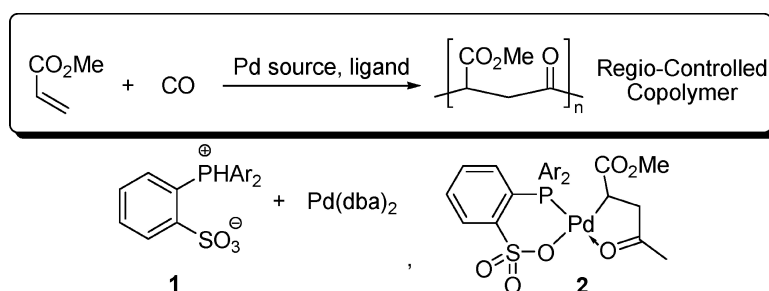


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## Regiocontrolled Copolymerization of Methyl Acrylate with Carbon Monoxide

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The use of polar vinyl monomers for coordination polymerization has been a major challenge for decades<sup>1</sup> because it potentially provides a wide variety of unique functionalized polymer architectures with precise structural control.<sup>2</sup> Late transition metal-catalyzed alternating copolymerization of olefins with CO is one of the most efficient processes that provides polar functionalized polymers by the coordination–insertion mechanism.<sup>3,4</sup> Several olefins bearing polar functional groups have been applied to the copolymerization.<sup>5</sup> However, no example had ever been reported for copolymerization of CO with polar vinyl monomers, the C–C double bond moiety of which is directly attached to polar groups, until our recent report on the copolymerization of vinyl acetate with CO.<sup>6</sup>

Methyl acrylate is one of the most important and readily available polar vinyl monomers. However, application of methyl acrylate for coordination polymerization has only been achieved for copolymerization with ethylene and  $\alpha$ -olefins.<sup>7</sup> Despite considerable efforts devoted toward copolymerization with CO, all of the reports described observation of a five-membered chelate substituted by a methoxycarbonyl group at the  $\alpha$ -position (**C**), formed by migratory insertion of CO into the Pd–Me bond of **A** and subsequent 2,1-insertion of methyl acrylate (Scheme 1). Previous studies also identified several serious obstacles to the copolymerization, including (i) suppressed CO coordination by strong intramolecular ketone coordination in **C**,<sup>8b</sup> (ii) low nucleophilicity of the  $\alpha$ -carbon impaired by the electron-withdrawing group in **D**, even if existed,<sup>8b,9</sup> and (iii) low coordination ability of the C–C double bond of methyl acrylate.<sup>7a,10,11</sup>

In this report, we describe the first example of alternating copolymerization of methyl acrylate with CO. The resulting copolymer has a high level of head-to-tail regularity, which has not been achieved for polar vinyl monomer/CO copolymerization.

The alternating copolymers of methyl acrylate with CO were obtained using catalysts generated *in situ* by combination of Pd(dba)<sub>2</sub> and phosphine–sulfonic acid ligand (**1**).<sup>12,13</sup> Treatment of methyl acrylate with 6.0 MPa of CO at 70 °C for 20 h in the presence of the Pd(dba)<sub>2</sub>/**1a** catalyst afforded the copolymer with  $M_n = 30\,000$  (Table 1, entry 1). Methoxy-substituted ligand **1a** offers both higher activity and higher molecular weights of the copolymers than does unsubstituted **1b** (entries 1, 2). The turnover frequency of the copolymerization was dependent on the CO pressure (entries 1, 4, 5). An increase in CO pressure led to an enhancement in catalytic activity, which may suggest the high barrier for CO coordination–insertion into the chelate **C**.

The alternating structure of the copolymer was confirmed by mass spectrometry and NMR spectroscopy. MALDI-TOF mass spectrometry of the low-molecular-weight product (Table 1, entry 3) shows signal intervals with 114 indicating the formation of alternating copolymer. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the resulting

### Scheme 1

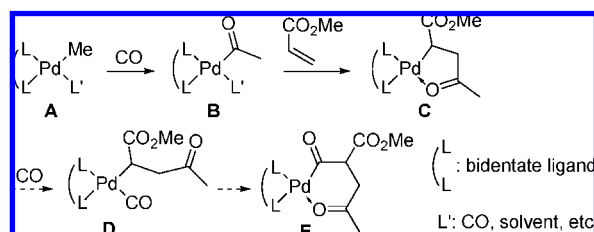
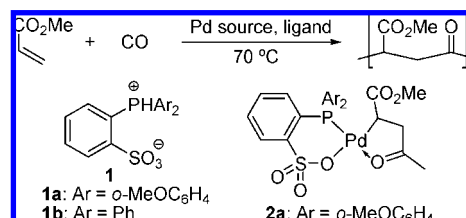


Table 1. Alternating Copolymerization of Methyl Acrylate with CO<sup>a</sup>



entry	Pd source	ligand	$P_{CO}$ (MPa)	time (h)	TOF (h <sup>-1</sup> )	$M_n$ ( $\times 10^3$ )	$M_w/M_n$
1	Pd(dba) <sub>2</sub>	<b>1a</b>	6.0	20	21	30	1.6
2	Pd(dba) <sub>2</sub>	<b>1b</b>	6.0	20	6.0	26	1.2
3	Pd(dba) <sub>2</sub>	<b>1a</b>	6.0	0.5	39	3.1	1.1
4	Pd(dba) <sub>2</sub>	<b>1a</b>	3.0	20	16	21	1.6
5	Pd(dba) <sub>2</sub>	<b>1a</b>	8.0	20	24	17	1.7
6	<b>2a</b>	–	6.0	20	25	24	1.6
7	<b>2a</b>	–	6.0	0.5	57	3.5	1.1

<sup>a</sup> Conditions: 0.010 mmol of Pd source, 0.012 mmol of ligand, 2.5 mL of methyl acrylate, 70 °C. The product contained poly(methyl acrylate) with less than 1 wt %.

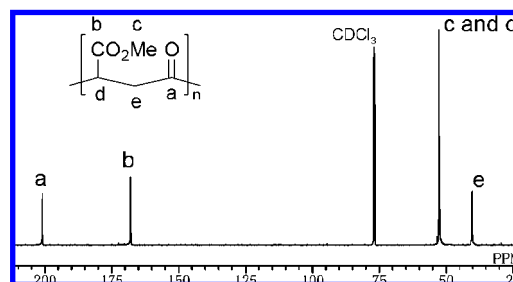
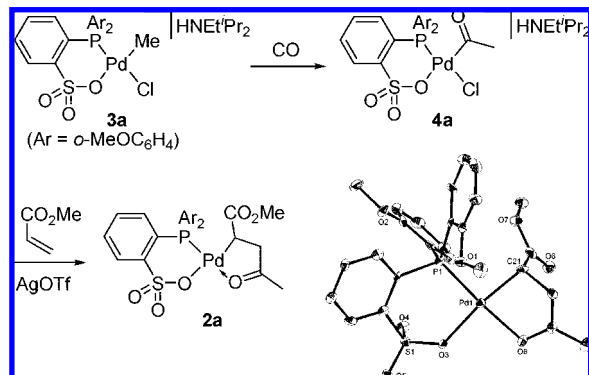


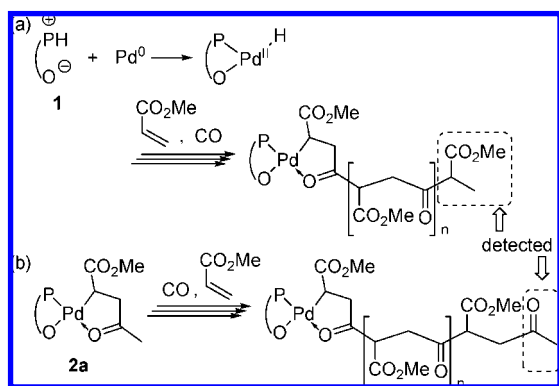
Figure 1. <sup>13</sup>C NMR spectrum of poly(methyl acrylate-*alt*-CO) (in CDCl<sub>3</sub>).

copolymers were in good agreement with the alternating structure but were distinct from those of poly(methyl acrylate).<sup>14</sup> The highly controlled head-to-tail structure of the copolymer was also suggested by the NMR spectra. In fact, the <sup>13</sup>C NMR spectrum (Figure 1) exhibits only one relatively sharp signal in the carbonyl region ( $\delta = 201.0$ ), which can be interpreted as a regiocontrolled copolymer on the basis of comparisons with model compounds and other olefin/CO copolymers.<sup>15</sup>

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**Figure 2.** Synthesis and molecular structure of **2a**. Hydrogen atoms are omitted. Selected bond distances (Å): Pd(1)–C(21) 2.042(6), Pd(1)–O(8) 2.137(4), Pd(1)–O(3) 2.106(4), Pd(1)–P(1) 2.2163(17).



**Figure 3.** Plausible mechanism of copolymerization of methyl acrylate with CO catalyzed by (a) **1** and Pd(0) or (b) **2a**.

To investigate the mechanism of the copolymerization, a five-membered chelate species (**2a**) corresponding to **C** in Scheme 1 was isolated using **1a** (Figure 2). Exposure of **3a**<sup>13b</sup> to ambient CO pressure quantitatively provided acetyl palladium complex **4a**.<sup>13d</sup> 2,1-Insertion of methyl acrylate into the Pd–C bond of **4a** proceeded in the presence of AgOTf to yield  $\gamma$ -ketoalkylpalladium complex **2a** in 60% yield. No formation of the 1,2-insertion product was observed. The structure of **2a** was determined by NMR and X-ray crystallography. The Pd–C (2.042(6) Å) and Pd–O (2.137(4) Å) bond lengths in the five-membered chelate are similar to those of reported examples of **C** bearing neutral bidentate ligands (Pd–C, 2.046–2.059 Å; Pd–O, 2.112–2.161 Å).<sup>8f,g</sup> Copolymerization of methyl acrylate with CO was also successfully initiated and catalyzed by **2a** (Table 1, entries 6, 7).

A plausible mechanism for the regiocontrolled alternating copolymerization is shown in Figure 3.<sup>16</sup> When a mixture of **1** and Pd(dba)<sub>2</sub> was used, the reaction was initiated by formation of a Pd–H bond via protonation of the Pd(0) species, followed by insertion of methyl acrylate. Further insertion of CO and 2,1-insertion of methyl acrylate in an alternating fashion leads to the formation of the alternating copolymer. In fact, a 1-methoxycarbonylethyl group was detected at the initiating end by <sup>1</sup>H NMR for relatively low molecular weight copolymers (Table 1, entry 3), as a result of the 2,1-insertion of methyl acrylate into the Pd–H bond.<sup>15</sup> In contrast, copolymers formed with **2a** (entry 7) showed the signal for an acetyl initiating end group, instead of the 1-methoxycarbonylethyl group. It is noteworthy that this system conquered the difficulties in coordination and insertion of CO to the five-membered chelate of **C**, which had never been accomplished using other ligands.<sup>8</sup>

The strong tendency for 2,1-insertion of methyl acrylate into the Pd–C bond, leading to the head-to-tail structure, was consistent with density functional theory (DFT) calculations<sup>11,13c</sup> and experimental observations<sup>7a</sup> using an  $\alpha$ -diimine ligand or **1a**. However, the origin of the difference in regioregularity between methyl acrylate/CO and vinyl acetate/CO copolymerization is still unclear. According to the DFT calculation on the  $\alpha$ -diimine Pd system by Goddard and co-workers,<sup>11</sup> the preference for 2,1-insertion into a Pd–C bond over 1,2-insertion is greater for methyl acrylate by 1.2 kcal/mol than for vinyl acetate. Although the energy difference may suggest a disparity in regioregularity, further studies are necessary to clarify the difference.

In summary, the first highly regiocontrolled copolymerization of a polar vinyl monomer with CO is reported, using methyl acrylate as a comonomer. Further mechanistic investigations by experimental and computational methods are currently in progress.

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**Supporting Information Available:** Experimental procedures and characterization (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (15) See Supporting Information.
- (16) Copolymerization via a radical process seems to be denied. See Supporting Information.

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