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Synthesis of Polyethylene with in-chain α,β-Unsaturated Ketone and Isolated Ketone Units by Pd-catalyzed Ring-opening Copolymerization of Cyclopropenones with Ethylene

Xiaoming Wang, Falk William Seidel, and Kyoko Nozaki*

Abstract: Although various functionalized units can be incorporated into polyolefins via transition-metal catalyzed coordination copolymerizations of non-functionalized olefins with polar functional monomers, the incorporated functional units are largely limited to a C1 unit from CO or C2 units from vinyl monomers. Here we report the Pd-catalyzed copolymerization of ethylene with cyclopropenone, leading to incorporation of C3 units with functional groups in chain, that are α , β -unsaturated ketones. Coordination-insertion of the carbonyl group and ring opening of the strained three-membered ring is proposed as the key steps in the mechanism. Under a different condition an isolated ketone structure was afforded as the major carbonyl unit, which could be generated by the copolymerization of ethylene with in-situ formed CO from cyclopropenone.

Rapidly growing demand of functionalized polyolefins in various areas has accentuated the need for the development of new polymerization chemistry for the ready introduction of functionalized groups into polyolefins.^[1] In recent years latetransition-metal catalyzed polymerization has become an attractive strategy for the synthesis of functionalized polyolefins via a direct copolymerization of non-functionalized olefins with polar monomers (Scheme 1a).^[2] Particularly palladium/phosphine-sulfonate complexes Pd[P-O] have been proven to be tolerant toward a large scope of polar monomers to produce highly linear functional polyethylenes.^[3] However the polar co-monomers utilized to date are mainly limited to vinyl compounds and/or carbon monoxide.^[4] We became interested in the development of alternative pathways based on new incorporation mechanisms to introduce functional groups into polyolefins, using monomers other than polar vinyl compounds.

Currently, cyclopropenones are receiving significant attention as an important activated coupling partner in organic synthesis (Scheme 1b).^[5] Cyclopropenones show a zwitterionic resonance structure in which a negative charge is located on the oxygen and a positive charge on the three-membered ring, that is stabilized by a 2-electron aromaticity. Accordingly cyclopropenones bear an extremely electrophilic carbonyl group which has been used in insertion reactions with nucleophilic organo-metal species.^[6] The strained ring can be opened by the subsequent β -carbon elimination to form an α , β -unsaturated

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ketone unit. As another reaction pathway, decomposition is known for cyclopropenone to generate alkynes and CO under high temperature pyrolysis, UV irradiation or in the presence of catalysts.^[7] The ring-opening coupling reactions of cyclopropenones with olefins were also reported to form fivemembered cycloaddition products via a strain-driven oxidative addition of the C-C bond to a transition metal as the key step.^[8,9] Although the chemistry of cyclopropenones has been extensively investigated in synthetic methodology, their application as polar monomers in olefin polymerization remains rather unexplored.^[10] Herein we report the first application of a C3 polar monomer to the olefin copolymerization through palladium-catalyzed ring-opening copolymerization of cyclopropenones with ethylene. The copolymers have highly linear structures with novel in-chain α , β -unsaturated ketone units. In addition, the reaction could be switched to afford an in-chain isolated ketone incorporated polyethylene under a different condition, incorporating the in-situ generated CO.^[7] Both of the α,β -unsaturated ketone and isolated ketone units constitute sites for introducing interestina anchoring further functionalities.^[11] The photo-degradability of the products suggested that the α,β -unsaturated ketone units in the copolymer can be partially cleaved.



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entry	cat.	T (°C)	yield (g) ^[b]	activity (kg/mol.h)	<i>M</i> n (g/mol) ^[c]	<i>M</i> w/ <i>M</i> n ^[c]	i.r. of α (%) ^[d]	i.r. of β (%) ^[d]	$\alpha/\beta^{[e]}$	Tm ^[f]
1	Α	80	0.526	4.4	5,400	2.6	1.93	1.04	1.8	110.7
2	в	80	1.420	11.8	7,600	2.1	0.69	0.20	3.4	
3	С	80	0.976	8.1	7,600	2.3	0.85	0.35	2.4	
4	D	80	2.035	16.9	25,300	2.5	1.01	0.17	5.9	119.8
5	D	60	0.896	7.5	50,600	1.8	0.41	0.04	10.2	
6	D	120	1.446	12.0	13,800	2.4	0.85	0.93	0.9	
7 ^[g]	D	80	0.275	2.3	5,500	1.6	3.35	1.39	2.4	
8 ^[h]	D	80	0.408	3.4	3,800	1.7	4.19	1.53	2.7	85.1 / 96.6

[a] A mixture of the catalyst (0.01 mmol) and cyclopropenone **1a** (1.0 mmol) in toluene (10.0 mL) was stirred under ethylene atmosphere (3.0 MPa) in a 50 mL autoclave. [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 in mol% determined by ¹H-NMR analysis. [e] The ratio was determined by ¹H-NMR analysis. [f] Melting temperatures determined by differential scanning calorimetry (DSC) analysis. [g] 1.0 MPa ethylene. [h] 5.0 mmol cyclopropenone **1a**.

Our mechanistic hypothesis begins with the olefin polymerization by Pd[P-O] (Scheme 1c). A Pd catalyst may initiate the polymerization of ethylene to generate a long alkyl palladium complex I. The Pd-C bond might undergo migratory insertion into the carbonyl group of the cyclopropenone, and a subsequent β -carbon elimination of intermediate II gives a ringopened alkenyl intermediate III. Further chain propagation from III with ethylene is proposed to be favorable to afford a novel α,β -unsaturated ketone incorporated polyethylene.Other possibilities are discussed in the Supporting Information..

Copolymerization of ethylene with commercially available diphenylcyclopropenone (1a) was successfully accomplished with Pd[P-O] catalysts A-D (entries 1-4, Table 1). The polymers were purified by precipitation with MeOH to give them in an essentially pure form as solids. NMR analysis of these four obtained polymers clearly supported that a substantial amount of 1a was successfully incorporated into the polymer chain in two different forms (named α and β). Unit α was assessed to be the proposed α,β -unsaturated ketone and unit β was evaluated to be an isolated ketone structure which might be generated by the copolymerization of ethylene with in-situ formed CO from cyclopropenone. For example, the ¹H NMR spectrum of the copolymer corresponding to entry 4 (Figure 1a) showed the characteristic resonances of the α,β -unsaturated ketone unit (α) at 2.58 (t) (B), 2.47 (t) (F), and 7.17-6.99 (aromatic range) ppm. Quantitative ¹³C NMR analyses also showed the resonance of ketone at 206 ppm (E), total of ten peaks for the aromatic carbons and alkenyl carbons at 144-126 ppm, and carbons at αand β -positions of C=O or C=C (F, B, A, G) (Figure 1b). The signals for unit β were found at 2.41 (t) (I) ppm in ¹H-NMR spectrum and 210 ppm (H) in ¹³C-NMR spectrum. It should be noted that the two phenyl groups are cis in unit α , suggesting that intermediate III does not undergo isomerization in the catalysis. No obvious incorporation of the polar monomer is seen at either chain ends. Quantitative ¹³C NMR analysis of the obtained polymers from entries 1-4 (Table 1) revealed that the reactions produced predominantly linear polymers containing less than one branch per 1000 carbon atoms in their polyethylene backbone. The results of the copolymerization including activity, Mn and the ratio of α/β , are highly related to the catalysts used. The complexes bearing alkylphosphine ligands exhibited higher catalytic activity than arylphosphine ligand (entries 2-4 vs 1). Catalysts B and C afforded similar copolymers with higher Mn and activities than catalyst A.

Copolymerization of ethylene with **1a** catalyzed by **D** generated the highest activity, *M*n and the ratio of α/β in the initial survey, albeit with the reduction in the incorporation ratio (Table 1, entry 4 vs 1-3).



Figure 1. Assignment of characteristic NMR resonances. (a) ¹H NMR spectrum of the copolymer in Table 1, entry 4. (b) Quantitative ¹³C NMR spectrum of the copolymer in Table 1, entry 4. (c) ¹H NMR spectrum of the copolymer after the UV irradiation (d) ¹H NMR spectrum of the copolymer in the terpolymerization with AAc (allyl acetate) at 80 °C with catalyst **D**. (e) ¹H NMR spectrum of the copolymer of ethylene with 1a at 120 °C with catalyst **C**. (f) ¹H NMR spectrum of the polyketone from the copolymerization of ethylene with dimesitylcyclopropenone (1e).

Detailed investigations of the reaction conditions were further carried out using catalyst ${\bf D}.$ ${\it M}\!n$ of the copolymer was increased

electron-donating groups (*p*-methoxyphenyl and ethyl) can preferably stabilize the cyclopropenone's zwitterionic resonance structure, leading to a diminished reactivity and stronger

Table 2. Copolymerization of ethylene and cyclopropenone using Pd catalyst D^[a]

$ + R \xrightarrow{O}_{R} \xrightarrow{catalyst \mathbf{D}}_{toluene, 80 °C} \xrightarrow{O}_{R} \xrightarrow{O}_{R$											
entry	cyclopropenone (R)	yield (g) ^[b]	activity (kg/mol.h)	Mn (g/mol) ^[c]	Mw/Mn ^[c]	i.r. of α (%) ^[d]	i.r. of β (%) ^[d]	$\alpha/\beta^{[e]}$			
1	1b (R = p-methoxyphenyl)	0.436	3.6	4,000	2.4	0.88	<0.10	-			
2	1c (R = <i>p</i> -Bromophenyl)	1.467	12.2	11,200	2.4	0.34	0.10	3.4			
3 ^[f]	1d (R = Ethyl)	0.479	4.0	5,200	3.3	0.34	<0.10	-			

[a] A mixture of the catalyst **D** (10.0 µmol) and cyclopropenone (1.0 mmol) in toluene (10.0 mL) was stirred under ethylene atmosphere (3.0 MPa) in a 50 mL autoclave. [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 in mol% determined by ¹H-NMR analysis. [e] The ratio was determined by ¹H-NMR analysis. [f] 0.5 mmol **1d** was used.

to 50,600 by lowering the reaction temperature to 60 °C with lower incorporation ratio and a higher ratio of α/β (Table 1, entry 5). Increasing the polymerization temperature from 80 °C to 120 °C resulted in a significant drop in *M*n and activity but evidently higher incorporation ratio of unit β (Table 1, entry 6). Increasing the ratio of [comonomer, 1a] vs *P*[ethylene] by decreasing the pressure of ethylene (entry 7) and/or raising the amount of 1a (entry 8) led to an increase in the α and β incorporation ratio with a decrease in catalytic activity, molecular weight and the ratio of α/β .

Notably, the differential scanning calorimetry (DSC) analysis of the copolymers obtained from entry 1 and 4 revealed endothermic peaks at Tm = 110.7 °C and 119.8 °C, respectively. The copolymer from entry 8 showed two endothermic peaks at Tm = 85.1 °C and 96.6 °C. All of them are significantly lower than highly linear PEs in the observed MW range.^[12] The photo-degradability of the copolymer obtained from entry 4 was further tested under UV light. The *M*n of the recovered polymer was decreased to 15,600 and the PDI was turned to be 4.0. The ¹H NMR analysis also showed that the signals B and F due to the enone moiety decreased (For details, see SI). These results suggested that the α , β -unsaturated ketone units of the copolymer were partially decomposed by the irradiation.^[13]

Terpolymerization of ethylene with **1a** and a polar vinyl monomer (allyl acetate; AAc) was further tested using catalyst **D** to investigate the relative activities of these two polar monomers. Figure 1c clearly showed that both polar monomers were successfully incorporated in the main chain of the obtained copolymer, suggesting that two different incorporation mechanisms are compatible together. Compared with AAc, much lower [**1a**] (0.10 M **1a** vs. 1.85 M AAc) in the present catalysis led to higher **1a** incorporation than AAc (1.24% vs. 0.60%), highlighting the high activity of **1a** towards the copolymerization with ethylene.

To further investigate the scope and versatility of the copolymerization, cyclopropenone derivatives **1b-d** were examined under the standard conditions. As shown in Table 2, all the co-monomers smoothly underwent the copolymerization with relative lower incorporation ratio than **1a**. Namely, the reactions using diarylcyclopropenone with electron-donating groups **(1b)** and diethylcyclopropenone **(1d)** gave similar results regarding the activities and *M*n, which were much lower than the reaction using comonomer **1c** and/or **1a**. It is proposed that

coordination of the polarized ketone to the catalyst.

As shown above, an isolated ketone unit (β) is generated in a linear polyethylene chain as a minor structure. Actually, the production of non-alternating/isolated CO and ethylene copolymers is one of the main aims in polyketone research in order to obtain new materials since non-alternating polyketones exhibit lower melting points as compared to perfectly alternating materials.^[4] Since 2002, it was reported that the use of Pd[P-O] catalysts enables successive insertion of several ethylene units into the growing polyketone chain for the synthesis of nonperfectly alternating copolymerization of CO and ethylene.[14,15] Although low content of CO was used in these cases, the obtained polyketones still contain significant alternating units which show strong inter-chain dipolar interactions. On the contrary, CO can be slowly generated in situ by the decarbonylation of cyclopropenone in this study. In order to obtain a non-alternating polyketone, the copolymerization of 1.0 MPa ethylene with 1.0 mmol 1a at 120 °C was carried out using catalyst C. The reaction led to the formation of a copolymer with units β as the dominant polar structures (Figure 1d, i.r. 1.80%, 9 ketone groups per 1000 CH₂ units, Mn 4,100). Unit α is at trace amount by ¹³C-NMR analysis. Besides these, copolymerization of ethylene with in situ formed diphenylacetylene was also detected (Figure 1d, for details, see SI). In order to decrease the copolymerization of ethylene with this alkyne, dimesitylcyclopropenone (1e) bearing bulky mesityl groups was synthesized and tested. The copolymer obtained showed isolated ketone units are dominant (Figure 1e, i.r. 1.29%, 6 ketone groups per 1000 CH₂ units, Mn 3,500), without a distinct alternating polyketone structure. Since the properties of polyketone are highly related to the microstructure, this finding offers opportunity for the studies of the structure-property relationships in polykeone research area.^[16]

In conclusion, the copolymerization of ethylene and C3 polar monomer (cyclopropenone) using palladium (II) phosphine-sulfonate catalysts was successfully achieved. Cyclopropenone was incroporated into the main chain by the proposed insertion-ring opening mechanism, generating a novel α , β -unsaturated ketone structure, which was photodegradable. The terpolymerization of ethylene, cyclopropenone and allyl acetate suggested that both of these two polar comonomers can be incorporated into the main chain by their respective mechanisms.

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In addition, benefiting from the slow in situ release of CO from cyclopropenone, polyethylene bearing isolated ketone units in chain was also obtained as the major component in this copolymerization, which may contribute to the studies of their structure-property relationships.

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Keywords: Copolymerization • C3 polar monomer • Cyclopropenones • Pd catalyzed • Polyethylene

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A C3-polar monomer unit was successfully incorporated into a polyethylene chain for the first time by the Pd catalyzed copolymerization of cyclopropenones with ethylene. A polyethylene containing α,β -unsaturated ketone units in chain was obtained possibly via the coordination-insertion of the carbonyl group and ring opening of the strained three-membered ring of cyclopropenone. Under a different condition an isolated ketone structure was afforded as the major carbonyl unit, which could be generated by the copolymerization of ethylene with in-situ formed CO from cyclopropenone.