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Polar additive triggered chain walking copolymerization of ethylene and fundamental polar monomers†

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Copolymerization of ethylene with polar monomers to produce functionalized polyethylenes is important but is a great challenge by using the seminal cationic α -diimine palladium(II) catalyst. A wide range of polar monomers generally shut down the reaction because of the underlying β -X elimination events and formation of stable chelates. In this contribution, a polar additive strategy was developed to overcome these issues. A large excess of a nitrile compound that acted as a polar additive triggered copolymerizations of ethylene with fundamental polar vinyl and allyl monomers, including methyl acrylate, vinyl acetate, butyl vinyl ether, allyl acetate, *tert*-butyl 3-butenate, butyl allyl ether, allyl chloride, acrylic anhydride, allyl acrylate, and allyl methacrylate, mediated by one α -diimine palladium(II) catalyst. This avoided a tedious hunting on a one-to-one catalyst. Catalytic activities, copolymer molecular weights, branching densities and microstructures, and co-monomer incorporations could be modulated by varying the amount of the polar additive. Possible mechanistic insights were proposed on the basis of these copolymerization results.

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Introduction

How to prepare functionalized polyethylenes by a convenient and controllable copolymerization method of ethylene and polar monomers using transition metal catalysts is a longstanding challenge because of both the presence of undesired side reactions and the negative effect of polar functional groups.^{1–12} In the library of catalysts used, less-oxophilic late transition metal palladium (Pd(II)) catalysts stood out, enabling the copolymerization of fundamental polar monomers required in industry. Thus far, phosphine–sulfonate Pd(II) catalysts were the most outstanding catalysts, which introduced a wide range of important polar vinyl and allyl monomers into the polyethylene chain, such as methyl acrylate (MA), vinyl acetate (VAc), butyl vinyl ether (BVE), butyl allyl ether (BAE), allyl acetate (AAc), *etc.*^{4,13,14}

In contrast, seminal α -diimine Pd(II) catalysts (**cPd** in Chart 1) that produced branched polyethylenes *via* the unique feature of “chain-walking” suffered from a very narrow scope of polar monomers, mainly including acrylates.^{15–24} In 2014, Takeuchi *et al.* developed macrocyclic binuclear α -diimine

Pd(II) catalysts (**dPd** in Chart 1), which enabled the copolymerization of *tert*-butyl 3-butenate (*tBB*).²⁵ In 2016 and 2017, Chen *et al.* broadened polar monomers to allyl ether and allyl acetate using bulky α -diimine Pd(II) (**bPd** in Chart 1)²⁶ and second-coordination α -diimine Pd(II) catalysts (**sPd** in Chart 1).²⁷ Recently, our group revealed an all-rigid α -diimine Pd(II) catalyst (**Pd** in Chart 1),^{28–30} which achieved the copoly-

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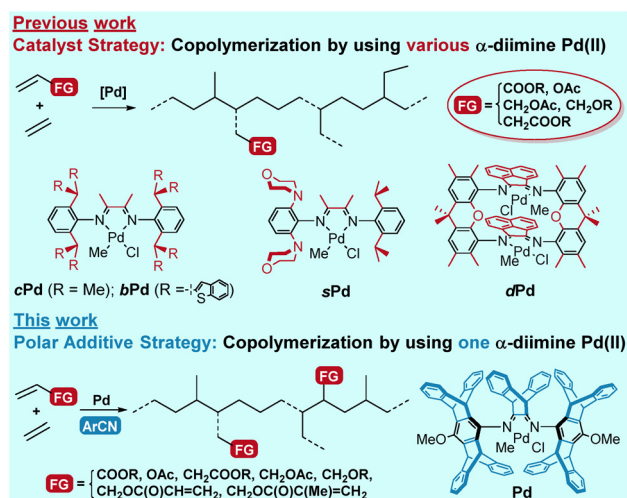


Chart 1 Chain walking copolymerization of ethylene with fundamental co-monomers including polar vinyl and allyl monomers.

merization of VAc *via* key inverted regio-chemistry. These various catalysts greatly expanded the library of polar monomers used in the α -diimine Pd(II)-mediated olefin copolymerization; however, the copolymerization of a given polar monomer usually required the given one-to-one catalyst. How to copolymerize a broad scope of polar monomers by the use of one α -diimine Pd(II) catalyst was long-sought and remained challenging.

Very recently, the Harth group^{31,32} and we³³ independently showed that an excess of polar additives (or ancillary ligands) such as nitrile compounds drastically altered the reactivity or branching in α -diimine Pd(II)-mediated olefin polymerizations. We thus envisioned that polar additives should alter the reaction pathway of polar monomers in olefin copolymerization as well. This might induce the incorporation of challenging polar monomers into the polyolefin chain. Here, we report how to trigger the α -diimine Pd(II)-catalyzed copolymerization of ethylene with a series of fundamental polar monomers by using a polar additive as the ancillary ligand.

Results and discussion

In α -diimine Pd(II)-catalyzed chain walking copolymerization of ethylene and polar monomers, some possible events occurred: (1) the functional group (FG) competed to coordinate to the metal active center, which hindered the coordination of the double bond in polar monomers or ethylene and thus slowed the chain growth (Chart 2, (a)); (2) β -heteroatom-elimination (BXE) after the insertion of polar monomers and the subsequent chain walking occurred to result in the deactivation of active species (Chart 2, (b)); and (3) the formation of stable chelates after the insertion of polar monomers impeded the insertion of incoming monomers such as ethylene (Chart 2, (c)). These underlying events severely limited the use of α -diimine Pd(II) catalysts in the copolymerization of ethylene and polar monomers.

To overcome these issues, a polar additive strategy rather than a catalyst strategy was utilized. The preferred nitrile compound *p*-tolunitrile was selected as the polar additive because of its suitable coordinating ability. We firstly tested the effect of the polar additive (PA) on the copolymerization of ethylene

and MA using Pd (Table S1†). Compared to the reaction of ethylene and MA without the addition of the polar additive, increasing the ratio of [PA]/[Pd] from 10, 20, to 50 led to higher catalytic activities and copolymer molecular weights (52 kDa to 94 kDa), and lower branching densities (154 brs/1000 C to 64 brs/1000 C) and incorporations of co-monomers (2.3 mol% to 0.7 mol%). However, when [PA]/[Pd] was higher and reached 100, the catalytic activity and polymer molecular weight decreased. This could be attributed to the competitive coordination of *p*-tolunitrile with ethylene and MA, which possibly altered the pathway of reaction and reduced the poison effect of MA. These results indicated that the polar additive definitely affected the copolymerization reaction. Thus, a broad scope of polar monomers were further studied.

E-AAc copolymerization triggered by the polar additive

Allyl acetate (AAc) was a typically polar allyl monomer, which was difficult to copolymerize with ethylene using α -diimine Pd(II) catalysts,²⁷ due to the formation of a stable five-membered chelate during insertion chain walking (Chart 2, (c)).²⁹ At 8 bar of ethylene and 30–90 °C, Pd was not able to mediate the copolymerization of ethylene and AAc (0.5 mol L⁻¹) (Table 1). Likewise, adding 1 equiv. of *p*-tolunitrile ([PA]/[Pd] = 1) to the reaction also did not trigger the copolymerization, and no polymer was isolated. In contrast, when [PA]/[Pd] reached 100, the copolymerization was switched on at 30–90 °C. Altering the ratio of [PA]/[Pd] from 100, 250, 500 to 1000 resulted in the change of catalytic activities, polymer molecular weights, branching densities, and incorporations (Fig. 1). Overall, a higher ratio of [PA]/[Pd] lowered the incorporation of AAc, but a higher reaction temperature elevated the incorporation of AAc.

To obtain the possible reaction pathways (see Fig. S1†), the microstructure of E-AAc copolymers was fully identified by ¹H/¹³C NMR (Fig. 2), ¹H-¹³C COSY, ¹H-¹³C HSQC, and ¹H-¹³C HMBC NMR spectroscopy (Fig. S19–S23†). The distribution of AAc on the polymer chain was quite complicated; both main-chain incorporation (*M*_{AAc}; Fig. 2, **b** and **d**) and end-of-branch functionalization (*T*_{AAc}; Fig. 2, **a** and **c**) were observed at a ratio of 64% : 36%. Among the four existing structures, structure **a** originating from the 2,1-insertion of AAc and subsequent chain walking was the major one and the identifiable -OCH₂ group gave a resonance at 4.05 ppm (*t*) in the ¹H NMR spectrum and 64.82 ppm in the ¹³C NMR spectrum. Structure **b** appeared at 4.85 ppm (-OCH-, ¹H) and 74.61 ppm (-OCH-, ¹³C), which was equal to the corresponding structure of E-VAc copolymers, as expected.²⁹ Notably, structure **b** was also derived from the 2,1-insertion of AAc and subsequent chain walking *via* an opposite direction. However, structure **c** originated from the 1,2-insertion of AAc and subsequent chain walking, showing signals at 3.94/3.86 ppm (-OCH₂, ¹H) and 69.69 ppm (-OCH₂, ¹³C). In addition, **d** (¹H: 3.97 ppm (*d*), ¹³C: 67.52 ppm) was a typical structure of AAc 1,2-insertion followed by no chain walking, and agreed with the structure of the E-AAc copolymer obtained using phosphine-sulfonate Pd(II) catalysts.³⁴ In previous E-AAc copolymerizations catalyzed

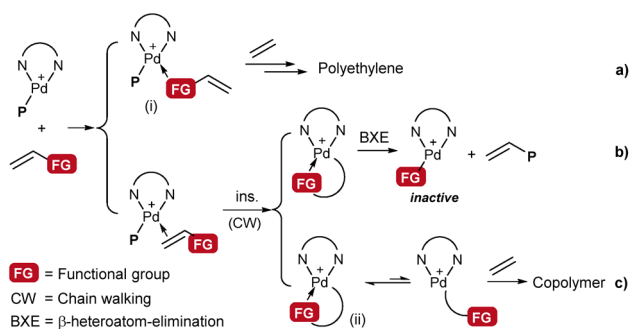


Chart 2 Possible events in the α -diimine Pd(II)-catalyzed chain walking copolymerization of ethylene and polar monomers.

Table 1 Effect of the polar additive on the copolymerization of ethylene and AAC with Pd^a

Entry	[PA]/[Pd]	T (°C)	Act. ^b	M _w ^c (10 ³)	M _w /M _n ^c	brs ^d	X ^e (mol%)
1	0	30	—	—	—	—	—
2	1	30	—	—	—	—	—
3	100	30	2.1	28	1.16	37	0.2
4	250	30	1.8	23	1.15	24	0.1
5	500	30	1.3	19	1.16	18	0.1
6	1000	30	1.0	14	1.12	14	<0.1
7	0	50	—	—	—	—	—
8	1	50	—	—	—	—	—
9	100	50	2.2	42	1.56	41	0.4
10	250	50	3.1	45	1.31	23	0.3
11	500	50	3.5	52	1.34	18	0.1
12	1000	50	2.8	46	1.53	16	<0.1
13	0	70	—	—	—	—	—
14	1	70	—	—	—	—	—
15	100	70	2.9	31	1.92	52	0.7
16	250	70	4.1	43	1.63	31	0.4
17	500	70	4.7	50	1.60	23	0.3
18	1000	70	4.4	44	1.56	18	0.2
19	0	90	—	—	—	—	—
20	1	90	—	—	—	—	—
21	100	90	1.4	12	1.68	77	1.3
22	250	90	2.4	22	1.80	44	0.7
23	500	90	3.6	30	1.67	33	0.5
24	1000	90	4.0	29	1.72	24	0.3
25 ^f	0	50	—	—	—	—	—
26 ^f	10	50	0.1	16	1.79	93	0.3
27 ^f	50	50	0.1	9	1.80	92	0.2
28 ^f	250	50	—	—	—	—	—

^a Reaction conditions: Pd catalyst (10 μmol), NaBARF (1.5 equiv.), toluene/CH₂Cl₂ (28 mL/2 mL), time (8 h), AAC (0.5 mol L⁻¹); all entries are based on at least two runs, unless noted otherwise. ^b Activity is in the unit of 10³ g mol⁻¹ h⁻¹. ^c Determined by GPC in 1,2,4-trichlorobenzene at 150 °C. ^d brs = number of branches per 1000 C, as determined by ¹H NMR spectroscopy. ^e X = incorporation of AAC in the copolymer, as determined by ¹H NMR spectroscopy. ^f cPd is used.

by α-diimine Pd(II) catalysts, the formed chelate and/or β-OAc elimination (Chart 2) usually prohibited the reaction. Now, the polar additive alters the reaction pathways and thus provides interesting structures.

To probe the universality of the polar additive on affecting α-diimine Pd(II)-catalyzed copolymerization, we backed to the classical Brookhart catalyst cPd. There was no isolated polymer without the polar additive; in contrast, adding 10 equiv. or 50 equiv. of the polar additive successfully switched on the copolymerization of ethylene and AAC (Table 1, entries 25–28).

Copolymerization of ethylene and broader polar monomers enabled by the polar additive

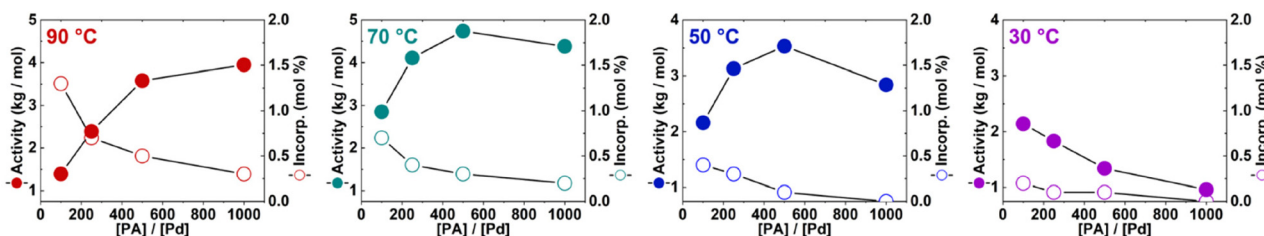
In order to investigate the compatibility of the polar additive effect, a broad scope of polar allyl and vinyl monomers including *tert*-butyl 3-butenolate (*t*BB), *n*-butyl allyl ether (BAE), allyl chloride (ACl), *n*-butyl vinyl ether (BVE), acrylic anhydride (AA), allyl acrylate (AIA), allyl methacrylate (AMA) and vinyl acetate (VAc) were studied (Table 2).

Fundamental polar allyl monomers *t*BB, BAE and ACl were found to be inactive in ethylene polymerization using Pd previously.²⁹ After adding 1000 equiv. of *p*-tolunitrile, the copolymerization of ethylene and *t*BB was switched on and the corresponding E-*t*BB copolymer with a *t*BB incorporation of 0.7 mol% was produced (Table 2, entry 2). The ¹³C NMR spectrum in which δ(C=O) is 172.83 ppm and δ[-OC(CH₃)₃] is 79.62 ppm confirmed the successful incorporation of *t*BB, as further evidenced by the ¹H NMR spectrum (Fig. 3). The control experiment without the polar additive did not produce any isolated polymer (Table 2, entry 1). The microstructure of E-*t*BB was quite simple and clear. Both the CH₂ (green, 1.65 ppm) and CH₂C(O) (blue, 2.25 ppm) signals indicated that *t*BB was only incorporated at the end of branches, as identified by the ¹H-¹³C HSQC/HMBC NMR spectra (Fig. S34–S39†).²⁵ The 2,1-insertion of *t*BB followed by chain walking should be responsible for the incorporation.

For BAE, similar results were observed, but with a lower activity, polymer molecular weight and polar monomer incorporation. In the microstructure of the E-BAE copolymer, BAE was distributed both in the main chain and at the end of branches in a ratio of 60% : 40% (Fig. S40–S42†). Fig. S3† exhibits the proposed insertion mechanism and the corresponding incorporation pattern in the E-BAE copolymerization triggered by the polar additive. Unfortunately, the copolymerization of ethylene and ACl was not triggered by the polar additive, and only pure polyethylene was produced without the incorporation of the polar group.

Polar monomers BVE and AA were further studied in ethylene copolymerizations. Catalytic activities by adding the polar additive were observed, but there were no incorporations of polar monomers in the polymers (Table 2, entries 7–10).³⁵

Similar to BVE and AA, polar diolefins AIA and AMA were also previously reported as poison agents, which terminated Pd mediated ethylene copolymerization because the allyl side in monomers underwent 1,2-insertion and chain walking to

**Fig. 1** Effect of the polar additive on the catalytic activities and the incorporations of the co-monomer in E-AAC copolymerization.

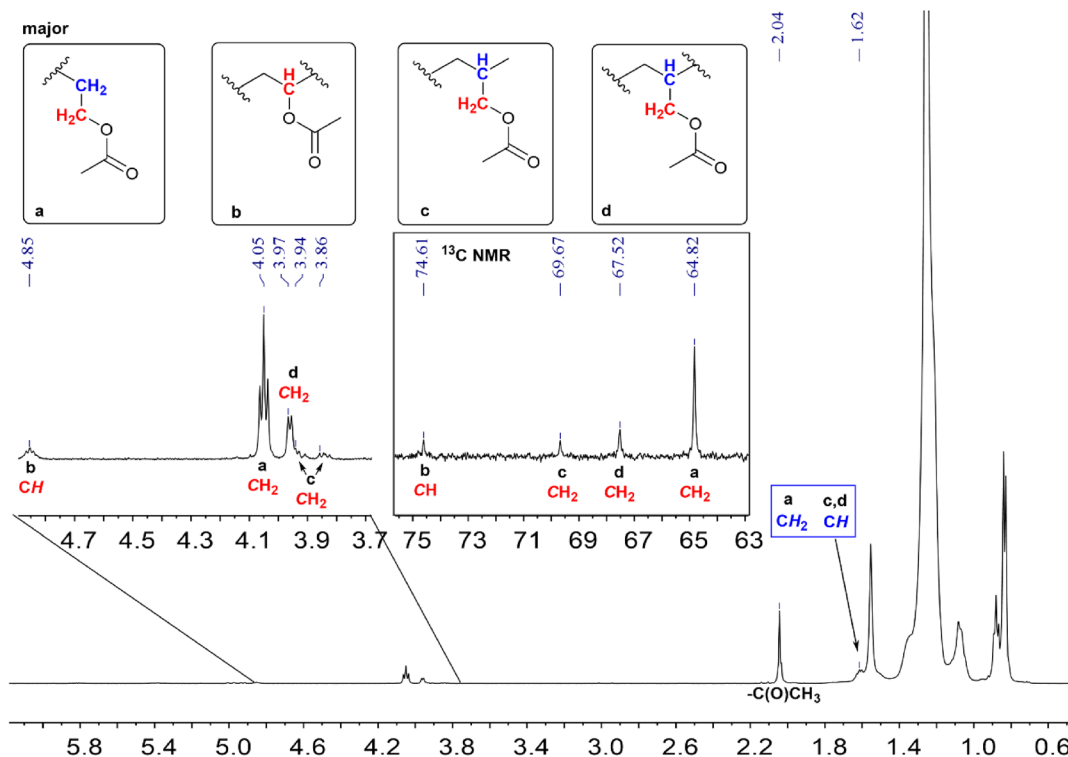


Fig. 2 ^1H NMR spectrum (500 MHz, 298 K, CDCl_3) and the key part of ^{13}C NMR spectrum (125 MHz, 298 K, CDCl_3) of the E-AAc copolymer in Table 1, entry 21.

Table 2 Effect of the polar additive on the copolymerization of ethylene and polar monomers with Pd^a

Entry	PM	[PA]/[Pd]	Act. ^b	M_w^c (10^3)	M_w/M_n^c	brs ^d	X^e (mol%)
1	<i>t</i> BB	0	—	—	—	—	—
2	<i>t</i> BB	1000	7.3	42	1.71	21	0.7
3	BAE	0	—	—	—	—	—
4	BAE	1000	0.7	11	2.06	25	0.2
5	ACL	0	—	—	—	—	—
6	ACL	1000	0.8	18	1.87	23	<0.1
7	BVE	0	—	—	—	—	—
8	BVE	1000	1.5	18	1.78	31	<0.1
9	AA	0	—	—	—	—	—
10	AA	1000	6.3	26	1.90	27	<0.1
11	AIA	0	—	—	—	—	—
12	AIA	1000	3.2	30	2.13	23	0.5
13	AMA	0	—	—	—	—	—
14	AMA	1000	3.0	28	1.76	22	0.5
15	VAc	0	—	—	—	—	—
16	VAc	50	2.5	23	1.89	91	0.3
17	VAc	100	5.0	43	1.83	56	0.1
18	VAc	1000	6.7	51	1.74	22	<0.1

^a Reaction conditions: catalyst (10 μmol), NaBARF (1.5 equiv.), toluene/ CH_2Cl_2 (28 mL/2 mL), time (8 h), temperature (90 $^\circ\text{C}$), polar monomer (0.5 mol L^{-1}); all entries are based on at least two runs, unless noted otherwise. ^b Activity is in the unit of 10^3 g mol^{-1} h^{-1} . ^c Determined by GPC in 1,2,4-trichlorobenzene at 150 $^\circ\text{C}$. ^d brs = number of branches per 1000 C, as determined by ^1H NMR spectroscopy. ^e X = incorporation of a polar monomer in the copolymer, as determined by ^1H NMR spectroscopy.

form stable five-membered chelates. This was reminiscent of the similar insertion chemistry of AAc.²⁹ In contrast, by adding the polar additive we successfully obtained the expected E-AIA and E-AMA copolymers (Table 2, entries 12 and 14). The incorporations of AIA and AMA were clearly observed in the ^1H NMR spectra (Fig. S46–S49[†]).^{36,37} Combining with the IR spectra (Fig. S52 and S53[†]), we found that only one double bond was introduced into the polymer chain and the other was intact; in other words, only acyclic structures were observed. This was not in agreement with previous reports using phosphine–sulfonate Pd(II) catalysts in the case of AIA.^{36,37} Both the incorporated allyl group and the incorporated acrylate group into the copolymer chain appeared at a ratio of 88% : 12%. It seemed that the electron-rich allyl group showed stronger binding affinity relative to the electron-deficient acrylate group. As expected, when AMA is employed in ethylene copolymerization, only the allyl incorporating structure was observed due to the larger steric hindrance of methacrylate *versus* acrylate.

In our previous works,²⁹ we reported the ultra-highly branched main-chain functionalized ($M_{\text{VAc}}:T_{\text{VAc}} = 99\%:1\%$) E-VAc copolymer synthesized by chain-walking copolymerization using Pd at 30 $^\circ\text{C}$. However, at 90 $^\circ\text{C}$ the copolymerization did not produce any polymer product, even though Pd was stable under these conditions. By the use of the polar additive, E-VAc copolymers with substantially lower branching densities were obtained at 90 $^\circ\text{C}$. VAc was distributed both in the main chain and at the end of branches in a ratio of 58% : 42%,

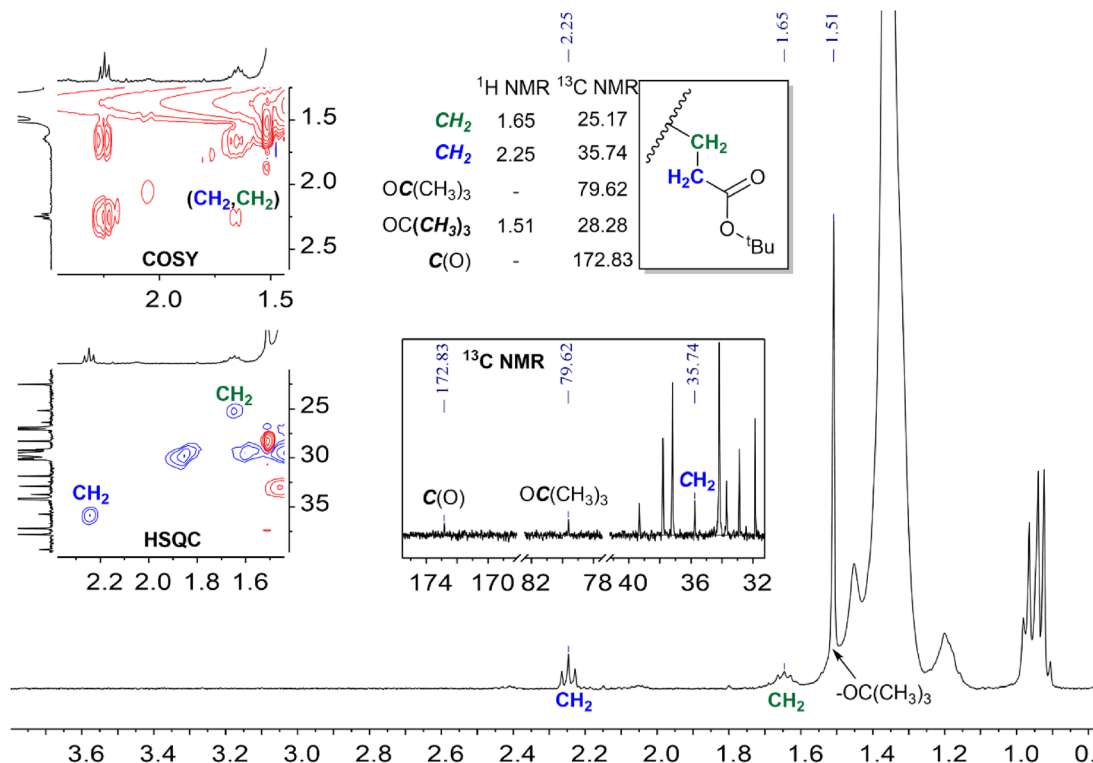


Fig. 3 NMR spectra (400 MHz, 383 K, C₂D₂Cl₄) of the E-tBB copolymer in Table 2, entry 2.

which was totally different from the previous E-VAc copolymer but was similar to both the main chain and the end of branch structures in E-MA copolymers.^{38,39} This again revealed that the polar additive influenced the insertion regio-chemistry and chain walking (Fig. S2†).

Possible mechanistic insights

Based on these copolymerization results, a possible mechanism was proposed to explain the “switch on” effect of the polar additive on the copolymerization of ethylene and polar monomers (Fig. 4).^{4,8} In the absence of the polar additive, when the copolymerization of ethylene and polar monomers was shut down, it was usually attributed to some key issues including the β-X elimination events (Fig. 4, BXE) (for example: β-OR elimination after the 1,2-insertion of vinyl ether or β-OR elimination after the 1,2-insertion of allyl ether and subsequent chain walking; β-OAc elimination after the 1,2-insertion of vinyl acetate or β-OR elimination after the 1,2-insertion of allyl acetate and subsequent chain walking; β-Cl elimination after the 1,2-insertion of vinyl chloride or β-Cl elimination after the 1,2-insertion of allyl chloride and subsequent chain walking) and the formation of stable chelates (Fig. 4, iv) (for instance: the formation of the strong five-membered chelate originating from the 2,1-insertion of vinyl acetate or the 1,2-insertion of allyl acetate and subsequent chain walking).

In contrast, when adding the polar additive (a large excess of *p*-tolunitrile) to the copolymerization reaction, different

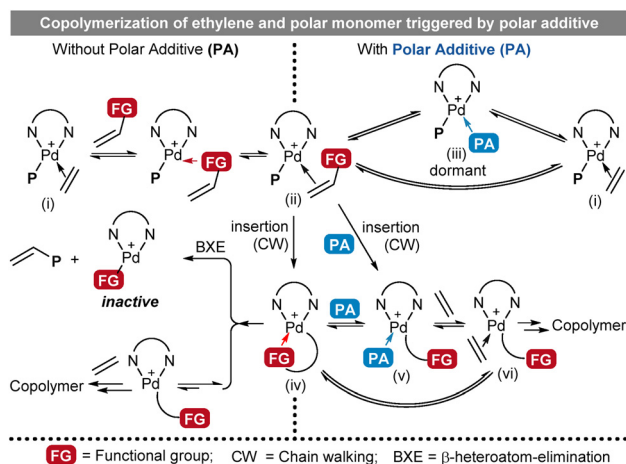


Fig. 4 Proposed mechanisms of the copolymerization of ethylene and polar monomers with and without the addition of the polar additive.

pathways occurred (Fig. 4). Firstly, the polar additive competed with polar monomers with a weak binding affinity to coordinate to active species (Fig. 4, iii), thus retarding the coordination and insertion of polar monomers. As a result, the reaction proceeded to produce a polymer, but in which the incorporation of polar monomers was not observed. For example, allyl chloride (ACl) belonged to this case. Secondly, the polar additive altered the insertion regio-chemistry (1,2-ins. or 2,1-ins. or both) of polar monomers and affected the β-H elimin-

ation process, thus triggering the copolymerization and enabling the incorporation of polar monomers. For example, allyl acetate (AAc) could be assigned to this case. The strong five-membered chelate originating from the 1,2-insertion of AAc and chain walking shut down the reaction without the polar additive; however, the addition of the polar additive enabled the emergence of both the 1,2- and 2,1-insertions to produce copolymers with various microstructures derived from 1,2- and 2,1-insertions (Fig. 2). Thirdly, the polar additive assisted to open the formed chelates (Fig. 4, v), thus promoting the chain propagation and incorporation of polar monomers. For example, the copolymerization of *tert*-butyl 3-butenolate (*t*BB) agreed with this case. The formed chelate after the 2,1-insertion of *t*BB was opened by the polar additive to initiate the following chain walking and chain propagation. Notably, both the alternation of insertion regio-chemistry and the opening of chelates enabled by the polar additive simultaneously took place usually. As for the reduction of the branching density, we assume that it could be attributed to the fact that *p*-tolunitrile possessing a moderate binding affinity with metal active species suppressed the β -agostic interaction and slowed down the chain walking rate, thus affecting the branching density.

Conclusions

In summary, we have developed a polar additive strategy rather than a catalyst strategy to address issues including the β -X elimination events and the formation of stable chelates in the α -diimine Pd(II)-mediated copolymerization of ethylene and polar monomers. By adding the well-designed nitrile compound as the polar additive to the reaction, a broad scope of fundamental polar monomers that were not copolymerized using the classical Brookhart catalyst **cPd** could be triggered to participate in ethylene copolymerizations. The polar additive influenced the catalytic activity, polymer molecular weight, branching density, co-monomer incorporation, and polymer microstructure. Possible mechanistic insights including competitive binding with polar monomers, alternation of insertion regio-chemistry and chain walking, and opening of chelates were proposed in the presence of the polar additive. Notably, this strategy could also be applied to the classical Brookhart catalyst **cPd**, suggesting an important generality. Thus, this work advanced the chain-walking copolymerization of ethylene with polar monomers to produce functionalized polyethylenes.

Conflicts of interest

There are no conflicts to declare.

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