New Ring-Opening Polymerization via a π-Allylpalladium Complex. 2. Novel Proton-Transfer Polymerization of Vinylcyclopropane Derivatives Having Two Electron-Withdrawing Substituents

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ABSTRACT: Vinylcyclopropane derivatives, **1a-d**, which have two electron-withdrawing groups such as ethoxycarbonyl, cyano, and phenylsulfonyl on the cyclopropane rings, were polymerized in the presence of a Pd(0) catalyst. Both the vinyl group and the cyclopropane ring participated in the polymerization with ring opening. The key intermediate of the polymerization is a π-allylpalladium complex which is generated by the oxidative addition of a Pd(0) complex to the monomer. The propagating end is a methyne proton activated by two electron-withdrawing substituents. The polymerization proceeds via novel intermolecular proton transfer through the π-allylpalladium complex.

Introduction

With Pd catalysts, a large number of various synthetic reactions have been developed.[1] In some of these reactions, a π-allylpalladium complex plays the role of a key intermediate. Nucleophilic substitution at an allylic position via a π-allylpalladium complex, which has electrophilic reactivity, constitutes the fundamental reaction (Scheme I). This reaction has brought a new idea for polymerization to us, *i.e.*, when a leaving group X is bound to the original molecule, an intermolecular nucleophilic attach of X may give rise to a ring-opening polymerization. In this context, monomers are designed to be cyclic compounds which have an appropriate functional group at an allylic position. Thus, we have contrived three types of monomers shown as (A)–(C) in Scheme II. They are subjected to the oxidative addition by a Pd(0) complex to generate a π-allylpalladium complex which has two electrophilic sites and one nucleophilic site. Polymerization is initiated by the attack of a nucleophile to the electrophilic site.

Among the various monomers designed, a vinylcyclopropane derivative, **1a**, gave us the first success in the new ring-opening polymerization (Scheme III).[2] The key intermediate was π-allylpalladium complex **2a**, and polymer **3a** was produced via an interesting mechanism (*vide infra*). This paper deals with further investigation including the polymerization of other related vinylcyclopropane derivatives **1b-d**, which have two electron-withdrawing substituents such as ethoxycarbonyl, cyano, and phenylsulfonyl on the cyclopropane rings.

Radical (for **1a-c**) as well as anionic (for **1b** and **1c**) polymerization is known; the former is performed by complicity of the C=C bond with the cyclopropane ring, *i.e.*, 1,5-type ring-opening polymerization,[3] whereas the latter is performed by participation of the cyclopropane ring alone, *i.e.*, 3,5-type ring-opening polymerization.[4] The new ring-opening polymerization described here produced polymer **3** whose structure is the same as the radical polymerization. All the C=C bonds in the main chain are exclusively of the trans configuration.

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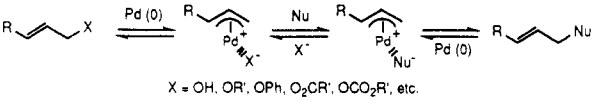
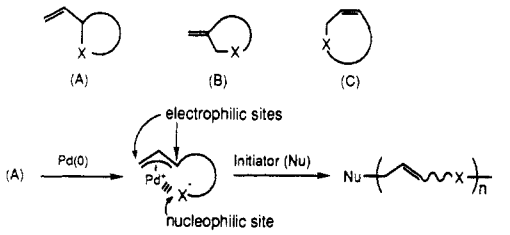
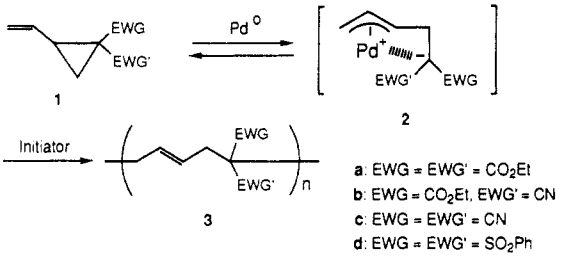
Scheme I



Scheme II. General Structures of Monomers and a General Reaction Scheme



Scheme III



Experimental Section

Materials. The monomers **1a-d** were prepared by literature procedures,[3,5] and **1a-c** were purified twice by careful distillation. $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylidene acetone) was prepared by an ordinary procedure.[6] Bis(diphenylphosphino)ethane (dppe) was purified by recrystallization from MeOH–$CHCl_3$. THF was dried over $LiAlH_4$ and freshly distilled under Ar before use. CH_3CN and DMSO dried over CaH_2 were distilled under Ar and stored over molecular sieves, 3 Å (Merck). Other commercially available reagents were purified by distillation or recrystallization according to ordinary methods.

Measurement. The following columns were employed for GPC analysis: Shodex AC-803 and K-802 (Showa Denko) using $CHCl_3$ as eluent and TSK-Gel G2500HXL and G4000HXL (Tosoh) using DMF–0.4% Et_3N as eluent. Calibration curves for GPC were made on the basis of polystyrene standards. VPO was carried out in $CHCl_3$ at 40 °C.

Polymerization. A typical procedure for the polymerization of **1a** has already been described in a previous paper.[2] Other

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Table I. Pd-Catalyzed Ring-Opening Polymerization of 1a[a]

run	solvent	[I]/[M], %	time, h	yield,[b] %	M_n(GPC)[c]
1	CH_3CN	7.5	18	51	3800
2	CH_3CN	0	24	(conv 54%)	
3	DMSO	6.3	24	69	3800
4	DMSO	0	24	21	9100
5	THF	5.0	25	0[d]	

[a] Catalyst: $Pd_2(dba)_3$·$CHCl_3$–2dppe (0.5 mol %). Initiator: diethyl malonate. Temp: room temperature. [b] Methanol-insoluble polymer. [c] Eluent: $CHCl_3$. [d] Almost all of 1a was consumed, but methanol-insoluble polymer was not obtained.

momomers, **1b-d**, were similarly polymerized. $Pd_2(dba)_3$·$CHCl_3$ (5.2 mg, 5×10^{-3} mmol) and dppe (4.0 mg, 1×10^{-2} mmol) were stirred in 1.6 mL of THF, CH_3CN, or DMSO for a while under Ar. Then, an initiator (0–10 mol % for the monomer) and, subsequently, the monomer (1 mmol) were added. The progress of the reaction was monitored by GLC (**1b** and **1c**) or TLC (**1d**). After complete conversion of the monomer, the product polymer was isolated as follows. In the case of **3b** and **3c**, the reaction mixture was poured into diethyl ether to give a precipitate, which was collected by centrifugation and dried *in vacuo*. In the case of **3d**, $CHCl_3$ was added into the reaction mixture, and the $CHCl_3$-insoluble polymer was separated by filtration and dried *in vacuo*. The filtrate was concentrated and poured into diethyl ether to precipitate the ether-insoluble polymer, which was collected by centrifugation and dried *in vacuo*. A solution of the isolated polymer sometimes contained a small amount of an insoluble material (Pd black), then, which was separated off.

Spectroscopic Data of the Polymers. ^1H NMR spectra of **3a-c** were identical with those of polymers which were previously prepared by the radical polymerization.[3] Spectroscopic data of **3d** are as follows: ^1H NMR (DMSO-d_6, tops of broad peaks) δ 2.86 (4H), 5.75 (2H), 7.54 (4H), 7.68 (2H), 7.97 (4H); ^{13}C NMR (DMSO-d_6) δ 32.3, 88.9, 126.8, 128.7, 130.9, 134.8, 136.1; FT-IR (KBr, cm^{-1}) 3067 (w), 1582 (w), 1447 (m), 1333 (s), 1309 (s), 1143 (s), 1077 (m), 999 (w), 969 (m), 758 (m), 727 (m), 689 (m).

Results and Discussion

The results of the polymerization of each monomer are summarized in Tables I–IV, respectively. All the monomers, **1a–d**, were polymerized at room temperature in the presence of a catalytic amount (0.5 mol % for the monomer) of $Pd_2(dba)_3$·$CHCl_3$–2dppe. Although most of the polymerizations took place even without the initiator of the corresponding active methylene compound, the addition of the initiator, whose effect depended on the monomer and the solvent, generally promoted the polymerization and was convenient in controlling the molecular weight of the product polymer. Since, theoretically, an initiator is necessary for the polymerization, it is assumed that the polymerization without an initiator is initiated by a species generated *in situ*.[7] The reaction solvents of CH_3CN, DMSO, and THF interestingly exerted a remarkable influence on the polymerizations. Not only the polarity but also the coordinating property to Pd affects the reactivity of a π-allylpalladium complex as well as the nucleophilicity of the propagating end.

As mentioned in our previous paper,[2] the polymerization of the diester type monomer **1a** took place in CH_3CN as well as in DMSO, and in particular it was well-controlled in CH_3CN with the addition of the initiator of diethyl malonate (Table I). On the contrary, the reaction in THF did not produce methanol-insoluble polymer but methanol-soluble oligomer along with unidentified materials. Presumably, a side reaction generating an initiator[7] more frequently occurred in THF to produce the oligomer.

The monoester–mononitrile type monomer, **1b**, was polymerized in various solvents, whether with or without an initiator of ethyl cyanoacetate. However, the addition of initiator reduced the molecular weight of the product polymer (Table II). M_n values estimated by GPC were much larger than those by VPO. The discrepancy is due to high polarity of the C≡N group, as often observed in the case of polar polymers including the polymers **3c** and **3d** (*vide infra*).

Table II. Pd-Catalyzed Ring-Opening Polymerization of 1b[a]

run	solvent	[I]/[M], %	time, h	yield,[b] %	M_n VPO	M_n GPC[c]
1	CH_3CN	5.16	28.5	43	3500	5 800
2	CH_3CN	2.19	28.5	55	5100	12 800
3	CH_3CN	0	28.5	52	5500	15 600
4	DMSO	5.08	24.5	58		9 200
5	DMSO	0	24.5	69		15 400
6	THF	5.10	24.5	55		6 000
7	THF	0	24.5	75	6300	20 400

[a] Catalyst: $Pd_2(dba)_3$·$CHCl_3$–2dppe (0.5 mol %). Initiator: ethyl cyanoacetate. Temp: room temperature. [b] Diethyl ether-insoluble polymer. [c] Eluent: $CHCl_3$.

Table III. Pd-Catalyzed Ring-Opening Polymerization of 1c[a]

run	solvent	[I]/[M], %	time, h	yield,[b] %	$\overline{DP}$(^1H NMR[c])
1	CH_3CN	10.6	2	97	12.3
2	CH_3CN	0	4	47[d]	
3	DMSO	4.9	18	no reaction	
4	DMSO	0	18	no reaction	
5	THF	9.02	4	97	12.2
6	THF	0	4	64[d]	

[a] Catalyst: $Pd_2(dba)_3$·$CHCl_3$–2dppe (0.5 mol %). Initiator: malononitrile. Temp: room temperature. [b] Diethyl ether-insoluble polymer. [c] Calculated on the relative intensity of the signals due to the polymer units to that due to the terminal groups. [d] The main products are the cyclic oligomers.

As for the polymerization of the dinitrile type monomer **1c**, no reaction took place in DMSO even at a temperature of 150 °C. It is assumed that DMSO strongly stabilizes and deactivates the π-allylpalladium complex **2c**, which is originally more stable than **2a** and **2b** due to the stronger electron-withdrawing property of a cyano group than an ester one. On the contrary, the reaction of **1c** in CH_3CN as well as in THF produced the polymer **3c**, which precipitated during the polymerization. Even though **3c** produced was oligomeric, it was slightly soluble in DMF and DMSO at room temperature. The ^1H NMR spectra (in DMSO-d_6) of the polymers, which were prepared in the presence of the initiator of malononitrile (10 mol % for **1c**), showed a triplet peak (δ 4.93, J = 6.35 Hz) assignable to the dicyanomethyne proton, which is assumed to be located at the polymer terminals. On the basis of the integral ratio of this peak to peaks due to the polymer unit, the value of the degree of polymerization was calculated, which was found to be in good agreement with the feed ratio of the initiator to the monomer (runs 1 and 5 in Table III). On the other hand, the polymeric material produced without the addition of the initiator showed no peak around δ 4.93 in the ^1H NMR spectrum. GPC analysis (DMF) indicated the main part of this product was a lower molecular weight material than the polymer prepared with the addition of the initiator. In the mass spectrum, peaks due to the cyclic tetramer (m/e 472), trimer (m/e 354), and dimer (m/e 236) were observed. The production of these cyclic oligomers is definitely ascribed to the reaction between π-allylpalladium complexes **2c**.

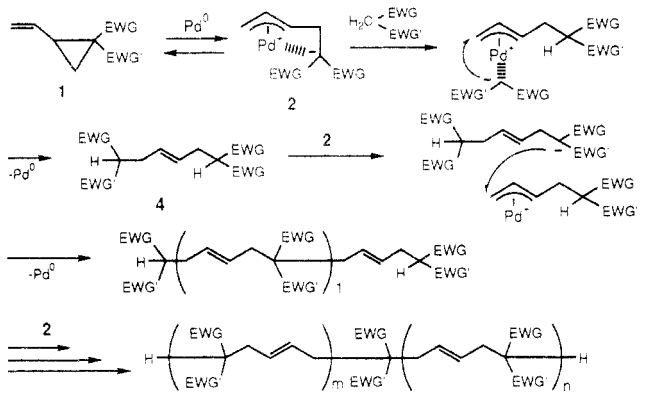
The polymerization of the disulfonyl type monomer **1d** took place in THF at room temperature, but heating was required in CH_3CN and in DMSO (Table IV). The less

Table IV. Pd-Catalyzed Ring-Opening Polymerization of 1d[a]

run	solvent	[I]/[M], %	temp, °C	time, h	yield, % (M_n) $CHCl_3$-insol	yield, % (M_n) Et_2O-insol
1	CH_3CN	5.0	rt	12	0	0
2	CH_3CN	5.0	80	4	14	80 (1850[b])
3	CH_3CN	0	80	4	0	46 (1510[b])
4	DMSO	5.0	rt	12	0	0
5	DMSO	5.0	80	20	0	38
6	THF	5.0	rt	13	81 (17 000[c])	17
7	THF	0	rt	36	75 (20 000[c])	11

[a] Catalyst: $Pd_2(dba)_3{\cdot}CHCl_3$–2dppe (0.5 mol %). Initiator: bis(phenylsulfonyl)methane. [b] VPO. [c] GPC (eluent: DMF–0.4% Et_3N).

Scheme IV



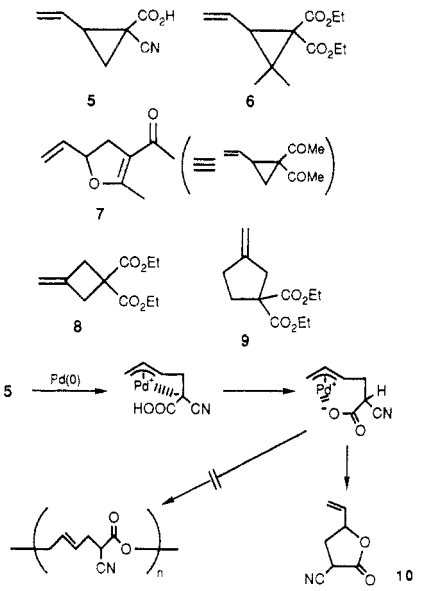
EWG, EWG' = electron-withdrawing groups

polar solvent made the polymerization faster. In any cases, addition of bis(phenylsulfonyl)methane as the initiator strongly promoted the polymerization. The product polymer **3d** was separated into $CHCl_3$-insoluble and -soluble portions by molecular weight; the former was soluble in hot DMF and DMSO.

Pd-catalyzed reactions of **1a** and **1d** are known; 1,5-addition of secondary amines or active methylene compounds and cycloaddition with electron-deficient olefins proceed via the π-allylpalladium intermediates **2a** and **2d**.[5,8,9] Thus, Scheme IV reveals the polymerization mechanism in the presence of the initiator. The key intermediate is the π-allylpalladium complex **2**, which is generated by oxidative addition of Pd(0) to monomer **1**. In the initiation, an active methylene proton of the initiator transfers to the nucleophilic site of **2**, and subsequent reductive elimination of Pd(0) produces the adduct **4**. Since the two methyne protons of **4** are also able to be transferred to **2**, repetition of the same element reaction as the initiation gives rise to production of the polymer. Accordingly, the propagating end is an active methyne proton, whose intermolecular transfer is taken to lead to the polymerization.[10]

We tried the polymerization employing other similar monomers, **5-9** (Scheme V). To our disappointment, the Pd-catalyzed reaction of **5** produced no polymer but lactone **10**, and others, **6-9** were inert under various conditions. However, further investigation employing a different type of monomer is ongoing.[11]

Scheme V



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References and Notes

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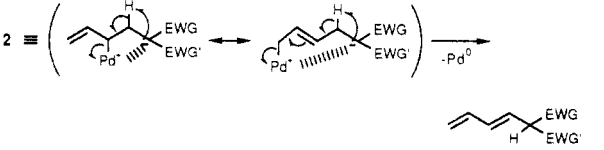
(7) Although there is no evidence, the most reasonable reaction to generate an initiator is the isomerization of the monomer via the π-allylpalladium complex as shown in the following scheme. This reaction involves a β-hydrogen elimination process which often occurs to organometallic compounds. A 1,2-pentadiene derivative generated has an active methyne proton to initiate the polymerization.



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(10) The evidence that the polymer end has an active methyne proton has been mentioned in the previous paper.[2]
(11) The third report of this series, which deals with the very unique polymerization of a cyclic carbamate, has already been published: Suzuki, M.; Ii, A.; Saegusa, T. *Macromolecules* **1992**, *25*, 7071.