

Palladium-Complex-Promoted Living Polymerization of 2-Alkoxy-1-methylenecyclopropanes. Synthesis of Linear and Cyclic Polymers and Block Copolymers Having Alkoxy and Vinylidene Groups

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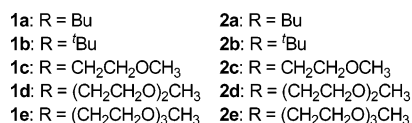
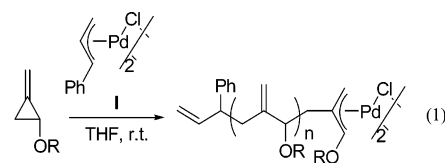
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Summary: Living ring-opening polymerization of 2-alkoxy-1-methylenecyclopropanes has been achieved by π -allyl Pd complexes to afford polymers having alkoxy and vinylidene groups in the repeating units. A cyclic dinuclear Pd complex has been synthesized and utilized for the synthesis of cyclic polymers and block copolymers with narrow molecular weight distribution.

Cyclic polymers are expected to show unique morphology and physical properties, such as smaller hydrodynamic volume and high glass transition temperature, in the solid state and in solution due to topological restraint of the molecular chain and intermolecular interaction being weaker than that in the corresponding linear polymers.¹ Intramolecular coupling of the terminals of linear telechelic polymers, formed by living radical, anionic, and cationic polymerization of styrene, acrylates, and THF, was reported to produce the cyclic polymers under high-dilution conditions.² This method was employed also for the preparation of cyclic block copolymers of styrene and diene as well as of acrylic esters and amides.³ Cyclodepolymerization of bisphenol A polysulfone under high-dilution conditions also forms the cyclic polymer.⁴ Another approach to the cyclic polymers is ring enlargement of cyclic initiators via successive insertion of monomers into a bond in the cyclic molecule, although examples of living ring enlargement polymerization are limited.^{5,6} Recently, methylenecyclopropanes have been reported to polymerize in the presence of transition-metal complexes to afford unique polymers having an olefin func-

tionality or three-membered ring in the repeating units.^{7,8} In this paper, we report ring-opening living polymerization of 2-alkoxy-1-methylenecyclopropanes promoted by dinuclear Pd complexes and its application for synthesis of new linear and cyclic polymers and block copolymers.

$[(\pi\text{-PhC}_3\text{H}_4)\text{PdCl}]_2$ (**I**) initiates polymerization of 2-butoxy-1-methylenecyclopropane (**1a**) at room temperature to produce a polymer with vinylidene groups (**2a**), as shown in eq 1. The



structure of the repeating units and their head-to-tail linkage are well regulated, similar to the polymers of 2-aryl-1-methylenecyclopropanes.⁷ The GPC measurement of **2a** after the polymerization was completed ($[\mathbf{1a}]/[\text{Pd}] = 50$) showed a unimodal elution pattern with a molecular weight ($M_n = 9000$, $M_w/M_n = 1.08$) that is significantly higher than the value calculated from the monomer-to-Pd ratio ($M_n(\text{calcd}) = 6300$).⁹ The polymers after treatment with NaOH (aq), AgOAc, and

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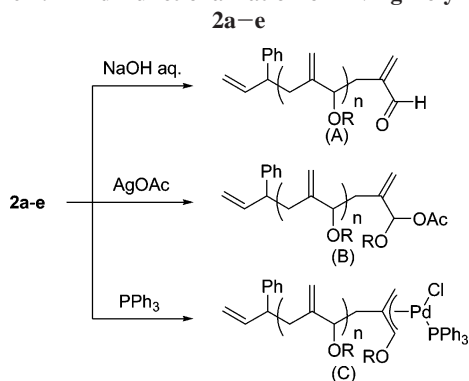
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(9) The molecular weight of **2a** (after treatment with PPh₃) ($M_n = 5700$) estimated by GPC calibrated with a polystyrene standard is almost similar to that estimated by NMR ($M_n = 6300$) on the basis of the relative intensity ratio of the CH₂= group in the main chain and the terminal Ph group.

Scheme 1. End Functionalization of Living Polymers of



PPh_3 have molecular weights close to the calculated value, $M_n = 5500$ ($M_w/M_n = 1.06$), $M_n = 5400$ ($M_w/M_n = 1.09$) and $M_n = 5900$ ($M_w/M_n = 1.05$). These results are explained according to the reactions shown in Scheme 1. NaOH , AgOAc , and PPh_3 convert the living polymer end to an aldehyde group (A in Scheme 1), hemiacetal ester group (B), and PPh_3 -coordinated Pd complex (C), respectively. The higher molecular weight of the original polymer in GPC as compared to those of A–C is ascribed to the structure with the Pd_2Cl_2 core bonded to two polymer chains.

Polymerization in the presence of pyridine ($[\text{pyridine}]/[\text{Pd}] = 1.5$) does not affect the molecular weight of the polymer, indicating that dimeric structure of the growing end is maintained in the presence of pyridine. An increase in the ratio of $[\mathbf{1a}]$ to $[\text{Pd}]$ from 50 to 400 in the polymerization leads to a linear increase of the molecular weight up to $M_n = 43\,000$ ($M_w/M_n = 1.11$) (Figure 1).

The growing polymer end is stable and does not decompose during the polymerization. The stability of the polymer end was confirmed by the polymer growth caused by stepwise addition of the new monomer. Polymerization promoted by **I** with $[\mathbf{1a}]/[\mathbf{I}] = 50$ for 15 h in air by using undistilled commercial THF as the solvent causes complete consumption of the monomer and formation of the polymer with $M_n = 5000$ ($M_w/M_n = 1.05$). Addition of new monomer ($[\mathbf{1a}]/[\mathbf{I}] = 100$) and polymerization for an additional 18 h led to a polymer with $M_n = 15\,000$ ($M_w/M_n = 1.11$). **I** also promotes living ring-opening polymerization of the methylenecyclopropanes having *t*-Bu group (**1b**) and mono- (**1c**), di- (**1d**), and triethylene glycol (**1e**) substituents.

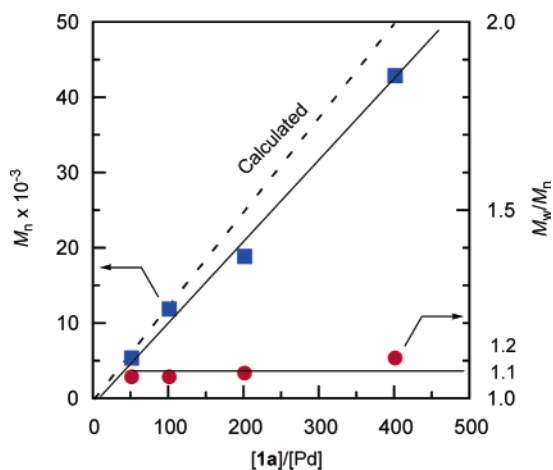
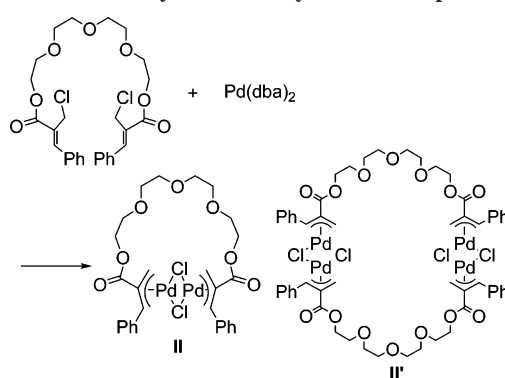


Figure 1. M_n and M_w/M_n values of the polymer of **1a** plotted against the initial monomer-to-Pd molar ratio. Conditions: in THF, room temperature. The dashed line shows the molecular weights calculated from $[\mathbf{1a}]_0/[\text{Pd}]$.

Scheme 2. Synthesis of Cyclic Pd Complexes



Initial polymerization of **1e** ($[\mathbf{1e}]/[\text{Pd}] = 70$) by **I** followed by addition of **1a** ($[\mathbf{1a}]/[\text{Pd}] = 70$) to the living polymer affords a block copolymer having hydrophobic OBU and hydrophilic $\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{Me}$ groups ($M_n = 11\,000$, $M_w/M_n = 1.08$).

This polymerization was applied to synthesis of the cyclic polymer of **1a** by using a cyclic dinuclear (π -allyl)palladium complex as the initiator. Initial attempts to prepare the cyclic initiator **II** by oxidative addition of tetraethylene glycol bis(α -(chloromethyl) cinnamate) with $\text{Pd}(\text{dba})_2$ ($\text{dba} = \text{dibenzylideneacetone}$) resulted in the formation of a mixture of **II** and a small amount of **II'**, having a ring with a double size of **II** (Scheme 2). These compounds were characterized by common NMR spectroscopy as well as CSI-MS (coldspray ionization mass spectroscopy)¹¹ (Figure 2) and DOSY (diffusion-ordered NMR spectroscopy)¹² spectra. Complexes with a molecular weight higher than that of **II'** were not formed. Attempted separation of **II** from **II'** by column chromatography was not successful. The polymerization of **1a** by a mixture of **II** and **II'** ($[\mathbf{1a}]/[\text{Pd}] = 70$) in THF forms the product with a bimodal GPC pattern (Figure 3a). The molecular weight of the higher elution peak top (29 000) is almost double of the lower one (15 000), indicating that the fractions with lower and higher molecular weight are due to the polymers formed by **II** and **II'**, respectively. Addition of excess PPh_3 to the polymer solution changes the bimodal elution pattern to a unimodal one with a molecular weight ($M_n = 16\,000$, $M_w/M_n = 1.05$) which is close to that calculated from the **1a**-to-Pd molar ratio ($M_n(\text{calcd}) = 18\,000$). All of these results suggest that polymerization initiated by **II** and **II'** takes place separately in a living fashion and that

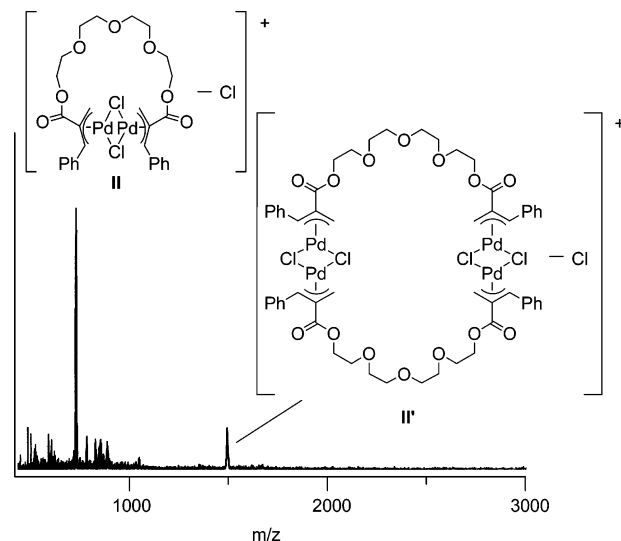


Figure 2. CSI-MS spectrum of the cyclic Pd complexes **II** and **II'**.

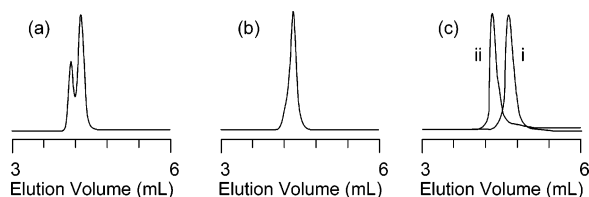


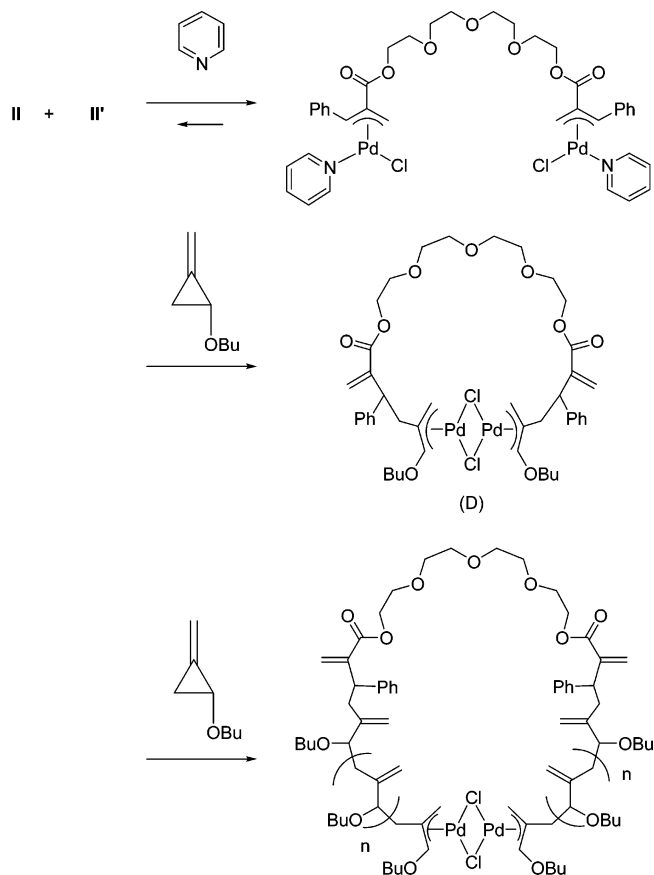
Figure 3. GPC profiles of the polymer obtained by a mixture of **II** and **II'** (a) in the absence and (b) in the presence of pyridine. (c) GPC of block copolymer of **1a** and **1e** in the presence of pyridine (i) after addition of the first monomer ($[1a]/[Pd] = 35$) and (ii) after addition of the second monomer ($[1e]/[Pd] = 35$).

coordination of PPh_3 to Pd converts the cyclic polymers to a linear one having two $Pd(Cl)PPh_3$ fragments.

The polymerization of **1a** by the mixture of **II** and **II'** in the presence of pyridine ($[1a]/[Pd] = 70$, $[pyridine]/[Pd] = 1.5$), however, leads to the formation of a polymer with a unimodal elution pattern (Figure 3b, $M_n = 14\,000$, $M_w/M_n = 1.09$) after complete consumption of the monomer. The molecular weight of the polymer was almost similar after treatment with HCl to remove pyridine from the solution, while addition of PPh_3 to the solution increases the molecular weight of the polymer by GPC to $M_n = 15\,000$ ($M_w/M_n = 1.07$). These results indicate that a cyclic polymer with a unimodal GPC pattern is formed and that the reaction of PPh_3 with a Pd_2Cl_2 core converts it into a linear polymer with two $PdCl(PPh_3)$ ends. Scheme 3 depicts the mechanism for formation of the cyclic initiator and growth of the cyclic living polymer. Coordination of pyridine to palladium converts the mixture of **II** and **II'** into a linear complex with two $PdCl(pyridine)$ ends. Insertion of monomer into the $Pd-\pi$ -allyl bonds produces a cyclic dinuclear Pd complex (**D**), predominantly, which initiates the growth of the cyclic polymer. $[(\pi\text{-allyl})PdCl]_2$ was reported to be in equilibrium with monomeric $(\pi\text{-allyl})PdCl(pyridine)$ in the presence of pyridine, whereas introduction of an electron-donating group at the π -allyl ligand shifts the equilibrium to formation of the dinuclear complex. Figure 3c shows a GPC pattern during block copolymerization of **1a** and **1e** under the same conditions as for Figure 3b. The molecular weight of the polymer after the reaction of the first monomer (**1a**), $M_n = 5300$, $M_w/M_n = 1.07$, increases after the polymerization of the second monomer (**1e**), $M_n = 12\,000$, $M_w/M_n = 1.13$.

The glass transition temperature of the cyclic poly(**1a**) ($T_g = -65.3\text{ }^\circ\text{C}$) and poly(**1e**) ($T_g = -91.7\text{ }^\circ\text{C}$) is lower than that of the corresponding linear polymers, **2a** ($T_g = -55.3\text{ }^\circ\text{C}$) and **2e** ($T_g = -74.3\text{ }^\circ\text{C}$). The cyclic polymers in this study show a small difference in the GPC hydrodynamic volume from the linear polymers composed of the same repeating unit (<10%) and T_g values lower than the linear ones. Although many cyclic polymers show a larger difference of the GPC hydrodynamic volume (20–30%) and higher T_g values as compared to the

Scheme 3. Mechanism of Formation of a Cyclic Polymer with Controlled Molecular Weight



values for the linear polymers,² cyclic poly(MMA) was reported to exhibit a hydrodynamic volume close to that of linear poly(MMA) and a T_g lower than for the linear species.¹³

In summary, we found Pd-promoted living ring-opening polymerization of 2-alkoxy-1-methylenecyclopropanes and succeeded in the synthesis of cyclic polymers and block copolymers that contain vinylidene and alkoxy groups in every repeating unit.

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Supporting Information Available: Text, figures, and schemes giving experimental details, characterization data, and additional reaction details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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