Living Ring-Opening Polymerization of 2-Alkoxy-1-methylenecyclopropanes Initiated by Pd Complexes

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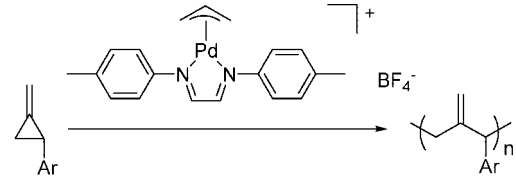
Received April 26, 2008; Revised Manuscript Received June 21, 2008

ABSTRACT: Pd complexes with a chelating diimine ligand promote ring-opening polymerization of 2-alkoxy-1-methylenecyclopropanes to produce the polymers having vinylidene and alkoxy substituents for every three-carbon unit. $^{13}C\{^1H\}$ NMR spectra of the produced polymers show the well-regulated structures with head-to-tail connection of the repeating units. [(π-Allyl)PdCl]$_2$ initiates living polymerization of 2-alkoxy-1-methylenecyclopropanes (alkoxy: OBu, O^{t}Bu, OMe) to afford the polymers with narrow molecular weight distribution. Molecular weight of the polymer was controlled over a wide range by changing the initial monomer-to-initiator molar ratio. Direct measurement of the growing polymer of 2-butoxy-1-methylenecyclopropane by NMR and GPC indicates that the polymer molecule has a dimer structure with a Pd_2Cl_2 core and two π-allyl−Pd bonds. Treatment of the growing polymer with nucleophilic reagents, such as NaOH/MeOH, NaOH/H_2O, AgOAc, and NaCMe(COOEt)$_2$−PPh_3, cleaves the π-allyl−Pd bonds and forms the polymers having organic functional groups at the terminal. The macromonomer having an α,β-unsaturated aldehyde terminal copolymerizes with styrene in the presence of AIBN to afford the polymer having oligo(**1a**) side chains. Photoirradiation of the polymer of 2-butoxy-1-methylenecyclopropane having the π-allyl−Pd bonds in the presence of chelating N-ligands causes coupling of the π-allylic polymer ends to produce the organic polymer.

Introduction

Addition polymerization of vinyl monomers provides the common and convenient method for syntheses of the polymers composed of carbon backbone and a substituent, derived from the monomer molecule, in every repeating unit of the polymer chain. Physical properties of the polymers, such as melting and/or glass transition temperatures, mechanical properties, affinity to surface of the solid, and solubility in solvents, are significantly influenced by the kind of the substituents of the polymer. For example, poly(vinyl ether)s, produced by cationic polymerization of vinyl ethers, have alkoxy group in every two-carbon unit of the polymer chain.[1] The polymer with oligo(ethyleneoxy) groups are soluble in water due to the hydrophilic substituents, while the polymer with alkyl chain at the oxygens shows no solubility in water. The carefully designed block copolymers, formed by living polymerization, exhibit unique properties and perform as intelligent materials.[2]

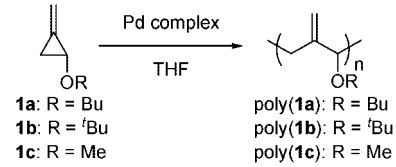
Recently, we reported that cationic Pd−diimine complexes, which were known to initiate efficient olefin polymerization,[3] promoted ring-opening polymerization of 2-aryl-1-methylenecyclopropanes to afford the polymers with vinylidene and aryl groups in the repeating units (eq 1).[4] Scheme 1 shows the proposed mechanism for the polymerization, giving the polymer with a regioregular structure. Initial 2,1-insertion of C=C double bond of the monomer into the π-allyl−Pd bond forms a cyclopropylpalladium intermediate which undergoes β-alkyl elimination to generate a new π-allyl−Pd bond. Repetition of these cycles of insertion and bond cleavage regulates positions of the vinylidene and aryl groups in the structural units. Analogous polymerization of 2-alkoxy-1-methylenecyclopropanes would afford the polymers having the alkoxy group in every three-carbon unit of the polymer chain. Herein, we present Pd(II) complex-initiated ring-opening polymerization of 2-alkoxy-1-methylenecyclopropanes to yield the living polymers whose end group can be functionalized easily to produce the polymer having various end groups. A part of the study has been reported in a preliminary form.[5]



(1)

Results and Discussion

Ring-Opening Polymerization of 2-Alkoxy-1-methylenecyclopropanes Initiated by Pd Complexes. Polymerization of 2-alkoxy-1-methylenecyclopropanes (**1a**−**1c**) initiated by Pd complexes produces the polymers −(CH_2−C(=CH_2)−CH(OR))$_n$− (poly(**1a**) R = Bu, poly(**1b**) R = ^{t}Bu, poly(**1c**) R = Me), as shown in eq 2. Chart 1 summarizes Pd complexes used



1a: R = Bu
1b: R = ^{t}Bu
1c: R = Me

poly(**1a**): R = Bu
poly(**1b**): R = ^{t}Bu
poly(**1c**): R = Me

(2)

in this study. Cationic Pd complexes with a chelating diimine ligand, **I** and **II**/NaBARF (BARF = B{$C_6H_3(CF_3)_2$}$_4^-$), were reported to promote ring-opening polymerization of 2-phenyl-1-methylenecyclopropane, as shown in our previous papers.[4] Complexes **III** and **IV** contain the tridentate N-ligands which are employed in the Fe and Co catalysts for ethylene polymerization.

Polymerization of 2-butoxy-1-methylenecyclopropane (**1a**) initiated by the cationic complexes **I** and **III**/NaBARF yields poly(**1a**) with low molecular weights (M_n = 1500 and 1300) (Table 1, runs 1 and 2). Neutral Pd complexes with diimine ligands (**II**, PdCl(Me)(bpy)) and the complexes with a tridentate N-ligand (**III**, **IV**) also promote the polymerization of **1a** (runs

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10.1021/ma800941f CCC: $40.75
Published on Web 08/12/2008

Scheme 1. Mechanism for the Ring-Opening Polymerization of 2-Aryl-1-methylenecyclopropane

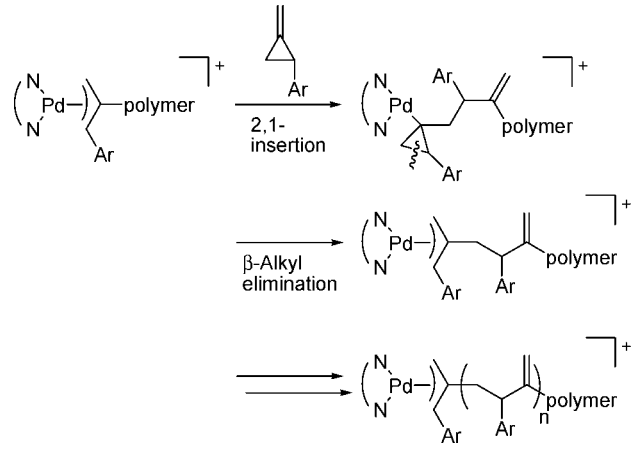


Chart 1. Pd Complexes Used in This Study

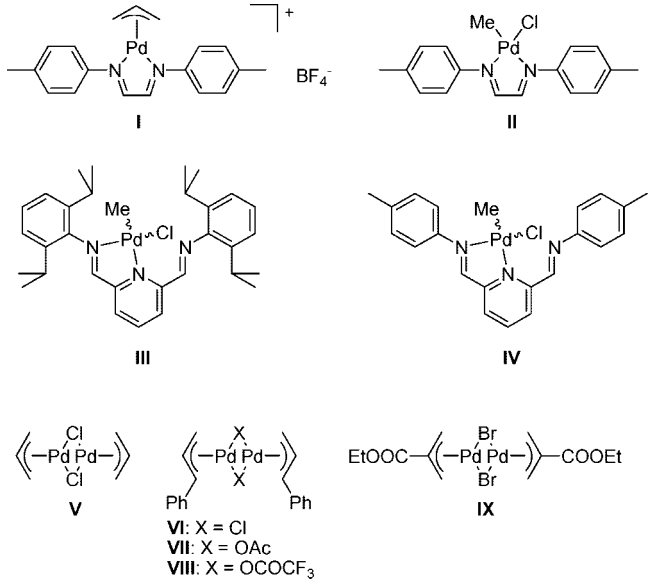


Table 1. Polymerization of 2-Alkoxy-1-methylenecyclopropanes by Pd Complexes[a]

run	monomer	initiator	time/h	conv/%[b]	M_n[c,d]	M_w/M_n[c,d]	M_n[c,e]	M_w/M_n[c,e]
1	**1a**	**I**	1	quant	1500	1.41		
2	**1a**	**III** + NaBARF	6	quant	1300	1.71		
3	**1a**	**II**	6	quant	12000	1.26		
4	**1a**	PdCl(Me)(bpy)	6	83	8700	1.36		
5	**1a**	**III**	6	91	13000	1.11		
6	**1a**	**IV**	6	95	15000	1.14		
7	**1a**	**V**	18	quant	14000	1.15	9000[f]	1.09
8	**1a**	**VI**	7	93	14000	1.07	8200[f]	1.03
9	**1a**	**VII**	12	—[g]	1200	1.54		
10	**1a**	**VIII**	3	quant	2500	1.81		
11	**1a**	**IX**	12	95			6600[f]	1.06
12	**1b**	**VI**	4	92	7300	1.18[h]	6800[f]	1.05
13	**1c**	**VI**	40	quant			6000[i]	1.11

[a] Reaction conditions: [**1a**]/[Pd] = 70, [Pd] = 25 mM in THF at room temperature. [b] Determined by ^{1}H NMR. [c] Determined by GPC. [d] Without quenching. [e] After quenching. [f] Quenched with NaOH/MeOH and measured without further purification. [g] Structure is not fully characterized. [h] Bimodal molecular weight distribution. [i] Quenched with AgOAc.

3−6). GPC analyses of the reaction mixture without quenching show molecular weight of the product with M_n = 12 000−15 000 with narrow molecular weight distribution (M_w/M_n = 1.11−1.26).

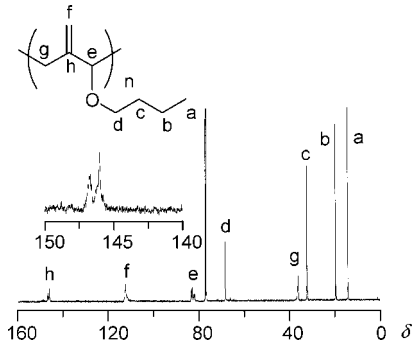


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of poly(**1a**) obtained by the polymerization of **1a** by **III** ([**1a**]/[Pd] = 70) in THF at room temperature (without quenching).

Figure 1 contains $^{13}C\{^1H\}$ NMR spectrum of poly(**1a**). The ^{1}H NMR signal at δ 5.03 and the $^{13}C\{^1H\}$ NMR signals at δ 112.4−112.8 correspond to the hydrogens and carbon nuclei of the $=CH_2$ group. The $^{13}C\{^1H\}$ NMR signals of the quaternary carbon of the $C=CH_2$ group and CH carbon are observed as pairs of peaks at δ 145.5−147.2 and δ 81.4−83.8, respectively. Two peaks of each carbon signal are assignable to *racemo* and *meso* diads of the repeating units. CH_3 and CH_2 carbon signals are observed at reasonable positions. All these NMR data indicate that the produced polymer has a well-regulated head-to-tail sequence of the single repeating unit, $-CH_2-C(=CH_2)-CH(OBu)-$. The polymerization of **1a** in the presence of catalytic amount of dinuclear π-allylpalladium complexes with bridging chloro ligands, **V** and **VI**, in THF consumes the monomer in 18 h (runs 7 and 8). Direct GPC measurement of the reaction mixture indicates formation of the polymer with M_n = 14 000 (M_w/M_n = 1.15 and 1.07). Quenching the product by addition of a MeOH solution of NaOH (excess) causes decrease of the M_n values of the polymer to 9000 and 8200, respectively, keeping the narrow molecular weight distribution (M_w/M_n = 1.09 and 1.03, respectively). The degree of polymerization calculated from the molecular weight after quenching (Dp = 71 and 65) agrees with that estimated from the molar ratio of the monomer to Pd used in the polymerization (70). π-Allylpalladium complexes with bridging acetate and trifluoroacetato ligands, **VII** and **VIII**, afford the polymer with low molecular weights (runs 9 and 10). The polymer obtained by **VII**, however, showed a different ^{1}H NMR spectrum from poly(**1a**) prepared by using the reactions initiated by **V** and **VI**. A Pd complex with ester group at the allyl ligand, **IX**, promotes the polymerization of **1a** to give poly(**1a**) with the controlled structure and molecular weight (run 11). Thus, neutral complexes are found to be suitable for the catalyst for the polymerization. Cationic complexes and π-allylpalladium carboxylate complexes afford the polymer with low molecular weight, possibly because of the frequent chain transfer of the growing species via reductive elimination.

Figure 2 plots change in molecular weights of poly(**1a**) during the polymerization using **VI** as the initiator and compares the results before and after the quenching with excess NaOH/MeOH. The M_n values of the polymer without quenching increase proportionally to conversion of the monomer with keeping almost constant M_w/M_n (1.0−1.1). The M_n value of poly(**1a**) obtained after quenching also increases with increase of the monomer conversion and is close to the calculated value based on the ratio of the reacted monomer to Pd. The molecular weight of poly(**1a**) is successfully controlled over a wide range by changing the initial molar ratio of **1a** to Pd in the polymerization.[5] For example, the polymerization of **1a** using **VI** with a molar ratio of [**1a**]/[Pd] = 400 affords poly(**1a**) with M_n and M_w/M_n of 43 000 and 1.11 (after quenching with NaOH/MeOH).

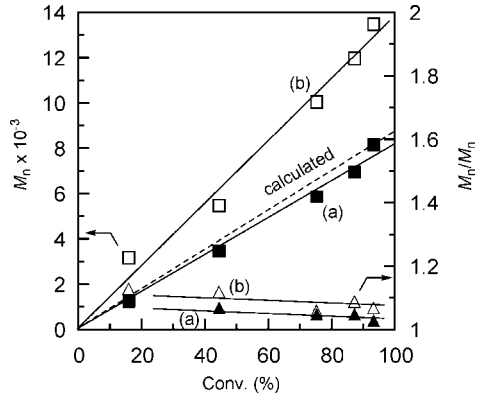


Figure 2. Relationship between M_n, M_w/M_n, and conversion of **1a** in polymerization promoted by **VI** ([**1a**]/[Pd] = 70, THF at room temperature). Results are shown for (a) after quenching with NaOH/MeOH and (b) before the quenching. Dotted line corresponds to the M_n calculated from the monomer to Pd ratio.

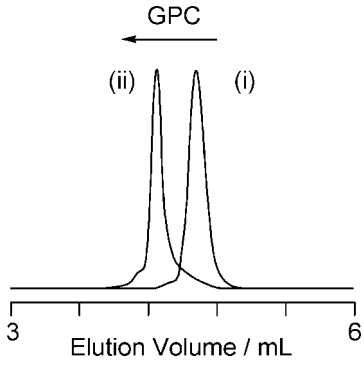


Figure 3. Two-stage polymerization of **1a** by **VI** in air using undistilled THF as the solvent. GPC profiles of the polymers formed (i) at the first stage ([**1a**]/[Pd] = 50) and (ii) at the second stage ([**1a**]/[Pd] = 100).

The molecular weight is comparable to the value calculated from the monomer to Pd ratio ($M_{n,calc}$ = 50 000).

Living polymerization of **1a** promoted by **VI** proceeds smoothly even under air, and commercial THF can be used as the solvent without further purification. New addition of the monomer to the living polymer causes smooth polymer growth. The first-stage polymerization of **1a** ([**1a**]/[Pd] = 50) produces poly(**1a**) with M_n = 5000 and M_w/M_n = 1.05 (after quenching with NaOH/MeOH), and subsequent addition of **1a** (100 equiv to Pd) to the reaction mixture resumes the polymerization to cause quantitative monomer conversion and affords the polymer with a higher molecular weight (M_n = 15 000 and M_w/M_n = 1.11, after quenching with NaOH/MeOH), as shown in Figure 3. There are some tails in the higher molecular weight region of the polymer, which may due to the product that does not react with NaOH/MeOH and keeps dinuclear structure having a Pd(μ-Cl)$_2$Pd core (vide infra). Similar two-stage polymerization in purified THF in Ar produces the poly(**1a**) with M_n = 5500, M_w/M_n = 1.06 (the first stage, ([**1a**]/[Pd] = 50)) and M_n = 16 000, M_w/M_n = 1.11 (the second stage, ([**1a**]/[Pd] = 100)). These results indicate that π-allyl−Pd bonds of the growing polymer are stable toward air and moisture, while they undergo smooth insertion of the monomer molecules.

The polymerization of **1a** probably involves 2,1-insertion of the monomer into the π-allyl−Pd bond and subsequent ring expansion, similarly to the polymerization of 2-aryl-1-methylenecyclopropanes, shown in Scheme 1. The first-order plots of the polymerization of **1a** promoted by **VI** in THF-d_6 at 0−40 °C as well as Arrhenius plots of the rate constants show good

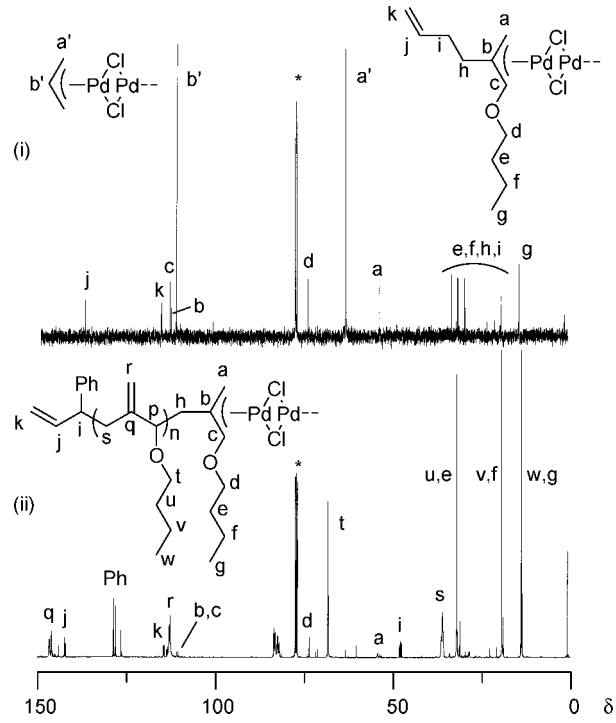


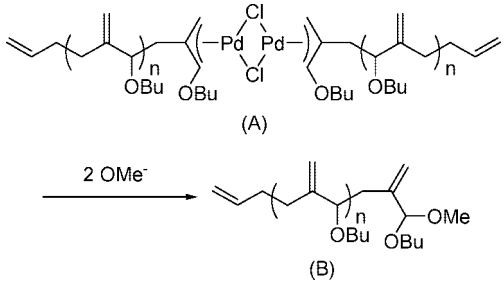
Figure 4. $^{13}C\{^1H\}$ NMR spectra of the reaction mixtures of (i) **V** and **1a** ([**1a**]/[Pd] = 1/10) and (ii) **VI** and **1a** ([**1a**]/[Pd] = 10/1).

linearity.[6] The observed rate constant at 40 °C is 2.3 × 10^{-4} s^{-1} with Pd concentration of 25.0 mM (k_{obsd}/[Pd] = 9.2 × 10^{-6} s^{-1} (mmol Pd)$^{-1}$). The activation energy of the polymerization is determined as 67.0 kJ mol^{-1}, which is close to that of 2-phenyl-1-methylenecyclopropane promoted by **I** (67.6 kJ mol^{-1}). The polymerization of **1a** in CH_2Cl_2 (k_{obsd} = 2.3 × 10^{-4} s^{-1} at 25 °C) occurs faster than the reaction in THF, while the reaction becomes slower in toluene (k_{obsd} = 5.5 × 10^{-5} s^{-1} at 25 °C).

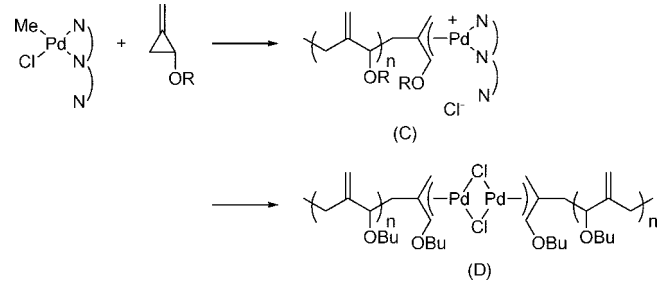
The following NMR studies of the growing polymer initiated by **V** revealed actual structure of the terminal group. A $CDCl_3$ solution of **V** and **1a** ([Pd] = 2 mM, [**1a**]/[Pd] = 1/10) was subjected to $^{13}C\{^1H\}$ NMR measurement. At 1 h after preparation of the mixture, signals due to **1a** becomes negligible, and new signals appeared clearly, as shown in Figure 4 (i). Large signals at δ 62.8 and 111.1 are due to **V** remained intact in the reaction mixture. The spectrum with the DEPT technique revealed that new signals at δ 53.3, 112.9, and 112.7 corresponded to CH_2, CH, and quaternary carbons, respectively, and were assigned to the signals of the π-allylic group bonded to Pd center. Another reaction mixture of **1a** with **VI** ([**1a**]/[Pd] = 10/1) exhibits the signals at δ 54.3, 110.2, and 110.5, which are assigned to the allylic polymer end-bonded to Pd (Figure 4 (ii)). Signals of the repeating units and 1-phenylallyl group of the initiating end group of the oligomer are observed at reasonable positions. NMR studies of the oligomer formed after addition of NaOH/MeOH revealed the terminal structure having actual end groups, as mentioned later. These results indicate that poly(**1a**) formed by the reaction using **V** has a structure shown in Scheme 2A, and the π-allyl−Pd end groups are bridged by two Cl ligands, similarly to **V**. The quenching process changes the π-allyl−Pd bond to the unsaturated acetal group via nucleophilic addition of OMe to the π-allyl ligand, as shown in Scheme 2B.

Different molecular weights before and after addition of NaOH/MeOH are explained on the basis of polymer structures, as follows. Polymer with structure A (Scheme 2) has a molecular weight higher than the calculated one from the monomer to Pd

Scheme 2. Structure of Poly(1a) before and after Quenching with NaOH/MeOH



Scheme 3. Polymerization of 2-Alkoxy-1-methylenecyclpropanes by Pd Complex with N-Ligand



ratio due to its dinuclear structure having a Pd(μ-Cl)$_2$Pd core. Addition of NaOH/MeOH to the polymer changes not only structures of the end group to C(=CH$_2$)−CH(OBu)(OMe) structure (vide infra) but also the molecular weight which becomes close to the calculated value from the monomer/Pd ratio. Reaction of nucleophilic reagents with π-allylpalladium complexes form new C−C, C−N, and C−O bonds, which are commonly used in synthetic organic reactions[7] as well as in polymer synthesis.[8]

NMR measurement of the growing polymer formed by the Pd complexes with chelating ligand shows structure of actual structure of the catalyst. Complex **III** contains 2,6-bisiminopyridine as a bidentate chelate ligand, as shown by ^{1}H NMR spectroscopy (Figure 5 (i)). Addition of **1a** to the solution ([**1a**]/[**III**] = 5) and reaction for 30 min causes decrease of the signals of the coordinated ligand in aromatic hydrogen region (Figure 5 (ii)). Concomitant growth of new signals due to the free ligand is also observed, indicating that the bisiminopyridine ligand undergoes dissociation during the polymerization. GPC analysis

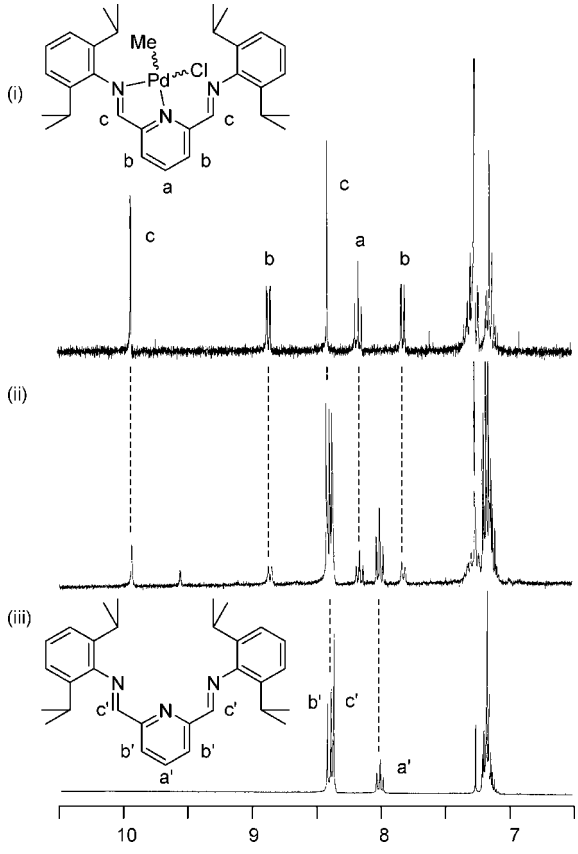


Figure 5. ^{1}H NMR spectra in CDCl$_3$ (aromatic region) of (i) **III**, the reaction mixture of **III** and **1a** ([**1a**]/[**III**] = 5, reaction time = 2 h), and (iii) the free ligand.

of the polymer obtained by using **IV** as the catalyst ([**1a**]/[**IV**] = 50), after addition of 1 M NaOH (MeOH solution) to the reaction mixture, shows a single sharp elution with M_n = 5300 and M_w/M_n = 1.07. This is close to the value calculated from relative amount of the reacted monomer and the initiator (6300). In contrast, GPC of the polymer, measured without addition of quenching agent, shows a larger molecular weight with somewhat broadened distribution (M_n = 8600, M_w/M_n = 1.14). The molecular weight of the growing polymer as well as the above results indicates formation of the polymer with the dimer structure having a Pd$_2$Cl$_2$ group, similarly to the polymer starting from **V** (Scheme 2A).

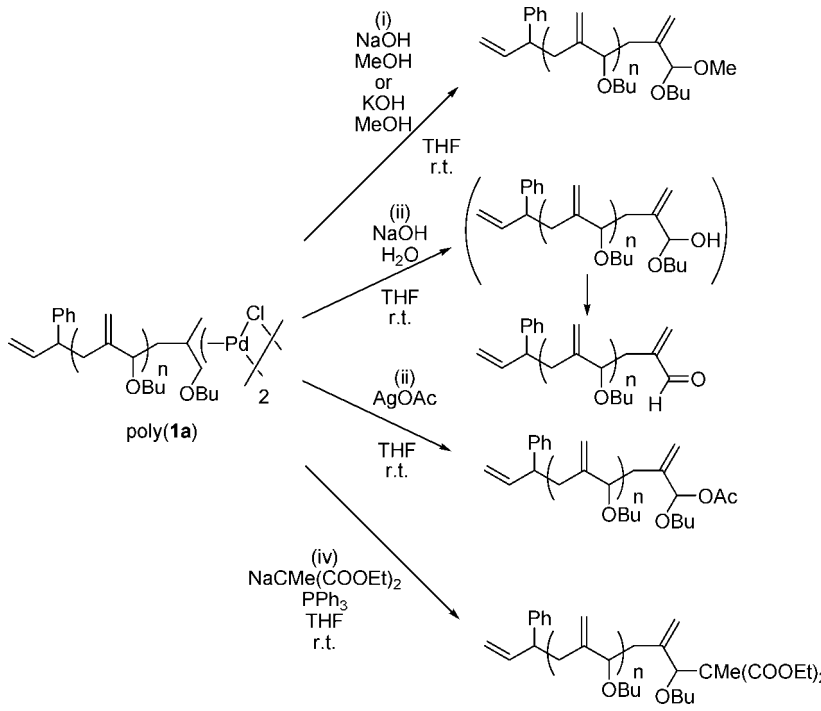
Thus, the Pd complex with N-ligand causes dissociation of the ligand and dimerization to give a (π-allyl)PdCl species, as shown in Scheme 3. Insertion of monomer molecules into the Pd−Me bond of the complexes may produce the cationic π-allylpalladium complex with the N-ligand (C). The intermediate complex is not observed in the NMR spectra probably due to instant decoordination of the chelating ligand and dimerization, forming (D) during the reaction.

2-Alkoxy-1-methylenecyclopropanes **1b** and **1c** also polymerize in the presence of a catalytic amount of **VI**. The polymerization of **1b** by **VI** proceeds faster than that of **1a** under similar conditions (Table 1, run 12). The obtained polymer after treatment with NaOH/MeOH showed narrow molecular weight distribution of the product. The polymerization of **1c** by **VI** proceeds more slowly than that of **1a** to give poly(**1c**) with narrow molecular weight distribution (M_w/M_n = 1.1) (run 13). Higher reactivity of **1b** than **1a** and **1c** can be ascribed to the bulky O^{t}Bu group of the monomer. The π-allyl−Pd bond of the growing end (Scheme 1) may be destabilized by the bulky substituent and isomerized into a more reactive σ-allyl−Pd bond.

Ni complexes with π-allyl ligands having alkoxy substituents were known to promote smooth polymerization of various allene derivatives,[9] although use of these types of complexes to synthetic organic reactions is quite limited.[10] π-Allylpalladium complexes having alkoxy substituents on the π-allyl ligand have only a few precedents.[11] This study demonstrated that the complexes with alkoxy-π-allyl ligand function as the good catalyst.

Functionalization and Coupling of the Terminal Group of the Polymer. The living polymer of the methylenecyclopropane derivatives contains the Pd−π-allyl bond at the growing polymer end. Reaction of nucleophilic reagents to the π-allyl−palladium complexes may cause cleavage of the Pd−C bond and formation of new bonds and introduce the functional group to the polymer end.[9] Scheme 4 summarizes reactions of the polymer end group. Poly(**1a**) formed by using **VI** as the initiator ([**1a**]/[Pd] = 20, quantitative monomer conversion) is employed for end-functionalization and characterization of the formed polymer. Treatment of the polymer with a methanol solution of NaOH (1.0 M), followed by purification using column chromatography (silica gel, ethyl acetate/hexane (1/1) eluent),

Scheme 4. End-Functionalization of Poly(1a)[a]

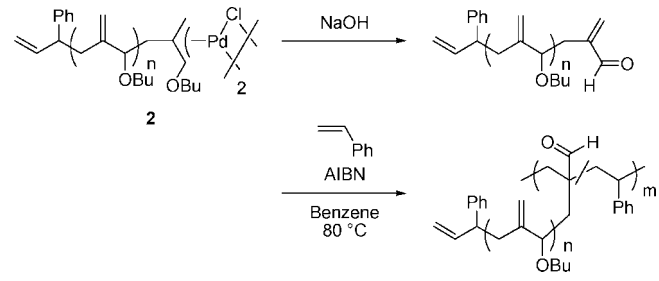


[a] For information on reaction conditions, see the Experimental Part.

affords the end-functionalized polymer as colorless oil (i). ^{1}H NMR spectrum of the polymer shows the signals due to the repeating $-CH_2C(=CH_2)CH(OBu)-$ units and smaller signals at δ 4.75 and 5.98. The former signal is assigned to the CH hydrogen of the terminal acetal group, $-CH(OBu)(OMe)$, while the latter is due to $=CH$ hydrogen of the vinyl group at the initiating end. The acetal group is probably formed via nucleophilic attack of MeO^- anion at the π-allyl carbon bonded to both Pd and OBu group and is confirmed by the $^{13}C\{^1H\}$ NMR spectrum of the polymer, which exhibits the acetal carbon at δ 104.1. The relative intensity of the acetal CH group to the vinyl CH group is 1:1.17, indicating that the Pd$-\pi$-allyl bond of end group of the living polymer is converted to the acetal group quantitatively. The degree of polymerization (Dp) of the polymer, determined from relative ^{1}H NMR peak intensity ratio of the CH signal of $=CH_2$ group of the polymer chain to the acetal end group, is 17, which is close to the monomer-to-Pd molar ratio (20). The polymer quenched by addition of NaOH(aq) shows the ^{1}H NMR signals at δ 9.51, 6.34, and 6.04, which are assigned to CHO and $=CH_2$ hydrogens of α,β-unsaturated aldehyde terminal group (ii). Initial nucleophilic reaction of OH^- to the Pd$-\pi$-allyl end group of the polymer forms the polymer with a hemiacetal group, which is isomerized into the more stable aldehyde group. Addition of AgOAc to the living polymer converts the polymer end to a hemiacetal ester group (iii). The reaction of $NaCMe(COOEt)_2$ with the living chain in the presence of PPh_3 produces the polymer having the $-CMe(COOEt)_2$ end group (iv).

The polymer having the unsaturated aldehyde end group can be used as a macromonomer. The macromonomer **2** synthesized by the reaction of **1a** with **VI** ([**1a**]/[Pd] = 20) and quenching with NaOH(aq) (0.14 g, M_n = 2200, M_w/M_n = 1.12) reacts with styrene (0.11 g) in the presence of AIBN (3.2 mg) at 80 °C to afford the poly(**2**-*co*-styrene) after pouring the solution to large amount of MeOH to remove unreacted **2** and styrene. The polymer contains the repeating units from **1a** and from styrene in 1:2.2 ratio (M_n = 9800, M_w/M_n = 1.74) (Scheme 5). The $C{=}CH_2$ groups of poly(**1a**) are intact during the radical

Scheme 5. Copolymerization of 2 and Styrene



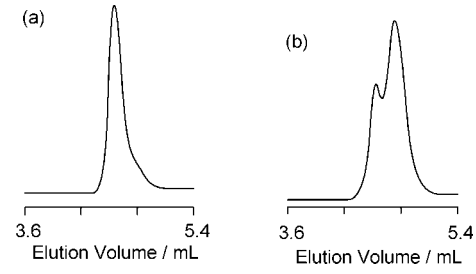


Figure 6. GPC trace of poly(**1a**) after photoirradiation in the presence of (a) TMEDA ([**1a**]/[Pd] = 26) and (b) 1,10-phenanthroline ([**1a**]/[Pd] = 42) ([Pd] = 0.78 mM, 10 °C, 3 h).

polymerization. T_g of poly(**1a**) is −57 °C, whereas that of poly(**2**-*co*-styrene) showed T_g at 31 °C. A similar copolymer is obtained from styrene and macromonomer having an α,β-unsaturated ester group in the initiating end, which is prepared by using **IX** as the initiator and quenched by NaOH/MeOH.

Dinuclear π-allylpalladium complexes with bridging chloro ligands were reported to undergo photoinitiated coupling of the two allyl groups to form a new C−C bond.[12] Analogous coupling of the living polymers of 2-alkoxy-1-methylenecyclopropanes is expected to afford the organic polymers having both terminal groups derived from the initiator. Photoirradiation (200

Table 2. Photoirradiation of Living Poly(1a) and Poly(1c)

						before irradiation[b]		after irradiation	
run	polymer	ligand	solvent[a]	[Pd]/mM	temp/°C	M_n[c]	M_w/M_n[c]	M_n[c]	M_w/M_n[c]
1	poly(**1a**)	1,10-phenanthroline	THF	3.1	10	5600	1.09	10200	1.13
2	poly(**1a**)	1,10-phenanthroline	THF	0.78	10	3200	1.09		bimodal
3	poly(**1a**)	1,10-phenanthroline	toluene	0.78	10	3600	1.10	7000	1.11
4	poly(**1a**)	1,10-phenanthroline	CH_2Cl_2	0.78	10	7300	1.08		bimodal
5	poly(**1a**)	1,10-phenanthroline	THF	0.78	−15	3900	1.08	7600	1.10
6	poly(**1a**)	1,10-phenanthroline	THF	0.78	−45	5500	1.11	10800	1.09
7	poly(**1a**)	1,10-phenanthroline	THF	0.78	−78	5200	1.06		bimodal
8	poly(**1a**)	1,10-phenanthroline	toluene	0.78	−15	2700	1.16	4800	1.15
9	poly(**1a**)	1,10-phenanthroline	toluene	0.78	−78	3600	1.15		bimodal
10	poly(**1a**)	TMEDA	THF	0.78	10	3400	1.07	6200	1.12
11	poly(**1a**)	pyridine	THF	3.1	10	6300	1.10		bimodal
12	poly(**1a**)	bipyridine	THF	3.1	10	3300	1.09		bimodal
13	poly(**1a**)	1,2-diaminocyclohexane	THF	3.1	10	4800	1.08		bimodal
14	poly(**1c**)	1,10-phenanthroline	THF	3.1	10	4800	1.07	8800	1.10

[a] Solvent used for photoirradiation. [b] Poly(**1a**) was prepared by the polymerization of **1a** with **VI** in the initial molar ratio [**1a**]/[Pd] of 26−70. [c] Determined by GPC after quenching with PPh_3 and without further purification.

W mercury xenon lamp) of poly(**1a**), obtained by the polymerization promoted by **VI**, changed structure and molecular weight of the polymer. Figure 6a depicts the GPC trace of the polymer (0.78 mM in THF) after irradiation in the presence of TMEDA. The unimodal elution and the molecular weight (M_n = 6200), which agrees well with the value that is twice of the calculated from the monomer-to-Pd ratio (3400, [**1a**]/[Pd] = 26), indicate that two π-allyl ligands of the polymer undergo coupling, leading to the high molecular weight polymer. The polymer obtained after the irradiation in the presence of 1,10-phenanthroline shows bimodal elution (M_n = ca. 4100 and ca. 8100). The polymer is probably a mixture of the molecules formed via coupling of the π-allylic group bonded to Pd and those whose π-allyl−Pd bonds are decomposed without coupling. Table 2 summarizes these results (runs 2 and 10) together with the results of irradiation under different conditions. 1,10-Phenanthroline enhances coupling of the π-allyl ligands and affords the polymer with unimodal elution at 3.1 mM concentration (run 1). At lower concentration of the polymer, complete coupling of the π-allyl end groups requires optimization of temperature and solvent (runs 2−9). TMEDA completes the coupling even at lower concentration of the polymer (run 10). Pyridine, 2,2′-bipyridine, and 1,2-diaminocyclohexane do not enhance the photoassisted coupling (runs 11−13). Poly(**1c**) also undergoes coupling of the π-allyl groups bonded to Pd (run 14).

The partial structure of the polymer resulting from the photoassisted coupling is investigated by the NMR analyses of poly(**1c**) with a low molecular weight. The living polymer of **1c** (M_n = 690, M_w/M_n = 1.09, after quenching with PPh_3[13]) is irradiated in the presence of TMEDA for 3 h at 10 °C. The molecular weight of the polymer after the irradiation and subsequent addition of PPh_3 is increased to 1100 (M_w/M_n = 1.31). Figure 7 compares the $^{13}C\{^1H\}$ NMR spectra of the reaction mixture before and after the photoirradiation. Signals at δ 110.2, 110.5, and 54.4 are observed before the photoirradiation and assigned to the ^{13}C nuclei of the π-allyl group bonded to the Pd center. Photoirradiation of the solution causes disappearance of the above signals and growth of new peaks at δ 142.9 and 59.2. These new peaks are assigned to the $=CH_2$ carbon of the vinylidene group and OCH_3 carbon, respectively. ^1H NMR and $^1H-^{13}C$ COSY spectra indicate that the former signal correspond to the ^1H NMR signal at δ 5.77. Comparison of the positions of the ^1H and ^{13}C NMR signals after the photoirradiation with model compounds (3,4-dimethoxy-1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene, and 1-methoxy-2-methylpropylene) indicates that the polymer contains a vinyl ether structure (Chart 2E) formed via C−C coupling. Previous studies on similar photoassisted coupling of the π-allyl group bonded

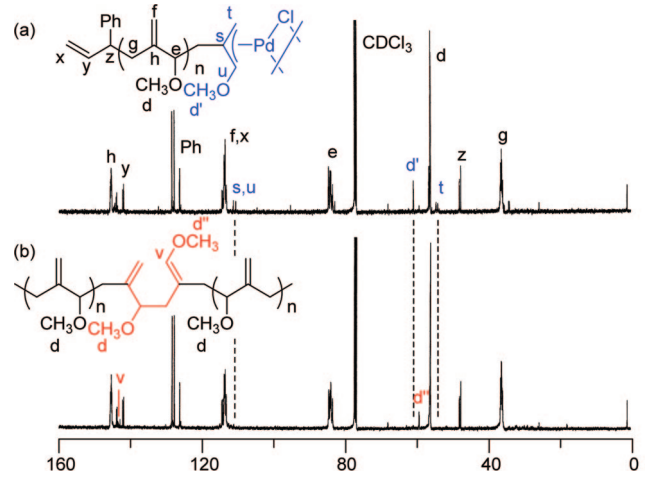
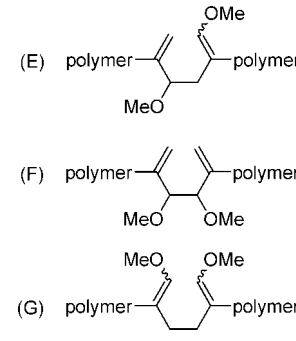


Figure 7. NMR spectra poly(**1a**) (a) before and (b) after photoirradiation in the presence of TMEDA ([**1a**]/[Pd] = 16, [Pd] = 0.78 mM, 10 °C, 3 h).

Chart 2. Possible Structure of the Polymer after Coupling of π-Allyl Groups



to the Pd centers indicated that the C−C coupling of the monosubstituted allyl ligand formed the structure (F) via head-to-head coupling of the substituted allyl groups as the major product.[12a] The results of this study indicate that the coupling of the π-allyl ligands with alkoxy substituents forms the structure (E) exclusively or form (E), (F), and (G) randomly.

Conclusion

Living ring-opening polymerization of 2-alkoxy-1-methylenecyclopropanes in this study is initiated by dinuclear π-al-

lylpalladium complexes. The polymerization has several advantages: facile preparation of the initiator, smooth polymer growth even under air, and living polymerization from each Pd center of the initiator to yield the polymer with desired molecular weights. The living polymer has a π-allyl−Pd bond at the growing polymer end, which is stable at ambient temperature but readily reacts with nucleophilic reagent to afford the end-functionalized polymers. Coupling of the two π-allyl groups of the growing polymer takes place in the presence of a N-ligand under photoirradiation. Polymerization of the functionalized monomers and their copolymerization will be presented in the next paper together with the polymer properties.

Experimental Part

Materials and Measurements. THF and anhydrous solvents such as CH_2Cl_2 and toluene were used as received. [(π-PhC_3H_4)PdCl]$_2$ (**VI**) was synthesized as reported.[14] Diimine[15] and bisiminopyridine ligands,[16] Pd complexes,[3,17] and NaBARF[18] were synthesized as reported.

NMR spectra (^{1}H and ^{13}C) were recorded on a Varian Mercury 300 or JEOL JNM-500 spectrometer. The peaks were referenced to $CHCl_3$ in the $CDCl_3$ solvent (δ 7.26) for ^{1}H and $CDCl_3$ (δ 77.0) for ^{13}C. Gel permeation chromatography (GPC) was performed at 40 °C on a TOSOH HLC-8020 high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV−vis detector, using THF as eluent at a flow rate of 0.6 mL min^{-1} with TSKgel SuperHM-L and SuperHM-M columns. The molecular weights were calibrated on the basis of polystyrene standards. M_n (M_w/M_n): 1 110 000 (1.08), 707 000 (1.05), 354 000 (1.02), 189 000 (1.04), 98 900 (1.01), 37 200 (1.01), 17 100 (1.01), 9830 (1.02), 5870 (1.02), 2500 (1.05), 870 (1.10), and 500 (1.14). DSC and TG were recorded on a Seiko DSC6200R and Seiko TG/DTA6200R, respectively.

Synthesis of 2-Butoxy-1-methylenecyclopropane (1a) and 2-*tert*-Butoxy-1-methylenecyclopropane (1b). 2-Butoxy-1-methylenecyclopropane (**1a**) and 2-*tert*-butoxy-1-methylenecyclopropane (**1b**) were synthesized in two steps starting from butyl vinyl ether and *tert*-butyl vinyl ether, respectively, according to the reported procedure for 2-aryl-1-methylenecyclopropanes.[19]

2-Butoxy-1-methylenecyclopropane (**1a**) (yield = 30%). ^{1}H NMR ($CDCl_3$): δ 5.71, 5.50 (2H, s, $=CH_2$), 3.69 (1H, m, OCH), 3.54 (2H, t, OCH_2), 1.62 (2H, m, CH_2), 1.26 (2H, m, CH_2), and 0.94 (3H, t, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 132.9, 106.6, 70.7, 52.5, 31.6, 19.3, 13.8, and 12.3.

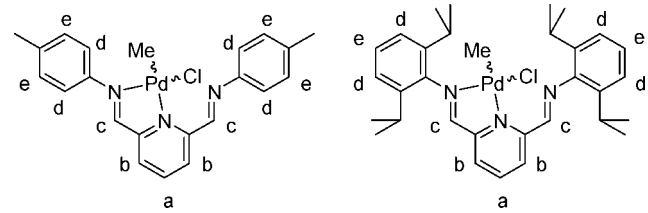
2-*tert*-Butoxy-1-methylenecyclopropane (**1b**) (yield = 98%). ^{1}H NMR ($CDCl_3$): δ 5.64, 5.48 (2H, s, $=CH_2$), 3.64 (1H, m, OCH), 1.26 (9H, s, $C(CH_3)_3$), and 0.9−1.2 (2H, m, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 133.8, 106.7, 75.1, 46.2, 28.2, and 12.9.

Synthesis of 2-Methoxy-1-methylenecyclopropane (1c). 2-Methoxy-1-methylenecyclopropane (**1c**) was synthesized by the reaction of 1-bromo-2-chloromethylcyclopropane and methanol according to the reported procedure (22%).[20] ^{1}H NMR ($CDCl_3$): δ 5.72, 5.50 (2H, s, $=CH_2$), 3.68 (1H, m, OCH), 3.42 (3H, s, CH_3), and 1.39−1.23 (2H, m, CH_2).

Synthesis of Pd Complex with Bisiminopyridine Ligands (III and IV). To a 25 mL Schlenk flask containing 2,6-diformylpyridinebis(4-methylanil) (0.25 mmol, 0.0734 g) and PdCl(Me)(cod) (0.25 mmol, 0.0663 g) under Ar was added CH_2Cl_2 (1 mL) by a syringe, and the mixture was stirred at room temperature. The initial clear yellow reaction solution became a suspension, which was stirred overnight. The precipitate was filtered and washed with ether to give **IV** (0.0744 g, 0.16 mmol, 63% yield). **III** was synthesized similarly.

^{1}H NMR data ($CDCl_3$) of **III**: δ 9.93 (1H, s, C_c), 8.86 (1H, dd, C_b), 8.40 (1H, s, C_c), 8.16 (1H, t, C_a), 7.81 (1H, dd, C_b), 7.31−7.10 (6H, m, C_d and C_e), 3.28 (2H, m, C *H*Me$_2$), 3.01 (2H, m, C *H*Me$_2$), 1.30 (3H, d, CH_3), 1.21 (6H, d, CH_3), 1.13 (3H, d, CH_3), and 0.85 (3H, s, $PdCH_3$).

^{1}H NMR data ($CDCl_3$) of **IV**: δ 10.28 (1H, s, C_c), 8.75 (1H, d, C_b), 8.48 (1H, s, C_c), 8.06 (1H, t, C_a), 7.77 (1H, d, C_b), 7.62 (2H, d, C_d or C_e), 7.26 (4H, m, C_d or C_e), 7.09 (2H, d, C_d or C_e), 2.40 (6H, s, CH_3), and 1.02 (3H, s, $PdCH_3$).



Polymerization of 2-Butoxy-1-methylenecyclopropane (1a) by [(π-PhC_3H_4)PdCl]$_2$ (VI). Typically, to a 25 mL Schlenk flask containing a THF solution (1 mL) of **VI** complex (0.0125 mmol, 3.2 mg) under Ar was added 2-butoxy-1-methylenecyclopropane (**1a**) (0.875 mmol, 0.112 g) by a syringe, and the mixture was stirred at room temperature for 18 h. The portion of the reaction mixture was taken out by a syringe. Monomer conversion and molecular weight of the product were determined by NMR and GPC measurements, respectively, of the aliquot. The reaction mixture was quenched by adding 1 M NaOH in MeOH (ca. 1 mL) and stirred overnight. After solvents were removed by evaporation, the residue was chromatographed on silica gel (hexane/ethyl acetate) to afford a polymer as oil. Poly(**1b**) was prepared by using 2-*tert*-butyl-1-methylenecyclopropane (**1b**) as the monomer and isolated by pouring the reaction mixture to a large amount of MeOH.

NMR data. Poly(**1a**): ^{1}H NMR ($CDCl_3$): δ 5.0 (2H, m, $=CH_2$), 3.8 (1H, m, OCH), 3.4 (1H, m, OCH_2), 3.2 (1H, m, OCH_2), 2.2 (2H, m, CH_2C), 1.5 (2H, m, CH_2), 1.3 (2H, br, CH_2), and 0.9 (3H, br, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.7 (*C*=), 112.9 (=CH_2), 82.8 (OCH), 68.5 (OCH_2), 36.2 (CH_2C), 32.5 (CH_2), 19.8 (CH_2), and 14.5 (CH_3). Poly(**1b**): ^{1}H NMR ($CDCl_3$): δ 4.9 (2H, m, $=CH_2$), 4.2 (1H, m, OCH), 2.3 (2H, m, CH_2), and 1.1 (9H, s, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.4 (C=), 112.0 (=CH_2), 75.7 (OCH), 73.8 (OCH), 37.4 (CH_2C), and 28.8 (CH_3). Poly(**1c**): ^{1}H NMR ($CDCl_3$): δ 5.1 (2H, m, $=CH_2$), 3.8 (1H, m, OCH), 3.2 (3H, br, CH_3), and 2.2 (2H, br, CH_2).

Kinetic Study of the Polymerization of 2-Butoxy-1-methylenecyclopropane (1a) by [(π-PhC_3H_4)PdCl]$_2$ (VI). Typically, to a 25 mL Schlenk flask containing a THF-d_8 solution (0.5 mL) of **VI** (0.0125 mmol, 3.2 mg) was added 2-butoxy-1-methylenecyclopropane (**1a**) (0.875 mmol, 0.112 g) by a syringe under Ar at −78 °C. The reaction mixture was transferred to an NMR tube, cooled at −78 °C, and subjected to NMR measurement at predetermined temperature periodically to estimate monomer conversion. For the kinetic study of the polymerization in CH_2Cl_2 and toluene, the polymerization was conducted in a Schlenk flask, and portions of the reaction mixture were taken out by a syringe and were subjected to NMR measurement. The results are shown in the Supporting Information (Figure S1).

End-Functionalization of Poly(1a). Typically, to a 25 mL Schlenk flask containing a THF solution (1 mL) of [(π-PhC_3H_4)PdCl]$_2$ complex (0.0125 mmol Pd, 3.2 mg) under Ar was added 2-butoxy-1-methylenecyclopropane (**1a**) (0.875 mmol, 0.112 g) by a syringe, and the mixture was stirred at room temperature for 18 h. The reaction mixture was quenched by adding 1 M NaOH in MeOH (ca. 1 mL) and stirred overnight. After solvents were removed by evaporation, the residue was chromatographed on silica gel (hexane/ethyl acetate) to afford a polymer having C(=CH_2)−CH(OBu)(OMe) terminal group. Similar quenching with 1 M NaOH(aq), AgOAc (excess amount), and $NaCMe(COOEt)_2$ (1 M THF solution)/PPh_3 afforded the polymer with C(=CH_2)−CHO, C(=CH_2)−CH(OBu)(OAc), and C(=CH_2)−CH(OBu){$CMe(COOEt)_2$} groups, respectively.

Polymer with C(=CH_2)−CH(OBu)(OMe) terminal group: ^{1}H NMR ($CDCl_3$): δ 4.75 (s, C*H*(OBu)(OMe)), 5.25, 5.12 (s, $=CH_2$), and 3.30, 3.27 (s, OCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.8 (C=), 114.9 (=CH_2), 104.1 (*C*H(OBu)(OMe)), 53.6, 52.9 (OCH_3), and 53.6, 52.9 (OCH_3).

Polymer with C(=CH_2)−CHO terminal group: ^{1}H NMR ($CDCl_3$): δ 9.51 (s, CHO) and 6.34, 6.04 (s, $=CH_2$). ^{13}C{^{1}H}

NMR ($CDCl_3$): $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 194.2 (CHO) and 136.0 ($=CH_2$).

Polymer with $C(=CH_2)-CH(OBu)(OAc)$ terminal group: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.5 (C=O), 98.4 (*C*H(OBu)(OAc)), and 20.9 (CH_3).

Polymer with $C(=CH_2)-CH(OBu)\{CMe(COOEt)_2\}$ terminal group: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.5 (C=O), 61.1, 61.2 ($COOCH_2$), 59.1 (*C*Me(COOEt)$_2$), and 14.5 ($COOCH_2CH_3$).

Copolymerization of 2 with Styrene. Typically, to a 25 mL Schlenk flask containing macromonomer **2** with α,β-unsaturated aldehyde terminal group (0.14 g, M_n = 2200, M_w/M_n = 1.10), styrene (2.2 mmol, 0.25 mL), AIBN (3.2 mg), and benzene (1.1 mL) was heated at 80 °C for 12 h under Ar. The reaction mixture was poured into MeOH to afford poly(**2**-*co*-styrene). The molar ratio of the repeating unit from **1a** and styrene was estimated by the relative intensity ratio of the signal due to $=CH_2$ group and phenyl group to be 1:2.2. M_n = 9800, M_w/M_n = 1.74.

Poly(**1a**-*g*-styrene): ^1H NMR ($CDCl_3$): δ 7.5−6.3 (Ph), 5.0 ($=CH_2$), 3.8 (OCH), 3.4 (OCH_2), 3.2 (OCH_2), 2.2 (CH_2C), 2.0−1.1 (CH_2 and CH), and 0.9 (CH_3).

Coupling of π-Allyl Ligands of the Living Poly(1a). Typically, to a 25 mL Schlenk flask containing a THF solution (1 mL) of $[(\pi\text{-}PhC_3H_4)PdCl]_2$ complex (0.0125 mmol Pd, 3.2 mg) under Ar was added 2-butoxy-1-methylenecyclopropane (**1a**) (0.32 mmol, 0.041 g) by a syringe, and the mixture was stirred at room temperature. A portion of the reaction mixture was taken out by a syringe and was subjected to NMR to confirm the completion of the polymerization. THF (15.6 mL) and TMEDA (0.0188 mmol, 2.8 μL) were added, and the reaction mixture was subjected to a freeze−pump−thaw cycle and was irradiated by a 200 W mercury xenon lamp in Ar and thermostated at 10 °C for 3 h. The resulting reaction mixture was added PPh_3 and subjected to GPC measurement.

Acknowledgment. The present work was partly supported by The Kao Foundation For Arts and Sciences, a Grant-in-Aid No. 18750094 for Scientific Research on Priority Area, the Ministry of Education, Science, Sports and Culture, Japan, and by a grant program in 2008 (No. 05A25502) from the New Energy and Industrial Technology Development Organization (NEDO) under the Ministry of International Trade and Industry, Japan.

Supporting Information Available: Kinetic study and GPC profiles of the polymerization of **1a** by **VI**. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA800941F