolymer without extraction was monomodal with narrow molecular weight distribution (M_w/M_n = 1.29) (Figure 1), indicative of true diblock copolymer, which was further confirmed by solvent extraction experiment. For example, we found that this copolymer was insoluble in THF at room temperature, excluding the existence of PIP and atactic PS; whilst this copolymer was also insoluble in acetone by refluxing. The ^{13}C NMR spectrum of the copolymer sample exhibits strong and sharp singlets at 145.12 (*ipso*-Ph, sPS), 43.44 ($S_{\alpha\alpha}$, methylene), 40.35 ($T_{\beta\beta}$, methine) ppm attributed to the syndiotactic (*rrrr* > 99%) PS block,[12] and resonances at 32.05, 26.25, 23.36 ppm arising from the *cis*-1,4 regulated PIP block (80.5%).[11] In addition, the copolymer showed a T_g at −54 °C and a melting point (T_m) at 268 °C originating from the high *cis*-1,4 PIP block and crystalline sPS block, respectively.

In order to explore whether the copolymerization of IP and St could be accessed, both monomers were mixed in toluene at 20 °C under the St feed molar fraction varying from 10 mol % to 90 mol %. All these copolymerizations went smoothly with high activities to afford multiblock IP−St copolymers with moderate molecular weights (M_n = (1.3−8.2) × 10^4) and molecular weight distributions (M_w/M_n = 1.41−1.95) (Table 1, runs 6−10). Correspondingly the St content (x_S) in these copolymers varied from 6.1 mol % up to 83.0 mol % with the St feed fractions albeit slightly lower. The monomer competitive polymerization ratios were deduced from the Fineman−Ross plot to be r_{St} = 3.1 and r_{IP} = 23.9 (Figure 2),[13] respectively, suggesting that both St−St sequences and IP−IP sequences were preferred to form in the copolymerization. The high product ($r_{St}r_{IP}$ = 74.1) of the reactivity ratios certainly revealed multiblocked microstructure of the resultant IP−St copolymers.[9g] The ^{13}C NMR spectrum of a representative copolymer (Table 1, run 8, x_S = 48.0 mol %) displayed strong singlets at 145.13, 43.44, and 40.36 ppm and the resonances at 32.05, 26.25, 23.36 ppm arising from the sPS blocks and *cis*-1,4-PIP blocks, respectively (Figure 3). Noteworthy was that the T_m values of these multiblock copolymer was obviously lower than that of the aforementioned IP−St diblock

Table 1. Copolymerization of Isoprene (IP) with Styrene (St) Catalyzed by $(C_5Me_4\text{-}C_5H_4N)Lu(\eta^3\text{-}C_3H_5)_2$ $(1)/[Ph_3C][B(C_6F_5)_4]$[a]



run	St fed [mol %]	t [min]	convn [%]	activity[b]	St found[c] [mol %]	microstructure[c] cis-1,4 [%]	trans-1,4 [%]	3,4 [%]	M_n[d] [10^4]	M_w/M_n[d]	T_g[e] [°C]	T_m[e] [°C]
1[f]	0	15	100	136	0	80.8	6.3	12.9	4.6	1.07	−53	–
2[g]	0	30	100	136	0	80.3	7.0	12.7	9.0	1.05	−51	–
3[h]	0	30	100	272	0	80.0	7.0	13.0	17.8	1.10	−52	–
4[i]	0	15/15	100	136	0	80.6	6.6	12.8	9.1	1.09	−52	–
5[j]	50	15/5[k]	100	66	50.0	80.5	9.2	10.3	3.9	1.29	−54	268
6	10	30	94	134	6.1	79.7	8.1	12.2	1.3	1.68	−55	–
7	20	30	81	122	10.5	78.3	9.8	11.9	3.0	1.86	−50	–
8	60	30	67	120	48.0	75.4	14.6	10.0	8.2	1.41	–	240
9	80	30	61	118	71.4	71.2	19.7	9.1	6.4	1.67	–	243
10	90	30	44	88	83.0	68.5	26.9	7.6	5.3	1.95	–	246

[a] Polymerization conditions: Lu (10 μmol); [Lu]/[B] = 1/1 (mol/mol); toluene (5 mL); [IP + St]/[Lu] = 1000/1 (mol/mol); T_p = 20 °C, unless otherwise noted. [b] Given in kg of polymer $(\text{mol}_{Lu}\ h)^{-1}$. [c] Measured by ^1H and ^{13}C NMR spectra in $C_2D_2Cl_4$. [d] Determined by GPC in THF at 40 °C against polystyrene standard for polyisoprene and in 1,2,4-trichlorobenzene at 150 °C against polystyrene standard for copolymers. [e] Determined by DSC. [f] [IP]/[Lu] = 500/1 (mol/mol). [g] [IP]/[Lu] = 1000/1 (mol/mol). [h] [IP]/[Lu] = 2000/1 (mol/mol). [i] After polymerization of 0.34 g (500 equiv) of IP for 15 min, another 0.34 g (500 equiv) of IP was added and the mixture was stirred for a further 15 min. [j] Sequential copolymerization: 0.085 g (125 equiv) of IP was added first followed by St (0.13 g, 125 equiv). [k] Sequential polymerization time.

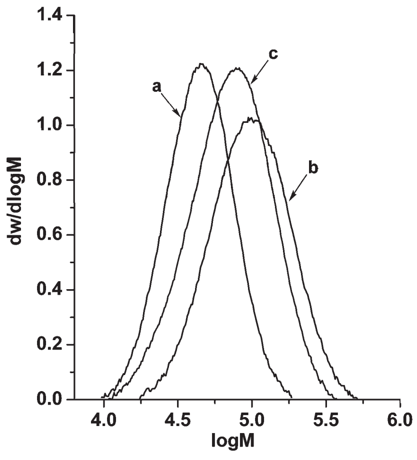


Figure 1. (a) IP−St diblock copolymer (x_S = 50.0 mol %, Table 1, run 5), (b) IP−St multiblock copolymer (x_S = 48.0 mol %, Table 1, run 8), and (c) St−IP−BD multiblock terpolymer (x_S = 36.6 mol %, Table 2, run 5).

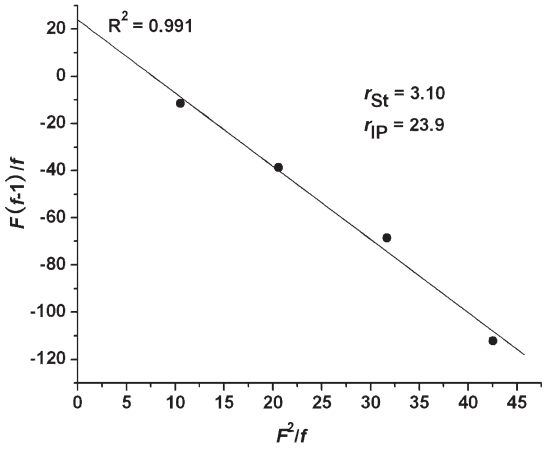


Figure 2. Finemann−Ross plot for the copolymerization of IP and St with $1/[Ph_3C][B(C_6F_5)_4]$ at 20 °C and least-squares best-fit line (F = [St]/[IP] in feed, f = [St]/[IP] in copolymer).

copolymer,[8b,d,9f,9g] which became invisible when the St content was lower than 10.5 mol %. Meanwhile no T_g could be observed when the IP content was lower than 52.0 mol %.[8d,9g] Thus, we demonstrated that by means of a cationic lutetium coordination catalyst, a new family of IP−St diblock and multiblock copolymers comprising flexible *cis*-1,4-PIP blocks and crystallizable sPS blocks has been obtained for the fist time, as far as we are aware.

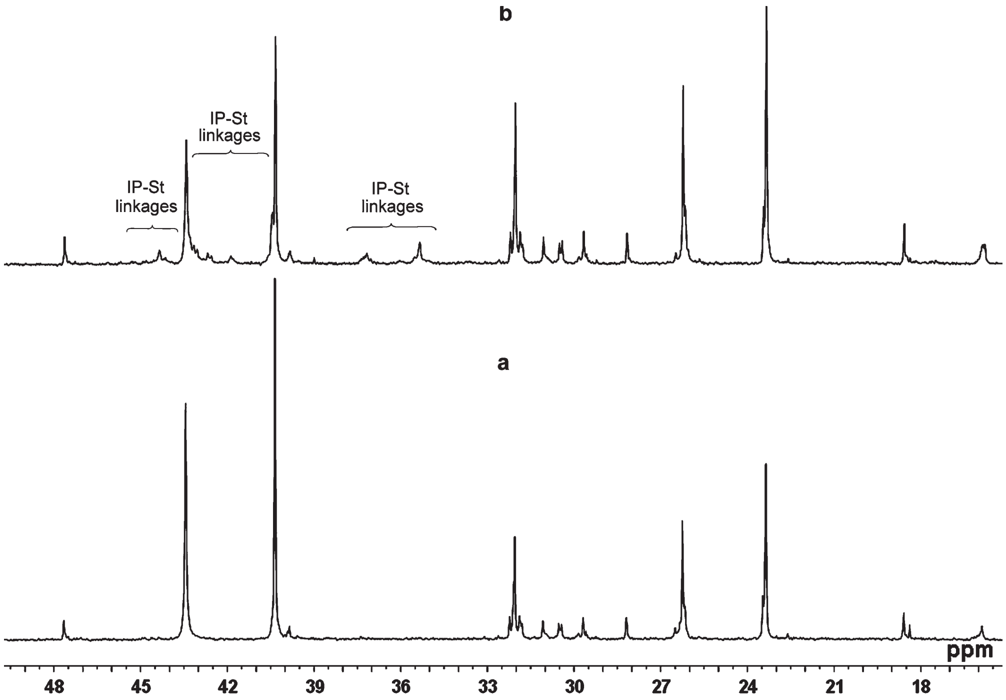


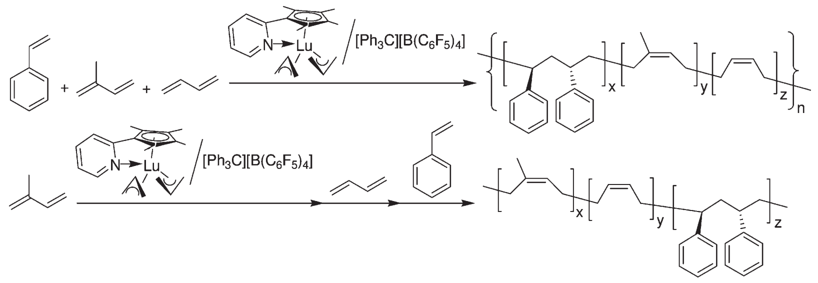
Figure 3. Aliphatic region of the ^{13}C NMR spectra ($C_2D_2Cl_4$, 25 °C): (a) IP−St diblock copolymer (x_S = 50.0 mol %, Table 1, run 5) and (b) IP−St multiblock copolymer (x_S = 48.0 mol %, Table 1, run 8).

Terpolymerization of Styrene with Isoprene and Butadiene. Intrigued by the above results, the terpolymerization of St with IP and BD was carried out by "one-pot" in toluene at 20 °C under different St/IP/BD feed ratios. Delighted to us, the terpolymerizations performed successfully and completed with high conversions (74−85%) in high activities 111−144 kg $(\mathrm{mol_{Lu}\ h})^{-1}$ to give terpolymers selectively. Solvent fractionation experiment revealed that the impurities were negligible. All the GPC traces of the isolated crude terpolymers were monomodal (M_n = (4.8−8.8) × 10^4) and the molecular weight distribution remained within a narrow range (M_w/M_n = 1.32−1.50) (Figure 1). The composition of the terpolymer could be adjusted swiftly by changing the St/IP/BD feed ratios, although under the same monomer feed ratio the incorporation rate of St was slightly lower than those of BD and IP owing to its slow competitive rate (Table 2, runs 2−6). In fact we could readily prepare a family of terpolymers with designed St or IP or BD contents to satisfy the requirment of versatile material.

More importantly, we concerned very much about the microstructures of the obtained terpolymers. The ^{13}C NMR spectrum of a chosen terpolymer sample (Table 2, run 4, x_S = 35.5 mol %) is shown in Figure 4, which gives strong singlets at 145.13, (**33**) 43.44, and (**26**) 40.36 ppm,[12] suggesting the presence of syndiotactic St−St blocks. Meanwhile the intense resonances at (**21**) 32.05, (**7**) 26.25, (**3**) 23.36 ppm (*cis*-1,4, 75.2%), (**25**) 39.85, (**9**) 26.50, (**1**) 15.88 ppm (*trans*-1,4), (**36**) 47.66, (**18**) 29.69, (**2**) 18.59 ppm (3,4-), and (**17**) 28.19, (**19**) 30.43 ppm are assignable to the PIP units,[11] and those resonances at (**11**) 27.27 ppm (*cis*-1,4, 96.8%) and (**22**) 32.54 ppm (*trans*-1,4)[14] for the PBD segments are also detected. More remarkably, we can observe signals at (**35**) 44.38, (**34**) 44.16, (**32**) 43.19, (**31**) 43.07, (**30**) 42.70, (**29**) 42.57, (**28**) 41.89, (**27**) 40.45, (**24**) 37.20, (**23**) 35.36, (**8**) 26.36, and (**6**) 26.07 ppm originating from the linkages of PIP with PS;[9f] the very weak signals at (**13**) 27.36, (**12**) 27.33 and (**4**) 25.04 ppm are attributed to the corresponding joints of PBD and PS;[8f] the intense resonances at (**20**) 31.73, (**16**) 27.85, (**15**) 27.63, (**14**) 27.57, (**10**) 27.22 and (**5**) 25.70 ppm are assignable to the PIP and PBD connections[7i] that also show up in the ^{13}C NMR spectrum of IP−BD random copolymer (Table 2, run 1; see Supporting Information). All these data suggested that the terpolymerization performed in precisely regio- and stereocontrolled manner to yield multiblock St−IP−BD terpolymer with crystalline syndiotactic St−St blocks, moderate *cis*-1,4 (up to 77.7%) PIP sequences and high *cis*-1,4 (up to 97.5%) PBD units. In consistence with the multiblocked microstructure, all the terpolymers had single T_g and (or) T_m. The T_g value increased with the decrease of BD/IP feed ratios (Figure 5); while the T_m value dropped reasonably with the decrease of St feed fraction and the peak of T_m disappeared when the St content in terpolymer was 18.2 mol % (Table 2, runs 2−6).[9f,g,10a]

To confirm further that the microstructure of above-mentioned terpolymers was multiblock not triblock, the sequential terpolymerization of IP, BD and St was performed, which yielded the corresponding ABC-type triblock copolymer selectively (Table 2, run 7). This terpolymer was insoluble in THF at room temperature, excluding the existence of PIP, PBD, and atactic PS. Its ^{13}C NMR spectrum (Figure 4) exhibits strong and sharp singlets at 145.12, 43.45, and 40.36 ppm assigned to the sPS block (*rrrr* > 99%) that gives a T_m at 265 °C; the *cis*-1,4 (80.1%) PIP block shows chemical shifts at 32.06, 26.25, and 23.37 ppm corresponding to a T_g value at −57 °C; the overwhelming strong resonance at 27.27 ppm is attributed to the highly *cis*-1,4 (95.9%) PBD block in consistence with the very low T_g value of −105 °C. No signals for the junctions between PIP and PS and PBD were detectable. Such a highly regio- and stereoselective triblock terpolymer, *cis*-1,4-PIP-*b*-*cis*-1,4-PBD-*b*-sPS, was unprecedented, to the best of our knowledge, which was a solid proof for our successful synthesis of highly regio- and stereoregulated St−IP−BD multiblock terpolymers.

Table 2. Terpolymerization of Styrene (St) with Isoprene (IP) and Butadiene (BD) Catalyzed by $(C_5Me_4{-}C_5H_4N)Lu(\eta^3\text{-}C_3H_5)_2$ (1)/$[Ph_3C][B(C_6F_5)_4]$[a]



run	St/IP/BD in feed[b] [10^{-5} mol]	t [min]	conv. [%]	act.[c]	St/IP/BD in terpolymer[d] [mol %]	microstructure[d] *cis*-1,4 [%] in PIP	*cis*-1,4 [%] in PBD	M_n[e] [10^4]	M_w/M_n[e]	T_g[f] [°C]	T_m[f] [°C]
1	0/500/500	30	100	122	0.0/50.0/50.0	80.2	97.1	3.8	1.19	−80	–
2	125/125/125	10	85	144	31.3/35.2/33.5	74.3	97.0	4.8	1.39	−84	243
3	125/250/250	20	85	111	18.2/41.7/40.1	77.7	97.5	6.2	1.50	−85	–
4	250/250/125	20	74	111	35.5/43.6/20.9	75.2	96.8	5.9	1.47	−72	250
5	250/125/250	20	79	114	36.6/22.8/40.6	73.8	97.0	6.5	1.46	−91	251
6	250/250/250	20	78	132	29.4/35.0/35.6	74.5	97.0	8.8	1.32	−81	242
7[g]	250/250/250	40/10/10	81	46	23.0/38.5/38.5	80.1	95.9	6.6	1.66	−105, −57	265

[a] Polymerization conditions: Lu (10 μmol); [Lu]/[B] = 1/1 (mol/mol); toluene + styrene + isoprene + butadiene =5 mL; T_p = 20 °C, unless otherwise noted. [b] Molar ratio to Lu. [c] Activity: given in kg of polymer $(\text{mol}_{Lu}\ h)^{-1}$. [d] Measured by ^{1}H and ^{13}C NMR spectra in $C_2D_2Cl_4$. [e] Determined by GPC in THF at 40 °C against polystyrene standard for IP−BD random copolymer and in 1,2,4-trichlorobenzene at 150 °C against polystyrene standard for terpolymers. [f] Determined by DSC. [g] Sequential terpolymerization: 0.17 g (250 equiv) of IP was first polymerized for 40 min, then 0.135 g (250 equiv) of BD was added and the mixture was stirred for 10 min, finally 0.26 g (250 equiv) of St was added and the polymerization reaction was stirred for a further 10 min.

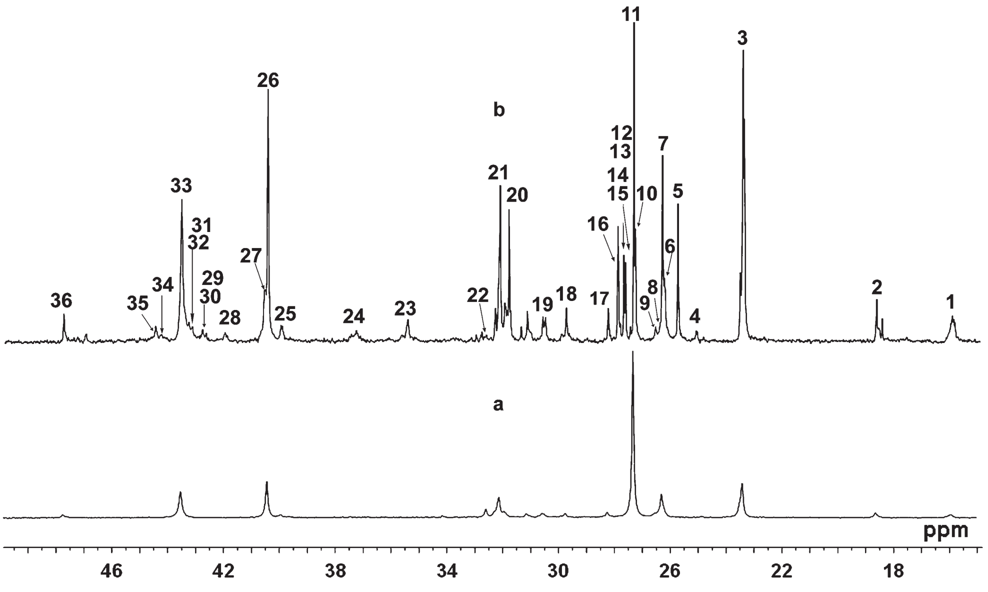


Figure 4. Aliphatic region of the ^{13}C NMR spectra ($C_2D_2Cl_4$, 25 °C): (a) IP−BD−St triblock terpolymer (x_S = 23.0 mol %, Table 2, run 7) and (b) St−IP−BD multiblock terpolymer (x_S = 35.5 mol %, Table 2, run 4).

■ CONCLUSIONS AND PERSPECTIVES

In summary, we have demonstrated that by means of a cationic linked-half-sandwich lutetium-based coordination catalyst, the terpolymeization of styrene−isoprene−butadiene has been successfully accomplished by "one-pot" for the first time. The resultant terpolymer is multiblocked, in which the PS blocks are highly syndiotactic and crystallizable and both the PIP and PBD segments are highly flexible *cis*-1,4 regulated, in striking contrast to that prepared by anionic polymerization. Morever, the composition of these terpolymers can be adjusted facilely by changing

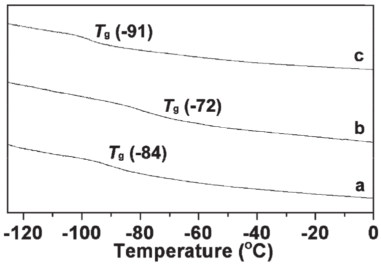


Figure 5. DSC curves of the St−IP−BD multiblock terpolymer: (a) x_{BD} = 33.5 mol % (Table 2, run 2), (b) x_{BD} = 20.9 mol % (Table 2, run 4), and (c) x_{BD} = 40.6 mol % (Table 2, run 5).

the monomer feed ratios without addition of extra electron donor, or addition of a chain tranfer, or raising the polymerization temperature, or varing the polarity of the solvent, which results in variable glass transition temperatures and melting points of the obtained terpolymers. Such novel terpolymers could not be obtained with any other coordination catalysts so far. Further works will focus on the study of the mechanical aspect of these terpolymers to explore whether they can open the door to potentially generate a new type of "integral rubber".

■ EXPERIMENTAL SECTION

General Procedures and Materials. All manipulation were performed under a nitrogen atmosphere using standard Schlenk techniques or a MBraun glovebox. Toluene was distilled from sodium/benzophenone under nitrogen and degassed thoroughly prior to use. Styrene (Aldrich) and isoprene (Aldrich) were dried over CaH_2 under stirring for 48 h and distilled under reduced pressure before use. Polymerization grade 1,3-butadiene was dried by passing through a column filled with activated molecular sieves (4 Å) and then dissolved in toluene at −30 °C. $[Ph_3C][B(C_6F_5)_4]$ was synthesized following the literature procedures.[15]

Typical Procedure for Isoprene Homopolymerization. A detailed polymerization procedure (Table 1, run 2) is described as a typical example. In a glovebox, 4.6 mg of complex **1** (10 μmol) was dissolved in 5 mL of dry and degassed toluene. Then 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μmol) was added under stirring to give a pale yellow solution. After a few minutes, isoprene (0.68 g, 10 mmol) was added and the reaction was carried out at 20 °C for 30 min to generate a viscous solution. The reaction was then terminated by the addition of a small amount of acidic methanol containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as an antioxidant reagent. The resulting polymer was poured into a large quantity of methanol and then dried under vacuum at room temperature to a constant weight (0.68 g, 100%).

Typical Procedure for Block Copolymerization of Isoprene with Styrene. A typical block copolymerization reaction is given as follows (Table 1, run 5). In the glovebox, a toluene solution (2 mL) of $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μmol) was added to a toluene solution (3 mL) of complex **1** (4.6 mg, 10 μmol) in a 25 mL flask. The mixture was stirred at 20 °C for a few minutes, and isoprene (0.085 g, 1.25 mmol) was first added under vigorous stirring. After 15 min of polymerization, styrene (0.13 g, 1.25 mmol) was then added to the polymerization solution. The copolymerization continuously proceeded for an additional 5 min and then was terminated by the addition of a small amount of acidic methanol containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as an antioxidant reagent. The mixture was poured into methanol (200 mL) to precipitate the copolymer product. The copolymer was collected by filtration, and dried under vacuum at 40 °C to a constant weight (0.215 g, 100%).

Typical Procedure for Copolymerization of Isoprene and Styrene. A typical copolymerization reaction is given below (Table 1, run 8). In the glovebox, a toluene solution (2 mL) of $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μmol) was added to a toluene solution (3 mL) of complex **1** (4.6 mg, 10 μmol) in a 25 mL flask. The mixture was stirred at 20 °C for a few minutes, and then the mixture of 0.624 g (6 mmol) of styrene and 0.272 g (4 mmol) of isoprene was added under vigorous stirring. After 30 min, the reaction was terminated by the addition of a small amount of acidic methanol containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as an antioxidant reagent. The mixture was poured into methanol (200 mL) to precipitate the copolymer product. The copolymer was collected by filtration, and dried under vacuum at 40 °C to a constant weight (0.60 g, 67%).

Typical Procedure for Tercopolymerization of Styrene with Isoprene and Butadiene. A typical terpolymerization reaction is given below (Table 2, run 4). In the glovebox, a toluene solution (2 mL) of $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μmol) was added to a toluene solution (2 mL) of complex **1** (4.6 mg, 10 μmol) in a 25 mL flask. The mixture was stirred at 20 °C for a few minutes, and the mixture of 0.26 g (2.5 mmol) of styrene and 0.17 g (2.5 mmol) of isoprene and 0.0675 g (1.25 mmol) of butadiene was added under vigorous stirring. After 20 min, the reaction was terminated by the addition of a small amount of acidic methanol containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as an antioxidant reagent. The mixture was poured into methanol (200 mL) to precipitate the terpolymer product. The terpolymer was collected by filtration, and dried under vacuum at 40 °C to a constant weight (0.37 g, 74%).

Typical Procedure for Block Terpolymerization of Isoprene with Butadiene and Styrene. A typical triblock terpolymerization reaction is given as follows (Table 2, run 7). In the glovebox, a toluene solution (2 mL) of $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μmol) was added to a toluene solution (2 mL) of complex **1** (4.6 mg, 10 μmol) in a 25 mL flask. The mixture was stirred at 20 °C for a few minutes, and isoprene (0.170 g, 2.5 mmol) was first added under vigorous stirring. After 40 min of polymerization, butadiene (0.135 g, 2.5 mmol) was then added to the polymerization solution. The polymerization continuously proceeded for an additional 10 min and finally styrene (0.26 g, 2.5 mmol) was added to the polymerization solution. After 10 min of polymerization, the polymerization was terminated by the addition of a small amount of acidic methanol containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as an antioxidant reagent. The mixture was poured into methanol (200 mL) to precipitate the copolymer product. The terpolymer was collected by filtration, and dried under vacuum at 40 °C to a constant weight (0.458 g, 81%).

Characterization. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polyisoprene and IP−BD random copolymer were measured by a TOSOH HLC-8220 GPC with THF as eluent at 40 °C. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of copolymers and terpolymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220 type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 °C. 1,2,4-trichlorobenzene (TCB), containing 0.05 w/v % 2,6-di-*tert*-butyl-*p*-cresol (BHT) was employed as the solvent at a flow rate of 1.0 mL min^{-1}. The calibration was made by polystyrene standard Easi Cal PS-1 (PL Ltd.).

The ^1H NMR and ^{13}C NMR spectra of polyisoprene, copolymers and terpolymers were recorded on a Bruker AV600 (FT, 600 MHz for ^1H; 150 MHz for ^{13}C) spectrometer in $C_2D_2Cl_4$ at 25 °C.

T_g or T_m of polyisoprene and isoprene−styrene copolymers were measured through DSC analyses, which were carried out on a Q 100 DSC from TA Instruments under nitrogen atmosphere at a heating and cooling rates of 10 °C/min (temperature range: −80 to +300 °C). T_g or T_m of terpolymers were measured through differential scanning calorimetry (DSC) analyses, which were carried out on a Perkin−Elmer

Diamond differential scanning calorimeter at a heating and cooling rates of 10 °C/min (temperature range: −140−150 °C) and on a Q 100 DSC from TA Instruments under nitrogen atmosphere at a heating and cooling rates of 10 °C min^{-1} (temperature range: −80−300 °C).

Wide-angle X-ray diffraction (WAXD) patterns of copolymer and terpolymer samples in the range 2θ = 4°−40° were obtained with an automatic Philips instrument using the nickel-filtered Cu Kα radiation.

■ ASSOCIATED CONTENT

S Supporting Information. ^{1}H and ^{13}C NMR spectra, DSC curves, and WAXD spectra for selected copolymers and terpolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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