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Chain Transfer to Toluene in Styrene Coordination Polymerization

Fei Lin,[a,b] Zhaohe Liu,[a,b] Meiyan Wang,[c] Bo Liu,[a] Shihui Li*[a] and Dongmei Cui*[a,b]

Abstract: Chain transfer reaction is rather important in coordination polymerization regarding to catalytic efficiency, adjustment of molecular weight and control of chain structure. To date, chain transfer to H_2, Al-, Mg- and Zn alkyl compounds and *β*-H elimination are the commonly encountered modes. We report herein a novel chain transfer to toluene. By introducing fluorine atoms into the *β*-diketimine ligands, an inert catalytic system for styrene (St) coordination polymerization was transferred into the highly active one. The activity increased with the increase of fluorine number in the ligands. Surprisingly, the molecular weights of resultant polystyrenes are very low (M_n = 2000 – 6600 Da) despite of St loadings, corresponding up to 121 chains per active species. The mechanisms were investigated by DFT simulation, MALDI-TOF MS, isotope tracing experiment and 2D NMR spectrum analyses, which revealed that the fluorine activated the polymerization and directed chain transfer to toluene.

Polystyrene (PS), one of the most widely used plastics, can be fabricated by radical, ionic or coordination polymerization. For the past decades, in order to endow PS with versatile physical properties, extensive investigations have been paid to innovate organometallic catalysts to control PS microstructures,[1] such as the groups 3 and 4 metallocenes,[2] half-metallocenes[3] constrained-geometry-configuration(CGC) complexes.[4] Comparatively, complexes anchoring non-cyclopentadienyl ligands are less promising. Except the highly active and specific selective titanium catalysts attached to bis-phenolate ligands,[5] those bearing acetylacetonate[6] and Schiff-base[7] ligands show low activities. We reported very recently that the rare-earth metal complexes attached to quinolyl aniline ligands exhibit low activities[8] while those bearing *β*-diimine ligands are completely inert although they can be activated by polar *ortho*-methoxystyrene monomers.[9] Therefore, to unveil the dilemma of resembling η^5-coordination mode of the non-Cp ligands is a rather challenging topic.

On the other hand, chain transfer to monomer, initiator and some solvents usually happen in free radical and cationic polymerizations, which are less controllable and considered as side reactions. On contrary, chain transfer in a coordination polymerization displays various advantages over the single-component catalytic systems, which is requisite regarding to adjust molecular weight, functionalize chain end and form multi-blocked or topological chain structures. From application viewpoint, chain-transfer is a key factor to evaluate whether a catalyst can be industrialized, since it is beneficial to the precious metal-based catalysts by propagating more chains from one metal center. Thus, chain transfer in coordination polymerization has gathered an upsurge in research interest in the past decades such as *β*-H elimination, or addition of H_2 or Al-, Mg- and Zn alkyl compounds for some properly designed organometallic precursors.[10] However, chain transfer to toluene is rather rare, because toluene is usually inert in a polymerization process and widely used as the reaction medium, although toluene can be transferred to important industrial chemicals via C-H activation by using the late transition metal catalysts.[11] Recently, a progress had been made on developing anisole as chain transfer agent in St coordination polymerization by using the cationic half-sandwich rare-earth metal complexes.[12] To date, the only chain transfer to toluene was reported by Busico group in 2016 for propylene polymerization using Cp-phosphinimide Ti catalysts.[13] The chain transfer follows radical mechanism: homolysis of Ti-C bond arouses polypropenyl radical to abstract benzylic proton; the obtained benzyl radical combines with Ti cationic species to initiate propylene coordination polymerization. Thus, chain transfer to solvent in coordination polymerization is still an open research area.

Herein, we report a series of newly designed rare-earth complexes chelating to fluorine substituted *β*-diketimine ligands, which, surprisingly, display high activity for St polymerization, contrary to their completely inert analogues without fluorine substituent. More strikingly, the unprecedented chain-transfer to toluene has been achieved to afford very low molecular weight PS that are important coatings and additives. This work provides a new avenue of transferring inert systems to active ones and an unprecedented method of fabricating oligomers via chain-transfer to solvent, which refreshes the coordination chemistry.

We reported previously CGC complexes (Py-CH_2-Flu)Ln(CH_2SiMe_3)$_2$(THF)$_n$ catalyze highly efficient (co)polymerizations of styrene[14] and its derivatives.[15] Whilst the non-Cp *β*-diketimine stabilized precursors (BDI)Ln(CH_2SiMe_3)$_2$(THF) (Ln = Sc, Y, Lu) are completely inert.[9] Therefore, we designed a series of electron-withdrawing *β*-diketimine ligands containing different fluorine substituents (**a**-**e**) (Scheme 1). Straightforward metathesis reaction between Sc(CH_2SiMe_3)$_3$(THF)$_2$ and **a**-**e**, respectively, afforded scandium complexes **1**-**5**. X-ray diffraction analyses revealed the overall molecular structure of **1**-**5** is a THF solvated monomer (Figures S1-S5 and Table S1). Noticeably, with the fluorine number increasing, the methylene carbon resonances of CH_2SiMe_3 shift obviously downfield from 41.71 to 45.18 ppm, in agreement with the strong electron-withdrawing effect of fluorine atoms.

Surprisingly, all complexes **1**-**5** in combination with [Ph_3C][B(C_6F_5)$_4$] were able to catalyze St polymerization in toluene. Interestingly, with the increase of fluorine number in *β*-diketiminato skeleton, the catalytic activity of the corresponding complex became higher, reaching the highest (260.2 kg of polymer/(mol_{Sc}·h)) for complex **5** by converting 5000 equiv. of St completely into polymer within 2 h (Table 1, entries 1-5).

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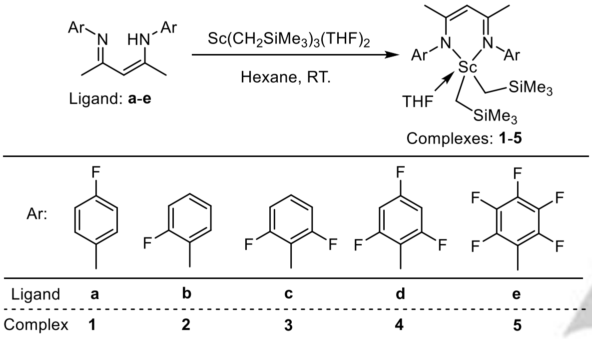
Table 1. Styrene polymerization catalyzed by precursors **1**-**5**.

Entry[a]	Precursor	[St]/[Sc]	t (h)	Conv. (%)	Activity[b]	$M_{n,\ calcd}$[c] (×10³)	$M_{n,\ exp}$[d] (×10³)	M_w/M_n[d]	Chains/Sc
1	**1**	1000	2	4.5	2.3	4.7	6.6	1.52	0.7
2	**2**	1000	2	13.1	6.8	13.6	5.7	1.64	2.4
3	**3**	1000	2	42.1	21.9	43.8	4.6	1.70	9.5
4	**4**	1000	2	70.0	36.4	72.8	3.5	1.79	20.8
5	**5**	1000	1	100	104.1	104.1	2.4	2.30	43.4
6	**5**	2000	1	100	208.2	208.2	2.9	2.21	71.8
7	**5**	5000	2	100	260.2	520.8	4.3	2.11	121.1

[a] Polymerization conditions: Ln (10 µmol), 1:1 [catalyst]/$[Ph_3C][B(C_6F_5)_4]$ mixture (molar ratio), toluene/monomer = 3/1 (v/v), Tp = 20°C, unless otherwise noted. [b] Given in kg of polymer/(molSc·h). [c] $M_{n,calcd}$ = [St]/[Sc]×104.1×conv (%). [d] Determined by GPC in THF at 40 °C against polystyrene standard.



Scheme 1. Synthesis of fluorine-containing *β*-diketiminate rare-earth metal complexes **1**-**5**.

These results meant, by tuning the substituents of ligands, we successfully transformed inert catalysts into highly active ones. To investigate the reason behind, the LUMO energies of the active species based on these complexes (Figure S6 for complex **1**) were simulated by DFT. Obviously, the two phenyl groups from the ligands bearing more fluorine atoms contribute significantly to the active species by lowering the LUMO energies from -0.16434 au for **1** to -0.18974 for **5** au (Figure S7 and Table S2). Thus, the energy gap (ΔE) between the HOMO of St and the LUMO of the active species became narrower varying from 0.06154 au to 0.03614 au, in agreement with the enhancement of the catalytic activity from 2.3 kg/(mol·h) for **1** to 104.1 kg/(mol·h) for **5** (Table 1). Apparently, the electron-withdrawing fluorine atoms dramatically increase the Lewis acidity of the active metal center, which facilitates the coordination of the vinyl group to accelerate St polymerization.

Under the St-to-Sc ratio of 1000:1, the molecular weights of the polymers obtained from precursors **1**-**5** were different, decreasing with the increase of fluorine number. However, this difference can be completely ignored as compared to the huge deviations of these measured molecular weights ($M_{n,\ exp}$) from the theoretic ones ($M_{n,\ calcd}$), which are surprisingly low and with slightly broadened distribution (Table 1, entries 1-5). Moreover, increasing the ratio to 5000:1, a polymer with $M_{n,\ exp}$ (4.3×10³ Da) of 2 orders of magnitude lower than $M_{n,\ calcd}$ (520.8×10³ Da) was still generated (Table 1, entries 6 and 7), indicating a strong chain transfer reaction proceeded in this polymerization system. Thus, up to 120 times of chain transfer took place in the polymerization procedure, alternatively, one active metal center grew 120 polymer chains. This arises a question: which type of chain transfer reaction happens in this system?

The matrix assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) is a powerful method to identify the polymer chain ends and ascertain the chain transfer type. The MALDI-TOF MS spectrum of polystyrene isolated from precursor **5** shows two sets of molecular ion peaks with the same spacing of a St unit (*m/z* = 104.15) between the adjacent peaks (Figure 1). The blue peaks with low responds are resulted from polystyrene terminated by *β*-H elimination. The red peaks with high responds correlate to polystyrene with H and Ph-CH_2- as both chain ends, which seem to be generated from the rare chain transfer to toluene.

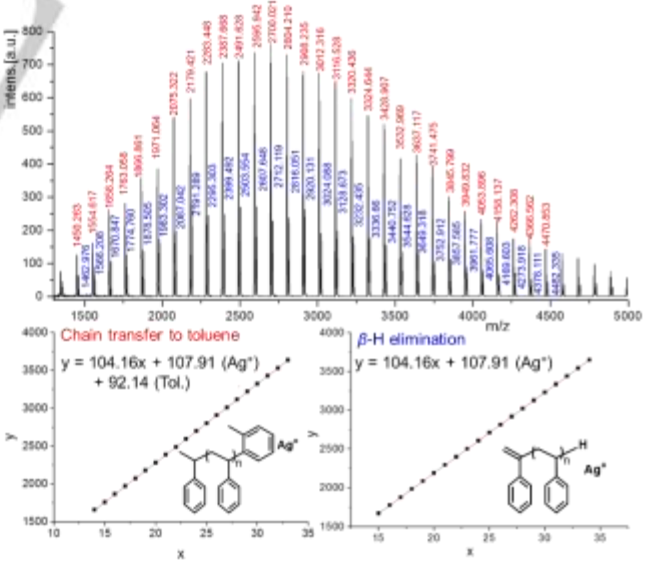


Figure 1. MALDI-TOF mass spectrum of polystyrene (Table 1, entry 5).

There are two possible chain transfer pathways due to the different chemical nature of methyl-H (sp^3-C-H) and phenyl-H (sp^2-C-H) in a toluene molecule as shown in Scheme 2. Path a:

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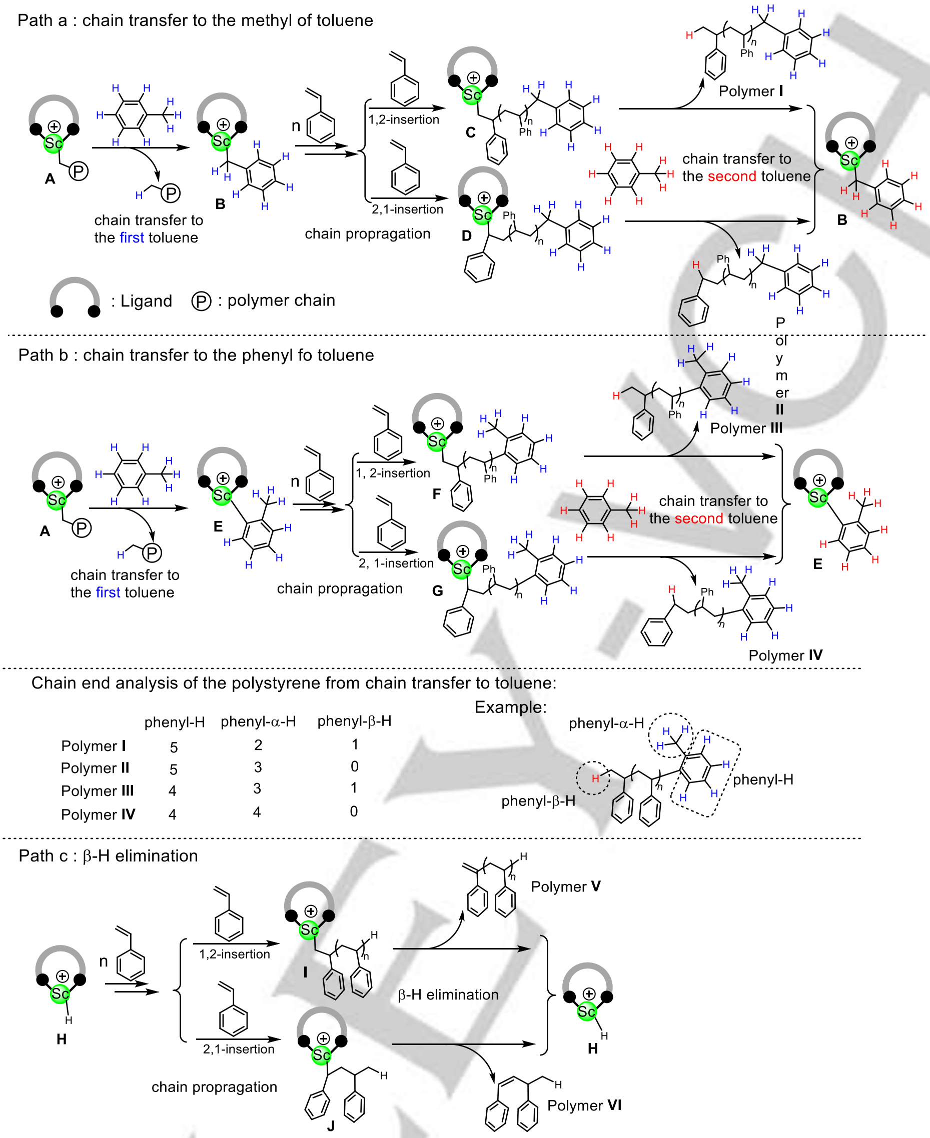

	phenyl-H	phenyl-α-H	phenyl-β-H
Polymer **I**	5	2	1
Polymer **II**	5	3	0
Polymer **III**	4	3	1
Polymer **IV**	4	4	0

Scheme 2. Possible chain transfer reactions of styrene coordination polymerization in this study.

chain transfer reaction takes place between the active species **A** and the *sp*^{3}-C-H of toluene to afford the new scandium benzyl active species **B**. 1,2- and 2,1-insertions of St to **B** lead to the intermediates **C** and **D**, respectively. The second chain transfer reactions proceed between **C**/toluene and **D**/toluene to recover the active species **B** and give polymers **I** and **II**, respectively. Path b: chain transfer reaction takes place between the active species **A** and the *sp*^{2}-C-H of toluene to afford the new active species **E**. The following 1,2- and 2,1-insertions of St to **E** provide the intermediates **F** and **G**, respectively. The subsequent *sp*^{2}-C-H bond activation (deprotonation) of toluene in **F** and **G** yield polymers **III** and **IV**, respectively, by releasing the scandium phenyl species **E**. With respect of the **Sc-H** active species (**H**) arising from the *β*-H elimination, it is minor present (Scheme 2, path c). **Sc-H** initiates 1,2- or 2,1-insertion of St to afford polymer **V** or **VI**. As depicted in Scheme 2, the resultant polymers **I-VI** possess chain ends of phenyl-*α*-H, phenyl-*β*-H and phenyl-H in different ratios.

To distinguish the chain ends, the polymerization was performed in toluene-*d*$_8$ with precursor **5** to give the deuterium-incorporating polystyrene (Table 2, entry 1, *vide infra*). The ^{2}H-NMR spectrum reveals the integral intensity ratio of phenyl-D: phenyl-*α*-D : phenyl-*β*-D to be 3.84:3:1 (Figure 2), corresponding to the chain end style of polymer **III**, where St propagates into polymer chain *via* 1,2-insertion mode and chain transfer to toluene through *ortho*-*sp*^{2}-C-H activation.[16] 1,2-Insertion is unusual for most catalytic systems,[17] which becomes the main mode here possibly because it is sterically favored than 2,1-insertion, since the two C_6F_5 groups and the penultimate phenyl ring of active polymeric species encounter mutual repulsion.[18]

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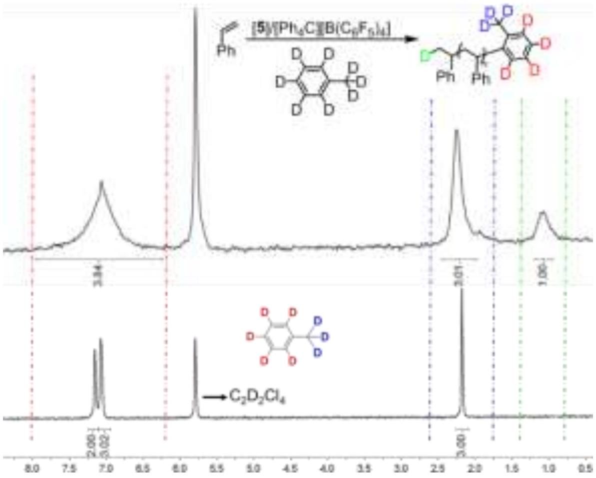


Figure 2. ^{2}H-NMR spectra of the deuterium-incorporating polystyrene (up) (Table 2, entry 1) and toluene-d_8 (down) ($C_2D_2Cl_4$ as the internal standard, $CHCl_3$, 25°C).

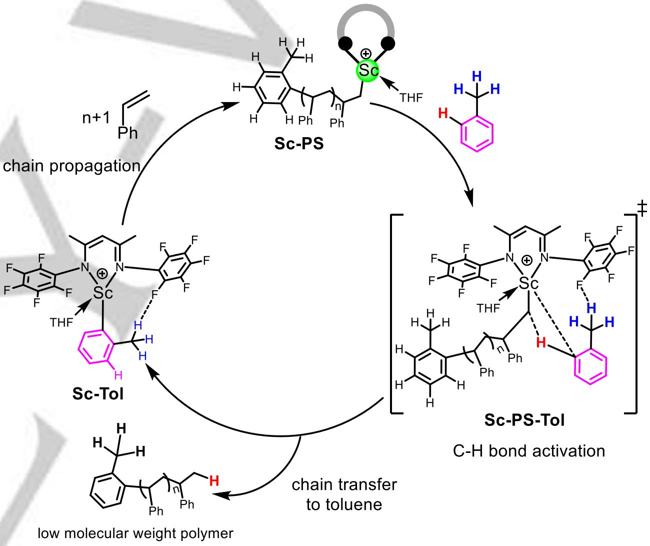
To clarify the driven force of chain transfer to toluene, some other solvents were employed as the polymerization medium. When benzene-d_6 was used, the molecular weight of the obtained polystyrene was still very low (Table 2, entry 2), however, no ^{2}H resonance was observed, indicating that the chain transfer to benzene didn't occur in this polymerization process. In addition, the MALDI-TOF MS spectrum shows only one set of molecular ion peaks (Figure S16), which corresponds to polystyrene terminated by *β*-H elimination. Thus, methyl group in toluene plays a pivotal role. To confirm this, *p*-xylene was used instead of toluene (Table 2, entry 3). As shown in Figures S17 and S18, the peaks at 20.92 and 21.25 ppm are attributed to the two methyl carbons C1 and C1' of *p*-xylene, indicative of chain transfer to *p*-xylene. When *p*-fluorotoluene, *p*-chlorotoluene and *p*-bromotoluene were used as the solvent in St polymerization, there were still no resonance of methyl carbon from toluene was detected although the molecular weights of the obtained polymers were rather low. This meant the isolated polystyrenes are *β*-H elimination products. Possibly the presence of halogen atom disturbs chain transfer to toluene.

Table 2. Styrene Polymerization Catalyzed by Precursor **5** in Different Solvents.

Entry[a]	Solvent	[St]/[Sc]	t (h)	Conv. (%)	$M_{n.exp}$[b] (×10^3)	M_w/M_n[b]
1	toluene-d_8	500	4	85.6	6.2	1.91
2	benzene-d_6	500	2	>99.9	5.8	2.08
3	*p*-xylene	500	4	>99.9	2.8	1.61
4	*p*-fluorotoluene	500	4	>99.9	7.0	2.03
5	*p*-chlorotoluene	500	4	>99.9	6.1	2.33
6	*p*-bromotoluene[c]	500	4	>99.9	6.7	2.17

[a] Polymerization conditions: Sc (10 μmol), 1:1 [Sc]/[Ph_3C][$B(C_6F_5)_4$] mixture (molar ratio), solvent/monomer = 3/1 (v/v), T_p = 20°C, unless otherwise noted. [b] Determined by GPC in THF at 40 °C against polystyrene standard. [c] The mixed solvents of 4-bromotoluene and hexane were used (4-bromotoluene/hexane = 2:1) because 4-bromotoluene is solid at the room temperature.

These results allowed us to elucidate the mechanism for the chain transfer to toluene (Scheme 3). The cationic scandium polystyrenyl active species **Sc-PS** adopts a toluene molecule via strong hydrogen-bond interaction between the fluorine atom and a methyl proton of the lower pK_a within toluene.[19] Meanwhile the scandium methylene moiety Sc-CH_2 catches *ortho*-phenyl-H to form the transition state **Sc-PS-Tol**. Thus, chain-transfer reaction, alternatively, deprotonation, take places to give polymer **III** and a new scandium phenyl active species **Sc-Tol**. In the process, methyl serves as the directing group and the propagating polymer chain has the priority to abstract the *ortho*-phenyl-H. Insertion-propagation of styrenes into **Sc-Tol** regenerates the active species **Sc-PS** to complete a catalytic cycle.



Scheme 3. Possible mechanism for chain transfer to toluene in styrene coordination polymerization catalyzed by precursor **5**.

In conclusion, we have developed a series of new scandium complexes chelated by fluorine-containing *β*-diketiminate ligands, which display increasing activities up to 260.2 kg polymer/(mol_{Sc}·h) for styrene polymerization with more fluorine atoms anchored on the ligands under the activation of [Ph_3C][$B(C_6F_5)_4$]. This is surprisingly contrary to their analogues bearing *β*-diketiminate ligands without a fluorine substituent, which are completely inert towards this polymerization. DFT calculations suggest the more the fluorine atoms are in the ligand, the lower the LUMO energy of the active species is, leading to the narrower energy gap between the HOMO of styrene and the LUMO of the active species and a higher activity. More excitingly, despite of monomer loading, the complexes give very low molecular weight polystyrenes due to the unprecedented chain transfer to toluene. The driving force for the chain-transfer is arising from the hydrogen bonding C−F···H−C between the fluorine and the methyl proton in toluene, which directs the active propagating polymer chain to abstract the *ortho*-H of toluene. This work sheds new lights on organometallic chemistry about how to design highly active catalysts and widens polymer science about chain transfer mechanism. It also paves a new avenue to access very low molecular weight polystyrene in the most convenient and cheapest method.

Acknowledgements

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Keywords: C-H activation •chain transfer• coordination polymerization • styrene polymerization •rare earths

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[16] The ortho-sp2-C-H activation by active species E was confirmed by ^{1}H (Figure S8), ^{13}C (Figure S9), HSQC (Figures S10-11) and HMBC (Figures S12-15) NMR analyses of an oligomeric polystyrene sample (Table 1, entry 5, M_n = 2400, M_w/M_n = 2.30). In the ^{13}C NMR spectra, the strong multi peaks within 144.5-146.5 ppm are related to the ipso-carbon *Cc* of the atactic polystyrene main chain; while the resonance at δ 20.89 ppm is assigned to methyl *C1* of the chain-end, which correlates to the methyl protons at δ 2.22 ppm in the HSQC spectrum. The resonance at δ 3.46 ppm can be assigned to the methine proton H8 connecting to the ortho-phenyl carbon *C7*, which correlates with *C8* at 47.87 ppm (Figures S12, S15). These evidences suggested that the active polystyrene chain transfers to the *ortho*-H of toluene, alternatively, the *ortho-sp*^{2}-C-H is prone to be abstracted.

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COMMUNICATION

The highly efficient chain transfer to toluene has been achieved for the first time in styrene coordination polymerization by using rare-earth metal precursors. The higher polymerization activity is attributed to the fluorine substitutents on the *ß*-diiminato ligands by lowering the LUMO energy of active metal center, which also direct the chain transfer to *ortho*-proton of toluene.

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