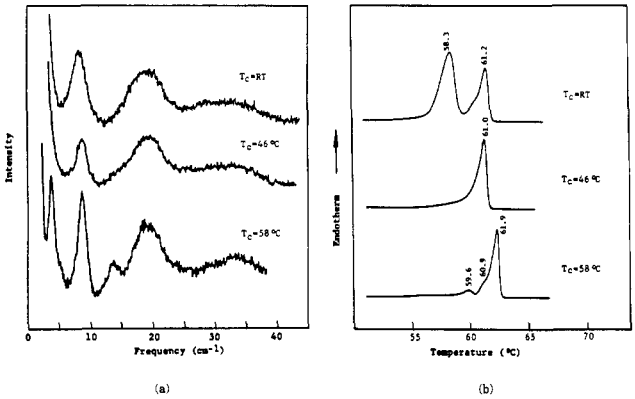

Figure 2. (a) Low-frequency Raman spectra and (b) DSC melting curves of PEO 5000 crystallized at different crystallization temperatures (T_c).

lengths of 274, 133, and 88 Å, respectively.

For the T_c = RT sample, the LAM band, SAXS spacing, and expected stem length (138 Å) clearly indicate the presence of F2(M) lamellae. The T_m = 58.3 °C peak in the DSC is assignable to this species, with the T_m = 61.2 °C peak being associated with F2(B) structures that develop on heating (at a heating rate of 0.5 °C/min, the lower T_m peak has a very small area compared to the higher T_m peak). For the T_c = 46 °C sample, the LAM peak, SAXS spacing, expected lamellar thickness (~2 × 138 Å), and T_m indicate the presence of F2(B) lamellae. (At a heating rate of 0.5 °C/min, this peak remains single and narrows and is located at the position of the higher T_c = RT peak.) For the T_c = 58 °C sample, the LAM peaks clearly show the presence of E (3.9 cm^{-1}), F2 (8.7 cm^{-1}), and F3 (13.5 cm^{-1}) molecules,[16] the SAXS spacing corresponds to essentially fully extended chains, and T_m = 61.9 °C is that associated with extended chain lamellae[16] (at a heating rate of 0.5 °C/min this peak remains single, narrows, and is 0.6 °C higher than T_m for the T_c = 46 °C sample). In view of the strong F2 LAM band together with an almost negligible F2(B) DSC peak, these results strongly suggest the presence of a single major species consisting of lamellae with E and F2(B) (and probably F3(T)) molecules mixed together.

These, and our other,[16] results thus indicate the existence of folded chain structures more complex than the simple IF lamellae proposed for PEO.[1-6] Our experiments do not, of course, distinguish between structures created initially at T_c and those that may form from these with increasing t_c. In fact, the M = 3000 results mentioned above clearly show the effect of t_c at T_c = RT, and comparable changes are seen with t_c for the M = 5000 sample at T_c = RT.[16] For both samples, however, prolonged annealing near the melting point does not eliminate the F2 LAM peak, leading to the possibility that pure E lamellae are not trivial to prepare.

The above conclusions could be confidently derived from the Raman spectra of PEO as a result of our normal mode analyses of the LAM in this helical polymer.[16] We plan to apply these insights to more detailed studies of the crystallization and annealing processes in this polymer.

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Registry No. PEO, 25322-68-3.

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New Ring-Opening Polymerization via a π-Allyl Complex. 1. Polymerization of Diethyl 2-Vinylcyclopropane-1,1-dicarboxylate Catalyzed by a Palladium(0) Complex

Palladium complexes catalyze a wide variety of useful synthetic reactions.[1] It is attractive and interesting to try to introduce some of these reactions into the field of polymerization chemistry. This communication deals with the new ring-opening polymerization of diethyl 2-vinylcyclopropane-1,1-dicarboxylate (1) in the presence of a Pd(0) complex (Scheme I).[2]

In organic synthesis, 1 is known to react in the presence of Pd(0) catalyst with some nucleophiles such as secondary amines[3] and active methylene compounds[4] as well as with electron-deficient olefins such as methyl acrylate[5] (Scheme II). The key intermediate of these reactions is a π-allyl complex, 2, which has two electrophilic sites and one nucleophilic site. It resembles zwitterionic intermediates having an electrophilic site and a nucleophilic one, which have conveniently been polymerized by a mechanism of the so-called "No Catalyst Copolymerization".[6] A speculation on the basis of the combination of this polymerization chemistry with the above organic synthesis involving π-allyl Pd complex[1,7] has brought about a new type of ring-opening polymerization of the present paper. It has been found that the binary system of a catalytic amount of a Pd(0) complex and an initiator such as diethyl malonate induces the ring-opening polymerization of a monomer, 1 (Scheme I).

The structure of the product polymer, 3, was established by spectroscopic analysis, which is identical with that of the polymer produced by free-radical ring-opening polymerization.[8] A typical procedure for the polymerization was as follows. $Pd_2(dba)_3{\cdot}CHCl_3$ (2.4 mg, 2.3 × 10^{-3} mmol, dba, dibenzylideneacetone) and 1,2-bis(diphenylphosphino)ethane (dppe, 1.8 mg, 4.5 × 10^{-3} mmol) were stirred in dry CH_3CN (0.8 mL) under argon atmosphere at room temperature for a while. The color changed from

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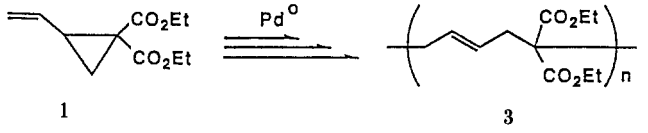
Table I
Ring-Opening Polymerization of 1 Catalyzed by Pd(0) Complex[a]

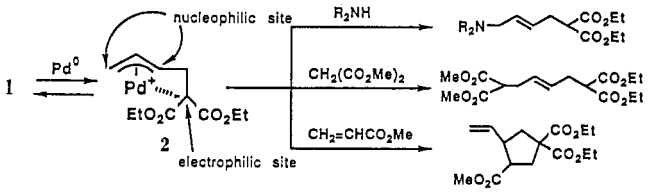
entry	initiator	solvent	[I]/[M]	temp	hours	yield,[b] %	M_n (GPC)
1	none	DMSO	0	room	24	21[c]	
2	$CH_2(CO_2Et)_2$	DMSO	0.063	room	24	69	3800
3	none	CH_3CN	0	room	24	(conv. 54%)	
4	$CH_2(CO_2Et)_2$	CH_3CN	0.075	room	18	51	3800
5	$CH_2(CO_2Et)_2$	CH_3CN	0.023	room	24	(conv. 73%)	
6	$CH_2(CO_2Et)_2$	CH_3CN	0.021	50 °C	11	25	4200
7	$CH_2(CO_2Et)_2$	CH_3CN	0.023[d]	room	24	52	4500
8	n-$BuNH_2$	CH_3CN	0.047	room	27	28	6500
9	aniline	CH_3CN	0.061	room	72	25	8200
10	AcOH	CH_3CN	0.057	room	17	no reaction	
11	$CH_2(COCH_3)_2$	CH_3CN	0.046	room	23	30	4000[e]
12	$CH_2(CN)_2$	CH_3CN	0.054	room	23	0	

[a] Catalyst, $Pd_2(dba)_3$·$CHCl_3$/dppe (Pd/1 = 0.01, P/Pd = 2); [M] = 0.63 mol/L. [b] 1 is consumed completely except for entries 3 and 5; the yield of methanol-insoluble polymer is shown. [c] See note 9. [d] [M] = 1.25 mol/L. [e] M_n = 4400 from VPO; M_n = 4700 from ^1H NMR.

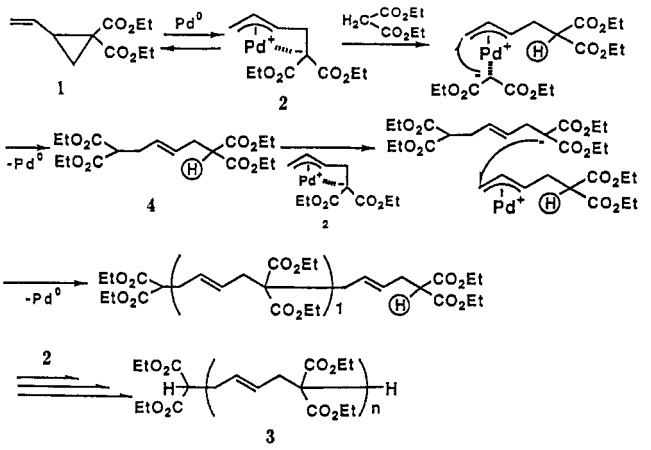
Scheme I



Scheme II



Scheme III



purple to orange. Then, diethyl malonate (6.0 mg, 0.038 mmol) and 1 (105 mg, 0.495 mmol) were added, and the mixture was stirred for 18 h at room temperature. After complete consumption of 1 was confirmed by GLC, iodomethane (9 mg, 0.063 mmol) was added and stirred overnight to react with dppe. The mixture was poured into methanol (16 mL), and the precipitate was collected by centrifugation. The obtained crude polymer was dissolved again in CH_2Cl_2, and the insoluble material (Pd black) was removed by centrifugation. Evaporation of CH_2Cl_2 from the clear solution gave a white, powdery polymer (54 mg, 51% yield).

First, this new polymerization of 1 was tried without any initiators. In DMSO, 1 was completely consumed after 24 h at room temperature in the presence of a catalytic amount (0.5 mol % for 1) of $Pd_2(dba)_3$·$CHCl_3$/dppe. However, the polymer was obtained in a low yield.[9] The addition of diethyl malonate was found to improve the reaction. With a small amount of diethyl malonate (6.9 mol % for 1), the polymer yield was increased to 69% (Table I). As is discussed later, malonate functions as the initiator.

In CH_3CN solvent instead of DMSO, the effect of malonate was more remarkable. In the absence of malonate, the reaction in CH_3CN was very slow and stopped at a halfway point. On the other hand, the presence of diethyl malonate (7.5 mol % for 1) gave rise to the complete consumption of 1, yielding the polymer (entry 4). When a small amount of diethyl malonate was added (2.3 mol %), the reaction stopped halfway again (entry 5). A concentration of the malonate initiator that was too low made the polymerization too slow, and the catalyst activity was lost before the complete conversion of 1. Heating at 50 °C promoted the reaction, however, producing the polymer in 25% yield (entry 6). The better yield of the polymer was achieved by the reaction at the higher concentration (twice) of the reagents, which favored the propagation of the polymerization (entry 7).

Other compounds such as amines and acetylacetone also acted as initiator, although the polymer yield was lower with these initiators. The presence of the initiator moiety in the polymer chain was established by ^1H NMR in the case of acetylacetone as the initiator. A small peak due to methyl protons of the acetyl group was observed. Moreover, on the basis of the integral ratio of this peak to others, the $\bar{M}_n$ of the polymer was calculated as 4700, which was in agreement with the value by VPO ($\bar{M}_n$ = 4400) and GPC ($\bar{M}_n$ = 4000).

The solvent had a decisive influence upon the reaction. In some solvents other than DMSO and CH_3CN, the polymer yield was low or zero even in the presence of diethyl malonate (5 mol %). The yield of the methanol-insoluble polymer was 17% ($\bar{M}_n$(GPC) = 3300) in DMF and 0%[10] in THF and PhCN, although 1 was completely consumed after 24 h at room temperature. In CH_3Ph and $CHCl_3$, the conversion of 1 itself was much slower and stopped at a halfway point.

The nature of the phosphine ligand of the Pd(0) complex is also important for the catalyst activity. Bidentate phosphine ligands such as dppe and dppb (1,4-bis(diphenylphosphino)butane) were effective (polymer yield 60%, $\bar{M}_n$ = 3200 with 5 mol % diethyl malonate initiator in DMSO), but monodentate ligands such as Ph_3P, Cy_3P, and $^nBu_3P$ were ineffective or much less effective. The consumption of 1 was not observed in the cases of Ph_3P and Cy_3P, and the polymer yield was low (23%, $\bar{M}_n$(GPC) = 3300) in the case of $^nBu_3P$.

The polymerization mechanism is shown in Scheme III. The oxidative addition of Pd(0) to the monomer 1 generates π-allyl complex 2, which reacts with the initiator,

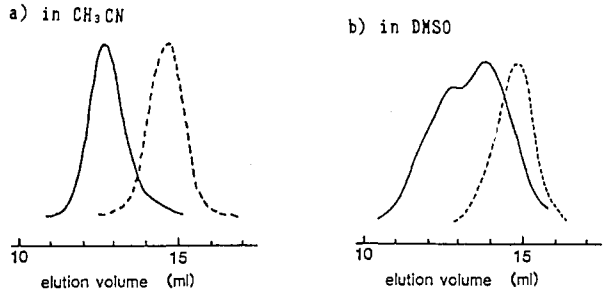


Figure 1. GPC curves of the polymer induced by the polymer initiator (—) and the starting polymer initiator (---).

diethyl malonate, to give adduct **4**. A nucleophilic site of **2** abstracts the methylene proton of diethyl malonate to generate malonate anion, which attacks the electrophilic site of **2** and the reductive elimination of Pd(0) takes place. Adduct **4** also has active protons, so that it continues to react with another π-allyl complex. Thus, the repetition of these elemental reactions gives rise to the production of polymer **3**.

As a support of the above mechanism of polymerization, it is worth mentioning that the isolated polymer **3** functioned as initiator; i.e., the isolated polymer **3** ($\bar{M}_n$ = 3300) (2 mol % for **1** based on the end groups) was stirred with the monomer **1** in CH_3CN, in the presence of a catalyst. After 24 h at room temperature, 88% **1** was consumed (GLC) and the polymer was obtained in 67% yield. A GPC curve of the produced polymer was found to be unimodal with a peak at a higher molecular weight region ($\bar{M}_n$ = 6300) (Figure 1a).

On the other hand, when the same reaction was carried out in DMSO, a GPC curve of the resultant polymer was bimodal (Figure 1b). This finding is explained assuming that the polymerization in DMSO was induced not only by the polymer initiator but also by a compound having an active proton which was probably derived by the isomerization of **1**.[11]

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Registry No. dppe, 1663-45-2; $Pd_2(dba)_3$, 51364-51-3; $CH_2(CO_2Et)_2$, 105-53-3; $BuNH_2$, 109-73-9; $CHCl_3$, 67-66-3; aniline, 62-53-3; diethyl 2-vinylcyclopropane-1,1-dicarboxylate, 7686-78-4.

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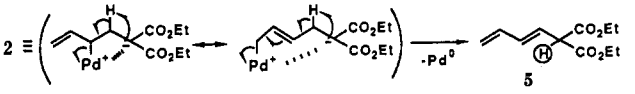
(9) Inadequate purification of **1** causes the polymer yield to increase. A small amount of contaminant, which has an active proton, probably acts as an initiator.
(10) A methanol-soluble oligomer, whose main structure is the same as that of the methanol-insoluble polymer, is produced along with the unidentified side reaction product.
(11) A plausible isomerization of the monomer **1** is β-hydrogen elimination in intermediate **2**, generating diene **5**.



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Linear Poly(quinoxalones)

Linear poly(quinoxalines) represent an important family of high-temperature materials.[1] Poly(quinoxaline)[2] (PQ) and poly(phenylquinoxaline)[3] (PPQ) have been the most widely studied quinoxaline-based polymers and are generally prepared by the reaction of bis(*o*-diamines) with bis(glyoxals) and bis(benzils), respectively. In contrast, poly(quinoxalone) (PQO) has received much less attention relative to PQ and PPQ. The formation of PQOs can be envisaged to occur by step-growth polymerization of a bis(*o*-diamine) with a difunctional α-ketocarboxylic acid derivative. The only documented synthesis of PQO entailed polymerization of *p*-phenylenediglyoxalic acid with 3,3′-diaminobenzidine (DAB) in phenyl ether at the reflux temperature, followed by heating the "prepolymer" under vacuum from 200 to 350 °C.[4] The resulting PQO had good thermal stability and was soluble in sulfuric acid. The polymerization was beset with several problems, including difficulty in preparing *p*-phenylenediglyoxalic acid in high yield and purity and its decarbonylation under the polymerization conditions.

A reinvestigation of PQO was undertaken since certain aspects of the PQO structure may be manifested in distinct properties relative to PPQ and PQ. The reaction of methyl phenylglyoxalate with *o*-phenylenediamine was studied to determine the best conditions for selective quinoxalone formation (Scheme I). We chose to use *N*-methylpyrrolidone (NMP), a basic polar aprotic solvent, as the reaction solvent for the model study since it would likely be a good solvent for the polymerization.[5] When the reaction was carried out in NMP at 150 °C, formation of a multitude of products occurred. However, when the reaction was conducted at 60 °C in the presence of trifluoroacetic acid as a catalyst (5–10 mol %) a single product was formed. The product was isolated as an off-white crystalline solid and was identified as the desired 3-phenylquinoxalone (**1**) (mp = 251–252 °C (lit.[6] 250–252 °C)). Other effective catalysts included *p*-toluenesulfonic acid, acetic acid, concentrated hydrochloric acid, and boron trifluoride etherate. Exclusive formation of **1** also occurred when methanesulfonic acid was substituted for NMP as the reaction solvent. The model study showed that the acid-catalyzed condensation of *o*-diamines and α-keto esters affords quinoxalones in both high yield and selectivity, indicative of a good polymer-forming reaction. By use of acid catalysis, the desired quinoxalone product is formed at temperatures well below the decarbonylation temperature of the α-keto ester monomer, eliminating this potential side reaction.

A single-step preparation of the bis(α-keto ester) monomer was achieved using a Friedel–Crafts acylation of

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