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Selective Chain-End Functionalization of Polar Polyethylenes: Orthogonal Reactivity of Carbene and Polar Vinyl Monomers in Their Copolymerization with Ethylene

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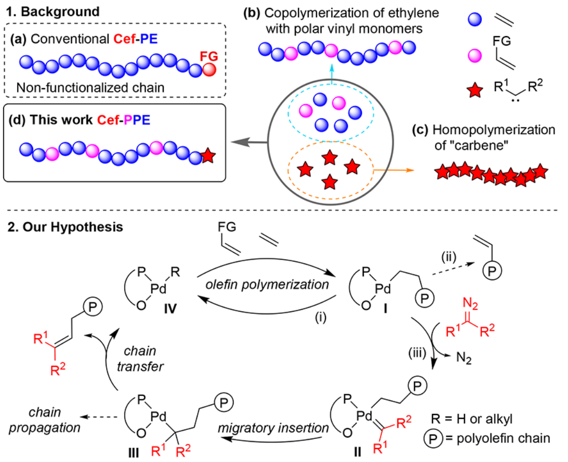
Supporting Information

ABSTRACT: Pd(II)-catalyzed copolymerization of ethylene, carbene species, and polar vinyl monomers is successfully developed for the first time to obtain chain-end-functionalized polar polyethylenes, with selective distribution of the polar vinyl monomers within the main chain and carbene at the chain-end. Notably, >99% chain-end-capping with the carbene species can be achieved under the optimized conditions. Mechanistic investigations suggest that the carbene precursor reacts with the generated alkyl palladium complex to terminate the growing chain-end and regenerate the catalyst.

Chain-end-functionalized polyethylenes (Cef-PEs) play a paramount role in the construction of complex macromolecular architectures (Scheme 1a).[1] Three general methods can be used to synthesize Cef-PEs: (1) controlled end-capping of living PE chains after living coordination polymerization of ethylene;[2] (2) chain-end functionalization via chain-transfer reactions during coordination−insertion polymerization of ethylene;[3] and (3) postmodification of the unsaturated chain-ends of preformed polyethylenes.[4] From the viewpoint of efficiency and productivity, method (1) inherently imposes a restriction that one catalyst molecule forms only one polymer chain.[2] Thus, chain-end functionalization via chain transfer (method (2)) is more preferable as a one-pot *in situ* approach and produces a large number of polymers per catalyst.[3] Early transition-metal catalysts such as group 3 and 4 metal complexes have been widely used for this chain-transfer chain-end functionalization: examples include σ-bond metathesis with the H−X bond or C−X bond of an amine (H−NR$_2$), borane (H−BR$_2$), alane (R−AlR$_2$), thiophene (H−C$_4$H$_3$S), etc.[3] Postmodification of preformed unsaturated chain-ends (method (3)) presents several disadvantages because quantitative chain-end unsaturation is required, and the chemical transformations are often hampered by the low concentration of the chain-end double bonds as well as the poor solubility of PEs.

Scheme 1. Copolymerization of Ethylene, Carbene, and Vinyl Monomers



Despite the significant progress in the synthesis of Cef-PEs, few examples can be applied to one-pot *in situ* chain-end functionalization of polar polyethylenes, which are statistical copolymers of ethylene and polar vinyl monomers. The reasons are as follows: (1) early transition-metal catalysts cannot be used, as they are poisoned easily by polar functional groups;[3] and (2) by using group 10 metal catalysts, the ethylene/polar vinyl monomer copolymerization takes place, but the alkylmetal species thus formed often undergoes β-hydride elimination, affording copolymers bearing a terminal vinyl group and/or in-chain C═C bonds.[5] The only functional group introduced successfully thus far is a furyl group in the copolymerization of ethylene and carbic anhydride, using vinylfuran as a chain-end functionalization reagent.[6]

In recent years, intensive efforts have been devoted to the development of late-transition-metal-catalyzed copolymerization of ethylene with polar monomers, which enables the incorporation of polar functional groups into polyethylene chains (Scheme 1b).[5] Particularly, palladium/phosphine−sulfonate complexes have been proven to be tolerant toward a large scope of polar monomers to produce highly linear copolyethylenes.[7] The unsymmetric ligand structure bearing a strong σ-donor and a weak σ-donor is proposed to play an indispensable role, suppressing chain-transfer reactions by β-hydride elimination. However, the polar comonomers utilized to date are limited to vinyl compounds[5] and/or carbon monoxide.[8] In this study, we envisioned that functionalized carbenes would be a novel class of comonomers for the

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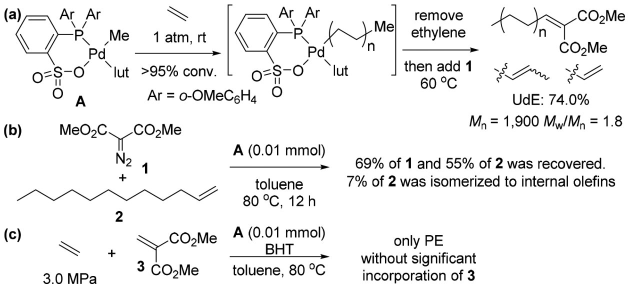
synthesis of such functionalized polymers. It is well known that carbenes can undergo migratory insertion into transition-metal−carbon bonds.[9] In addition, diazoacetates ($N_2{=}CHCO_2R$) can be polymerized under transition-metal catalysis, with the release of N_2 gas, to access functional polymethylenes, as pioneered by Ihara[10] and de Bruin[11] (Scheme 1c). These papers support our idea of using carbene comonomers. To the best of our knowledge, however, there is only one reported example of the successful copolymerization of ethylene with a carbene precursor, in the presence of a rhodium catalyst.[12] The copolymerization afforded a mixture of carbene homopolymers and carbene/ethylene random copolymers with only 2−11 mol % ethylene incorporation in the whole mixture, and the copolymers had many branches.

We hypothesized whether a stable carbene precursor such as dimethyl diazomalonate **1** could be used as a comonomer for selective chain-end functionalization. Our mechanistic hypothesis begins with olefin polymerization by well-known palladium/phosphine−sulfonate catalysts (Scheme 1). Continuous insertion of olefins (either ethylene or polar vinyl monomers) results in the formation of an alkyl palladium complex **I**. Three pathways from intermediate **I** can be considered: (i) chain propagation by subsequent olefin insertion, (ii) chain transfer via β-hydride elimination, and (iii) reaction with **1** to form Pd−carbene complex **II**. Once **II** is generated, key intermediate **III** may be formed by the migratory insertion of the carbene into the Pd−alkyl bond. We anticipated that owing to the steric hindrance of the ester-substituted carbon atom connected to the palladium atom, chain propagation from these carbene insertion intermediates might be suppressed. Accordingly, direct chain transfer from **III** would be favorable to afford chain-end-functionalized copolymers and generate the Pd−H species to reinitiate the olefin polymerization. The formation of a conjugate double bond in the malonic ester unit may also be a driving force.

To investigate the feasibility of our hypothesis, we first examined the homopolymerization of **1** using catalyst **A** at 80 °C. The results indicated no significant formation of homopolymethylene. Next, stepwise copolymerization of ethylene and **1** was performed (Scheme 2a). Complex **A** was reacted with 1.0 atm of ethylene at room temperature, which resulted in the formation of a palladium complex bearing a long alkyl chain, as detected by ^1H NMR analysis.[13] After excess ethylene was removed, **1** was added to the mixture. The reaction afforded a PE (M_w = 1900; M_w/M_n = 1.8) with diester (dE)-based end groups as the major chain-end (UdE, 74.0%) and alkenyl groups as the minor chain-end (26.0%). The incorporated dE was located entirely at the unsaturated chain-end, and no sequential incorporation of carbene was detected. In addition, no functionalized products from 1-dodecene **2** were detected in the reaction of 1-dodecene **2** and **1** in the presence of catalyst **A** (Scheme 2b). Only ∼7% of **2** was isomerized to the internal olefins. Thus, this suggests that the dE moiety is incorporated by carbene insertion to an alkylpalladium bond and subsequent β-hydride elimination, but not via the reaction of the carbene with 1-alkene as a transient intermediate.[14]

Scheme 2. Preliminary Mechanistic Investigations



Motivated by the above-mentioned results, we investigated the copolymerization of ethylene and carbene precursor **1** with palladium complexes **A**−**E** in toluene at 80 °C (Table 1, entries 1−5). All these reactions afforded dE-incorporated copolymers, thereby demonstrating that the palladium-catalyzed ethylene polymerization is compatible with **1**. The NMR analysis of these copolymers indicated that the majority of the incorporated dE is present as an unsaturated chain-end (UdE), and the minority of dE is present as a saturated chain-end (SdE). For example, the ^1H NMR spectrum of the copolymer corresponding to entry 3 (Figure 1a) clearly showed the characteristic resonances of the UdE chain-ends at 7.04 (t) (C), 3.86 (s) (A/B), 3.83 (s) (B/A), and 2.38 (m) (D) ppm, as well as those of SdE at 3.78 (s) (E) and 3.40 (t) (F) ppm. In the olefinic region, a vinyl group (a, b) and a 1-propenyl group ($-CH{=}CHCH_3$) (d) were also detected. Notably, the number of saturated chain-ends (sum of SdE and ethyl group) was equal to the number of unsaturated chain-ends (sum of UdE, $-CH{=}CH_2$, and $-CH{=}CHCH_3$), as determined by quantitative ^{13}C NMR analyses (see Supporting Information). These results provide important insights into the polymerization mechanism. The polymerization is initiated by ethylene insertion either into the Pd−CH_3 bond of complexes **A**−**E** or into a Pd−H bond generated by β-hydride elimination. Carbene insertion to a Pd−H bond is likely to be responsible for the formation of SdE structures. Notably, there is no notable incorporation of **1** into the main chains, suggesting that intermediate **III**, formed by carbene insertion into the Pd−alkyl species, does not undergo further chain propagation. This might be caused by the larger steric hindrance of **III** than the intermediate formed from the carbene insertion to the Pd−H species. The polymerization is possibly terminated by β-hydride elimination either from carbene-inserted palladium species **III** to form UdE or from alkylpalladium species **I** to form a terminal vinyl group (partial migration of the C−C double bond occurs).

As revealed by entry 1 in Table 1, the incorporated dE is entirely located at the unsaturated chain-end of the copolymer, rather than the saturated chain-ends (<1%), suggesting that the carbene precursor is less reactive than ethylene for insertion into the Pd−CH_3 (and Pd−H) bonds in the initiation step of the polymerization. The majority of the unsaturated chain-end was dE based, UdE (90.0%). As shown in entries 2 and 4 of Table 1, complexes **B** and **D** also produced low-molecular-weight copolymers with UdE as the major structure of the unsaturated chain-end, while complex **C** resulted in a decrease in UdE (entry 3). In the presence of complex **E**, the reaction afforded a copolymer with an especially high ratio of UdE (>99%), thus implying exclusive chain-end functionalization (entry 5). For the saturated chain-end, a relatively higher ratio of SdE (38.3%) was observed. Increasing the amount of the carbene precursor and decreasing the ethylene pressure improved the ratio of the chain-end functionalization with dE: UdE was improved to 93.4 and 99.0% when using catalyst **A** (entries 6 and 7), although M_n decreased in both cases.

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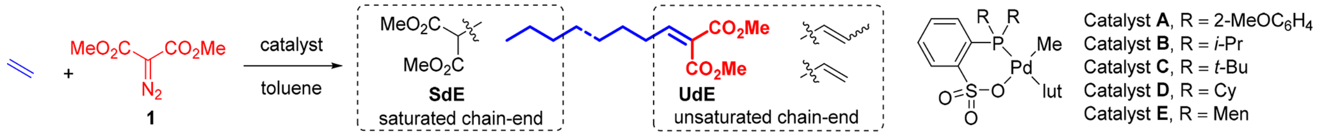
Table 1. Copolymerization of Ethylene and Dimethyl Diazomalonate Using Palladium Complexes[a]



entry	cat. (μmol)	"carbene" (mmol)	yield (g)[b]	activity (kg/mol·h)	M_n (g/mol)[c]	M_w/M_n[c]	i.r. (%)[d]	saturated chain-end, SdE (%)[e]	unsaturated chain-end, UdE (%)[f]	no. chains/Pd
1	**A** (4.0)	2.0	0.877	18.2	2,300	2.5	0.93	<1	90.0	95
2	**B** (4.0)	2.0	1.049	17.5	3,700	2.3	0.42	1.0	71.4	71
3	**C** (4.0)	2.0	1.500	31.2	6,400	4.2	0.10	13.0	17.6	58
4	**D** (4.0)	2.0	0.552	11.5	2,800	2.6	0.80	1.1	88.8	49
5	**E** (4.0)	2.0	0.038	0.8	4,700	2.6	0.64	38.3	>99	2
6	**A** (4.0)	4.0	0.448	9.3	1,500	2.3	1.24	<1	93.4	75
7[g]	**A** (4.0)	2.0	0.242	5.0	1,100	2.0	1.45	<1	99.0	55
8	**E** (10.0)	1.0	0.545	4.5	7,900	3.0	0.29	34.0	>99	7
9[h]	**E** (10.0)	1.0	0.583	4.8	15,400	2.5	0.11	10.3	>99	4

[a] A mixture of the catalyst (4.0 or 10.0 μmol) and dimethyl diazomalonate in toluene (10.0 mL) was stirred under an ethylene atmosphere (3.0 MPa) in a 50 mL autoclave at 80 °C. [b] Isolated yields after precipitation with methanol. [c] Molecular weights determined by size-exclusion chromatography using polystyrene standards and corrected by universal calibration. [d] Incorporation ratio of dE in mol %. [e] The saturated chain-ends containing dE in mol %. [f] The unsaturated chain-ends containing dE in mol %. [g] Ethylene atmosphere (1.0 MPa). [h] 50 °C.

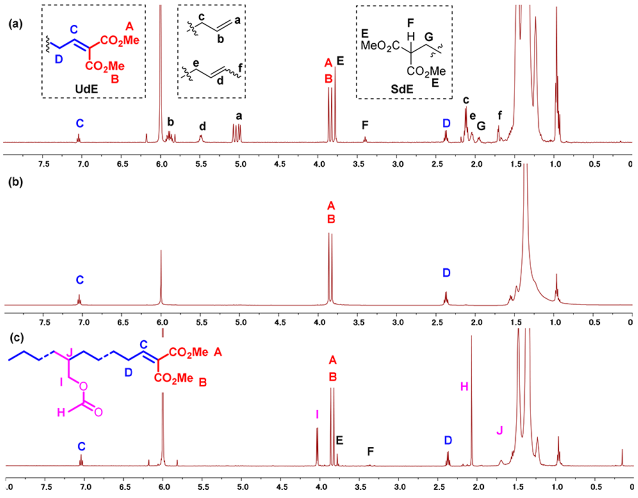


Figure 1. ^{1}H NMR spectrum of the copolymers obtained in entries 3 (a) and 7 (b) of Table 1 and entry 3 of Table 2 (c).

When using catalyst **E**, reducing the amount of **1** improved the activity and M_n appreciably, without significantly changing the selectivity (entry 8 vs entry 5). Decreasing the temperature from 80 °C to 50 °C resulted in a significant improvement of M_n (up to 15 400) while maintaining the excellent selectivity for UdE (>99%, entry 9).

Figure 1b shows a representative ^{1}H NMR chart for the product with selective chain-end functionalization (Table 1, entry 7): the characteristic resonances for UdE are detected as the exclusive structure of the unsaturated chain-end. Quantitative ^{13}C NMR analyses of the obtained polyethylenes from entries 7 and 8 (Table 1) revealed that the reactions produced predominantly linear polymers containing less than one branch per 1000 carbon atoms in their polyethylene backbone. It is noteworthy that the present catalytic system produces more than one chain per Pd catalyst (chain transfer, 2−95 chains/Pd), highlighting the higher efficiency compared to that of end-capping in living coordination polymerization.

Expecting the formation of intermediate **III** in the mechanism outlined in Scheme 1, we synthesized dimethyl methylenemalonate **3** and used it for copolymerization with ethylene (Scheme 2c). However, the reaction only afforded the polyethylene without significant incorporation of **3**. The steric hindrance of **3** may have prevented the insertion of the carbon−carbon double bond into the Pd−alkyl bond.[15] The difference in reactivities between **1** and **3** in the copolymerization with olefins highlights the significance of the unique reactivity of carbenes toward transition metals. Two other carbene precursors, ethyl diazoacetate and α-benzoyl sulfur ylide, were also tested in the copolymerization with ethylene. However, the reactions only afforded PE without significant incorporation of the polar monomers (for details, see the Supporting Information).

A variety of typical polar vinyl monomers were incorporated successfully with orthogonal reactivity of the dimethyl diazomalonate **1** in the terpolymerization with ethylene using catalyst **E**. Under pressure-reactor conditions, the exposure of catalyst **E** to 3.0 MPa of ethylene, 1.0 mmol of **1**, and 2.0 mL of allylic acetate (AAc) at 80 °C resulted in the formation of a novel heterofunctionalized PE (Table 2, entry 1). Notably, high selectivity of the AAc in the main chain (>99%) and dE-based unsaturated chain-end (>99%) was achieved. The ^{1}H NMR spectrum of the obtained copolymer (Figure 1c) clearly showed the orthogonal distribution of the AAc within the main chain and carbene at the unsaturated chain-end. Increasing the amount of AAc significantly improved the incorporated ratio of AAc, with little change in the AAc distribution (Table 2, entry 2). The yield and M_n of the copolymer were clearly improved when the reaction temperature was reduced to 50 °C (Table 2, entry 3). Furthermore, allylic chloride (AC), methyl acrylate (MA), and 3-butenylacetate (BAc) were applied in this terpolymerization. In general, the vinyl monomers and **1** exhibited excellent orthogonal selectivities, in that the vinyl monomers were incorporated selectively in the main chain, while the dE was incorporated preferentially at the unsaturated chain-end. It is noteworthy that very high ratios of unsaturated chain-ends with dE (90.1% and >99%) were also obtained in the presence of MA and BAc, respectively, as successful examples of unprecedented chain-end-functionalized polar polyethylenes (Table 2, entries 6 and 8).

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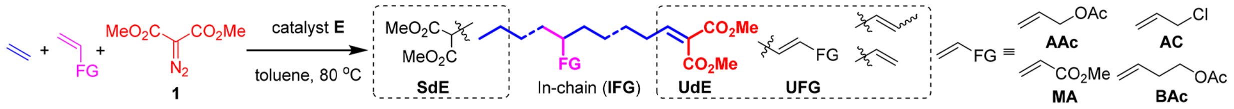
Table 2. Orthogonal Copolymerization of Ethylene, Carbene, and Vinyl Monomers Using a Palladium Complex[a]



entry	monomer (X mL)	yield (g)[b]	M_n (g/mol)[c]	M_w/M_n[c]	i.r. (%)[d] FG	i.r. (%)[d] dE	IFG/FG (%)[e]	saturated chain-ends, SdE (%)[f]	unsaturated chain-ends UdE (%)[g]	unsaturated chain-ends UFG (%)[h]
1	AAc (2.0)	0.078	14 000	2.1	0.36	0.21	>99	7.1	>99	<1
2	AAc (5.0)	0.056	9400	3.0	1.49	0.26	97.2	2.5	80.3	13.6
3[i]	AAc (2.0)	0.230	23 500	2.4	0.16	0.06	>99	6.0	87.7	<1
4[i]	AC (2.0)	0.103	18 000	2.0	0.57	0.10	>99	0.8	66.0	<1
5	AC (2.0)	0.084	12 000	2.3	0.62	0.16	>99	1.4	70.6	<1
6	MA (2.0)	0.449	10 100	3.3	0.65	0.23	97.9	17.8	90.1	6.3
7	MA (5.0)	0.450	8900	3.0	1.50	0.24	96.0	16.4	76.7	23.3
8	BAc (5.0)	0.203	9800	2.7	1.10	0.27	>99	11.3	>99	<1

[a] A mixture of the catalyst (10.0 μmol), monomer (X mL), and dimethyl diazomalonate (1.0 mmol) in toluene (10.0 − X mL) was stirred under an ethylene atmosphere (3.0 MPa) in a 50 mL autoclave at 80 °C. [b] Isolated yields after precipitation with methanol. [c] Molecular weights determined by size-exclusion chromatography using polystyrene standards and corrected by universal calibration. [d] Incorporation ratio of FG and dE in mol %. [e] Vinyl monomers in the main chain/all the incorporated vinyl monomers. [f] The saturated chain-ends containing dE in mol %. [g] The unsaturated chain-ends containing dE in mol %. [h] The vinyl monomers at the unsaturated chain-ends. [i] 50 °C.

In conclusion, highly efficient chain-end functionalization of polar polyethylenes was achieved successfully by the palladium-catalyzed copolymerization of ethylene, a carbene precursor, and vinyl monomers. A series of attractive heterofunctionalized PEs with selective distribution of the polar vinyl monomers within the main chain and carbene at the chain-end were obtained. The application of carbene into olefin copolymerization in this work would trigger the development of novel polyolefins that are inaccessible via traditional polymerization methods and stimulate future work for the development of novel carbene species and other types of polar monomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b10335.

Experimental procedures, characterization of polymers (PDF)

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Notes

The authors declare no competing financial interest.

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