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Simultaneous Chain-Growth and Step-Growth Polymerization of Methoxystyrenes by Rare-Earth Catalysts

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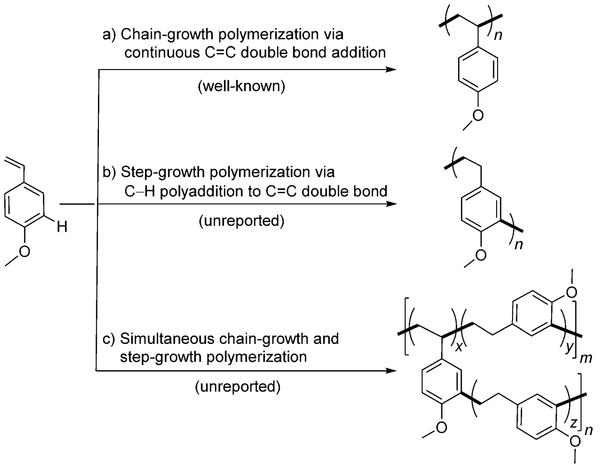
Abstract: *The simultaneous chain-growth and step-growth polymerization of a monomer is of great interest and importance because it can produce unique macromolecules which are difficult to prepare by other means. However, such a transformation is usually difficult to achieve in one polymerization system because chain-growth polymerization and step-growth polymerization proceed by different reaction mechanisms. Reported here is the simultaneous chain-growth and step-growth polymerization of para- and meta-methoxystyrenes catalyzed by half-sandwich rare-earth alkyl complexes, and the step-growth polymerization proceeds by the C–H polyaddition of anisyl units to vinyl groups. This unprecedented transformation affords a new family of macromolecules containing unique alternating anisole-ethylene sequences. In contrast to para- and meta-methoxystyrenes, ortho-methoxystyrene exclusively undergo syndiospecific, living chain-growth polymerization by continuous C=C bond insertion to give perfect syndiotactic poly(ortho-methoxystyrene) with high molecular weight and narrow polydispersity (rrrr* $> 99\,\%$, *M_n up to $280\ \mathrm{kg\,mol^{-1}}$, $M_w/M_n < 1.10$).*

Polymerization is a powerful tool for making synthetic polymer materials which are ubiquitous in modern industry and our daily life. Polymerization reactions can be generally classified into two categories, that is, chain-growth polymerization and step-growth polymerization.[1] Mechanistically, chain-growth polymerization proceeds by reaction between a growing chain end and monomers, while step-growth polymerization occurs by reactions among chain-end groups, monomers, and the resulting oligomer and polymer products. The simultaneous occurrence of these two types of polymerization in one reaction system is usually difficult, because of their different reaction mechanisms.[2] As the simultaneous chain-growth and step-growth polymerization of a monomer can produce unique polymer architectures which are difficult to prepare by other means, the search for efficient catalyst systems enabling such unique transformations is of great interest and importance.

Methoxystyrenes are commercially available, well-known styrenic monomers. The chain-growth polymerization of methoxystyrenes by various initiators and catalysts, including cationic,[3] anionic,[4] and radical[5] reagents as well as rare-earth and titanium complexes,[6] has been well documented (Scheme 1a). However, the polymerization of a methoxystyrene monomer in a step-growth fashion has not been reported previously. We have previously shown that half-sandwich rare-earth alkyl complexes serve as efficient catalysts for the chain-growth polymerization and copolymerization of a wide range of monomers, including styrenes, through continuous C=C bond insertion.[7,8] Very recently, we found that the same type of half-sandwich rare-earth catalyst can also catalyze the step-growth copolymerization of 1,4-dimethoxybenzene with 1,4-divinylbenzene by intermolecular C–H polyaddition of the anisyl unit to the vinyl group of the styrene moiety.[9] These findings invoked much interest in the polymerization behaviors of methoxystyrenes, which have both an anisyl group and a styrene unit in one molecule, with the half-sandwich rare-earth catalysts. In principle, if the activation of an *ortho*-C–H bond of the anisole unit by the rare-earth alkyl species and subsequent addition of the resulting rare-earth metal anisyl species to the C=C double bond of the styrene unit could take place, the step-growth polymerization of a methoxystyrene monomer would be possible (Scheme 1b).



Scheme 1. Possible polymerization patterns of *para*-methoxystyrene.

Herein, we report our studies on the polymerization of *para*-, *meta*-, and *ortho*-methoxystyrenes by half-sandwich rare-earth catalysts. We found that the simultaneous chain-growth and step-growth polymerization of *para*- and *meta*-

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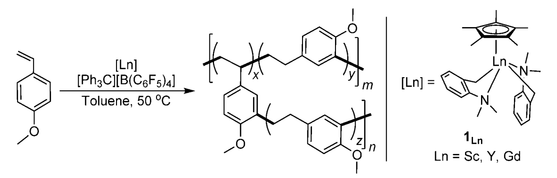
methoxystyrenes could be achieved by using an appropriate rare-earth catalyst, in which the step-growth polymerization proceeded by the C−H polyaddition of anisole units to vinyl groups (Scheme 1 c). This unprecedented transformation led to formation of a new family of macromolecules containing unique alternating anisole-ethylene sequences. In contrast, *ortho*-methoxystyrene exclusively underwent syndiospecific, living chain-growth polymerization by continuous C=C bond insertion, and gave perfect syndiotactic poly(*ortho*-methoxystyrene) with high molecular weight and narrow polydispersity.

The polymerization of *para*-methoxystyrene was first examined at 50 °C by using half-sandwich rare-earth alkyl complexes ($\mathbf{1_{Ln}}$; Ln = Sc,[10a] Y,[10b] Gd[10c]) with $[Ph_3C][B(C_6F_5)_4]$ as a cocatalyst. In the case of $\mathbf{1_{Sc}}$ with 40 equivalents of *para*-methoxystyrene, a polymer product was obtained in 88 % yield in 24 hours, but a significant portion (35 %) of this polymer product was insoluble in both THF and hot dichlorobenzene (145 °C; Table 1, entry 1). We suspected that this poor solubility might be due to the high activity of $\mathbf{1_{Sc}}$ towards continuous C=C bond insertion, and could result in formation of poorly soluble, long syndiotactic polymer sequences.[8a] We then examined the yttrium and gadolinium complexes, $\mathbf{1_{Y}}$ and $\mathbf{1_{Gd}}$, respectively, which were known to show much lower activity for continuous C=C bond insertion than their scandium analogue.[7,8a] Under the same reaction conditions, $\mathbf{1_{Y}}$ quantitatively yielded a THF-soluble polymer product with $M_n = 4.06\ \mathrm{kg\,mol^{-1}}$ and $M_w/M_n = 5.29$ (entry 3). The gadolinium catalyst $\mathbf{1_{Gd}}$ showed even better performance, and afforded a THF-soluble polymer with much higher molecular weight, $M_n = 16.2\ \mathrm{kg\,mol^{-1}}$, and narrower molecular weight distribution, $M_w/M_n = 2.45$ (entry 11). Quantitative polymer formation of higher monomer feeds ([M]/[Ln] = 100 and 300) could also be achieved (entries 14 and 15), thus demonstrating the high efficiency of this catalyst system. It is also noteworthy that the higher monomer feeds resulted in lower molecular weight under the same reaction conditions (entries 11, 14, and 15), which is in contrast with what was usually observed in chain-growth polymerization reactions, but in agreement with the involvement of a step-growth polymerization mechanism.[1,9]

To establish the microstructure of the polymer products, the ^{1}H, ^{13}C, DEPT135, HSQC, and HMBC NMR spectroscopic analyses were conducted (see the Supporting Information). As a representative example, the ^{1}H, ^{13}C, and DEPT135 NMR spectra of a polymer with $M_n = 16.2\ \mathrm{kg\,mol^{-1}}$ and $M_w/M_n = 2.45$ (Table 1, entry 11) are shown in Figure 1. In the aliphatic region of the ^{1}H NMR spectrum, besides a strong

Table 1: Simultaneous chain-growth and step-growth polymerization of *para*-methoxystyrene by half-sandwich rare-earth catalysts.[a]



Entry	Ln	[M]/[Ln][b]	t [h]	Yield [%][c]	M_n[d] ($\times 10^3$)	M_w/M_n[d]	T_g [°C][e]	**CC/CH**[f]
1	$\mathbf{1_{Sc}}$	40	24	88	2.51 g	4.25[g]	n.d.[h]	33:67
2	$\mathbf{1_{Y}}$	40	12	71	2.88	4.91	30	5:95
3	$\mathbf{1_{Y}}$	40	24	100	4.06	5.29	40	3:97
4	$\mathbf{1_{Gd}}$	40	0.3	11	3.91	1.33	n.d.[h]	40:60
5	$\mathbf{1_{Gd}}$	40	0.6	25	6.06	1.49	20	29:71
6	$\mathbf{1_{Gd}}$	40	1	36	8.04	1.52	20	18:82
7	$\mathbf{1_{Gd}}$	40	2	60	11.0	1.96	29	12:88
8	$\mathbf{1_{Gd}}$	40	4	89	13.5	2.35	29	10:90
9	$\mathbf{1_{Gd}}$	40	8	100	15.9	2.36	33	8:92
10	$\mathbf{1_{Gd}}$	40	12	100	16.1	2.43	32	8:92
11	$\mathbf{1_{Gd}}$	40	24	100	16.2	2.45	33	8:92
12[i]	$\mathbf{1_{Gd}}$	40+40	4+20	100	20.3	3.36	34	5:95
13	$\mathbf{1_{Gd}}$	80	24	100	15.3	2.91	29	9:91
14	$\mathbf{1_{Gd}}$	100	24	100	15.1	3.28	31	9:91
15	$\mathbf{1_{Gd}}$	300	24	100	10.9	2.06	29	8:92

[a] Reaction conditions: [Ln] (0.025 mmol), $[Ph_3C][B(C_6F_5)_4]$ (0.025 mmol), [M] 0.5 mol L^{-1}, 24 h, unless otherwise noted. [b] Molar ratio of monomer feed/catalyst. [c] Yield of isolated product. [d] Determined by GPC in THF at 40 °C against a polystyrene standard. [e] Measured by DSC. [f] Ratio of segments formed by continuous C=C insertion (**CC**) to those by C−H addition (**CH**). [g] THF-soluble part (65 %) of the polymer product. [h] n.d. = Not determined. [i] The second monomer feed (40 equiv) was added after polymerization of the first feed was carried out for 4 h, and the mixture was stirred for 20 h.

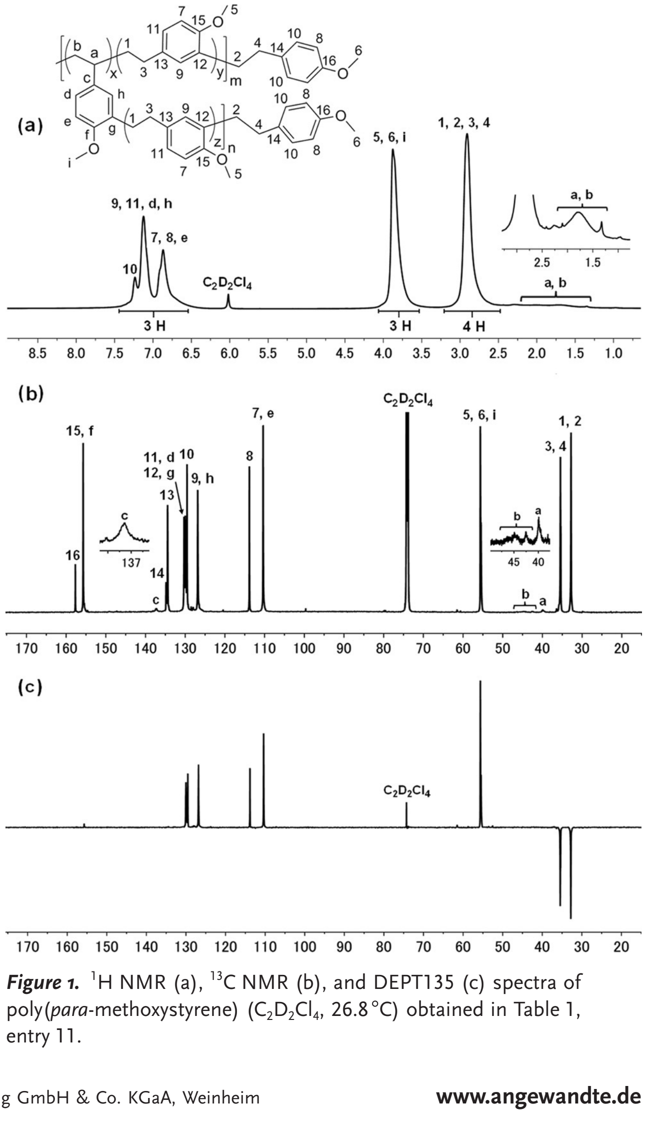
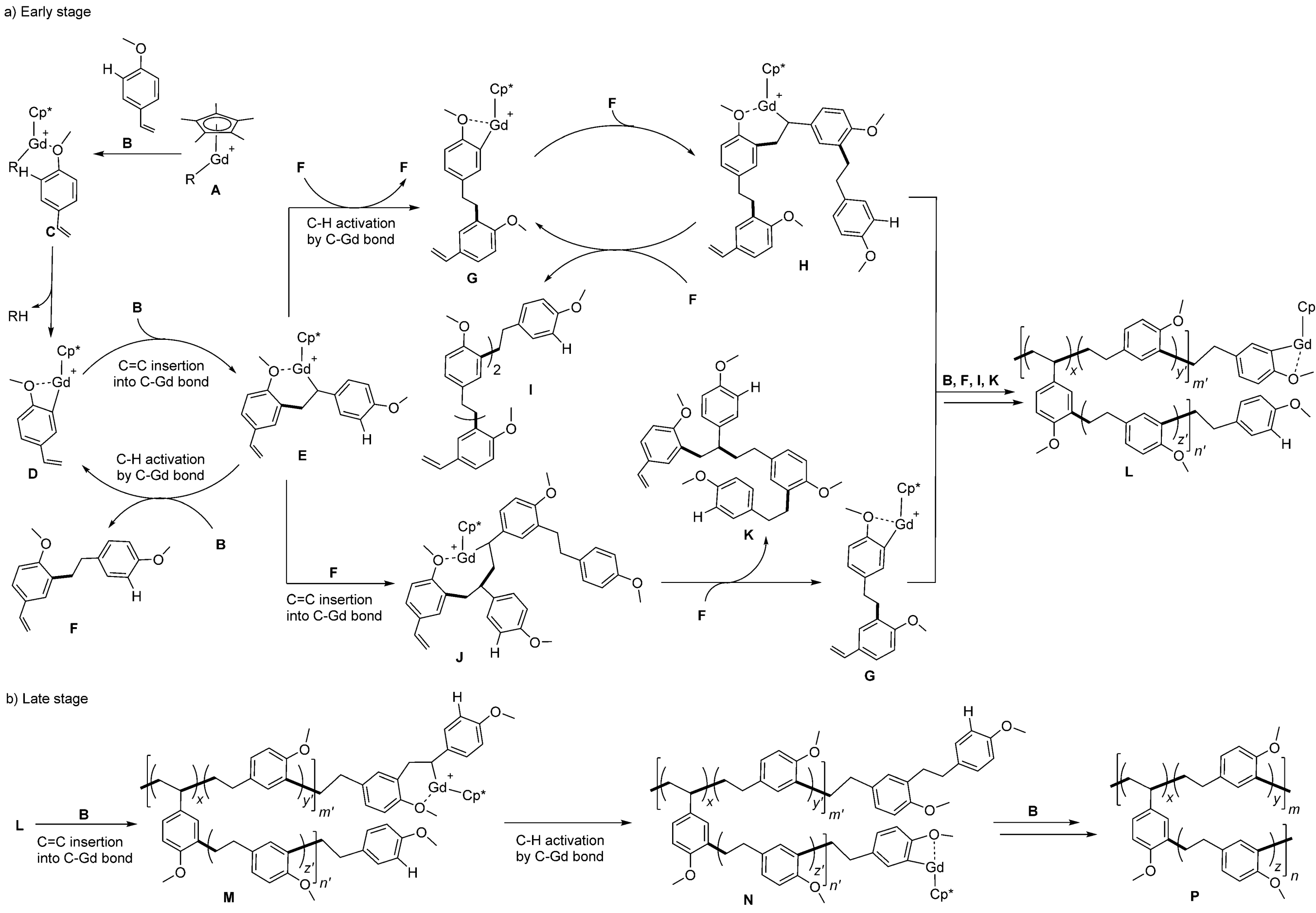


Figure 1. ^{1}H NMR (a), ^{13}C NMR (b), and DEPT135 (c) spectra of poly(*para*-methoxystyrene) ($C_2D_2Cl_4$, 26.8 °C) obtained in Table 1, entry 11.

broad signal at $\delta = 3.89$ ppm, which is assignable to the methoxy groups, a strong broad signal at $\delta = 2.88$ ppm is also observed (Figure 1a). This broad ^{1}H NMR peak corresponds to two ^{13}C NMR signals at $\delta = 32.8$ and 35.5 ppm in the HSQC NMR spectrum (see Figure S4), and the latter showed inverted signals in the DEPT135 spectrum (Figure 1c), thus indicating that methylene units (CH_2) should be predominant in the polymer chain. These results together with the integration of the ^{1}H NMR spectrum as well as the ^{13}C NMR spectrum strongly suggest that the polymer mainly contains alternating anisole-ethylene sequences connected at the 2,4-positions of the anisole unit (see Figures S4 and S5), which could be formed by the *ortho*-C−H addition of the anisole unit to the vinyl group of *para*-methoxystyrene. In addition to these major peaks, there are weak signals at $\delta =$ 1.30–1.80 ppm in the ^{1}H NMR spectrum and at $\delta = 39.0$–47.0 and 137.3 ppm in the ^{13}C NMR spectrum, which could be assigned to the typical sequences formed by the continuous C=C bond insertion (chain-growth polymerization) of *para*-methoxystyrene.[6] These NMR data suggest that both C−H addition (major) and continuous C=C insertion (minor) could be involved in the formation of this polymer product. The ratio of the segments formed by the continuous C=C insertion (**CC**) and those by the C−H addition (**CH**) was estimated to be about 8:92 from the integration ratio of the ^{13}C NMR signals at $\delta = 137.3$ ppm (**CC**) and at $\delta = 134.4$ and 134.8 ppm (**CH**; Figure 1).

To gain more information about the present reaction, the polymerization of 40 equivalents of *para*-methoxystyrene using $\mathbf{1_{Gd}}$ was investigated for different periods of time (Table 1, entries 4–11). When the polymerization was carried out for 0.3 hours, a polymer product with $M_n = 3.91$ kg mol^{-1} and $M_w/M_n = 1.33$ was obtained in 11% yield (entry 4). The GC-MS analysis of the reaction mixture confirmed a predominant amount of the unreacted monomer with a trace of dimer, thus suggesting that the possible dimer products could be quickly transformed into oligomer/polymer products after they were generated from the monomer. The ^{1}H NMR spectrum of the polymer product did not show any signals assignable to a dimethylaminobenzyl group, thus suggesting that the aminobenzyl ligand in the original Gd catalyst was not incorporated into the polymer. This occurrence could be due to the initial rapid C−H activation (deprotonation) of the anisole unit of *para*-methoxystyrene by the Gd–benzyl bond in the catalyst to release *o*-$MeC_6H_4NMe_2$.[8g,9,11] Signals assignable to vinyl protons in the ^{1}H NMR spectrum were negligible (see Figure S8). The ratio of the segments formed by the continuous C=C insertion (**CC**) to those by the C−H addition (**CH**) in this polymer was about 40:60 as shown by the ^{13}C NMR spectrum (see Figure S9). As the reaction time was prolonged, the monomer conversion steadily increased, thus reaching 100% in 8 hours (entries 5–9). The molecular weight of the resulting polymers significantly increased as the monomer conversion was raised. After the conversion reached 100%, a prolonged reaction time did not lead to significant increase of the molecular weight, and the **CC**/**CH** ratio remained constant (entries 9–11). It is also worth noting that when the monomer conversion was raised from 11 to 100%, the **CC**/**CH** ratio in the resulting polymers dropped significantly from 40:60 to 8:92 (entries 5–9). This outcome suggests that the continuous C=C insertion (**CC**) may take place mainly at the early stage of the polymerization process, and the C−H addition to a vinyl group (**CH**) could be predominant at the late stage of the process. More remarkably, when another feed of 40 equivalents *para*-methoxystyrene was added after the polymerization of the first feed (40 equiv) was carried out for 4 hours with 89% conversion, a polymer product with a significantly higher molecular weight, $M_n = 20.3$ kg mol^{-1}, was obtained quantitatively in 20 hours (entries 8 and 12). The **CC**/**CH** ratio in the resulting polymer decreased from 10:90 (entry 8) to 5:95 (entry 12). These results strongly suggest that the polymerization in the second step should take place mainly through the C−H addition of the anisole units in the polymer products formed in the first feed to the vinyl group of *para*-methoxystyrene (added at the second feed and left in the first feed). When 80 equivalents of *para*-methoxystyrene was fed in one step rather than in two separate steps (40 + 40), the resulting polymer product showed a lower molecular weight ($M_n =$ 15.3 kg mol^{-1}; entry 13; see also entries 11, 14, and 15), thus suggesting again the involvement of a step-growth polymerization mechanism.

On the basis of the above experimental results, a possible scenario for the polymerization of *para*-methoxystyrene by $\mathbf{1_{Gd}}$ is shown in Scheme 2. The coordination of the methoxy group of *para*-methoxystyrene (**B**) to the Gd atom in **A**, which was generated by the reaction of the dialkyl complex $\mathbf{1_{Gd}}$ with $[Ph_3C][B(C_6F_5)_4]$, affords **C**. The *ortho*-C−H bond activation (deprotonation) of the anisole unit by the Gd–aminobenzyl (R) species in **C** should give the anisyl species **D** with release of RH. Insertion of the vinyl group of **B** may lead to **E**, which deprotonates **B** at the Gd−C σ-bond to release the dimer **F** and regenerate **D**. The analogous deprotonation of **F** by **E** would afford a new Gd–anisyl species **G**, which upon insertion of the vinyl group of **F** could give **H**. The subsequent deprotonation of **F** by **H** would yield the tetramer **I** and regenerate **G**. In contrast, insertion of the vinyl group of **F** into **E** may also take place to give **J**, which upon deprotonation of **F** by the Gd−C σ-bond would generate **G** and release the tetramer **K**, which possesses a subunit formed by continuous insertion of two C=C bonds. Repetition of the analogous reactions among **B** and **D**–**K** as well as the resulting products would lead to the formation of oligomer(s) like **L** which possesses multiple branches of alternating anisole-ethylene sequences bearing the Gd–anisyl species at a chain end(s). The vinyl-group-free terminal anisole unit(s) in **F** and the tetramers **I** and **K** could be more reactive than the anisole unit in **B** in terms of coordination of the methoxy group to the metal center and the subsequent *ortho*-C−H activation, because **B** bears an electron-withdrawing vinyl group.[8g] The reactivity of the vinyl group in **F**, **I**, and **K** could also be higher than that of **B**, because **F**, **I**, and **K** possess a electron-donating saturated -CH_2CH_2- substituent. Consequently, at a certain point of the reaction, no vinyl groups (very few, if any) could exist in the oligomer products, while a certain amount of **B** remains unreacted (Table 1, entry 4; see Figure S8). Therefore, the insertion of the vinyl group of **B** into the Gd−anisyl bond in **L** (to give **M**) followed by the

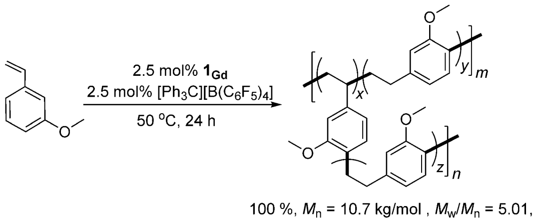


Scheme 2. Possible scenario for the simultaneous chain-growth and step-growth polymerization of *para*-methoxystyrene by a gadolinium catalyst.

deprotonation of the anisole unit in an oligomer chain end (to give a new anisyl species such as **N**), could be a predominant event at this stage. Such a chain propagation process, that is, C–H addition of an anisole unit in the oligomer chain ends to **B**, would then continue until all monomers (**B**) are consumed, and finally give **P**. This scenario could explain the experimental observations that the higher conversion of the monomer resulted in higher molecular weight and lower **CC/CH** ratio in the resulting polymers (Table 1). Obviously, both the monomer/catalyst feed ratio and the monomer/oligomer ratio have a significant influence on the molecular weight of the polymer products. The higher molar ratio of monomer to the oligomers without a vinyl unit would give a higher molecular weight because the chain propagation could steadily proceed through the monomer insertion into a C–H bond of an anisole unit at the oligomer chain-ends (Figure 1b). Therefore, the polymerization of *para*-methoxystyrene in two separate steps gave a higher molecular weight than that in one step with the same total feed (Table 1, entries 12 and 13).

Similar to *para*-methoxystyrene, the polymerization of *meta*-methoxystyrene could also take place in a simultaneous chain-growth and step-growth fashion in the presence of the $\mathbf{1}_{\mathbf{Gd}}$ catalyst. A quantitative conversion of 40 equivalents of *meta*-methoxystyrene was achieved in 24 hours at 50 °C, thus affording a polymer product with $M_n = 10.7\ \text{kg mol}^{-1}$ and $M_w/M_n = 5.01$ (Scheme 3). The polymer contained alternating anisole-ethylene sequences connected at the 2,5-positions of an anisole unit formed by *ortho*-C–H addition of the anisole unit to the vinyl group of *meta*-methoxystyrene. The **CC/CH** ratio in this polymer was 19:81.

In contrast with *para- and meta*-methoxystyrene, the polymerization of *ortho*-methoxystyrene by $\mathbf{1}_{\mathbf{Gd}}$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] occurred exclusively in a chain-growth fashion by

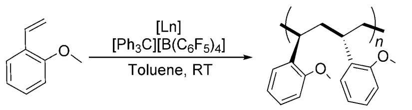


100 %, M_n = 10.7 kg/mol , M_w/M_n = 5.01, T_g = 24 °C, **CC/CH** = 19:81

Scheme 3. Simultaneous chain-growth and step-growth polymerization of *meta*-methoxystyrene by a gadolinium catalyst. **CC** = segments formed by continuous C=C bond insertion, **CH** = segments formed by C–H addition to C=C bonds.

continuous C=C insertion, thus affording syndiotactic-rich poly(*ortho*-methoxystyrene) (*rrrr* = 85 %)[6b] at either room temperature or 50 °C (Table 2, entry 1). The yttrium catalyst $\mathbf{1}_\mathbf{Y}$ showed much higher syndiotactic selectivity (*rrrr* > 99 %) for this chain-growth polymerization under the same reaction conditions (entry 2). As the monomer/catalyst ratio was raised from 1:100 to 1:2000, the molecular weight of the resulting polymers linearly increased with very narrow molecular weight distribution ($M_w/M_n < 1.10$; entries 2–6), thus showing a living polymerization behavior. No C−H addition sequences were observed in these polymers, probably because of the difficulty in activation of the C−H bond *ortho* to the methoxy group in *ortho*-methoxystyrene. This observation is in agreement with what was observed previously in the reactions of *ortho*-substituted anisoles with half-sandwich rare-earth catalysts, where the activation of the *ortho* C−H bond in the anisole unit did not take place because of the steric influence of the substituent on the other *ortho* position.[11,12]

Table 2: Chain-growth polymerization of *ortho*-methoxystyrene.[a]



Entry	Ln	[M]/[Ln][b]	*t* [h]	Yield [%][c]	M_n ($\times 10^3$)[d]	M_w/M_n[d]	*rrrr* [%][e]	T_g/T_m[f]
1	$\mathbf{1}_\mathbf{Gd}$	100	2	100	12.6	1.05	85	70/–
2	$\mathbf{1}_\mathbf{Y}$	100	2	100	13.5	1.06	> 99	64/235
3	$\mathbf{1}_\mathbf{Y}$	300	2	100	37.8	1.08	> 99	76/242
4	$\mathbf{1}_\mathbf{Y}$	500	2	100	58.9	1.08	> 99	78/243
5	$\mathbf{1}_\mathbf{Y}$	1000	2	100	131	1.07	> 99	80/243
6	$\mathbf{1}_\mathbf{Y}$	2000	5	100	280	1.09	> 99	81/242

[a] Reaction conditions: [Ln] (0.025 mmol), $[Ph_3C][B(C_6F_5)_4]$ (0.025 mmol), monomer concentration 0.5 mol L^{-1}. [b] Molar ratio of monomer/catalyst. [c] Yield of isolated product. [d] Determined by GPC in *o*-dichlorobenzene at 145 °C against a polystyrene standard. [e] Determined by ^{13}C NMR spectroscopy. [f] Measured by DSC.

In summary, we have achieved for the first time the simultaneous chain-growth and step-growth polymerization of *para*- and *meta*-methoxystyrenes by using a half-sandwich rare-earth catalyst. The chain-growth polymerization by continuous C=C insertion and the step-growth polymerization by the C−H addition of anisole units to vinyl groups mainly occur at the early stage of the reaction, while the C−H addition of an anisole unit in the chain ends of the oligomer products to the vinyl group of the monomer in a chain-growth fashion predominates at the latter stage of the reaction, because the oligomer products are more reactive than the initial monomer. This unique transformation has led to the formation of novel macromolecules containing multiple branches of alternating anisole-ethylene sequences. In contrast, the polymerization of *ortho*-methoxystyrene occurs exclusively in a perfect chain-growth fashion solely through continuous C=C insertion without C−H activation being involved, because of the steric influence of the vinyl group which could hamper the *ortho*-C−H activation of the anisole unit. This work has demonstrated that rare-earth-catalyzed C−H activation and C=C bond insertion may provide unique opportunities for the construction of novel polymer architectures which are difficult to make by other means. Studies in this direction are currently in progress.

Acknowledgments

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Keywords: C−H activation · gadolinium · polymerization · rare-earth metals · reaction mechanisms

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