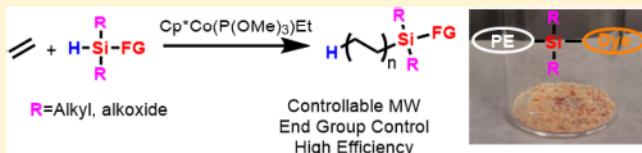


Introduction of Highly Tunable End-Groups in Polyethylene via Chain-Transfer Polymerization using a Cobalt(III) Catalyst

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ABSTRACT: Highly tunable end-functionalized polyethylene molecules are directly synthesized via chain-transfer polymerization of ethylene with silanes as chain-transfer agents catalyzed by a pentamethyl cyclopentadienyl cobalt phosphite alkyl catalyst. A series of polymerizations and kinetic studies of the different elementary steps involved in the catalytic cycle were performed to establish the methodology and to gain a deeper understanding of the reaction mechanism. The rate of the chain transfer, and thus the polymer length, can be tuned independently by varying the silane concentration or substituents. The combination of a chain-transfer methodology with a late transition-metal-based catalyst makes this system more compatible to polar functionality. This is highlighted by the introduction of an organic dye as end group to yield a colored polyethylene material.



INTRODUCTION

Polyethylenes (PEs) made by catalytic polymerization represent almost a quarter of the 300 million tons of polymers produced annually worldwide.¹ This strong market presence is due to the large availability of the inexpensive monomer and the broad mechanical properties achievable by tuning the polymer architecture. This tunability is illustrated by the various grades of polyethylene used in the production of pipes, packaging film, and fishing line, as each application requires unique material properties and thus polymer architectures (respectively, high-density polyethylene (HDPE)/toughness, linear low-density polyethylene (LLDPE)/transparency, and ultrahigh molecular weight polyethylene (UHMWPE)/strength). The control over the polyethylene architecture requires precise control over the catalyst and processes employed to vary the molecular weight, comonomer insertion, and branch incorporation of the polymer. Today this molecular precision is performed on a massive scale and is enabled by the tremendous knowledge gained on catalytic olefin polymerization.^{2–4} One of the remaining challenges in the field of olefin polymerization, however, is the introduction of polar groups into the polymer.^{5,6} This additional chemical tunability would offer another handle to adjust the properties of these already versatile materials, allowing, for example, improvements in their compatibility with other polymers or new lithographic materials.^{7–9}

Using catalytic copolymerization to introduce polar groups into polyethylene is difficult due to the high oxophilicity of the early transition-metal-based catalysts used in industry, as they tend to be completely deactivated by the heteroatoms of the polar monomers used.^{5,10} This incompatibility has motivated the development of less-sensitive catalysts. On the one hand, a few examples of group III- and group IV-based catalysts

tolerating some polar monomers have been reported, but the scope of compatible functional groups remains limited.^{11–13} Late transition-metal-based catalysts, on the other hand, offer a promising avenue, as they have been demonstrated to be significantly more stable toward polar monomers and solvents than their early transition-metal counterparts.^{5,10,14–23} While direct copolymerization with polar monomers using late transition metals is successful, high polar monomer loadings are required due to the poor copolymerization parameter with olefins, which results in low conversion of the polar monomer.^{5,16} The limitations of the copolymerization strategy triggered the development of alternative methods of incorporating polar groups into polyolefin chains. The chain-transfer polymerization (CTP) of olefin using polar chain-transfer agents (CTA) has been demonstrated as an efficient strategy to yield end-functionalized polymer chains.^{24,25} Seminal works from Marks established this strategy for early transition-metal- and lanthanide-based catalysts, successfully introducing silane, borane, phosphine, and amine as end groups onto polyethylene.^{24,26–33} Here again, the high oxophilicity of the metals employed to perform the catalysis limits the functionalization to at most one heteroatom per polymer chain. Other chain-transfer agents, such as metal alkyls (aluminum, zinc, magnesium), have also been implemented for the synthesis of functional polyolefins made by lanthanide, early and late transition-metal catalysts.^{24,25,34–37} In this case, the high electrophilicity of these CTAs is used to functionalize the polymer via multistep postpolymerization reactions.^{8,9} To directly introduce functional groups into polyethylene using CTP, it would be

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advantageous to use a system that is more stable toward heteroatoms, such as late transition-metal-based catalysts.

We herein report a chain-transfer polymerization strategy using a late transition-metal catalyst and polar chain-transfer agents to directly synthesize highly tunable end-functionalized linear polyethylenes. We recently reported the synthesis of end-functionalized amorphous polyethylene using chain-transfer polymerization catalyzed by a palladium diimine catalyst with silane as chain-transfer agent.³⁸ Here, using a cobalt catalyst, we further extend the type of polymeric architectures attainable by this method and deepen our understanding of the reaction mechanism by studying the kinetics of the key elementary steps involved in the chain-transfer polymerization. The merit of the chain-transfer strategy is the high efficiency of the reaction and the precision of the method (controlled placement of functional groups and molecular weight simultaneously). The advantage of using a late transition metal is highlighted by the stability of the system when using a silane-modified dye to synthesize a dye-labeled polyethylene. An overview of the various strategies to introduce functional groups into polyethylene is shown in Figure 1.

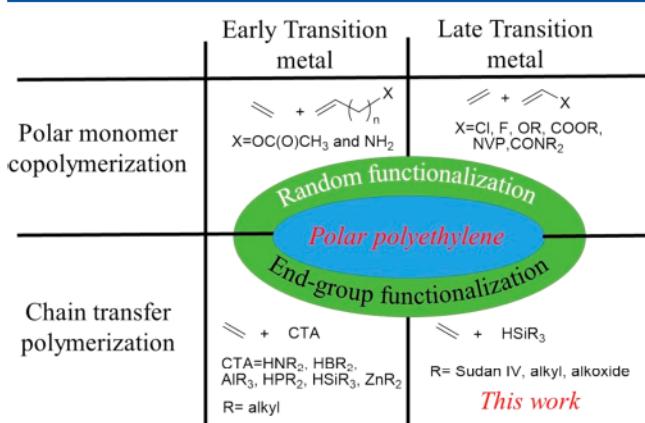


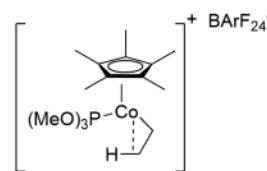
Figure 1. Overview of the strategies reported for the synthesis of polar polyethylene.

RESULTS AND DISCUSSION

Chain-Transfer Polymerization. A chain-transfer polymerization is a polymerization where chain termination occurs via the reaction of the catalyst with a chain-transfer agent that is not the monomer.²⁴ This reaction results in an end-functionalized polymer and in the formation of an organometallic complex capable of initiating the growth of a new end-functionalized polymer chain. To ensure the end-functionalization of all the polymer chains, it is necessary to develop a chain-transfer polymerization using a living polymerization catalyst, as this type of polymerization is free from other chain-transfer and termination events.³⁹ Because of their high propensity for β -hydride elimination, not many late transition-metal-based complexes have been reported in the literature to catalyze the living polymerization of ethylene.³⁹ One of the earliest examples of such a complex is the pentamethyl cyclopentadienyl cobalt phosphite alkyl catalyst referred to as Co-Et (Chart 1).^{40,41}

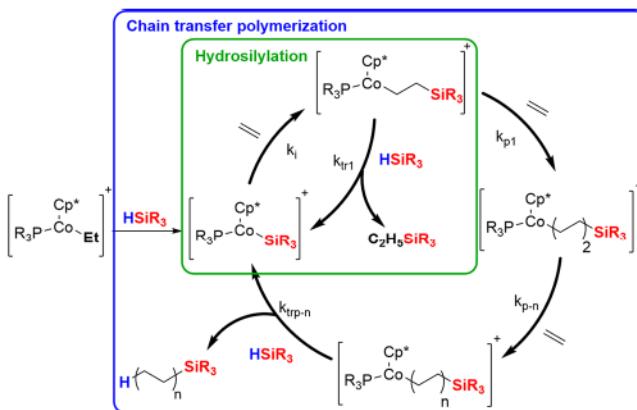
In addition to catalyzing the living polymerization of ethylene to yield linear polyethylene, Co-Et is most unique, as its resting state during the polymerization is a chelated four-membered ring issued from the agostic interaction between the

Chart 1. Co-Et Catalyst



cobalt metal center and a β -hydrogen (Chart 1).⁴⁰ Brookhart and co-workers investigated Co-Et extensively as a model catalyst to study the Cosee–Arlman mechanism.^{42,43} Later the same group reported the use of this catalyst for the catalytic hydrosilylation of hexene.⁴⁴ In this reaction the rate-determining step was demonstrated to be an intramolecular isomerization after insertion of hexene into the cobalt-SiR₃ species, meaning the reaction is zero order with respect to both silane and hexene. Silane addition to the cobalt alkyl complex is thought to follow a σ -bond metathesis mechanism.⁴⁴ The resulting cobalt silyl species could not be detected, suggesting that migratory insertion of hexene into the cobalt silyl is fast. The ability of complex Co-Et to catalyze the hydrosilylation of olefins and the living polymerization of ethylene suggests that silane could act as a chain-transfer agent for the polymerization of ethylene following the reaction mechanism drawn in Scheme 1.

Scheme 1. Reaction Mechanism for the Tandem Hydrosilylation and Chain-Transfer Polymerization of Ethylene



It is worth noting another paper by Brookhart, where the hydrosilylation of hexene is performed using Co-Et prior to pressuring the reaction mixture with ethylene to yield one chain of end-functionalized polyethylene per metal center.⁴⁵

Catalyst Co-Et was synthesized and isolated following literature procedure and used to catalyze the polymerization of ethylene at 40 psi.⁴⁶ The polymerizations were living as illustrated by the linear gain in yield and molecular weight observed over time as well as the decrease in \bar{D} over time as determined by high-temperature gel permeation chromatography (GPC; Table 1). The moderate decay of activity for longer reaction times is attributed to the partial precipitation of the semicrystalline PE in dichloromethane at room temperature.

On the basis of the previously reported hexene hydrosilylation study, which produced solely the hydrosilylation product, we postulated that the reaction of ethylene and silane catalyzed by Co-Et could result either in the corresponding

Table 1. Living Polymerization of Ethylene Initiated by Co-Et^a

entry	time (min)	TON ^b	yield (g)	Mn ^c (GPC) (g/mol)	D ^c
1	20	95	0.05	4300	1.6
2	40	175	0.10	7800	1.3
3	60	245	0.14	10 300	1.3
4	80	370	0.21	14 300	1.2

^aConditions: 20.7 μ mol of catalyst Co-Et; 50 mL of dichloromethane; 25 °C; 40 psi ethylene; reacted for differing amounts of time. ^bTON is based on gravimetric yield of polymer and moles of catalyst used.

^cMn and D were determined by GPC.

ethylene hydrosilylation product or in silane-terminated polyethylene.⁴⁴ We performed this reaction using 20.6 μ mol of Co-Et in 50 mL of CH_2Cl_2 at 25 °C for 3 h with 51 equiv of triethylsilane (HSiEt_3) under 40 psi ethylene (0.514 M). A milky white solution was collected upon ethylene pressure release; this turbidity is known to happen during ethylene polymerization, as the polymer is not soluble in the solvent and precipitates out. A white solid (0.17 g) was isolated upon precipitation in methanol and drying in *vacuo*. Analysis of the supernatant solution by gas chromatography confirmed the formation of some SiEt_4 (~2 TON) and the presence of unreacted HSiEt_3 (~70% of initial loading). Considering the consumption of silane and the low quantity of hydrosilylation product, we investigated if any silane had been incorporated at the end of the polyethylene chain. High-temperature ¹H NMR of the polymer shows linear polyethylene along with a peak at 0.52 ppm consistent with a tetra-alkyl silane end group. Note that no residual HSiEt_3 was detected in the isolated polymer confirming that the precipitation method efficiently removes any low molecular weight silanes. The formation of silane-terminated polyethylene suggests that silane acts as a chain-transfer agent for ethylene polymerization catalyzed by Co-Et. This was further confirmed by studying the degree of polymerization (DP) as a function of CTA concentration, as in a well-behaved chain-transfer system 1/DP varies linearly with CTA concentration (eq 1).⁴⁷ This relationship will also allow us to determine the rate constant of chain transfer $k_{\text{trp-n}}$ as discussed in a later section.

Equation 1. Theoretical dependence of DP on [silane].

$$\frac{1}{\text{DP}} = \frac{1}{\text{DP}_0} + \frac{k_{\text{trp-n}}[\text{silane}]}{k_{\text{p-n}}[\text{ethylene}]^n} \quad (1)$$

A series of polymerizations were performed at constant ethylene pressure, catalyst concentration, and temperature with varying amounts of HSiEt_3 in solution (Table 2). The DP of the polyethylene was determined by ¹H NMR using the ratio between the CH_2 's of the $\text{PE-CH}_2\text{-Si}(\text{CH}_2\text{CH}_3)_3$ end group and the methylene protons in the backbone; the trend in these DP's are consistent with the DP determined by GPC. As illustrated in Figure 2, the degree of polymerization of the polyethylene is inversely proportional to the concentration of silane, confirming that the tertiary silane is a chain-transfer agent for the catalytic polymerization of ethylene. It is also worth noting that the activity of the catalyst decreases as the concentration of silane is increased. We attribute this decay to the lower stability of the cobalt silyl species, which is consistent with the fact that the cobalt silyl species could not be isolated nor detected (*vide infra*).⁴⁸

We further confirmed that the silane is covalently attached to the polymer end by performing a ¹H DOSY NMR

Table 2. Effect of HSiEt_3 Concentration on DP with Catalyst Co-Et^a

entry	HSiEt_3 (mM)	yield (g)	TOF ^b (h ⁻¹)	DP ^c (NMR)	DP ^d (GPC)	D ^d
1	5.1	0.27	155	126	193	2.0
2	10.5	0.18	105	74	89	2.3
3	15.5	0.21	125	61	63	2.4
4	20.6	0.20	120	51	54	2.2
5	25.7	0.16	90	43	44	2.5
6	31.2	0.17	95	37	42	2.6
7	36.2	0.14	80	33	38	2.9
8	41.3	0.16	90	27	33	3.0

^aConditions: 20.7 μ mol of catalyst Co-Et; 50 mL of dichloromethane; 25 °C; 40 psi ethylene; reacted for 3 h. ^bTOF is based on gravimetric yield of polymer and moles of catalyst used. ^cDP was determined based upon Si end groups in the NMR, polymer yield, and moles of catalyst added (see Supporting Information). ^dDP and D were determined by GPC.

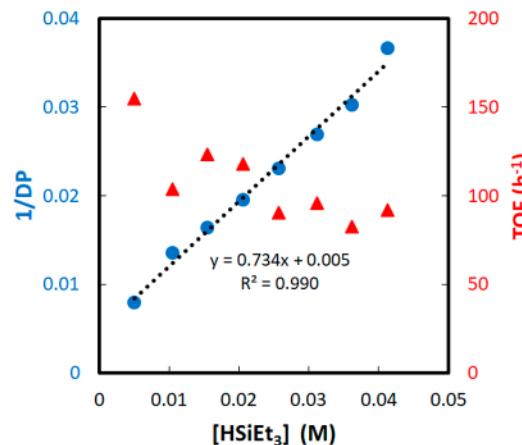


Figure 2. Plot of 1/DP (NMR) and catalyst activity vs triethylsilane concentration. The equivalent version using DP determined from GPC is provided in the Supporting Information.

experiment of the polymer, which shows that the diffusion rate of the Si-Et protons is similar to the diffusion rate of the protons belonging to the polyethylene (Table 3).

Table 3. Diffusion Coefficients for Polymer-SiEt₃

peak ^a (ppm shift)	diffusion coefficient (m ² /s)
solvent (5.920)	8.34×10^{-10}
PE CH_2 (1.271)	1.66×10^{-10}
PE CH_3 (0.882)	2.15×10^{-10}
PE- $\text{Si-CH}_2\text{-CH}_3$ (0.935)	2.06×10^{-10}
PE- $\text{Si-CH}_2\text{-CH}_3$ (0.521)	2.05×10^{-10}
silicone grease (0.07)	3.63×10^{-11}

^aConditions: see Supporting Information.

Kinetic Study. As the incorporation of the chain-transfer agent, and thus formation of the end-functionalized polymer, depends on two concomitant reactions, namely, chain growth and chain transfer, we proceeded to investigate the kinetics of the chain-transfer polymerization. With the Mayo equation the linear relationship between 1/DP and the CTA concentration (eq 1) provides information regarding the ratio of the rate constant of chain transfer $k_{\text{trp-n}}$ to the rate constant of chain propagation $k_{\text{p-n}}$ (see Scheme 1), assuming the ethylene

dependency of the polymerization is known. Therefore, a series of ethylene polymerizations were performed at varying monomer concentration to determine the order of ethylene (Figure 3).

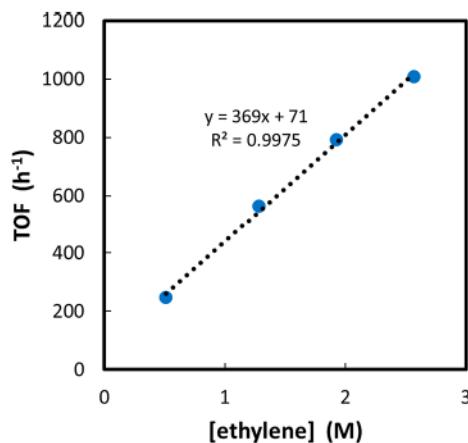


Figure 3. Dependency of activity of Co-Et as a function of ethylene concentration. Conditions: 20.7 μmol of catalyst Co-Et; 50 mL of dichloromethane; 25 $^{\circ}\text{C}$; varying ethylene pressure; reacted for 1 h to minimize polymer precipitation. TOF is based on gravimetric yield of polymer and moles of catalyst used.

The activity of the polymerization increases linearly with ethylene concentration showing that the polymerization is first order in ethylene in absence of silane, which allowed us to adjust the power dependency of the ethylene term in eq 1 to result in eq 2.

Equation 2. Theoretical dependence of DP on [silane].

$$\frac{1}{\text{DP}} = \frac{1}{\text{DP}_0} + \frac{k_{\text{trp}-n}[\text{silane}]}{k_{p-n}[\text{ethylene}]} \quad (2)$$

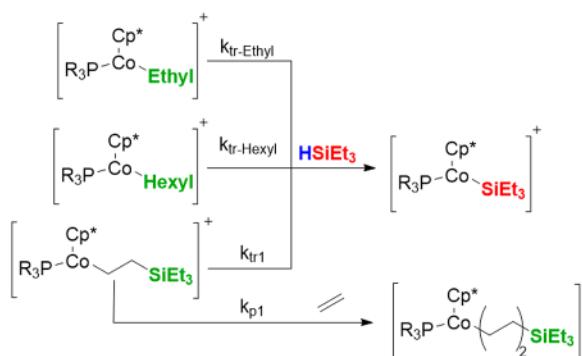
Equation 3. Relation between k_p and turnover frequency (TOF).

$$\text{TOF} = k_{p-n}[\text{ethylene}] \quad (3)$$

Using eq 3 and the solubility of ethylene under polymerization conditions, we determined the rate constant of propagation of Co-Et k_{p-n} to be 480 $\text{h}^{-1} \text{M}^{-1}$ (the 0.514 M point in Figure 3 was used to calculate this instead of the slope, as polymer precipitation at higher pressures consistently lowers the slope).¹⁸ Plugging k_{p-n} , the ethylene concentration, and the slope of the regression line from Figure 2 into eq 2 provides the rate constant of chain transfer $k_{\text{trp}-n} = 180 \text{ h}^{-1} \text{ M}^{-1}$. This confirms that the rate of chain transfer is faster than the rate of chain propagation, especially considering the large differences in [ethylene] (514 mM) and [silane] (5–40 mM). This result is consistent with the formation of polymer and the partial consumption of the silane.

A striking difference between our ethylene chain-transfer polymerization and Brookhart's hydrosilylation of hexene is that the rate of ethylene propagation is faster than σ -bond metathesis, while σ -bond metathesis is significantly faster than hexene insertion into a Co-alkyl chain (as evidenced by the absence of any consecutive insertions of hexene being observed). This selectivity motivated us to investigate in more detail the rates of the different elementary steps of the chain-transfer polymerization, summarized in Scheme 2.

Scheme 2. σ -Bond Metathesis and Ethylene Insertion of Cobalt Alkyl Species



As the cobalt catalyst contains an agostic bond, the rate of migratory insertion of ethylene into an ethyl group (polymer with a DP = 1) is slower than the rate of insertion into a butyl or longer group (polymer with a DP ≥ 2).^{43,49} We therefore investigated whether a similar effect is observed with the silane σ -bond metathesis using cobalt alkyl complexes with either an ethyl or a hexyl chain. We were also interested in studying the effects of the pendant silane group on the rate of ethylene insertion and silane addition by comparing the Co-Et to a Co-Et-SiEt₃ species.

The rate of cleavage of the cobalt–ethyl bond was determined by reacting Co-Et with 10 equiv of HSiEt₃ in CD₂Cl₂ at -46 $^{\circ}\text{C}$ and monitoring the disappearance of the agostic hydrogen signal (-12.2 ppm). As can be seen in Figure 4 the logarithm of the concentration of Co-Et decreases

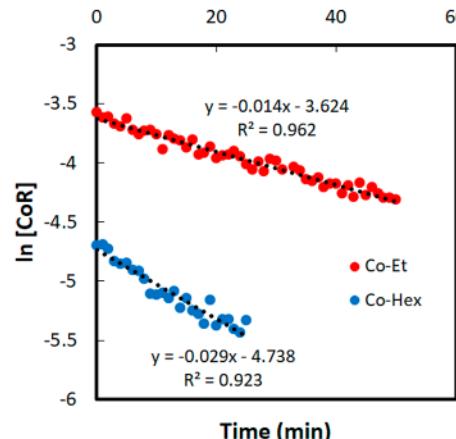


Figure 4. Differing rates of chain transfer with HSiEt₃ for Co-Et and Co-Hex.

linearly with time, suggesting a first-order reaction; using eq 4, we determined $k_{\text{tr-ethyl}} = 2.0 \text{ h}^{-1} \text{ M}^{-1}$ at -46 $^{\circ}\text{C}$ (Scheme 2). The reaction was confirmed to be first-order in silane by performing a second experiment with double the silane loading, which resulted in double the observed rate (Table S2 in the Supporting Information).

Equation 4. Rate of silane chain transfer.

$$\text{rate} = k_{\text{tr-R}}[\text{CoR}][\text{HSiEt}_3] \quad (4)$$

The cobalt hexyl complex Co-Hex was used as a model for the catalyst attached to a polymer chain; this was synthesized by performing the hydrogenation of hexene using Co-Et.

Under analogous conditions for Co-Et, the rate of cleavage for Co-Hex was monitored by the disappearance of the agostic hydrogens at -12.9 and -13.1 ppm to give $k_{\text{tr-hexyl}} = 4.0 \text{ h}^{-1} \text{ M}^{-1}$ at -46°C . The larger value of $4.0 \text{ h}^{-1} \text{ M}^{-1}$ for Co-Hex versus $2.0 \text{ h}^{-1} \text{ M}^{-1}$ for Co-Et demonstrates that σ -bond metathesis is faster when the cobalt center is attached to a longer alkyl chain. This is consistent with the observation made by Brookhart for the migratory insertion of ethylene.⁴³

Considering the impact of chain length on the rate of σ -bond metathesis, we decided to investigate the effect of the terminal silane group of the alkyl chain on the rate of chain transfer and ethylene insertion. The Co-Et-SiEt₃ complex was synthesized in situ by exposing a solution of Co-Et and 15 equiv of vinyl triethyl silane to 100 psi of H₂ for 30 min and then purging with argon to yield a mixture of Co-Et-SiEt₃ and Co-Et (80/20) as well as unreacted vinyl triethyl silane.⁴⁴ This solution was then cooled to -78°C , and either a solution of HSiEt₃ in CD₂Cl₂ was added or the headspace was purged with ethylene; both reactions are under flooded conditions to ensure pseudo-first-order kinetics. The samples were allowed to warm to the reaction temperature, and the rates of chain transfer or ethylene insertion were monitored by following the disappearance over time of the Co-Et-SiEt₃ agostic hydrogen at -10.40 ppm. The rate constants k_{tr1} and k_{p1} were determined at various temperatures and used to construct an Arrhenius plot (Figure 5) to extrapolate the rate constants to

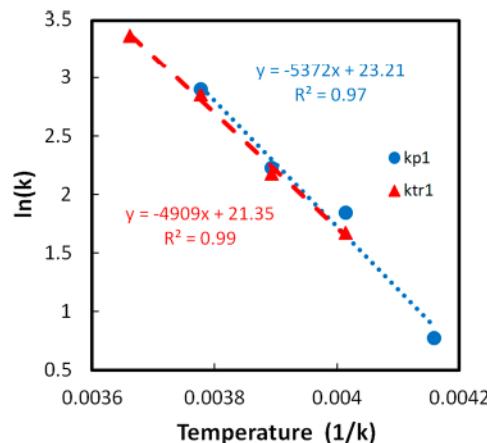


Figure 5. Arrhenius plot for Co-Et-SiEt₃ σ -bond metathesis with HSiEt₃ and insertion of ethylene.

room temperature ($k_{\text{tr1}} 133 \text{ M}^{-1} \text{ h}^{-1}$ and $k_{\text{p1}} 180 \text{ M}^{-1} \text{ h}^{-1}$). This shows that the pendant silane group of Co-Et-SiEt₃ slows the rate of ethylene insertion more than the rate of chain transfer when comparing to the rate constants determined from the Mayo equation for the Co-polymer species ($k_{\text{tr-p}} 180 \text{ M}^{-1} \text{ h}^{-1}$ and $k_{\text{p-p}} 480 \text{ M}^{-1} \text{ h}^{-1}$).

To complete our mechanistic study of the chain-transfer polymerization we attempted to measure the rate of insertion of ethylene into the cobalt silyl bond (k_i from Scheme 1). Although the three NMR chain-transfer rate studies with HSiEt₃ described above presumably yielded the desired cobalt silyl complex, no new peaks consistent with it were observed. This lack of signal is attributed to the instability of the Co-SiR₃ species, which is consistent with previous failed attempts to observe it.⁴⁸ The reaction of Co-Et with HSi(OEt)₃ was performed as a final attempt to characterize the corresponding cobalt silyl complex. We hypothesized that altering the

electronics of the silane could stabilize the desired complex. This reaction resulted in the release of ethane confirming the cobalt carbon bond cleavage and produced several new peaks in ¹H region ($-12.85, -13.1, -15.45, -16.3$ ppm) similar to other Co-R species. However, the absence of any cross peaks in the $\{^1\text{H}^1\text{H}\}$ gCOSY and $\{^1\text{H}^{29}\text{Si}\}$ gHMBC NMR suggests that the protons did not belong to the desired Co-Si(OEt)₃ species. Electrospray ionization (ESI) mass spectrometry of the crude reaction mixture was also unable to detect any signal consistent with a Co-SiR₃ species using either HSi(OEt)₃ or HSiEt₃. This lack of detection and the decay in polymerization activity observed at higher silane concentrations are consistent with the instability of this intermediary species. This completes our study of the kinetics of the chain-transfer mechanism; an overview of each rate constant is shown in Table 4, and we moved on to synthesizing functionalized polyethylene.

Table 4. Overview of Various Rate Constants

species	HSiEt ₃	ethylene
Co-Et	$2.0 \text{ h}^{-1} \text{ M}^{-1}$ (-46°C)	$6.5 \text{ h}^{-1} (-70^\circ\text{C})^a$
Co-Hex	$4.0 \text{ h}^{-1} \text{ M}^{-1}$ (-46°C)	$\sim 26 \text{ h}^{-1} (-70^\circ\text{C})^a$
Co-Et-SiEt ₃	$133 \text{ h}^{-1} \text{ M}^{-1}$ (25°C)	$180 \text{ h}^{-1} \text{ M}^{-1}$ (25°C)
Co-Polymer	$180 \text{ h}^{-1} \text{ M}^{-1}$ (25°C)	$480 \text{ h}^{-1} \text{ M}^{-1}$ (25°C)

^aThese rate constants have been reported in the literature and are included for comparison.⁴³ The rate constant is for the ethylene coordinated complex. The catalysts used are the Co-Et and Co-Pr BF₄ versions.

Functionalized Polyethylene. The primary goal for the development of this chain-transfer polymerization system was to efficiently introduce functional groups into polyethylene chains. To incorporate the largest fraction of functional groups, we investigated the effect of the silane substituent on the chain-transfer rate. As can be seen in Table 5 bulky silanes such as

Table 5. Substituent Effects of Various Silanes on DP^a

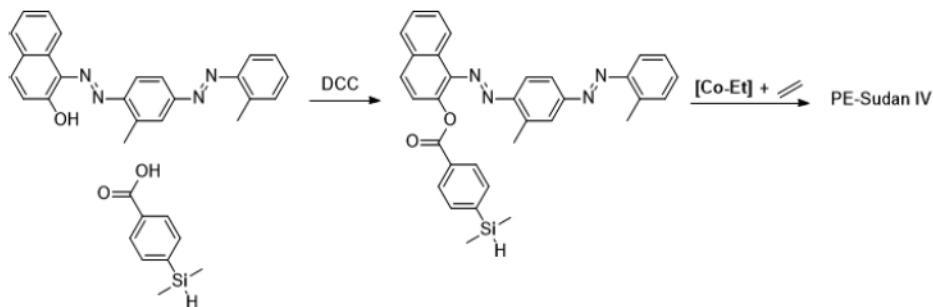
entry	silane	ethylene (psi)	TOF ^b h ⁻¹	DP ^c	Si/Co ^d
1	none	40	215	644 ^e	NA
2	HSiEt ₃	40	87	46	4.7
3	HSiEt ₂ Me	40	44	26	4.1
4	HSi(ⁱ Pr) ₃	40	184	ND ^f	0
5	HSiPh ₃	40	192	ND ^f	<0.3
6	HSi(OEt) ₃	40	11	ND ^f	ND
7	HSi(OEt) ₃	240	236	86	7.5

^aConditions: $20.7 \mu\text{mol}$ of catalyst Co-Et; 50 mL of dichloromethane; 20.65 mM silane; 25°C ; reacted for 3 h. ^bTOF is based on gravimetric yield of polymer and moles of catalyst used. ^cDP was determined by NMR. ^dMoles silane reacted per mol catalyst, determined by NMR and yield. ^eDP was determined by gravimetric yield. ^fDP was not determined, since there are too few Si ends to accurately determine it.

HSi(ⁱPr)₃ and HSiPh₃ (Table 5 Entry 4 and 5) are slow chain-transfer agents, and little to none of the silane reacts, Si/Co < 0.3; the less bulky HSiEt₂Me (Table 5 Entry 3) appears to be faster at chain transfer than HSiEt₃ as evidenced by the lower DP.

The activity of the catalyst in the presence of faster chain-transfer agents was observed to be systematically lower. We again attributed this decay in activity to the instability of the Co-Si intermediate. For example, when the electron-deficient

Scheme 3. Synthesis of Silane-Modified Sudan IV



HSi(OEt)_3 was used (Table 5 Entry 6) barely any polymer was recovered. Hypothesizing that the Co–Si intermediate is decomposing before ethylene can insert, increasing the rate of insertion should decrease the time spent in the unstable Co–Si form. Indeed, by increasing the ethylene pressure (Table 5 Entry 7) this resulted in higher polymer yields, beyond the expected ethylene polymerization first-order rate increase, signifying that more of the catalyst remained active. The polymer formed also contained a high amount of Si incorporation (7.5 Si/Co, 15% of silane loading). These high rates of chain transfer are valuable for introducing polar groups using a modified CTA.

Having tested the effects of the silane substituents on the rate of chain transfer we moved on to using the silane as a means to covalently link a dye (Sudan IV) to the end of the polyethylene (Scheme 3). A benzoic acid dimethyl silane was used for this purpose; the carboxylic acid allows easy attachment to a multitude of groups, while the two Me on the silane should increase the rate of chain transfer and thus incorporation.

We first demonstrated that the cobalt catalyst remains active in the presence of Sudan IV (Table 6 Entry 2) and that a



Figure 6. Sudan IV modified PE.

CONCLUSIONS

The chain-transfer polymerization of ethylene using silanes as chain-transfer agents and a cyclopentadienyl cobalt complex as catalyst to synthesize silane end-modified semicrystalline polyethylene was successfully developed. This expands upon our previous work with a palladium diimine chain-transfer system that made silane end-modified hyper-branched polyethylene. With the cobalt catalyst system we were able to control the molecular weight of the polymer by simply tuning the silane concentration, which shows that silanes are effective chain-transfer agents for ethylene polymerization. The rates of chain transfer and other key steps in the mechanism have been determined. Most unique to this catalyst is that the rates of chain transfer and ethylene insertion depend upon the length of the growing polymer chain on the cobalt center. The rate of chain transfer was also shown to vary with the silane substituents. In the case of certain chain-transfer agents, the instability of the cobalt silyl intermediate was shown to decrease the productivity of the catalyst. This decay could be partially circumvented by performing the reaction at higher ethylene pressure. The benefit of our late transition-metal chain-transfer system over other systems is its ability to incorporate heteroatoms besides the chain-transfer agent itself. We demonstrated this using a silane-modified Sudan IV dye (dye attached to CTA), which was successfully incorporated into the high density polyethylene. Our group is currently seeking to further extend the types of polymer composition and architecture that can be achieved with this technique.

EXPERIMENTAL SECTION

General Methods and Materials. All reactions were performed in oven-dried glassware using standard Schlenk line technique under a nitrogen or argon atmosphere. All solvents were dried using a solvent purification system; dichloromethane was additionally dried over molecular sieves for at least 2 days. All commercially obtained reagents were used as received unless otherwise noted; silanes were degassed by three freeze–pump–thaw cycles: sodium tetrakis[3,5-

Table 6. Dye-Modified Silane Experiments^a

entry	additive	ethylene (psi)	yield (g)	TOF ^b (h ⁻¹)	Si/Co ^c
1	none	40	0.37	215	NA
2	Sudan IV	40	0.27	154	NA
3	HSiMe_2Ph	40	0.07	43	0.3
4	HSiMe_2Ph	240	0.60	345	1.0
5	silane dye	240	0.35	203	0.2

^aConditions: 20.7 μmol of catalyst Co-Et; 50 mL of dichloromethane; 3 equiv of additive were used; 25 °C; reacted for 3 h. ^bTOF is based on gravimetric yield of polymer and moles of catalyst used. ^cMoles silane reacted per mol catalyst, determined by NMR and yield.

simpler version of the silane HSiMe_2Ph (Table 6 Entry 3) is capable of chain transfer; the lower than normal incorporation can be increased by increasing the ethylene pressure (Table 6 Entry 4). Nonetheless the chain-transfer polymerization using the Sudan IV-functionalized silane was performed at high ethylene pressure (Table 6 Entry 5) and resulted in an orange PE (Figure 6) with 0.2 equiv of the silane dye being incorporated as the end group as determined via ^1H NMR. As no residual starting silane is detected in the NMR, we concluded that the dye is covalently attached to the polymer and not just a blend; this was further confirmed by stirring the polymer in CH_2Cl_2 for several days, and no leaching of the dye was observed.

bis(trifluoromethyl)phenyl]borate (NaBArF_{24}) was purified by washing with dichloromethane and dried under high vacuum at 100 °C to remove water. $\text{H(OEt}_2\text{)}_2\text{BArF}_{24}$ and catalyst Co-Et were synthesized according to literature procedures.^{46,50} Conversion of ethylene (psi to M in CH_2Cl_2) was performed using the equation provided by Brookhart.⁵¹

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity 500 MHz, Bruker Ascend 500 MHz or Varian Unity Inova 600 MHz spectrometer. Spectra are reported in parts per million and referenced to the residual solvent signal. DOSY NMR were recorded on a Varian Unity Inova 600 MHz NMR equipped with a 5 mm Varian AutoTuneX probe; the procedure for DOSY NMR is described in detail in the *Supporting Information*. High-temperature NMRs were performed in 1,1,2,2-tetrachloroethane- d_2 . Gas chromatography was run using an Agilent Technologies 6850 GC equipped with a flame ionization detector. UV–Vis spectra were recorded using a Cary 50 Bio UV–visible spectrophotometer. ESI mass spectra were recorded using a Waters Quattro Ultima equipped with a quadrupole-hexapole-quadrupole. Air/water/temperature sensitive samples were done in water-free deoxygenated solvents and were synthesized right next to the mass spectrometer before being run.

Polymerization Procedure and Mathematical Analysis. All polymerizations were performed in a stainless steel 200 mL Büchiglasuster miniclave drive reactor. The reactor was dried under vacuum for 2 h and flushed with nitrogen. A 25 mL solution of silane (for experiments that used silane) in dichloromethane was syringed into the reactor. Subsequently 25.0 mg of catalyst Co-Et in 25 mL (50 mL if no silane) of dichloromethane was syringed into the reactor and immediately pressurized to the desired ethylene pressure with stirring. After the appropriate reaction time the ethylene pressure was released, and the reaction was quenched in methanol. The polymer was isolated by filtration and dried under vacuum (at 40 °C) overnight.

Determination of DP by NMR for Silane-Containing Polyethylene Samples. To accurately determine DP by NMR, one must account for the polymer chains that would have been formed by the initial Co-Et catalyst using eq 5 below. Mol ethylene is defined as the number of moles of ethylene that reacted = polymer yield g/28.05. The Si-coefficient is defined as the total number of hydrogens from CH_2 's that are attached to the Si in the polymer. For HSiEt_3 this would be 8; for HSi(OEt)_3 this would be 2.

$$\text{DP} = \frac{\text{mol ethylene}}{\text{mol CoEt} + \text{mol ethylene} \times \left(\frac{\text{Si-CH}_2 \text{ area / Si-coefficient}}{\text{PE area / 4}} \right)} \quad (5)$$

Determination of DP by GPC and Comparison with Values Determined by ^1H NMR. Gel permeation chromatography was performed by PolyAnalytik using a Tosoh HLC-8321GPC/HT at 145 °C equipped with two TSKgel HHR HT2 columns with trichlorobenzene as the mobile phase. Mn and polydispersity index (PDI) were determined using refractive index against polyethylene standards. Reported values are the average of two repeat runs. A representative chromatogram of the chain-transfer polymerization is shown in Figure S7 in the *Supporting Information*. The values of DP determined by GPC in Table 2 are the combination of all three peaks. The peak at 21 184 g/mol is consistent as if no chain transfer had occurred in the reactor, even though the combined peaks at 1516 g/mol are consistent if chain transfer did occur in the reactor. We hypothesize that the peak at 21 184 g/mol is due to a number of cobalt centers that had polymerized sufficiently that the formed polyethylene caused it to crash out of solution, before silane could cause chain transfer. This would protect it from chain transfer while still allowing it to polymerize. The values of DP as determined via NMR or GPC, Table 2, differ mostly at low loadings of silane. While the values of the two methods are different the trend is the same, as evidenced by the plot of 1/DP (from GPC) versus $[\text{HSiEt}_3]$ in Figure S3 in the *Supporting Information*.

Determination of the Number of Silanes that Reacted per Catalyst. Equation 6, below, was used to determine the equivalents of

silane that reacted per cobalt catalyst for Table 5 and the dye-labeled polymer. Si-Coefficient is as defined in eq 5.

$$\text{Si/Co} = \frac{\text{mol ethylene}}{\text{mol CoEt}} \times \left(\frac{\text{Si-CH}_2 \text{ area / Si-coefficient}}{\text{PE area / 4}} \right) \quad (6)$$

Low-Temperature NMR Kinetics. Co-Hex Catalyst Synthesis.

This was performed based on the literature procedure for the propyl version.⁴⁸ Under air/water-free conditions Co-Et (100.0 mg 0.0826 mmol) and a large excess of 1-hexene were dissolved in CH_2Cl_2 (20 mL). This was placed inside an oven-dried steel reactor, which was then pressurized with H_2 (100 psi) and reacted for 1 h. The pressure was released, argon was blown through the reactor to remove excess H_2 , and the solution was transferred to a glass flask. The solvent was removed in *vacuo* to yield a dark brown solid (43 mg, 41% isolated yield). Co-Hex was shown to be stable at -46 °C in absence of silane by monitoring the agostic ^1H peak -13.15 ppm over time; this is included in the *Supporting Information* as Figure S14. ^1H NMR at -46 °C (600 MHz, CD_2Cl_2) σ 7.67 (s, BArF_{24} Ar-ortho), 7.49 (s, BArF_{24} Ar-para), 4.06–3.65 (m), 3.59 (d, coordinated P(OMe)_3), 1.64 (s, C_5Me_5), 2.70–0.10 (m, aliphatic), -11.83 (m, agostic H), -12.12 (d), -12.45 (m), -12.62 (t), -12.88 (m, agostic H), -13.15 (d, agostic H), -14.26 (t, $\text{Cp}^*(\text{P(OMe)}_3)_2\text{Co-H}^+\text{BArF}_{24}^-$). The full ^1H NMR spectrum is provided in the *Supporting Information* as Figure S12. Three agostic hydrogens are observed, which are consistent with the agostic hydrogens observed by Brookhart in the propyl version.⁵² Figure S11 in the *Supporting Information* details the structures of the different agostic hydrogens. ^{31}P NMR at -46 °C (243 MHz, CD_2Cl_2) σ 157.145 (s, $\text{Cp}^*(\text{P(OMe)}_3)_2\text{Co-H}^+\text{BArF}_{24}^-$), 152.124 (s, P(OMe)_3 of Co-Hex), 145.781 (s), 130.956 (s). The ^{31}P NMR is provided in the *Supporting Information* as Figure S13.

Determination of Co-Et and Co-Hex Rate of Chain Transfer with HSiEt_3 . To an NMR tube 21.5 μmol of the catalyst Co-Et or Co-Hex dissolved in 0.25 mL of CD_2Cl_2 was added and fitted with a septum cap. The sample was then frozen in liquid nitrogen, and a 0.25 mL solution of HSiEt_3 was slowly added, which froze. The sample was then melted in a dry ice bath, shaken, and then added to the NMR (precooled to -78 °C). The NMR was warmed to the operating temperature of -46 °C and allowed to equilibrate thermally, and then data collection was started by following the disappearance of the agostic hydrogen signal. Final volume of the NMR sample was determined by marking a line where the solution is, filling the empty tube with acetone, and using the mass of acetone and the density to determine volume. The silane concentration and observed rate constants can be found in the *Supporting Information* in Table S2.

Determination of k_{tr1} and k_p for Co-Et-SiEt₃. The catalyst Co-Et-SiEt₃ has been reported previously and is synthesized in a similar manner.⁴⁴ The catalyst was prepared by dissolving 20.6 μmol of Co-Et and 15 equiv of vinyl triethyl silane in ~1 mL of CD_2Cl_2 . This was placed inside a vial fitted with a cap with a needle through it (the needle did not go into the solution; that way, when the pressure is released the solution does not squirt out). This vial was placed inside a small steel reactor inside the glovebox, sealed, and then brought out. This was hooked up to an H_2 cylinder and pressurized to 100 psi for 30 min at room temperature (RT), then depressurized, and argon was blown through the reactor to get rid of excess H_2 . The reactor was brought back into the glovebox, the vial was taken out, and the solution was added to an NMR tube equipped with a septum cap. This was then cooled to -78 °C and added to the NMR to pre lock and shim the NMR as well as to confirm that Co-Et-SiEt₃ was formed in a sufficient amount to perform kinetic experiments. The NMR tube was then taken out, placed in a dry ice bath, and then either had ethylene purged through the tube or a solution of HSiEt_3 (10 equiv) in CD_2Cl_2 added. The tube was then shaken, added to the NMR, and warmed to the desired temperature, and then data acquisition was started; rate of the reaction was monitored by following the disappearance of the agostic hydrogen at -10.40 ppm. There was no noticeable consumption of excess vinyl triethyl silane during the experiment. The determined rate constants are listed in Table S3 in

the Supporting Information. Control experiments show that the Co-Et₂SiEt₃ species is sufficiently thermally stable at the temperatures investigated and that its decomposition will not significantly contribute to the determined rate constants.

Synthesis of the Dye-Labeled Silane and Polymer. **Dye-Labeled Silane.** Under water-free conditions Sudan IV (0.4877 g), 4-(dimethylsilyl)benzoic acid (0.4554 g), synthesized according to literature;⁵³ *N,N'*-dicyclohexylcarbodiimide (0.5103 g), and 4-(dimethylamino)pyridine (0.0147 g) were combined and dissolved in dichloromethane (50 mL). The reaction was left to stir at room temperature for 24 h. The solution was filtered, and the filtrate was isolated, of which the solvent was removed in *vacuo* to give an orange/purple solid. This solid was purified by column chromatography (40% dichloromethane, 60% hexanes) to give a dark orange solid. Obtained 0.4302 g (62% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.745–7.275 (m, 17H Ar), 4.482 (sep, *J* = 4 Hz, 1H Si–H), 2.741 (s, 3H Ar–CH₃), 2.481 (s, 3H Ar–CH₃), 0.394 (d, *J* = 4 Hz, 6H Si–(CH₃)₂); Mass spec (ESI): M+H. Theoretical 543.22 Experimental: 543.5; UV-vis (CH₂Cl₂) λ_{max} = 385 nm, ϵ = 21 350 cm^{−1} M^{−1}.

Note: The silane carboxylic acid precursor used in this reaction displays two different Si–H species in the NMR but only one spot on the thin-layer chromatography (TLC). We believe these to be two different isomers, of which the major isomer is the para isomer as identified by ¹³C and two-dimensional (2D) NMR. Both of these isomers react with Sudan IV to make the silane-modified dye; the chemical shifts we report are for the major isomer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.organomet.8b00765](https://doi.org/10.1021/acs.organomet.8b00765).

All experimental methods, materials and characterization (PDF)

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Notes

The authors declare no competing financial interest.

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