Novel Palladium(0)-Catalyzed Polyaddition of Bifunctional Vinyloxiranes with 1,3-Diketones. Synthesis of New Polymers Bearing an Allyl Alcohol Moiety via π-Allylpalladium Intermediates

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Received November 1, 2001; Revised Manuscript Received January 23, 2002

ABSTRACT: Palladium(0)-catalyzed polyaddition of bifunctional vinyloxiranes [1,4-bis(2-vinylepoxyethyl)-benzene (**6a**) and 1,4-bis(1-methyl-2-vinylepoxyethyl)benzene (**6b**)] with 1,3-diketones [acetylacetone (**2**) and 1,3-indandione (**8**)] as carbon nucleophiles afforded new polymers having an allyl alcohol moiety in the main chain and ketone groups in the side groups. The molecular weights of polymers obtained from **6b** were higher than those of polymers from **6a**. It was suggested that the cause of formation of lower molecular weight polymers from **6a** is the β-hydrogen elimination of the π-allylpalladium intermediate generated by oxidative addition of Pd(0) to **6a**. The Pd(0)-catalyzed polyaddition of **6b** and **2** gave the corresponding polymer **7b** (M_n 9800) when $Pd_2(dba)_3{\cdot}CHCl_3$/dppf (dba, dibenzylideneacetone; dppf, 1,2-bis(diphenylphosphino)ferrocene) was used as a catalyst. By use of $Pd(PPh_3)_4$, the polyaddition of **6b** and **8** afforded the desired polymer **9b** with high molecular weight (M_n 67 600). The stereochemistries of all of the obtained polymers were confirmed as being in the *E*-configuration by the coupling constant of the vinyl proton ($-C(OH)C\mathbf{H}{=}CHCH_2-$); the *J* values were in the range 14.5−15.1. The *Z*-isomers were observed neither in the ^{13}C NMR spectra nor in the ^{1}H NMR spectra.

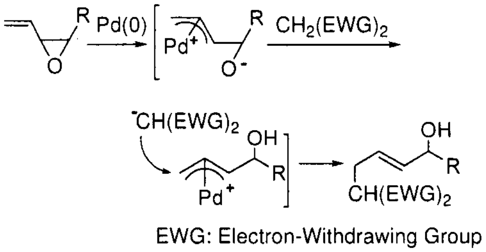
Introduction

Palladium-catalyzed allylic alkylation reaction using soft carbon nucleophiles is a very versatile carbon−carbon bond formation reaction in organic synthesis. A great variety of active methylene compounds can be used.[1] The substrates for this reaction commonly are allylic compounds such as allylic acetates and carbonates. The ring-opening reaction of vinyloxirane derivatives by organometallics has provided a valuable approach to allylic alcohols, which are useful for synthesis of functionalized compounds.[2] It is also known that a Pd(0)-catalyzed reaction of vinyloxiranes with pronucleophiles (NuH) such as carbon nucleophiles and amines gives synthetically useful (*E*)-allylic alcohols via π-allylpalladium intermediates.[3] In this reaction, the nucleophilic attack takes place selectively under neutral conditions at the terminal carbon (Scheme 1).

This Pd(0)-catalyzed reaction prompted us to explore the synthesis of new functional polymers. Although the palladium-catalyzed allylic alkylation reaction is widely used in organic synthesis, there are only a few reports of polymer synthesis via π-allylpalladium intermediates.[4] Polymers bearing hydroxy groups are important in coatings, adhesives, and polymeric reagents.[5] However, it is very difficult to synthesize a variety of polymers having hydroxy and other functional groups. There is a report of the preparation of such polymers reported by Nomura et al.[6]

Recently, we have reported as a preliminary communication that the palladium(0)-catalyzed polyaddition of a bifunctional vinyloxirane, 1,4-bis(2-vinylepoxyethyl)benzene (**6a**), and carbon nucleophiles can lead to the formation of new polymers having an allyl alcohol moiety in the main chain accompanying carbon−oxygen bond cleavage of the oxirane ring.[7] This is the first example of palladium-catalyzed polyaddition of bifunctional vinyloxirane with carbon nucleophiles. In this paper, we wish to report in detail the palladium-catalyzed polyaddition of bifunctional vinyloxiranes [**6a** and 1,4-bis(1-methyl-2-vinylepoxyethyl)benzene (**6b**)] and 1,3-diketones as carbon nucleophiles under various conditions.

Scheme 1



Experimental Section

Materials. Extra-pure grade reagents were used without further purification, unless otherwise stated. Tetrahydrofuran (THF) used as a solvent for polymerization was purified by distillation according to the usual method.

Measurement. IR spectra were recorded on a JASCO FT/IR-3 spectrometer. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker-DMX 500 with $CDCl_3$, acetone-d_6, or DMSO-d_6 as solvent and Me_4Si as an internal standard. Gel permeation chromatograms were taken with a Shimadzu HPLC LC-6A system equipped with two columns (Shim-pack GPC-802 and GPC-804), and tetrahydrofuran (THF) was used as an eluent at 45 °C.

Preparation of 1,4-Bis(2-vinylepoxyethyl)benzene (6a). A mixture of allyl bromide (44.8 g, 0.370 mol) and dimethyl sulfide (28.8 g, 0.463 mol) in water (25 mL) was stirred at room temperature overnight. Unreacted dimethyl sulfide was removed at reduced pressure. Isopropyl alcohol (80 mL) and

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10.1021/ma011900i CCC: $22.00

terephthalaldehyde (20.0 g, 0.149 mol) were added to the reaction mixture at room temperature, and subsequently, sodium hydroxide (16.9 g, 0.423 mol) in water (30 mL) was added dropwise at room temperature with vigorous stirring. After this mixture was stirred for 6 h, the resulting dimethyl sulfide was removed under reduced pressure and the solution was extracted with ether three times. The organic layer was washed with water and saturated sodium chloride successively and dried over anhydrous magnesium sulfate. The ether solution was distilled in vacuo to obtain **6a** (12.0 g, 38%): bp 120−122 °C/0.4 mmHg (lit.[8] 140 °C/0.1 mmHg); IR (neat) 3079, 2989, 1864, 1641, 1517, 1444, 1184, 987, 933, 879, 827 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.33−3.35 (−C=CCH− (trans), m, 1.2H), 3.65−3.68 (−C=CCH− (cis), m, 0.8H), 3.77 (−CHAr− (trans), d, J = 1.3 Hz, 1.2H), 4.23 (−CHAr− (cis), d, J = 4.2 Hz, 0.8H), 5.28−5.74 (CH$_2$=CH-, m, 6H), 7.26−7.33 (ArH, m, 4H).

Preparation of 1,4-Bis(1-methyl-2-vinylepoxyethyl)-benzene (6b). A mixture of allyl bromide (96.8 g, 0.800 mol) and tetrahydrothiophene (72.3 g, 0.800 mol) in water (30 mL) was stirred at room temperature overnight. Isopropyl alcohol (60 mL) and 1,4-diacetylbenzene (25.0 g, 0.154 mol) were added to the reaction mixture at room temperature, and subsequently, sodium hydroxide (32.0 g, 0.800 mol) in water (30 mL) was added dropwise at 0 °C with vigorous stirring. After being stirred overnight at room temperature, the reaction mixture was extracted with ether three times. The organic layer was washed with water and saturated sodium chloride successively and dried over anhydrous magnesium sulfate. The ether solution was evaporated to dryness. The crude product was purified by column chromatography on silica gel (hexanes−ethyl acetate, 4:1) to afford the title vinyloxirane **6b**. Further purification was made by distillation (19.9 g, 55%): bp 112−114 °C/0.2 mmHg; IR (neat) 3079, 2989, 1864, 1641, 1517, 1444, 1184, 987, 933, 879, 827 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 1.63−1.65 (CH$_3$, m, 6H), 3.27−3.62 (−C=CCH−, m, 2H), 5.10−5.93 (CH$_2$=CH−, m, 6H), 7.37 (ArH, s, 4H); ^{13}C NMR (acetone-d_6) δ 17.9, 24.8, 64.3, 67.3, 121.1, 121.2, 125.7, 126.0, 127.3, 127.5, 134.2, 135.0. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.13; H, 7.53.

Pd(0)-Catalyzed Reaction of 2-Phenyl-3-vinyloxirane (1) and Acetylacetone (2). To a solution of **2** (0.100 g, 1.0 mmol) and Pd(PPh$_3$)$_4$ (0.116 g, 0.10 mmol) in THF (5 mL) was added a solution of **1**[8] (0.292 g, 2.0 mmol) in THF (1 mL). After being stirred for 3 h at room temperature under argon, the reaction mixture was evapoporated to dryness. The residue was subjected to column chromatography on silica gel (hexanes−ethyl acetate, 1:1) to give the desired 2:1 adduct **3** (0.370 g, 94%): IR (neat) 3417, 3030, 2921, 1693, 1450, 1357, 1172, 971, 755 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 2.00 (CH$_3$, s, 6H), 2.55−2.64 (−CH$_2$−, m, 4H), 4.51 (OH, s, 2H), 5.05 (CH, s, 2H), 5.44−5.50 (−CH=C**H**CH$_2$−, m, 2H), 5.63 (−CHC**H**=CH−, dd, J = 15.1 and 6.1 Hz, 2H), 7.15−7.27 (ArH, m, 10H); ^{13}C NMR (acetone-d_6) δ 26.9, 33.9, 70.1, 73.9, 123.9, 127.1, 127.8, 128.6, 138.3, 144.5, 206.1; HRMS: calcd for $C_{25}H_{28}O_4$, 392.1988; found, 392.1991.

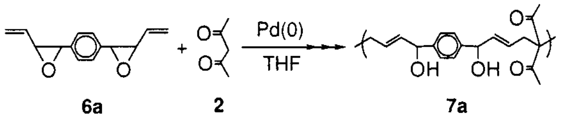
Pd(0)-Catalyzed Polyaddition of Bifunctional Vinyloxiranes 6 with Acetylacetone (2): A Typical Procedure. To a solution of **2** (0.201 g, 2.0 mmol) and Pd(PPh$_3$)$_4$ (0.023 g, 0.02 mmol) in THF (4 mL), a solution of **6a** (0.428 g, 2.0 mmol) in THF (2 mL) was added. The mixture was stirred at room temperature for 24 h under argon and poured into toluene (100 mL) to precipitate polymer (Table 1, run 6). The resulting polymer **7a** was filtered off, washed with toluene, and dried in vacuo (0.582 g, 93%) giving a pale yellow solid: IR (KBr) 3400, 3010, 2919, 2862, 1693, 1421, 1358, 1173, 1086, 972 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 2.01 (CH$_3$, s, 6H), 2.59 (−CH$_2$−, s, 4H), 4.51 (OH, s, 2H), 5.02 (−CH−, s, 2H), 5.42−5.48 (−CH=C**H**CH$_2$−, m, 2H), 5.60 (−CHC**H**=CH−, dd, J = 14.5 and 5.4 Hz, 2H), 7.21 (s, 4H); ^{13}C NMR (acetone-d_6) δ 27.0, 33.88, 70.1, 73.8, 123.8, 126.1, 138.2, 143.1, 206.0.

7b, a pale yellow-brown solid: IR (KBr) 3435, 2976, 2927, 1693, 1360, 1171, 1080, 974 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 1.54 (CH$_3$, s, 6H), 2.09 (CH$_3$C(=O), s, 6H), 2.66 (−CH$_2$−, d, J = 7.1 Hz, 4H), 4.39 (OH, s, 2H), 5.48−5.54 (−CH=C**H**CH$_2$−, m, 2H), 5.83 (−CC**H**=CH−, d, J = 15.1 Hz, 2H), 7.39 (ArH, s, 4H); ^{13}C NMR (acetone-d_6) δ 26.4, 28.8, 33.0, 69.6, 72.7, 120.0, 124.4, 141.9, 145.5, 205.4.

9a, a pale purple solid: IR (KBr) 34276, 3022, 2908, 1703, 1244, 975 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.44−2.48 (−CH$_2$−, m, 4H), 4.73 (OH, s, 2H), 5.21−5.30 (−CH=C**H**CH$_2$− and −CH−, m, 3H), 5.48 (−CHC**H**=CH−, dd, J = 15.0 and 5.7 Hz, 2H), 6.67 (ArH, s, 4H), 7.86−7.94 (ArH, m, 2H), 8.00 (ArH, s, 2H); ^{13}C NMR (DMSO-d_6) δ 37.2, 58.5, 72.5, 122.3, 123.2, 125.9, 136.8, 138.7, 142.2, 142.7, 203.5.

9b, a gray solid: IR (KBr) 3427, 1974, 2925, 1703, 1357, 1242, 976 cm^{-1}; ^{1}H NMR (DMSO -d$_6$) δ 1.14 (CH$_3$, s, 6H), 2.45−2.51 (−CH$_2$−, m, 4H), 4.99 (OH, s, 2H), 5.11−5.14 (−CH=C**H**CH$_2$−, m, 2H), 5.58 (−CC**H**=CH−, d, J = 15.1 Hz, 2H), 6.75 (ArH, s, 4H), 7.92 (ArH, s, 2H), 8.01 (ArH, s, 2H); ^{13}C NMR (DMSO-d_6) δ 29.9, 37.1, 58.8, 72.6, 119.7, 123.1, 124.6, 136.8, 142.3, 142.9, 145.6, 203.6.

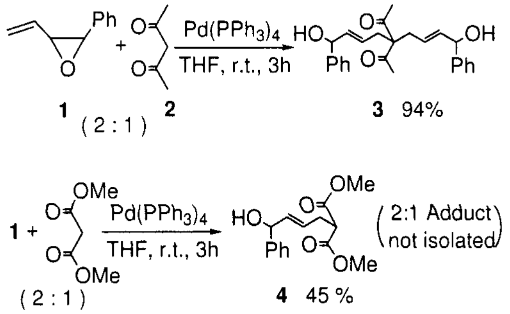
Table 1. Pd(0)-Catalyzed Polyaddition of 6a with Acetylacetone (2)



run	Pd(0)^a	temp (°C)	time (h)	yield (%)^b	M_n^{c}	M_w/M_n^{c}
1	Pd(PPh$_3$)$_4$ (5)	0	6	100	3400	2.73
2	Pd(PPh$_3$)$_4$ (5)	rt^d	6	98	3600	2.04
3	Pd(PPh$_3$)$_4$ (5)	rt	24	100	3600	2.46
4	Pd(PPh$_3$)$_4$ (5)	reflux	6	100	3300	2.17
5	Pd(PPh$_3$)$_4$ (1)	rt	6	0		
6	Pd(PPh$_3$)$_4$ (1)	rt	24	93	4700	2.31
7	Pd$_2$(dba)$_3$/4dppe (5)	rt	24	100	3400	2.49
8	Pd$_2$(dba)$_3$/4dppp (5)	rt	24	100	3700	2.37
9	Pd$_2$(dba)$_3$/4dppb (5)	rt	24	79	3500	3.03
10	Pd$_2$(dba)$_3$/4dppf (5)	rt	24	87	3800	3.43

[a] Numbers in parentheses: [Pd/**6a**] × 100. [b] Insoluble in toluene. [c] Estimated by GPC (based on PSt). [d] Room temperature.

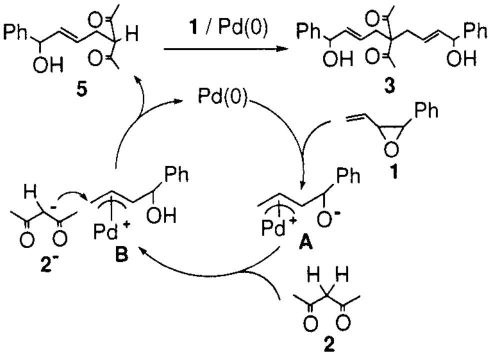
Scheme 2



Results and Discussion

1. Pd(0)-Catalyzed Polyaddition of Vinyloxirane 6a with Acetylacetone (2). It is known that the Pd(0)-catalyzed addition of vinyloxiranes with active methylene compounds affords 1:1 adducts in good yields (Scheme 1).[3] Although the adducts still have one active hydrogen, the formation of 2:1 adducts has not been reported yet. Hence, the Pd(0)-catalyzed addition of 2-phenyl-3-vinyloxirane (**1**) with acetylacetone (**2**) (pK_a 9)[9] was examined as a model reaction. The Pd(0)-catalyzed addition using 2 equiv of **1** to **2** was carried out at room temperature for 3 h in the presence of Pd(PPh$_3$)$_4$ (5 mol % for **1**). The desired 2:1 adduct (**3**) was isolated in 94% yield by flash column chromatography (Scheme 2). However, when dimethyl malonate (pK_a 13)[9] was employed as a carbon nucleophile under the same conditions, the corresponding 2:1 product was

Scheme 3



not isolated (Scheme 2). In this case, 1:1 adduct (**4**) was obtained in 45% yield. These results suggest that active methylene compounds with lower pK_a values are required to obtain 2:1 adducts in high yields. A plausible reaction mechanism of the formation of **3** is shown in Scheme 3. The oxidative addition of Pd(0) to vinyloxirane **1** affords π-allylpalladium intermediate **A**, which abstracts the methylene proton of **2** to generate carbanion **2**$^-$. Nucleophilic attack of **2**$^-$ on π-allylpalladium intermediate **B** gives the corresponding 1:1 adduct (**5**), which reacts with **1** to yield 2:1 adduct **3**. Although the pK_a value of **5** is higher than that of **2**, **5** seems to have a sufficient lower pK_a value for proton abstraction by intermediate **A**. In the case of reaction of **1** and dimethyl malonate, however, the expected 2:1 adduct was not obtained by reaction of 1:1 adduct **4** with **1**. Adduct **4** has a higher pK_a value than that of dimethyl malonate. It can therefore be presumed that π-allylpalladium intermediate **A** cannot abstract the active hydrogen of adduct **4** to produce the corresponding 2:1 adduct. Thus, acetylacetone as a carbon nucleophile is a good candidate for the polyaddition of bifunctional vinyloxirane, 1,4-bis(2-vinylepoxyethyl)benzene (**6a**).

Bifunctional vinyloxirane **6a** was synthesized by the phase-transfer reaction of an allyldimethylsulfonium salt with terephthalaldehyde according to the method reported in our previous paper.[8] The Pd(0)-catalyzed polyaddition of **6a** with **2** was carried out in THF under various conditions. The formed polymers were isolated by pouring the reaction mixtures into toluene. The results are summarized in Table 1. In the polyaddition using 5 mol % of $Pd(PPh_3)_4$ relative to **6a**, the desired polymers (**7a**) were obtained quantitatively (runs 1–4). The reaction temperature and the time did not affect the yield and average molecular weight (M_n) of **7a**. These results indicate that the polyaddition of **6a** and **2** is fast under these conditions. The decrease of amount of $Pd(PPh_3)_4$ required longer reaction time. The polyaddition at room temperature for 6 h did not afford **7a** when 1 mol % of $Pd(PPh_3)_4$ was used (run 5), although prolonged polymerization time (24 h) did (93%, M_n 4700) (run 6).

Next, the effect of the ligands, 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)propane (dppp), 1,2-bis(diphenylphosphino)butane (dppb), and 1,2-bis(diphenylphosphino)ferrocene (dppf) on the polyaddition was examined. The polyaddition of **6a** and **2** was carried out in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone; 2.5 mol % for **6a**). All of the ligands produced polymers with molecular weights in the range 3400–3800 (runs 7–10), which were very similar to the results using $Pd(PPh_3)_4$. The polyaddition using dppb produced polymer **7a** with somewhat lower yield than those of the polymers obtained with dppe, dppp, and dppf. These results indicate that the polyaddition of **6a** with **2** did not depend on the kind of the ligands employed. The polymers were soluble in acetone, THF, and DMSO. The structure of the polymers was confirmed by comparison with IR and NMR spectra of model compound **3**. All of the proton signals of **7a** could be assigned and were in good agreement with those of **3**. The signals due to methylene and vinyl protons were observed around 2.59, 5.42–5.48 (–CH=C**H**CH$_2$–), and 5.60 (–C**H**=CHCH$_2$–) ppm (Figure 1a). The observation of these protons reveals that carbon–oxygen bond cleavage of the oxirane ring occurred. Similarly, all of the carbon signals of **7a** could also be assigned and agreed well with those of **3**.[7] The stereochemistries of **3** and **7a** were confirmed as *E*-configuration by the coupling constant of the vinyl proton **d** of **7a**; the *J* values of **3** and **7a** were 15.1 and 14.5 Hz, respectively. The *Z*-isomers were observed neither in the ^{13}C NMR spectra nor in the ^{1}H NMR spectra of **3** and **7a**. These results demonstrate that the selectivity is exclusive as reported by Tsuji and Trost.[3] The IR spectra of both **3** and **7a** show the characteristic absorptions based on the hydroxy and carbonyl groups around 3400 and 1690 cm^{-1}, respectively. From the NMR and IR spectral data, we confirmed that the Pd(0)-catalyzed polyaddition of **6a** with **2** produced polymers having an allyl alcohol moiety in the main chain and carbonyl groups in the side groups.

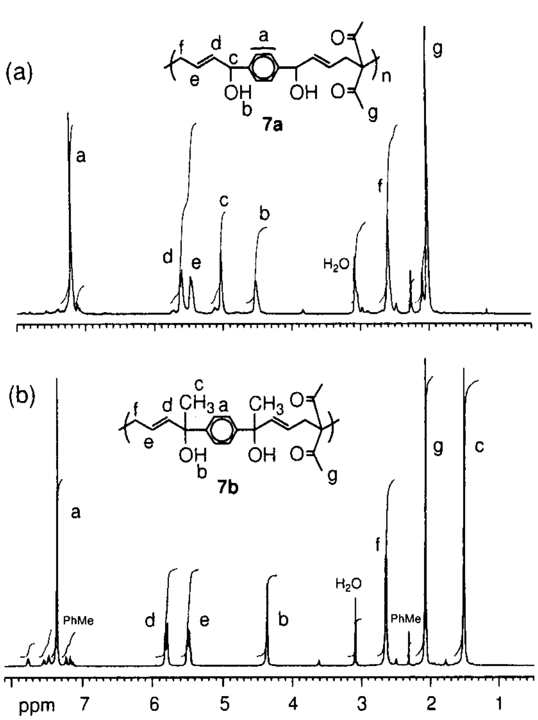
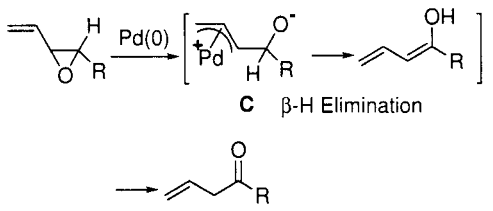


Figure 1. ^{1}H NMR spectra of **7a** and **7b** (acetone-d_6, 500 MHz).

In the polyaddition of **6a** and **2**, the molecular weights of the obtained polymers were not high. The main reason seems to be the occurrence of β-hydrogen elimination as a termination. It is known that palladium-catalyzed isomerization of vinyloxiranes in the absence of nucleophiles gives β,γ-unsaturated ketones via β-hydrogen elimination of intermediate **C** (Scheme 4).[10] By the oxidative addition of Pd(0) to vinyloxirane **1**, **A** is generated, which functions as a base and abstracts a proton of **2** in the presence of a pronucleophile

Scheme 4



Scheme 5

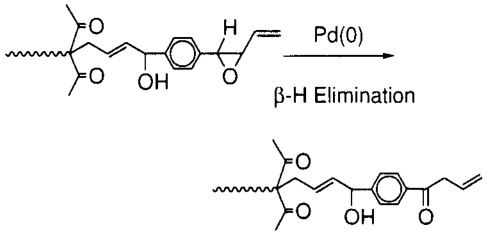
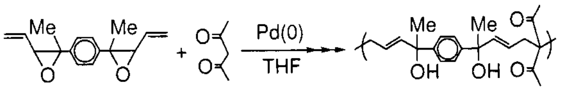


Table 2. Pd(0)-Catalyzed Polyaddition of 6b with Acetylacetone (2)



6b **2** **7b**

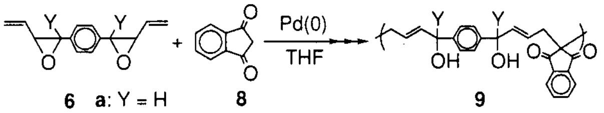
run	Pd(0)[a]	temp (°C)	time (h)	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	$Pd(PPh_3)_4$	0	6	76	3100	1.63
2	$Pd(PPh_3)_4$	rt[d]	6	100	4400	3.09
3	$Pd(PPh_3)_4$	rt	24	100	6000	3.48
4	$Pd(PPh_3)_4$	reflux	6	82	6300	2.83
5	$Pd_2(dba)_3$/4dppe	rt	24	92	9400	6.05
6	$Pd_2(dba)_3$/4dppp	rt	24	92	7900	5.69
7	$Pd_2(dba)_3$/4dppb	rt	24	75	10 000	6.55
8	$Pd_2(dba)_3$/4dppf	rt	24	87	9800	4.47

[a] Pd/**6b** = 0.05. [b] Insoluble in toluene. [c] Estimated by GPC (based on PSt). [d] Room temperature.

(Scheme 3). Intermediate **A** has a β-hydrogen atom at the benzylic position. The reaction of **1** using $Pd(PPh_3)_4$ (5 mol %) was also carried out at room temperature for 16 h in the absence of **2** in THF. Vinyloxirane **1** completely disappeared and the formation of a β,γ-unsaturated ketone was confirmed by the ^{1}H NMR spectrum of the reaction mixture; the characteristic signals of methylene protons of the ketone were observed (3.24 ppm, doublet, $J = 7.5$ Hz). As the polyaddition of **6a** and **2** proceeds, the amount of the propagating end groups having active hydrogen decreases. Therefore, the β-hydrogen elimination of the end groups bearing vinyloxirane moieties seems to take place at the final stage as shown in Scheme 5. The clear signals of such an unsaturated ketone group could not be detected in the ^{1}H and ^{13}C NMR spectra of **7a**.

2. Pd(0)-Catalyzed Polyaddition of Vinyloxirane 6b with 2. Second, the polyaddition of 1,4-bis(1-methyl-2-vinylepoxyethyl)benzene (**6b**) and **2** was examined. The π-allylpalladium intermediate generated by oxidative addition of Pd(0) to **6b** does not possess β-hydrogen. Consequently, the molecular weights of the polymers obtained from **6b** and **2** are expected to be higher than those of polymers **7a**. The polymerization of **6b** and **2** was conducted in THF under various conditions. Table 2 shows the results. The polyaddition using $Pd(PPh_3)_4$ (5 mol % for **6b**) afforded the expected polymers (**7b**) in good to excellent yields (runs 1−4). The reaction temperature and the time affected the average molecular weight (M_n) of **7b**, contrary to the polyaddition with **7a**. The M_n values of the obtained polymers increased from 3100 to 6300 with the temperature elevating from 0 °C to reflux (runs 1, 2, and 4). Although the M_n of **7b** obtained by polymerization for 6 h was 4400, prolonged reaction time (24 h) gave **7b** with higher molecular weight (M_n 6000) (runs 2 and 3). The molecular weights of the obtained polymers (runs 3 and 4) were higher than those of polymers **7a** from **6a** under the same conditions (runs 3 and 4 in Table 1).

Table 3. Pd(0)-Catalyzed Polyaddition of 6 with 1,3-Indandione[a]



6 **a**: Y = H
b: Y = Me
8 **9**

run	oxirane	Pd(0)	yield (%)[b]	M_n[c]	M_w/M_n[c]
1	**6a**	$Pd(PPh_3)_4$	87	9200	1.96
2	**6a**	$Pd_2(dba)_3$/4dppe	100	7500	2.28
3	**6b**	$Pd(PPh_3)_4$	80	67 600	3.17
4	**6b**	$Pd_2(dba)_3$/4dppe	95	25 000	4.07

[a] Conditions: Pd/**6** = 0.05, room temperature, 24 h. [b] Insoluble in toluene. [c] Estimated by GPC (based on PSt).

The polyaddition of **6b** and **2** was also carried out at room temperature for 24 h in the presence of $Pd_2(dba)_3\cdot CHCl_3$ (2.5 mol % for **6b**). Bidentate phosphine ligands (dppe, dppp, dppb, and dppf) were employed (runs 5−8). All of these ligands gave polymers with high M_n values ranging from 7900 to 10000, compared with the M_n values of polymers **7b** obtained by polymerization using $Pd(PPh_3)_4$. These results indicate that the bidentate phosphine ligands employed are more effective than PPh_3 in the polyaddition of **6b** and **2**.

Polymers **7b** were soluble in methanol, acetone, THF, and DMSO. The structure of the polymers was confirmed by IR and NMR spectra. The ^{1}H NMR spectrum of **7b** is illustrated in Figure 1b. All of the proton signals of **7b** could be assigned. The methylene and vinyl protons were observed around 2.66, 5.48−5.54 (−CH=C**H**CH$_2$−), and 5.83 (−C**H**=CHCH$_2$−) ppm. The signals based on vinyloxirane **6b** completely disappeared. The stereochemistry of **7b** as well as **7a** was confirmed as being in the *E*-configuration. The coupling constant of the vinyl proton **d** of **7b** was 15.1 Hz. The IR spectrum of **7b** exhibits the characteristic absorptions due to the hydroxy and carbonyl groups at 3435 and 1693 cm^{-1}, respectively.

Thus, we succeeded in obtaining polymers **7b** with higher molecular weights than those of polymers **7a** as expected.

3. Pd(0)-Catalyzed Polyaddition of Vinyloxiranes 6 with 1,3-Indandione 8. We found that the polyaddition of **6** with **2** as an acyclic 1,3-diketone afforded the desired polymers in good to excellent yields. Third, we examined the polyaddition of **6** using 1,3-indandione (**8**) as a cyclic 1,3-diketone. The results are shown in Table 3. The polyaddition of **6a** and **8** was carried out using $Pd(PPh_3)_4$ to afford the expected polymer (**9a**) (M_n 9200) in 87% yield, whereas polymer **9a** with somewhat lower M_n was obtained by polymerization using $Pd_2(dba)_3$/dppe (runs 1 and 2). The polymerization of **6b** and **8** gave polymers **9b** with much higher molecular weights. When $Pd(PPh_3)_4$ was used as a catalyst, the M_n value of the obtained polymer was

67 600 (run 3). Polymerization in the presence of $Pd_2(dba)_3$/dppe also afforded the desired polymer (run 4) of which the M_n value was 25 000. In both the polyaddition of **6a** and **6b**, the M_n values of **9a** and **9b** were high when $Pd(PPh_3)_4$ was employed. These results indicate that PPh_3 as the ligand is more effective than dppe, contrary to the polyaddition of **6b** and **2**. Polymers **9a** and **9b** were soluble in THF and DMSO. The structure was determined by IR and NMR spectra (Experimental Section). The stereochemistries of **9a** and **9b** were confirmed as being in the *E*-configuration by the coupling constant of the vinyl proton; the *J* values of **9a** and **9b** were 15.0 and 15.1 Hz, respectively. The *Z*-isomers could not be detected in the NMR spectra.

Conclusion

In this work, we found that the Pd(0)-catalyzed polyaddition of **6a** and **6b** with 1,3-diketones proceeded successfully to give new polymers having an allyl alcohol moiety in the main chain and could demonstrated the first example of palladium-catalyzed polyaddition of bifunctional vinyloxirane with carbon nucleophiles. It is suggested that the cause of formation of lower molecular weight polymers from **6a** is the β-hydrogen elimination of the π-allylpalladium intermediate generated by oxidative addition of Pd(0) to **6a**. In both the polyadditions using 1,3-diketones **2** and **8**, the molecular weights of polymers obtained from **6b** were higher than those of polymers from **6a**. In particular, the polyaddition of **6b** and **8** afforded polymer **9b** with high molecular weight (M_n 67 600). The stereochemistries of all of the polymers **7** and **9** were *E*-configuration. The *Z*-isomers were not observed in the NMR spectra. The spectral data of the obtained polymers demonstrated that the selectivity was exclusive.

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MA011900I