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Palladium/IzQO-Catalyzed Coordination—Insertion Copolymerization of Ethylene and 1,1-Disubstituted Ethylenes Bearing a Polar Functional Group

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ABSTRACT: Coordination–insertion copolymerization of ethylene with 1,1-disubstituted ethylenes bearing a polar functional group, such as methyl methacrylate (MMA), is a long-standing challenge in catalytic polymerization. The major obstacle for this process is the huge difference in reactivity of ethylene versus 1,1-disubstituted ethylenes towards both coordination and insertion. Herein we report the copolymerization of ethylene and 1,1-disubstituted ethylenes by using an imidazo[1,5-*a*]quinolin-9-olate-1-ylidene (IzQO)-supported palladium catalyst. Various types of 1,1-disubstituted ethylenes were successfully incorporated into the polyethylene chain. In-depth characterization of the obtained copolymers and mechanistic inferences drawn from stoichiometric reactions of alkylpalladium complexes with methyl methacrylate and ethylene indicate that the copolymerization proceeds by the same coordination–insertion mechanism that has been postulated for ethylene.

INTRODUCTION

Coordination-insertion copolymerization of ethylene and polar monomers has attracted much attention as a powerful method for the synthesis of functionalized polyethylenes. The presence of polar functional groups alters their physical and surface properties such as paintability and dyeability.¹ To date, group 10 metal catalysts bearing various ligands including α -diimine,² phosphine-sulfonate,³ bisphosphine monoxide, 4 and imidazo[1,5-a]quinolin-9-olate-1-ylidene (IzQO)⁵ have successfully copolymerized ethylene and polar monomers such as acrylates, vinyl acetate, and allyl monomers (Scheme 1a).^{1d} Copolymers of ethylene with 1,1-disubstituted ethylenes are expected to exhibit superior material properties and higher stability when compared to those with monosubstituted ethylenes.⁶ Thus, 1,1-disubstituted ethylenes such as methyl methacrylate (MMA) are highly lucrative comonomers. To this end, the challenge of coordination-insertion copolymerization of ethylene and 1,1-disubstituted ethylenes bearing a polar functional group has been the subject of ongoing investigation (Scheme 1b).

Scheme 1. Copolymerization of Ethylene and (a) Polar Vinyl Monomers and (b) 1,1-Disubstituted Ethylene Bearing a Polar Functional Group.



The major difficulty in copolymerization of ethylene with 1,1-disubstituted ethylenes is related to the coordination–

insertion steps: having higher steric demands than that of ethylene, the 1,1-disubstituted ethylenes generally show much lower reactivity towards coordination/insertion of a monomer and subsequent propagation. For example, Mecking and coworkers' attempts to copolymerize ethylene and MMA using palladium/phosphine-sulfonate complexes only resulted in exclusive formation of linear polyethylene even in the presence of substantial amounts of MMA.⁷ Gibson et al. successfully incorporated MMA into the polyethylene chain using nickel/phosphine-enolate catalysts; however, 2,1insertion of MMA resulted in chain termination, indicated by the formation of enolate-terminated polyethylene.⁸ Sen and colleagues reported that the activation enthalpy of MMA insertion into cationic palladium/a-diimine complexes is 4 kcal/mol higher than that of methyl acrylate (MA) insertion, explaining the inability of MMA to insert in a-diiminecatalyzed copolymerization reactions.9

Another concern in these transformations is the elucidation of the mechanism of copolymerization. Although there are some reports on the "coordination-insertion" copolymerization of ethylene and polar 1,1-disubstituted ethylenes,^{10,11,12} drawing conclusions inclined towards a coordinationinsertion mechanism might be erroneous, since most polar 1,1-disubstituted ethylenes are also susceptible to ionic or radical polymerization. For instance, Li and colleagues reported the copolymerization of ethylene and MMA by [(βketoiminato)NiPh(PPh₃)]/MMAO systems and suggested that coordination-insertion mechanism was operational (Scheme 2a).^{nb} By contrast, Mecking and coworkers have shown that a mixture of homopolymers, polyethylene and polyMMA (Scheme 2b), were formed when similar neutral nickel catalysts were used, indicating that the coordinationinsertion polymerization of ethylene and the radical polymerization of MMA proceeded simultaneously and independently.^{13,14} Furthermore, it was reported that similar [(salicylaldiminato)NiPh(PPh₂)] complexes produced multiblock

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copolymers by combining a coordination-insertion mechanism for ethylene and a radical mechanism for MMA (Scheme 2c).¹⁵ From the above, mechanistic conclusions of repetitive reports on ethylene/MMA copolymerization are often inconclusive and contradictory.

An inconclusive picture of polymerization process also exists on the other ethylene/1,1-disubstituted ethylene copolymerization. Recently, it was reported that palladium/phosphine-sulfonate complexes produced copolymers of ethylene and 1,1-disubstituted ethylenes bearing two polar functional groups, such as ethyl 2-cyanoacrylate and trifluoromethyl acrylic acid, which are claimed statistical copolymers as shown in Scheme 2a.¹² However, our comparison of spectroscopic data of their copolymers with those of some model compounds revealed inconsistencies (*vide infra*). Thus, we felt that the implied coordination-insertion mechanism needed further investigation.

Scheme 2. Polymer Structures Postulated for Ethylene/1,1-Disubstituted Ethylene Copolymers.

(a) Statistical copolymer via coordination-insertion copolymerization

(b) Mixture of homopolymers

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(c) Multiblock copolymer

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We chose the palladium complexes bearing an IzQO ligand (1) to perform coordination-insertion copolymerization of ethylene and 1,1-disubstituted ethylenes bearing a polar functional group, since previous reports from our group demonstrated that the same catalysts could efficiently incorporate polar monomers under even low concentration.^{5a} This choice was also warranted by its high durability under high temperature conditions, favoring incorporation of 1,1disubstituted ethylenes. Here, we report the copolymerization of ethylene with various 1,1-disubstituted ethylenes bearing a polar functional group (2), including MMA, using the palladium/IzQO catalyst (Scheme 3). In-depth NMR analyses of the obtained copolymers and comparison with model compounds revealed that these 1,1-disubstituted ethylenes were successfully incorporated into the main chain of polyethylene as depicted in Scheme 2a. By investigating stoichiometric reactions of palladium/IzQO complexes with MMA followed by reactions with ethylene, we conclusively demonstrate that the copolymerization proceeds via the coordination-insertion mechanism.

Scheme 3. Copolymerization of Ethylene and 1,1-Disubstituted Ethylenes Bearing a Polar Functional Group by Palladium/IzQO Complex 1.



RESULTS AND DISCUSSION

Copolymerization of Ethylene and 1,1-Disubstituted Ethylenes Bearing a Polar Functional Group. The copolymerization of ethylene and 1.1-disubstituted ethylenes 2 was investigated by using palladium/IzQO complex 1 (Table 1). Copolymerization of ethylene (2.0 MPa) and MMA (2a; 25 vol % in toluene) with 1 (10 µmol) was performed in the presence of BHT (200 mg) as a radical inhibitor to afford an ethylene/MMA copolymer with an MMA incorporation of 0.46 mol % (entry 1). When the concentration of MMA was increased to 50 vol % (entry 2) and 100 vol % (entry 3), the incorporation ratio was increased to 0.62 mol % and 0.85 mol %, respectively, although the polymerization activity and polymer molecular weight were decreased. Reducing the ethylene pressure from 2.0 to 1.0 MPa significantly changed the incorporation ratio of MMA up to 2.5 mol % (entry 4). The palladium/IzQO catalysts were also employed for the copolymerization of ethylene with other 1,1-disubstituted ethylenes bearing a polar functional group (entries 5-8 of Table 1). Methallyl monomers (CH₂=CMeCH₂X, where X = OR, NR₂, halogen, etc.), industrially produced from isobutene,¹⁶ are a potential class of candidates. Methallyl phenyl ether 2b was successfully incorporated to form the ethylene/2b copolymers with ca. 3-5 times higher activity than those of MMA

Table 1. Copolymerization of Eth	vlene and 1,1-Disubstituted Eth [,]	vlenes 2a–c by Palladium/Iz	OO Complex 1 ^a
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entry	comonomer	ethylene (MPa)	monomer (mL)	solvent (mL)	yield ^b (mg)	activity (g·mmol ⁻¹ ·h ⁻¹)	$M_{\rm n}^{\ c}$ (10 ³)	$M_{ m w}/M_{ m n}{}^c$	incorp. ^d (mol %)	T_{pm}^{e} (°C)
I ^f	2a (FG = CO ₂ Me)	2.0	2.0	6.0	130	0.87	8.7	1.8	0.46	104.1
2' f	2 a	2.0	4.0	4.0	101	0.67	8.6	1.7	0.62	106.6
3' _F	2a	2.0	8.0	0	49.1	0.33	2.2	2.1	0.85	108.6
4'	2a	1.0	8.0	0	23.7	0.16	0.8	2.9	2.5	br
5	2b (FG = CH_2OPh)	2.0	4.0	4.0	343	2.3	18	1.9	0.30	106.7
6	2b	2.0	8 .o	0	227	1.5	5.1	2.3	0.41	109.5
7	$2c (FG = CH_2CH_2OAc)$	2.0	4.0	4.0	315	2.1	27	1.7	0.11	107.0
8	20	2.0	8.0	0	127	0.85	18	1.9	0.23	102.8

^{*a*} A mixture of catalyst **1** (10 μmol), ethylene, and monomer **2a–c** in toluene was stirred in a 50-mL autoclave with glass tube for 15 h at 120 °C. ^{*b*} Isolated yields after precipitation with methanol. ^{*c*} Molecular weights determined by SEC using polysty-rene standards and corrected by universal calibration. ^{*d*} Molar incorporation ratios of polar monomers determined by ¹H NMR analysis. ^{*e*} Peak melting temperatures determined by DSC analysis. ^{*f*} Reaction was performed in the presence of BHT (200 mg).

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(entries 5 and 6). The 2b incorporation ratio could be increased up to 0.41 mol % by conducting the copolymerization at a higher concentration of **2b** (entry 6). This catalytic system was also applied to the copolymerization of homomethallyl monomers having a structure of CH₂=CMeCH₂CH₂X, which can be obtained from isobutene.¹⁷ 3-Methylbut-3-en-1yl acetate 2c (X = OAc), a volatile fragrant constituent of various fruits,¹⁸ produced ethylene/2c copolymers with activities comparable to those of 2b (entries 7 and 8). Similar to the copolymerizations with methacrylic and methallyl monomers, the incorporation ratio of 2c was increased to 0.23 10 mol % when the concentration was increased, albeit at the 11 expense of the polymerization activity and polymer molecu-12 lar weight.

13 Characterization of Ethylene/1,1-Disubstituted Ethylene Co-14 polymers. The structures of the obtained ethylene/MMA 15 copolymers were determined via in-depth NMR analyses including 1H, 13C, DEPT, COSY, HSQC, and HMBC experi-16 17 ments. In the ¹H NMR spectrum (Figure 1a), the proton signals of methoxy group A and methyl group C were observed 18 as a singlet at 3.697 and 1.186 ppm, respectively, while the 19 signals of methylene group E were observed as multiplets 20 around 1.67 and 1.45 ppm due to their diastereotopic charac-21 ter. The minor proton signals (ca. 2% of incorporated MMA 22 units) of methoxy groups observed at 3.71 ppm were also 23 observed and assigned as chain-end group through the com-24 parison with several model compounds (vide infra).^{19,20} In the 25 quantitative ¹³C NMR spectrum (Figure 1b), the signal of the 26 quaternary carbon at the α position of the carbonyl group 27 (**D**) and the signals of methylene carbons at the β and γ positions (E and F, respectively) were observed in the ratio of 1.0: 28 2.0 : 2.0.19 The characterization was also supported by 29 DEPT135 analysis, indicating that A and C are primary or 30 tertiary carbons, E and F are secondary carbons, and B and D 31 are quaternary carbons (Figure S22). Furthermore, the struc-32 tures of the obtained copolymers were confirmed by two-33 dimensional NMR analyses. The HSQC spectrum (Figure 34 S24) showed the cross signals between proton and carbon 35 signals for A, C, and E, and the HMBC spectrum (Figure S26) 36 revealed cross signals of methylene proton E (1.67 ppm) with 37 carbons **B** (177.5 ppm), **D** (45.9 ppm), and **F** (24.3 ppm). The-38 se results strongly indicated that the obtained polymers were without doubt statistical copolymers of ethylene and MMA, 39 and that MMA was mainly incorporated into the main chain 40 of polyethylenes as illustrated in Scheme 2a.¹⁹ It is worth 41 noting that no units in which multiple MMA are successively 42 inserted into the main chain were observed and that only 43 minor amounts of MMA units incorporated into the chain 44 ends were observed in the NMR spectra. As for the eth-45 ylene/2b copolymers and ethylene/2c copolymers, the struc-46 tures were determined in the same manner to confirm in-47 chain incorporation of these comonomers into polyethylene 48 chain (Figures S33–S49 and S50–S66, respectively).¹⁹ 49

Comparison of Ethylene/Methyl Methacrylate Copolymers and Model Compounds. In order to support the assignments, we compared the ¹H and ¹³C NMR spectra of the obtained ethylene/MMA copolymers and those of several model compounds shown in Figure 2, which were reasonably chosen from the mechanistic consideration (See Scheme S1 for de tail). ¹H and ¹³C NMR spectra of the copolymer obtained in this study and model compound I are shown in Figure 3.



Figure 1. (a) ¹H NMR and (b) Quantitative ¹³C NMR spectra of the ethylene/MMA copolymer obtained in entry 3 of Table 1 (1,1,2,2-tetrachloroethane-*d*₂, 120 °C).

All the characteristic signals were in accord with each other with great accuracy, again suggesting that a single unit of MMA was incorporated into the main chain of polyethylene during the chain propagation step (Scheme 2a). In addition, infrared (IR) spectra of the ethylene/MMA copolymer, model compound I, and commercial poly(methyl methacrylate) (PMMA) (Figures S70-S72) revealed that the carbonyl absorption of the copolymer was observed at 1734 cm⁻¹, which was almost identical to that of model compound I at 1732 cm ¹, but was different from that of PMMA (1722 cm⁻¹). The comparison of NMR spectra with model compounds II-VI provided important information on the chain-end structures (Table 2). For the ease of comparison, the chemical shifts of the methoxy group are focused. In the ¹H NMR spectrum of the ethylene/MMA copolymer, two types of signals corresponding to chain ends were observed in the ¹H NMR spectrum (3.706 and 3.714 ppm) as well as the aforementioned inchain signal at 3.697 ppm. These two signals are consistent with those of model compounds II, III, and IV and no signal corresponding to model compounds V and VI was observed. Quantitative ¹³C NMR spectra also revealed the methoxy signals of the copolymer corresponds to model compounds II, III, and IV. Thus, chain-end of the ethylene/MMA copolymer is confirmed as the structure corresponding to model compounds II, III, and IV.¹⁹

OMe

OMe





VI

OMe

Figure 2. List of model compounds.

Table 2. ¹H and ¹³C NMR Chemical Shifts (ppm) of the Methoxy Group of the Ethylene/MMA Copolymer Obtained in Entry 3 of Table 1 and Model Compounds II-VI.

	E/MMA copolymer	II	III	IV	V	VI
ΊΗ	3.697 (major) 3.706, 3.714 (minor)	3.708	3.705	3.717	3.783	3.802
¹³ C	50.8	51.1	50.8	50.9	55.6	51.5



Figure 3. ¹H NMR spectra of (a) the ethylene/MMA copolymer obtained in entry 3 of Table 1 and (b) model compound I (1,1,2,2-tetrachloroethane- d_2 , 120 °C). Quantitative ¹³C NMR spectra of (c) the ethylene/MMA copolymer obtained in entry 3 of Table 1 and (d) model compound I (1,1,2,2-tetrachloroethane- d_3 , 120 °C).

Table 3. ¹³C NMR Chemical Shifts (ppm) of Ethylene/MMA Copolymers and PMMA.^{*a*}



sample	condi- tion ^b	А	В	С	D	Е	F
E/MMA copolymer	[A]	50.8	177.5	21.3	45.9	39.1	24.2
(entry 3, Table 1)	[B]	50.6	177.0	21.5	46.1	39.5	24.7
	[A]	54.6-53.8 (m)	177.4-176.4 (m)	19.4–19.1 (m), 17.4 (br)	51.3	45.3-44.9 (m)	
commercial PMMA (TCI)	[B]	54.6-54.3 (m)	177.3-176.3 (m)	19.9–19.6 (m), 17.9 (br)	51.1	45.6-45.3 (m)	
	[C]	54.6-54.1 (m)	178.3-177.1 (m)	18.9 (br), 16.6 (br)	51.9	45.0-44.7 (m)	
E/MMA copolymer in ref. 11b	[B]	54.9	177.5	18.6	51.5	45.9	27.6
E/MMA copolymer in ref. 11c	[B]	54.6	177	18.3	51.3	45.9	not as- signed
E/MMA copolymer in ref. 10	[C]	54 [°]	179–177 (m)	not assigned	52 ^c	46-44 (m) ^c	not as- signed
E/MMA copolymer in ref. 11a	[C]	55 [°]	180	21.1, 18.8, 16.6	52 [°]	45.5, 44.8, 44.6	29.8

^{*a*} m = multiple signals, br = broad signal. ^{*b*} [A]: 1,1,2,2-tetrachloroethane- d_2 , 120 °C; [B]: 1,2-dichlorobenzene- d_4 , 120 °C; [C]: chloroform-d, ambient temperature. ^{*c*} Values read off the NMR spectra shown in the paper.

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Comparison with Commercial PMMA and Ethylene/Methyl Methacrylate Copolymers in Literature. As stated in the in-2 troductory part, there are some reports on the late transition-metal-catalyzed copolymerization of ethylene and MMA.^{10,11} Nonetheless, a comparison of our copolymers with those reported in literature^{10,11} as well as to commercial PMMA validated the originality of our copolymers. ¹³C NMR 6 chemical shifts of our ethylene/MMA copolymer, commercial PMMA, and reported ethylene/MMA copolymers^{10,11} are 8 summarized in Table 3. Our copolymer exhibited strikingly 9 different ¹³C NMR signals from those of the other 10 (co)polymers. In particular, the chemical environment of 11 methylene carbon E should be significantly different between 12 -ethylene-MMA-ethylene- and -(MMA)_n- units. The chem-13 ical shifts of carbon E in the reported copolymers were observed at 44-46 ppm, which significantly differ from that of 14 our copolymer (39.1 ppm) and rather resembled those of 15 commercial PMMA (45-46 ppm). Similar trends were ob-16 served in the chemical shifts of methoxy carbon A and quer-17 tanary carbon **D**. This strongly implies that all of the previ-18 ously reported ethylene/MMA copolymers in references^{10,11} 19 have successive MMA units in the main chain as shown in 20 Schemes 2b and/or 2c. These poly-MMA units would be 21 formed by the intermediacy of radical-related processes, con-22 sidering that coordination-insertion processes typically af-23 ford copolymers with random and statistical distribution of 24 each comonomers.

25 Comparison of Reported Ethylene/1,1-Disubstituted Ethylene 26 Copolymers and Model Compounds. It was reported in 2015 27 that the copolymerization of ethylene with difunctional 1,1disubstituted ethylenes was mediated by palladi-28 um/phosphine-sulfonate catalysts.¹² However, our compari-29 son with model compounds resulted in a conclusion contra-30 dictive to the authors' claim that the obtained copolymers 31 have a sequence of -ethylene-(1,1-disubstituted ethylene)-32 ethylene-. For example, Figures 4 and 5 show 'H and '3C 33 NMR spectra of (a) ethyl 2-cyano-2-hexylotanoate as a model 34 compound for in-chain incorporation of ethyl 2-35 cyanoacrylate, (b) poly(ethyl 2-cyanoacrylate),²¹ and (c) the 36 reported ethylene/ethyl 2-cyanoacrylate copolymer.^{12a} The 37 comparison showed that spectrum (c) rather resembled (b) 38 rather than (a), suggesting successive ethyl 2-cyanoacrylate units are present in the copolymer, which is different from 39 the polymer structures the authors proposed to have formed. 40 We also compared the NMR spectra for ethylene/2-41 acetamidoacrylic acid, ethylene/methyl 2-acetamidoacrylate, 42 and ethylene/2-bromoarylic acid copolymers and obtain es-43 sentially the same results.¹⁹ From the above consideration, 44 we strongly believe that the previously reported ethylene/1,1-45 disubstituted ethylene copolymers in references 12 did not 46 have the proposed sequence of -ethylene-(1,1-disubstituted 47 ethylene)-ethylene- (Scheme 2a), but contained blocky mi-48 crostructures generated by successive 1,1-disubstituted ethylene incorporation presumably via ionic/radical mecha-49 nisms (Schemes 2b and/or 2c). 50



Figure 4. ¹H NMR spectra of (a) ethyl 2-cyano-2hexylotanoate, (b) poly(ethyl 2-cyanoacrylate), and (c) ethylene/ethyl 2-cyanoacrylate copolymer in reference 12a (1,1,2,2-tetrachloroethane- d_2 , 130 °C). NMR spectrum (c) was adapted with permission from reference 12a. Copyright 2015 American Chemical Society.



Figure 5. ¹³C NMR spectra of (a) ethyl 2-cyano-2hexylotanoate, (b) poly(ethyl 2-cyanoacrylate), and (c) ethylene/ethyl 2-cyanoacrylate copolymer in ref. 12a (1,1,2,2tetrachloroethane- d_2 , 130 °C). Note: * = solvent impurities; # = monomer residue. NMR spectrum (c) was adapted with permission from reference 12a. Copyright 2015 American Chemical Society.

Stoichiometric Methyl Methacrylate Insertion. In order to elucidate the polymerization mechanism, a stoichiometric reaction of alkylpalladium complex 3 with MMA was performed (Scheme 4). The reaction of methylpalladium complex 3 with MMA in the presence of silver carbonate for 18 h at 75 °C led to the formation of MMA-inserted complex 4 in 93% NMR yield. This result indicates that MMA indeed underwent coordination and insertion into the palladiummethyl bond and that the same process occurs in other alkylpalladium species formed during the polymerization process. It should be noted here that no 2,1-insertion complex was detected by NMR spectroscopy, suggesting that MMA inserts into the palladium-alkyl bond of palladium/IzQO complexes exclusively in a 1,2-fashion.^{5a} Recrystallization furnished complex 4 in 45% yield as single crystals appropriate for X-ray crystallographic analysis.¹⁹ The molecular structure, shown in Figure 6, clearly indicates that 1,2-insertion of MMA into the palladium-methyl group of complex 3 occurred to form a five-membered-ring chelation. When compared to the reported MMA-inserted cationic complex bearing an α -diimine ligand,⁹ the observed angle for C1–Pd1–O1 is similar (81.21(13)° versus 81.41(19)°), while the observed bond length of Pd1–O1 is longer (2.124(3) Å versus 2.041(4) Å). These results suggest that the strong trans influence of the carbene ligand weakens the Pd1-O1 bond in neutral complex 4.

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Scheme 4. Synthesis of MMA-Inserted Complex 4 by the Reaction of Methylpalladium Complex 3 with MMA.



Figure 6. X-ray structure of complex **4** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1-C1 = 2.026(4), Pd1-C7 = 1.949(4), Pd1-O1 = 2.124(3), Pd1-O3 = 2.056(3), C7-Pd1-O3 = 90.44(14), C1-Pd1-O1 = 81.21(13).

Reactivity of MMA-Inserted Complex 4. The potential of MMA-inserted complex 4 to further incorporate ethylene was confirmed experimentally, as shown in Scheme 5. Upon heating complex 4 under 2.0 MPa ethylene pressure at 100 °C for a period of 1 h, a mixture of two kinds of polyethylene, 5 and 6, were obtained. Polymer 5 features a methoxycarbonyl $(-CH_2CMe_2CO_2Me)$ terminus while polymer 6 features a hydrogen terminus. The structures of polymer 5 were unambiguously characterized by NMR analyses; the ¹H NMR signals of the methoxycarbonyl group in polymer 5 (3.706 ppm) were in good accordance with those of model compound II (3.708 ppm).¹⁹

A mechanism for the formation of polymers **5** and **6** is proposed in Scheme 5. Ethylene coordination and insertion into complex **4** followed by chain propagation lead to the formation of **INT-2**, which bears the polymer chain with the methoxycarbonyl terminus. Polymer **5** is formed via chain termination of **INT-2**, and Polymer **6**, i.e. regular polyethylene, is obtained by polymerization initiated by palladium-hydride species, which was generated by β -hydride elimination during the polymerization process. From a MALDI-TOF-MS analysis of the supernatant of the reaction mixture, signals assignable to the palladium species formed by several consecutive insertions of ethylene into starting complex **4** [**4** + (ethylene)_n] (e.g. INT-1 and INT-2) were observed (Figure S75). These palladium species provide further convincing evidence for the insertion of ethylene into complex **4**.

It is worth noting that the condition required for the initiation of ethylene polymerization from **4** (2.0 MPa, 100 °C) is quite reasonable compared to the actual copolymerization conditions (1.0–2.0 MPa, 120 °C). Moreover, the mass balance of the methoxycarbonyl unit based on **4** was as high as 95%; the recovery of **4** was 86% while 9% of the methoxycarbonyl unit (65% from the 14% conversion of **4**) was found at the chain end of the obtained polyethylene. These results suggest that ethylene coordinated to the palladium center of complex **4** via de-chelation and subsequently inserted into the palladium–alkyl bond to successfully start chain propagation. Hence, the stoichiometric reactions of complex **3** with MMA followed by ethylene strongly support the coordination– insertion mechanism in the palladium/IzQO-catalyzed copolymerization of ethylene and MMA.

Scheme 5. Homopolymerization of Ethylene Using Complex 4.



Discussion on the Advantages of the Palladium/IzQO System towards Ethylene/MMA Copolymerization. Finally, we discuss the advantages of our palladium/IzQO systems over the other systems. In the previous reports,^{7,9} the trials of the copolymerization of ethylene and MMA using palladium/ α diimine complexes9 and palladium/phosphine-sulfonate complexes⁷ did not afford the corresponding copolymers, rather, only polyethylenes were obtained. This was attributed to the large differences of activation barriers between ethylene insertion and MMA insertion, which were experimentally determined to be 4 kcal/mol in palladium/ α -diimine systems⁹ and 5 kcal/mol in palladium/phosphine-sulfonate systems.⁷ On the other hand, our previous study revealed that the palladium/IzQO system can incorporate both electron-rich and -deficient polar monomers even under considerably low concentration, compared to the first two systems.^{5a} Such insensitivity of the palladium/IzQO system towards steric hindrance on alkenes can be further supported by its ability to polymerize 1-butene, which could not be pol-

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ymerized by palladium/phosphine-sulfonate system. Therefore, it could be postulated that the reactivity gap between ethylene and MMA arising from their steric difference is less emphasized in the case of palladium/IzQO system.

Another important feature of the palladium/IzQO system is selective 1,2-insertion of substituted ethylenes.^{5a} As for MMA, the above stoichiometric study revealed almost quantitative formation of the 1,2-inserted product (Scheme 4). As shown in Scheme 6, after 1,2-insertion of MMA, β -hydrogen elimination cannot occur because of the absence of β hydrogen in the resulting alkylpalladium species. In contrast, 2,1-insertion of MMA affords a species bearing multiple β hydrogens and stabilized tertiary alkyl chain-end hindering the following propagation, both of which lead to undesirable chain termination. Indeed, the previous report on the stoichiometric reaction of a palladium/phosphine–sulfonate complex with MMA proceeded in both 1,2- and 2,1-insertion fashion and the 2,1-insertion product was subject to facile β hydrogen elimination.⁷

Based on the discussion above, we conclude that our successful coordination-insertion copolymerization of ethylene and MMA by the palladium/IzQO system stems from the insensitivity towards steric hindrance and the selective 1,2insertion mode.

Scheme 6. Insertion of Methyl Methacrylate into a Palladium-Alkyl Bond during the Polymerization Process.



CONCLUSION

In summary, palladium/imidazo[1,5-a]quinolin-9-olate-1ylidene (Palladium/IzQO) catalysts were successfully applied to copolymerize ethylene with a series of polar functional group bearing 1,1-disubstituted ethylenes. For the first time, we obtained statistical copolymers of ethylene and 1,1disubstituted ethylene uniquely featuring nonsequential incorporation of the polar units into the main chain. The structures of the obtained copolymers were rigorously confirmed via thorough NMR spectroscopic analyses. In sharp contrast to earlier reports, our copolymers, containing sequences of ethylene-(1,1-disubstituted ethylene)-ethylene-, are devoid of undesirable blocky microstructures. Isolation of an MMAinserted complex obtained via a stoichiometric reaction of alkylpalladium complex with MMA supported the hypothesis that MMA can coordinate to the complex and then insert. Subsequent initiation of ethylene from the MMA-inserted complex showed that the chain propagation can indeed occur after the insertion of MMA. These mechanistic inferences, together with comparison our copolymers with model compounds and copolymers reported earlier, suggest that our study indeed offers the first report on the coordinationinsertion copolymerization of ethylene with 1,1-disubstituted ethylene.

EXPERIMENTAL SECTION

A General Procedure of the Copolymerization of Methyl Methacrylate with Ethylene (Table 1, entries 1-4). A 50-mL stainless steel autoclave was dried in an oven at 120 °C, and then cooled inside a glovebox under argon atmosphere. Complex 1 (5.7 mg, 10 µmol), BHT (200 mg), MMA (x mL; x = 2, 4, 8), and toluene (8-x mL) were added into the autoclave (NOTE: In order to avoid the formation of PMMA, MMA should be added directly to the bottom of the autoclave, so as not to touch the inner sidewall of the autoclave). After the autoclave was charged with ethylene (1.0-2.0 MPa), the reaction mixture was stirred in an isothermal heating block at 120 °C for 15 hours. After cooling to room temperature and venting redundant ethylene, the reaction was guenched by addition of methanol (ca. 20 mL). The formed precipitates were filtered, washed with methanol (NOTE: The product should be carefully washed because insufficient washing results in the formation of PMMA during the subsequent drying process), and dried under high vacuum for >3 hours at 100 °C to afford ethylene/MMA copolymers. The molecular weights and molecular weight distributions were determined by size exclusion chromatography. The incorporation ratio of polar monomers was determined by quantitative ¹H NMR analyses. The melting temperature was determined by DSC analysis.

A General Procedure of the Copolymerization of 1,1-Disubstituted Ethylenes with Ethylene (Table 1, entries 5-8). A 50-mL stainless steel autoclave was dried in an oven at 120 °C, and then cooled inside a glovebox under argon atmosphere. Complex 1 (5.7 mg, 10 µmol), 1,1-disubstituted ethylene (x mL; x = 2, 4, 8), and toluene (8-x mL) were added into the autoclave. After the autoclave was charged with ethylene (2.0 MPa), the reaction mixture was stirred in an isothermal heating block at 120 °C for 15 hours. After cooling to room temperature and venting redundant ethylene, the reaction was quenched by addition of methanol (ca. 20 mL). The formed precipitates were filtered, washed with methanol, and dried under high vacuum for >3 hours at 100 °C to afford ethylene/1,1-disubstituted ethylene copolymers. The molecular weights and molecular weight distributions were determined by size exclusion chromatography. The incorporation ratio of polar monomers was determined by quantitative ¹H NMR analyses. The melting temperature was determined by DSC analysis.

Preparation of Complex 3: Sodium {(SP-4-3)-(chlorido)[2-(2,6diisopropylphenyl)imidazo[1,5-α]quinolin-9-olato-κO-1-

ylidene-κC1](methyl)palladate}: To a mixture of 2-(2,6diisopropylphenyl)imidazo[1,5-a]quinolinium-9-olate (51.7 mg, 0.15 mmol) and sodium bis(trimethylsilyl)amide (30.3 mg, 0.17 mmol) in a 15-mL vial was added THF (7.5 mL) at room temperature and the mixture was stirred for 15 minutes at room temperature. To the resulting solution was added PdMeCl(cod) (39.8 mg, 0.15 mmol), and the mixture was stirred for 1 hour. The resulting mixture was passed through a plug of Celite with THF, and concentrated under reduced pressure to ca. 0.2 mL. The obtained solution was poured into hexane (ca. 10 mL) to form precipitates. After filtration and extraction with dichloromethane, the resulting solution was dried in vacuo. Then, complex 3 was obtained as a yellow solid (69.3 mg, 0.13 mmol, 88% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.42 (t, J = 7.8 Hz, 1H), 7.22 (d, J = 7.9 Hz, 1H), 7.106.95 (m, 6H), 6.77 (dd, J = 7.6, 1.5 Hz, 1H), 2.64 (sept, J = 6.7 Hz, 2H), 1.48 (d, J = 6.7 Hz, 6H), 1.10 (d, J = 6.7 Hz, 6H), 0.33 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 154.4, 149.8, 142.1 (2C), 133.9, 126.7, 126.5, 123.9, 123.7, 122.7, 122.3, 120.5 (2C), 119.3, 112.6, 112.0, 110.2, 25.1 (2C), 22.2 (2C), 20.4 (2C), -11.3; HRMS-ESI (m/z) calcd for C₂₄H₂₆ClN₂NaOPd ([M–Na⁺]⁻) 499.0774, found 499.0766.

Preparation of Complex 4: (SP-4-3)-[2-(2,6-diisopropylphenyl)imidazo[1,5-α]quinolin-9-olato-κO-1-ylidene-κC1][3-

methoxy-2,2-dimethyl-3-oxo-κO-prop-1-yl-κC1]palladium: To a solution of complex 3 (29.2 mg, 55.8 µmol) in THF (4.0 mL) in a 20-mL Schlenk tube were added MMA (297.1 µL, 2.79 mmol) and silver carbonate (15.4 mg, 55.8 µmol) at room temperature. In the dark, the mixture was stirred for 18 h at 75 °C. The yield of complex 4 was determined to be 93% by NMR analysis using 1,2,4,5-tetrabromobenzene as an internal standard (Figure S5). The resulting mixture was passed through a plug of Celite, and evaporated to dryness. The resulting solid was dissolved in diethyl ether, and filtered to remove some precipitates. Then, slow evaporation of the solvent afforded the crystal of complex 4 as pale yellow rectangular cylinders (14.2 mg, 45% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.44 (t, J = 7.8 Hz, 1H), 7.22–7.15 (m, 4H), 7.11 (d, J = 9.5 Hz, 1H), 7.02 (s, 1H), 6.96 (d, J = 9.5 Hz, 1H), 6.69 (dd, J = 7.2, 1.7 Hz, 1H), 3.89 (s, 3H), 2.63 (sept, J = 6.7 Hz, 2H), 1.35 (d, J = 6.7 Hz, 6H), 1.07 (d, J = 6.7 Hz, 6H), 0.98 (s, 6H), 0.48 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 189.8, 153.9, 151.1, 142.3, 133.9, 126.5, 126.2, 124.5, 123.6, 123.5, 121.7, 120.4 (2C), 118.3, 112.6, 109.6, 108.8, 51.6, 45.3, 27.1, 25.4 (2C), 25.0 (2C), 22.3 (2C), 20.0 (2C), 17.9; Anal. calcd for C₂₀H₃₄N₂O₃Pd C, 61.65; H, 6.07; N, 4.96 found C, 61.57; H, 6.25; N, 4.86.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org. Experimental procedures, characterization of palladium compounds and polymers, and crystallographic data for **4** (PDF)

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