

New ring-opening polymerization via a π -allylpalladium complex

4. Palladium-catalyzed decarboxylative polymerization of cyclic carbonate

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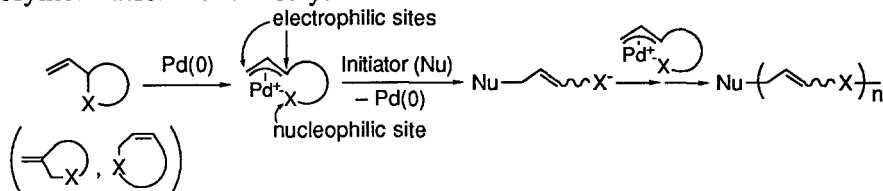
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Summary

A binary system of a palladium complex as catalyst and zinc alkoxide as initiator conducted a novel ring-opening polymerization of cyclic carbonate, i. e., 5,5-dimethyl-4-ethenyl-1,3-dioxan-2-one. The polymerization proceeded along with releasing carbon dioxide to produce the corresponding polyether. The π -allylpalladium complex generated from the monomer with the catalyst is the key intermediate for this new polymerization. The propagating end is zinc alkoxide, which nucleophilically attacks the monomer activated as the π -allylpalladium complex in the propagation.

Introduction

Palladium catalysts are famous for promoting a variety of unique and useful reactions (1). They are powerful also for polymer synthesis, as has been demonstrated by recent many reports including ours (2). Using palladium catalysts, we have been studying new ring-opening polymerization, which we have designed by linking reactions via π -allylpalladium intermediates (3) with polymerization chemistry.



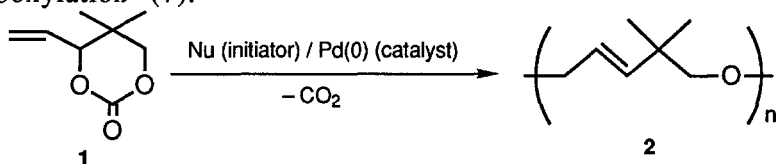
The above scheme shows our idea for the new polymerization. The monomer should have an appropriate leaving group at the allylic

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position in order to accept the oxidative addition of Pd(0). The π -allylpalladium complex generated is attacked by a nucleophilic reagent that is an initiator. In the propagation step, the leaving group acts as nucleophile in turn to conduct the polymerization.

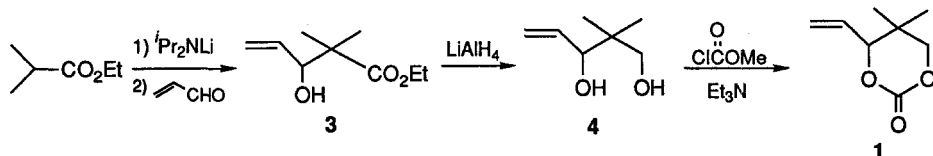
In this context, we have already reported ring-opening polymerization of vinylcyclopropanes activated with two electron-withdrawing groups (4) and of cyclic carbamate, 5,5-dimethyl-6-ethenylperhydro-1,3-oxazin-2-one (5). In the former polymerization, interestingly, the propagating end is an active methyne proton which transfers from the end to the end in the propagation step. In the latter that we have named multi-branching polymerization, amazingly, the propagating end increases in number with the progress of the polymerization releasing carbon dioxide, and hyper-branched polyamine is consequently produced. Herein we employ cyclic carbonate, i. e., 5,5-dimethyl-4-ethenyl-1,3-dioxan-2-one **1** (6) as the monomer for this new type of polymerization to extend its scope. Allylic carbonate is a typical substrate for the palladium-catalyzed reactions via π -allylpalladium intermediates (3). Consequently, as discussed below, we have found that **1** polymerizes to give polyether **2** along with releasing carbon dioxide. It should be mentioned that cyclic carbonate is generally polymerized with anionic or cationic initiators, some of which induced partial decarboxylation (7).



Experimental

Materials $i\text{Pr}_2\text{NH}$, Et_3N , and CH_2Cl_2 were dried over CaH_2 and distilled under N_2 . THF was dried over LiAlH_4 and freshly distilled under Ar before use. $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (dba: dibenzylideneacetone) was prepared by an ordinary procedure (8). EtOH was dried with magnesium ribbon and distilled under N_2 . Other commercially available reagents were used without further purification unless otherwise noted. Shodex[®] AC-803 and K-802 (Showa Denko) were employed as columns for GPC analysis using CHCl_3 as eluent. Calibration curves for GPC were made on the basis of polystyrene standards.

Monomer synthesis Monomer **1** was prepared according to the following three steps. All reactions were carried out under N_2 .



Ethyl 2,2-dimethyl-3-hydroxy-4-pentenoate (3) To a solution of $i\text{Pr}_2\text{NH}$ (47 ml, 336 mmol) in THF (200 ml) was added dropwise $n\text{BuLi}$ (1.6 M in hexane, 210 ml, 336 mmol) at 0 °C. Afterwards, two solutions of ethyl isobutyrate (39 g, 336 mmol) and acrolein (23 ml, 336 mmol) in THF (2 x 50 ml) were sequentially added at -78 °C at an interval of 1 hr. Soon after the addition of the latter solution, the reaction mixture was allowed to warm to room temperature. Then, water was added to the reaction mixture concentrated, and the organic layer extracted with ethyl acetate was dried over MgSO_4 . This solution was concentrated and distilled to give **2** (40 g, 69%): bp 105 °C / 14 mmHg; $^1\text{H NMR}$ (60 MHz, CDCl_3) δ 1.19 (s, 6H), 1.25 (t, 3H), 2.69 (s, 1H), 4.17 (m, 3H), 5.13-6.21 (m, 3H).

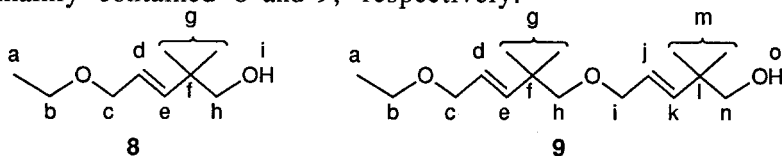
2,2-Dimethyl-4-pentene-1,3-diol (4) To LiAlH_4 (4.45 g, 117 mmol) suspended in THF (250 ml) was added dropwise a solution of **3** (20.15 g, 117 mmol) in THF (50 ml) at 0°C. The reaction mixture was refluxed for 2 hr, and then two portions of water (8.4 g and 4.2 g) were added at 0°C and under refluxing, respectively. After white powder was filtered off, the filtrate was dried over MgSO_4 . The solvent was completely evaporated under reduced pressure to give a colorless liquid, which exclusively contained **4** (quantitative yield): $^1\text{H NMR}$ (60 MHz, CDCl_3) δ 0.87 (s, 3H), 0.91 (s, 3H), 3.02 (s, 2H), 3.51 (s, 2H), 4.02 (br d, 1H), 5.11-6.29 (m, 3H). This crude product was used for the next step without further purification.

5,5-Dimethyl-4-ethenyl-1,3-dioxan-2-one (1) To a solution of **4** (9.72 g, 71.2 mmol) and Et_3N (79 ml, 570 mmol) in THF (250 ml) was added slowly a solution of methyl chloroformate (33 ml, 427 mmol) in CH_2Cl_2 (100 ml). After stirred at r.t. overnight, the reaction mixture was washed with water. The organic layer extracted with CH_2Cl_2 was dried over MgSO_4 and subjected to distillation to give **1** (6.54 g, 59%): bp 98 °C / 1.4 mmHg; $^1\text{H NMR}$ (60 MHz, CDCl_3) δ 1.02 (s, 3H), 1.04 (s, 3H), 4.03 (s, 2H), 4.59 (d, $J=6$ Hz, 1H), 5.24-5.87 (m, 3H); IR (neat, cm^{-1}) 1740, 1640, 987, 935; Anal. Calc: C 61.52, H 7.88, Found: C 61.44, H 7.88.

Polymerization The polymerization of **1** was carried out under Ar in a custom-made reaction tube, which consisted of two tubes (diameter = 18 mm, length = 12 cm) connected with each other through a canal (diameter = 8 mm, length=2 cm) at the position of 3 cm from the bottoms of the tubes. A typical procedure is as follows. In one of the tube, $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (31 mg, 0.03 mmol) and Ph_3P (63 mg, 0.24 mmol) were resolved in THF (3 ml). To this solution

was added **1** (312 mg, 2 mmol), and the mixture was stirred for half an hour. During this period, Et_2Zn (1.0 M solution in hexane, 50 μl , 0.05 mmol) was reacted with a THF-solution of EtOH (5.09 wt%, 90 mg, 0.01 mmol) for 15 min in another tube. Then, these two solutions were mixed well through the canal and stirred at r.t.. The reaction was monitored by measuring the IR spectrum of the reaction mixture in a liquid cell. The absorption peak due to the carbonyl group of **1** gradually faded out. On the basis of the relative intensity of this peak, the monomer conversion was roughly estimated; the IR spectra of **1** measured in THF at various concentrations gave the information for it. After the conversion of **1** was nearly complete, the reaction mixture was poured into hexane. The hexane-insoluble portion was collected by centrifugation (53 mg). On the other hand, from the hexane-soluble portion, the solvent was completely evaporated off. The residue (268 mg), pale brown viscous liquid, contained the product polymer: ^1H NMR (60 MHz, CDCl_3) δ 1.02 (s, 6H), 3.15 (s, 2H), 3.94 (d, $J=3.6$ Hz, 2H), 5.63 (br, 2H); ^{13}C NMR (22.6 MHz, CDCl_3) δ 24.6, 37.3, 72.4, 79.0, 123.8, 140.9; IR (neat, cm^{-1}) 975, 1120.

Stoichiometric reaction of 1 with $\text{Et}_2\text{Zn}-2\text{EtOH}$ To a solution of $\text{Pd}(\text{Ph}_3\text{P})_4$ (23.2 mg, 0.02 mmol) in THF (3.2 ml) was added sequentially EtOH (59 μl , 1 mmol), Et_2Zn (0.93 M in hexane, 540 μl , 0.5 mmol), and **1** (155 mg, 0.99 mmol). After 4 hr at r.t., HCl aq. (1.3 M, 5 ml) was added to the reaction mixture. The aqueous layer was subjected to extraction with four portions of CH_2Cl_2 (6 ml). The organic layer combined was dried over MgSO_4 and concentrated. Then, the residue was subjected to distillation by use of a Kugelrohr apparatus. Two fractions were collected; the first fraction (75~80 $^\circ\text{C}$ / 2.2 mmHg, 15 mg) and the second one (100~150 $^\circ\text{C}$ / 1.4 mmHg, 16 mg) mainly contained **8** and **9**, respectively.



Spectroscopic data (peak assignments): **8**: ^1H NMR (60 MHz, CDCl_3) δ 1.02 (s, H_g), 1.21 (t, $J=7.0$ Hz, H_a), 1.64 (br, H_i), 3.33 (s, H_h), 3.45 (q, $J=7.0$ Hz, H_b), 3.93 (br, H_c), 5.57 (br, H_d and H_e); ^{13}C NMR (22.6 MHz, CDCl_3) δ 15.2 (C_a), 23.7 (C_g), 38.3 (C_f), 65.6 (C_b), 71.5 (C_c and C_h), 125.6 (C_d), 140.0 (C_e); MS (70 eV) m/z (rel. intensity) 158 (M^+ , 0.1), 127 ($\text{M}^+-\text{CH}_2\text{OH}$, 20), 99 ($\text{M}^+-\text{EtOCH}_2$, 3.5), 85 ($\text{M}^+-\text{Me}_2\text{CCH}_2\text{OH}$, 36), 82 ($\text{M}^+-\text{EtO}-\text{CH}_2\text{OH}$, 100), 81 ($\text{M}^+-\text{EtO}-\text{CH}_3\text{OH}$, 91); **9**: ^1H NMR (60 MHz, CDCl_3) δ 1.02 (s, H_g and H_m), 1.21 (t, $J=7.0$ Hz, H_a), 1.85 (br, H_o), 3.12 (s, H_h), 3.33 (s, H_n), 3.45 (q, $J=7.0$ Hz, H_b), 3.93 (br, H_c and H_i), 5.57 (br, H_d , H_e , H_j , and H_k); ^{13}C NMR (22.6 MHz, CDCl_3) δ 15.1 (C_a), 23.7

(C_m), 24.5 (C_g), 37.3 (C_f), 38.3 (C_l), 65.4 (C_b), 71.6 (C_c and C_n), 72.1 (C_i), 79.3 (C_h), 123.8 (C_d), 125.7 (C_j), 139.6 (C_k), 141.2 (C_e); MS (70 eV) *m/z* (rel. intensity) 239 (M⁺-CH₂OH, 0.5), 197 (M⁺-Me₂CCH₂OH, 14), 127 (14), 95(21), 82 (100), 81 (44).

Results and discussion

It is expected that the polymerization of **1** must be conducted by a metal alkoxide or hydroxy group as the propagating end, as is also suggested by our previous studies (4, 5). Accordingly, we tested a number of nucleophiles that might act as the initiator in the presence of a Pd-catalyst: ⁿBuNH₂, ⁿBuLi, ⁿBuMgCl, MeOK, Ti(OEt)₄, Al(OEt)₃, B(OEt)₃, Bu₃SnOEt, Et₂Zn, and Et₂Zn-2EtOH. As the result, only the latter two reagents were effective for the polymerization, while others promoted no reaction or a set of complicated reactions. On the other hand, the stoichiometric reactions (1:2) of Et₂Zn and Et₂Zn-2EtOH with **1**, respectively, gave a complex mixture and distinguishable oligomeric products (vide infra). Therefore, we investigated the polymerization of **1** employing Et₂Zn-2EtOH as the initiator under various conditions (Table 1). The polymerization took place in THF with the aid of palladium-catalyst, i.e., Pd₂(dba)₃•CHCl₃-4Ph₃P. It was confirmed that, without the Pd-catalyst, Et₂Zn-2EtOH was incapable of initiating the polymerization. Room temperature was enough to promote the polymerization, however, which was accelerated by heating at 50°C. The reaction was kept up until the reaction mixture showed almost no IR absorbance peak due to the carbonyl group of monomer **1** at 1740 cm⁻¹. The product polymer was soluble even in hexane; the hexane-insoluble portion of the

Table 1. Ring-Opening Polymerization of 5,5-Dimethyl-4-vinyl-1,3-dioxane (**1**) Initiated with Et₂Zn-2EtOH in the Presence of Pd-Catalyst^{a)}

run	Et ₂ Zn-2EtOH (mol%)	temp. (°C)	time (h)	M _n GPC ^{b)}	M _n Calc. ^{c)}
1	5.0	r.t.	48	900	1120
2	2.5	r.t.	72	1440	2240
3	2.5	50	4.5	1680	2240
4	1.25	r.t.	48	1700	4480
5	1.25	50	4.5	1850	4480

a) Solvent = THF, Pd-catalyst = Pd₂(dba)₃•CHCl₃-4Ph₃P (1.5 mol% for **1**), dba:dibenzylideneacetone. The polymers were produced almost quantitatively.

b) Calibrated using Pst standards in CHCl₃. M_w/M_n = 1.3 ~ 1.4.

c) 112 (= MW of **1** - 44) x 100/(mol% of EtOH)

reaction mixture almost exclusively contained the Pd-catalyst with Ph₃P or dba, as was indicated by the ¹H NMR spectrum. Accordingly, the hexane-soluble portion was subjected to GPC analysis and spectroscopic measurement without further purification. It should be mentioned that to purify the product polymer is possible by use of preparative GPC (bed: Sephadex® LH-20, eluent: methanol).

The molecular weight of the product polymer was evaluated from a GPC elution profile detected by not UV but RI measurement, because a large UV-absorbance peak due to a low molecular weight contaminant prevented the evaluation by use of a UV detector. When the concentration of the initiator decreased, there was a tendency for the molecular weight of the product polymer to increase, however, not proportionally to the feed ratio of the initiator to the monomer (Table 1). It appears that a chain transfer reaction, which is discussed below, occurred.

The ^1H and ^{13}C NMR spectra of the hexane-soluble portion indicated that the product polymer was contaminated with Ph_3P or dba , however, no contaminant other than which was detected there (Figure 1). This is equivalent to saying that monomer 1 was quantitatively converted to the polymer. The NMR signals together with the IR spectrum defined the polymer structure to be polyether 2. The stereochemistry of the double bond is exclusively trans. This was revealed by the following observations; the IR spectrum showed an absorption band due to out-of-plane C-H bending vibration of a trans vinylene group at 975 cm^{-1} , and additionally the ^{13}C NMR spectrum implied that the polymer consisted of the sole unit.

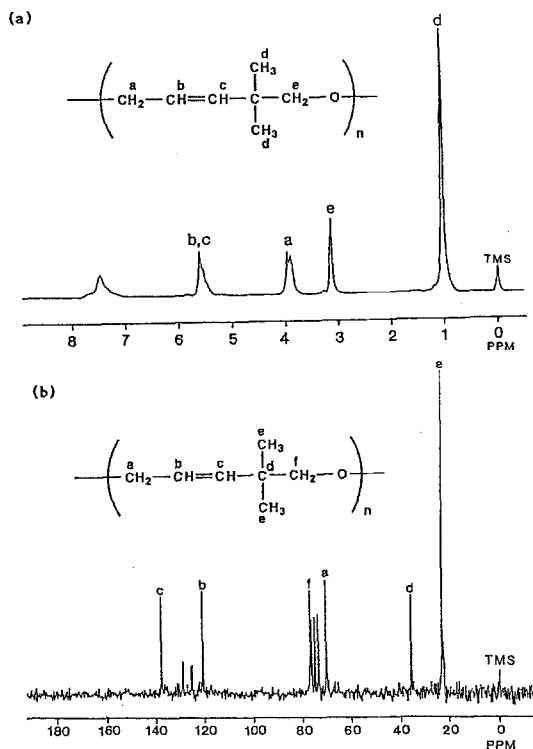
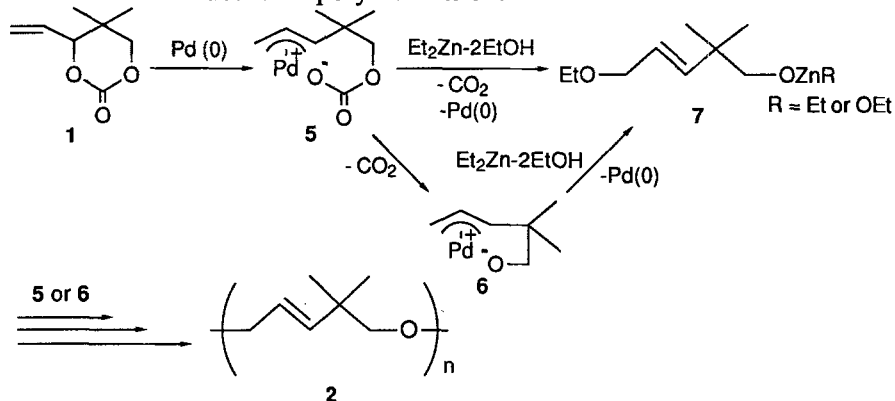
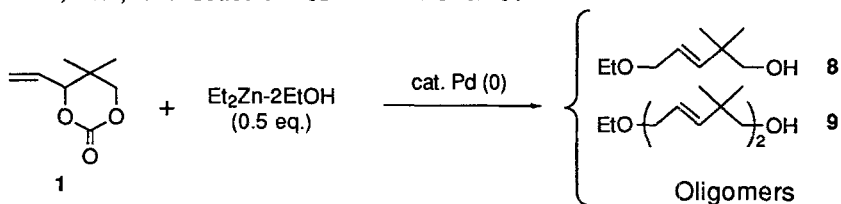


Figure 1. ^1H (a) and ^{13}C (b) NMR spectra (CDCl_3) of the hexane-soluble part (run 3 in Table 1).

The following scheme shows the polymerization mechanism. Monomer **1** accepts the oxidative addition of Pd(0) to generate π -allylpalladium complex **5** (**9**). On the other hand, the actual species for initiation are ethylzinc ethoxide and/or zinc diethoxide, which are generated in situ by the reaction of diethylzinc with ethanol (**10**). In the initiation step, these initiators attack an electrophilic site of **5** simultaneously or subsequently releasing carbon dioxide and regenerating Pd(0). There is another possibility about this process; carbon dioxide is liberated before the attack of the initiator to **5** to generate another π -allylpalladium complex, **6**, which then reacts with the initiator. The product is, anyway, adduct **7** that has the zinc alkoxide moiety. Accordingly, it is possible to repeat a similar process, which is the propagation, leading the production of polyether **2**. It seems that character and reactivity of the zinc alkoxide moiety as the propagating end is suitable for the selective reaction to conduct the polymerization.



This mechanism has been supported by the stoichiometric reaction of monomer **1** with $\text{Et}_2\text{Zn-2EtOH}$ (0.5 eq.). As shown in the following scheme, compounds **8** and **9** were isolated from the reaction mixture in the yields of 10% and 12%, respectively. These structures were defined by ^1H and ^{13}C NMR as well as mass spectroscopy (see Experimental). Compound **8** is the hydrolyzed product of **7**, and the production of **9** is reasonably ascribed to the first propagation reaction, i.e., the reaction of **7** with **5** or **6**.



We have to discuss about the above-mentioned result that the molecular weight of **2** did not increase proportionally with the decrease of the feed ratio of the initiator to the monomer. As one of

the possible causes for it, we speculated a back-biting reaction. The polymer chain accepts oxidative addition by Pd(0) at the position of the allylic ether to generate π -allylpalladium, and the propagating end, i.e., zinc alkoxide, attacks to this position to produce a cyclic oligomer. In order to investigate the possibility of this hypothesis, a model reaction was carried out; allyl neopentyl ether was mixed with $\text{Et}_2\text{Zn}-2^{\text{n}}\text{C}_8\text{H}_{17}\text{OH}$ under the same condition with that of the polymerization. In the result, however, no reaction occurred. This observation indicated that our speculation was out of bounds of possibility. Another possibility is that water not completely excluded from the polymerization system causes the molecular weight of the product polymer to decrease. However, it is difficult to prove it. In conclusion, the feature of the chain-transfer reaction is still unknown.

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This article is dedicated to one of the authors, the late Mr. Tetsuya Haruyama

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