

NOTES

Palladium(0)-catalyzed Synthesis of Unsaturated Polyethers from Bifunctional Vinyloxiranes and Bisphenol Analogues

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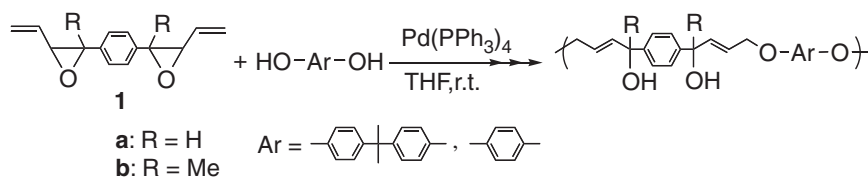
The Pd(0)-catalyzed reaction of vinyloxiranes with carbon nucleophiles is a very useful method for synthesis of functionalized compounds.^{1,2} On the other hand, relatively little is known about the Pd(0)-catalyzed reaction of vinyloxiranes with phenols because carbon-carbon bond formation reactions have received much attention in organic synthesis.^{3,4} We recently reported that the Pd(0)-catalyzed polyaddition of bifunctional vinyloxiranes [1,4-bis(2-vinylepoxyethyl)benzene (**1a**) and 1,4-bis(1-methyl-2-vinylepoxyethyl)benzene (**1b**)] with oxygen nucleophiles such as hydroquinone and bisphenol A could lead to the formation of new unsaturated polyethers containing an allyl aryl ether moiety and pendant hydroxyl groups (Scheme 1).⁵ Unsaturated polymers are of importance for synthesizing crosslinked polymers, and polymers with hydroxyl groups are also significant in functional polymers such as polymeric reagents.⁶ Accordingly, the unsaturated polyethers obtained from **1** and oxygen nucleophiles are regarded as a new type of functional polymers. Generally, it is very difficult to synthesize unsaturated polymers with hydroxyl and various functional groups by conventional polymerization methods.⁷ From the viewpoint of the development of a versatile synthetic method for such polymers, we have reported that the Pd(0)-catalyzed polyaddition of **1** and carbon nucleophiles is a very useful method for the synthesis of unsaturated poly-

mers having hydroxyl and functional groups.^{8,9} Polymer synthesis *via* π -allylpalladium intermediates has recently attracted attention. Suzuki reported the Pd(0)-catalyzed ring-opening polymerization of cyclic monomers such as vinylcyclopropanes.¹⁰ More recently, Nomura reported the Pd(0)-catalyzed allylic substitution polymerization using allylic monomers and malonic esters, which offers a new method of Csp³–Csp³ bond-forming polymerization of the monomers.^{11,12} In this article, we report the Pd(0)-catalyzed polyaddition of **1** and bisphenol analogues such as 4,4'-dihydroxydiphenyl ether and 4,4'-dihydroxybenzophenone for synthesizing unsaturated polyethers with functional groups in the main chain. The Pd(0)-catalyzed polyaddition of **1** was examined by use of bisphenol analogues having an electron-donating or electron-withdrawing group. The Pd(0)-catalyzed polyaddition of **1** and bisphenol analogues will be a more useful method for the synthesis of unsaturated polyethers bearing functional groups, if various bisphenol analogues can be used.

EXPERIMENTAL

Measurement

Fourier transfer infrared (FT-IR) spectra were obtained with a JASCO FT/IR-230 spectrometer. ¹H and ¹³C NMR spectra were measured on a Bruker-



Scheme 1. Pd(0)-catalyzed polyaddition of vinyloxiranes **1** and oxygen nucleophiles.

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DMX 500 or JEOL JNM-AL300 using dimethyl sulfoxide- d_6 (DMSO- d_6) as a solvent and Me₄Si as an internal standard. Gel permeation chromatography (GPC) measurements were performed on a TOSOH HLC8220 GPC system equipped with three columns (TSK-GEL SUPER HM-M, H3000, and H2000) using tetrahydrofuran (THF) as an eluent at 40 °C. Calibration curves for GPC were obtained using standard polystyrene samples.

Materials

Extra-pure grade reagents were used without further purification. Bifunctional vinyloxiranes **1** were prepared by the method reported in our previous paper.⁸ THF used as the solvent for the Pd(0)-catalyzed polyaddition was distilled from sodium/benzophenone ketyl under nitrogen prior to use.

Pd(0)-catalyzed Polyaddition of Bifunctional Vinyloxiranes (1) with Bisphenol Analogues: A Typical Procedure. To a yellow solution of Pd(PPh₃)₄ (0.058 g, 0.05 mmol) in THF (2 mL) 4,4'-dihydroxydiphenyl ether (**2c**; 0.202 g, 1.0 mmol) was added. To this mixture a solution of bifunctional vinyloxirane **1b** (0.242 g, 1.0 mmol) in THF (1 mL) was added. The mixture was stirred at room temperature under an Ar atmosphere. After 24 h, the reaction mixture was poured into toluene (100 mL) to precipitate the polymer (run 1 in Table II). The resulting polymer was filtered off, washed with toluene, and dried *in vacuo* (0.352 g, 79%) giving polymer **3bc**: IR (KBr): 3427, 3043, 2976, 2925, 2866, 1496, 1207, 1012, 833 cm⁻¹. ¹H NMR (300 MHz, DMSO- d_6): δ 1.53 (CH₃, s, 6H), 4.50 (–CH₂–, d, J = 5.1 Hz, 4H), 5.27 (OH, s, 2H), 5.79–5.88 (–CH=CHCH₂–, m, 2H), 6.09 (–CCH=CH–, d, J = 15.3 Hz, 2H), 6.86–6.94 (ArH, m, 8H), 7.36 (ArH, s, 4H). ¹³C NMR (75 MHz, DMSO- d_6): δ 29.5, 68.1, 72.4, 115.8, 119.2, 121.3, 124.5, 141.5, 145.7, 150.9, 154.0.

Polyester **3bd**: IR (KBr): 3415, 3030, 2974, 2925, 2864, 1591, 1489, 1236, 1009, 827 cm⁻¹. ¹H NMR (300 MHz, DMSO- d_6): δ 1.52 (CH₃, s, 6H), 4.53 (–CH₂–, d, J = 5.4 Hz, 4H), 5.28 (OH, s, 2H), 5.79–5.88 (–CH=CHCH₂–, m, 2H), 6.10 (–CCH=CH–, d, J = 15.3 Hz, 2H), 6.92 (ArH, d, J = 8.4 Hz, 4H), 7.23 (ArH, d, J = 8.4, 4H), 7.36 (ArH, s, 4H). ¹³C NMR (75 MHz, DMSO- d_6): δ 29.5, 67.9, 72.4, 115.7, 121.0, 124.5, 126.4, 132.4, 141.7, 145.7, 157.7.

Polyester **3be**: IR (KBr): 3429, 3041, 2974, 2927, 2866, 1599, 1506, 1252, 1165, 845 cm⁻¹. ¹H NMR (300 MHz, DMSO- d_6): δ 1.49 (CH₃, s, 6H), 4.61 (CH₂, br s, 4H), 5.80–5.85 (–CH=CHCH₂–, m, 2H), 6.10 (–CCH=CH–, d, J = 15.3 Hz, 2H), 7.02 (ArH, d, J = 8.1 MHz, 4H), 7.33 (ArH, s, 4H), 7.64 (ArH, d, J = 8.4 MHz, 4H). ¹³C NMR (75 MHz, DMSO- d_6): δ 29.5, 68.0, 72.4, 114.3, 120.7, 124.6, 130.0,

131.6, 142.1, 145.7, 161.5, 193.0.

Polyester **3bf**: IR (KBr): 3446, 2976, 2927, 2870, 1591, 1495, 1255, 1147, 1107, 980, 837 cm⁻¹. ¹H NMR (300 MHz, DMSO- d_6): δ 1.51 (CH₃, s, 6H), 4.63 (–CH₂–, d, J = 4.8 Hz, 4H), 5.79–5.87 (–CH=CHCH₂–, m, 2H), 6.12 (–CCH=CH–, d, J = 15.3 Hz, 2H), 7.10 (ArH, d, J = 7.5 MHz, 4H), 7.35 (ArH, s, 4H), 7.82 (ArH, d, J = 7.2 Hz, 4H). ¹³C NMR (75 MHz, DMSO- d_6): δ 29.4, 68.2, 72.4, 115.4, 120.3, 124.5, 129.1, 133.4, 142.3, 145.6, 161.8.

Polyester **3ac**: IR (KBr): 3383, 3045, 2974, 2870, 1498, 1207, 1057, 1011, 831 cm⁻¹. ¹H NMR (300 MHz, DMSO- d_6): δ 4.50 (CH₂, d, J = 3.9 Hz, 4H), 5.12 (CH, s, 2H), 5.46 (OH, d, J = 4.5 Hz, 2H), 5.84–6.00 (–CH=CH–, m, 4H), 6.82–6.93 (ArH, m, 8H), 7.33 (ArH, s, 4H). ¹³C NMR (75 MHz, DMSO- d_6): δ 67.9, 72.2, 115.8, 119.2, 124.0, 125.8, 137.1, 142.8, 150.9, 154.0.

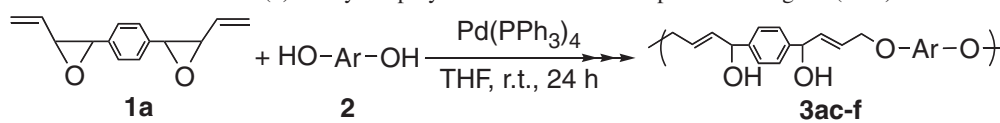
Polyester **3ad**: IR (KBr): 3381, 2972, 2870, 1591, 1489, 1236, 1061, 1007, 827 cm⁻¹. ¹H NMR (500 MHz, DMSO- d_6): δ 4.53 (CH₂, d, J = 4.0 Hz, 4H), 5.18 (CH, s, 2H), 5.57 (OH, s, 2H), 5.87–5.98 (–CH=CH–, m, 4H), 6.93 (ArH, d, J = 8.1 MHz, 4H), 7.26 (ArH, d, J = 8.6 MHz, 4H), 7.28 (ArH, s, 4H). ¹³C NMR (125 MHz, DMSO- d_6): δ 68.0, 72.6, 116.9, 124.0, 126.4, 126.8, 132.9, 137.9, 143.2, 158.1.

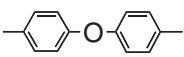
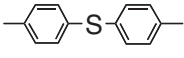
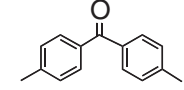
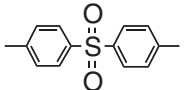
Polyester **3ae**: IR (KBr): 3400, 3037, 2868, 1599, 1506, 1248, 1165, 1001, 928, 847 cm⁻¹. ¹H NMR (500 MHz, DMSO- d_6): δ 4.66 (CH₂, br s, 4H), 5.16 (CH, d, J = 5.2 Hz, 2H), 5.93–6.04 (–CH=CH–, m, 4H), 7.08 (ArH, d, J = 8.5 MHz, 4H), 7.32 (ArH, s, 4H), 7.70 (ArH, d, J = 8.5 MHz, 4H).

Polyester **3af**: IR (KBr): 3429, 3103, 3059, 2918, 1591, 1495, 1294, 1255, 1147, 1105, 978, 833 cm⁻¹. ¹H NMR (500 MHz, DMSO- d_6): δ 4.62 (CH₂, br s, 4H), 5.19 (CH, d, J = 5.2 Hz, 2H), 5.80–5.85 (–CH=CH–, m, 4H), 7.09 (ArH, d, J = 8.1 MHz, 4H), 7.28 (ArH, s, 4H), 7.84 (ArH, d, J = 8.6 MHz, 4H).

RESULTS AND DISCUSSION

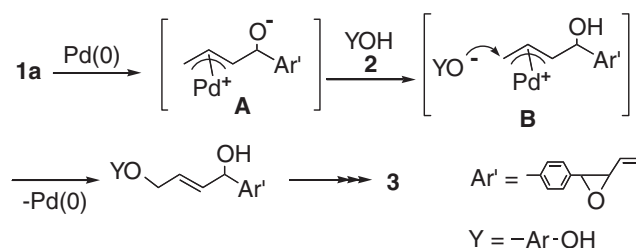
In our previous paper, we reported that the Pd(0)-catalyzed polyaddition of bifunctional vinyloxirane **1a** with hydroquinone and bisphenol A could afford the corresponding unsaturated polyethers with hydroxyl groups when Pd(PPh₃)₄ was used.⁵ Pd₂(dba)₃·CHCl₃/1,2-bis(diphenylphosphino)ethane (dppe) as a catalyst (where dba is dibenzylideneacetone) was not effective, and the yields and number-average molecular weights (M_n) of the obtained polyethers were lower than those of the polyethers obtained by polymerization using Pd(PPh₃)₄. Therefore, the Pd(0)-catalyzed polyaddition of **1a** and bisphenol analogues was examined in THF under an Ar atmosphere in the

Table I. Pd(0)-catalyzed polyaddition of **1a** and bisphenol analogues (**2c-f**)^a


Run	2 (Ar =)	Yield ^b (%)	M_n^c	M_w/M_n^c
1	c 	95	2200	1.43
2	d 	86	2500	1.81
3	e 	80	680	1.45
4	f 	35	910	1.70

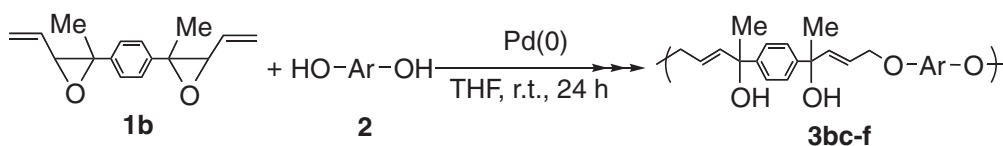
^aConditions: **1a** (1.0 mmol), **2** (1.0 mmol), Pd(PPh₃)₄ (5 mol % for **1a**), THF (3 mL). ^bInsoluble in toluene. ^cEstimated by GPC (based on PSt).

presence of Pd(PPh₃)₄. The formed polymers were isolated by the pouring of the reaction mixture into toluene. The results are summarized in Table I. 4,4'-Dihydroxydiphenyl ether (**2c**), which has an ether linkage having an electron-donating function, afforded the desired unsaturated polyether (**3ac**) in a 95% yield by polymerization at room temperature for 24 h ($M_n = 2200$; run 1). The Pd(0)-catalyzed polyaddition of **1a** and 4,4'-dihydroxydiphenyl sulfide (**2d**) also gave the corresponding polyether (**3ad**) with sulfide bonds in the main chain in a good yield ($M_n = 2500$; run 2). The structures of **3ac** and **3ad** were confirmed by NMR and IR. Signals based on the methylene protons of **3ac** and **3ad** appeared at 4.50 and 4.53 ppm, respectively. Signals due to the methine proton [-CH(OH)-] of the polymers were also observed at 5.12 and 5.18 ppm, respectively. In the IR spectra, absorptions based on the hydroxyl groups of **3ac** and **3ad** were observed around 3383 and 3381 cm⁻¹, respectively. These spectral data revealed that the polyaddition of **1a** using **2c** and **2d** proceeded successfully similar to that of **1a** using hydroquinone and bisphenol A. Next, 4,4'-dihydroxybenzophenone (**2e**) and 4,4'-dihydroxydiphenyl sulfone (**2f**), which have an electron-withdrawing group, were examined as oxygen nucleophiles. The Pd(0)-catalyzed polyaddition of **1a** and **2e** was conducted at room temperature for 24 h, and a toluene-insoluble product was obtained. However, the M_n value of the product **3ae** was very low ($M_n = 680$; run 3). The polyaddition of **1a** and **2f** also gave a toluene-insoluble product **3af**, but the yield and M_n value were low (35%, $M_n = 910$; run 4). **1a** was completely consumed in this case. **3af** was not obtained by polymerization of **1a** and **2f**

**Scheme 2.** Polymerization mechanism.

for 6 h, and the presence of **1a** was ascertained by NMR. These results indicate that **2e** and **2f** are not suitable substrates for the polyaddition with **1a**. The reason is not clear at this stage. **2e** and **2f** have a carbonyl and sulfonyl groups as an electron-withdrawing group, respectively. Therefore, the phenoxide ions generated by hydrogen abstraction of the π -allylpalladium intermediate (**A**) seem not to have sufficient nucleophilicity. It can therefore be presumed that nucleophilic attack of the phenoxide ions generated from **2e** and **2f** onto intermediate **B** were slow (Scheme 2). In the ¹H NMR spectra of the obtained oligomeric products, the methylene and methine protons due to **3ae** and **3af** were observed, and signals based on the bifunctional vinyloxirane **1a** disappeared completely. The IR spectra of **3ae** and **3af** showed the characteristic absorptions based on the hydroxyl groups. These spectral data supported the structures of **3ae** and **3af**.

Second, we examined the Pd(0)-catalyzed polyaddition between bisphenol analogues **2c-f** and bifunctional vinyloxirane **1b**. In the polyaddition of **1b** and bisphenol A, the desired unsaturated polyether could be obtained by polymerization using Pd₂(dba)₃·CHCl₃/dppe as well as Pd(PPh₃)₄.⁵ Therefore,

Table II. Pd(0)-catalyzed polyaddition of **1b** and bisphenol analogues **2c–f**^a

Run	2 (Ar=)	Pd(0)	Yield ^b (%)	M_n^c	M_w/M_n^c
1	c	Pd(PPh ₃) ₄	79	10600	2.88
2	c	Pd ₂ (dba) ₃ ·CH ₃ Cl/dppe	98	13800	3.00
3	d	Pd(PPh ₃) ₄	76	9600	2.35
4	d	Pd ₂ (dba) ₃ ·CH ₃ Cl/dppe	98	6300	3.21
5	e	Pd(PPh ₃) ₄	100	2500	2.06
6	e	Pd ₂ (dba) ₃ ·CH ₃ Cl/dppe	0		
7	f	Pd(PPh ₃) ₄	53	1200	2.10
8	f	Pd ₂ (dba) ₃ ·CH ₃ Cl/dppe	0		

^aConditions: **1b** (1.0 mmol), **2** (1.0 mmol), Pd(0) (5 mol % for **1b**), THF (3 mL). ^bInsoluble in toluene.

^cEstimated by GPC (based on PSt).

Pd(PPh₃)₄ and Pd₂(dba)₃·CHCl₃/dppe were employed as catalysts. The polyaddition of **1b** and **2c–f** was carried out in THF at room temperature for 24 h in the presence of a Pd(0) catalyst (5 mol % for **1b**). Table II shows the results. The yields and M_n values of the obtained polyethers (**3bc–f**) were largely affected by the kinds of bisphenol analogues employed. Unsaturated polyethers with high M_n values were obtained by polymerization using **2c** and **2d** as oxygen nucleophiles. The Pd(0)-catalyzed polyaddition of **1b** and **2c** was carried out in the presence of Pd(PPh₃)₄ and afforded the corresponding polyether (**3bc**) in a 79% yield ($M_n = 10600$; run 1). The yield and M_n value of polyether **3bc** were higher when dppe was used as a ligand instead of PPh₃ (98%, $M_n = 13800$; run 2). The similar tendency was observed in the Pd(0)-catalyzed polyaddition of **1b** and hydroquinone.⁵ The polyaddition of **1b** with **2d** was conducted by use of Pd(PPh₃)₄ and gave the desired polyether (**3bd**) with a high M_n value ($M_n = 9600$; run 3). When dppe was employed as a ligand, however, the M_n value of **3bd** decreased ($M_n = 6300$; run 4), in contrast to the polyaddition **1b** and **2c**. The structures of **3bc** and **3bd** were confirmed based on the NMR and IR spectral data (see the Experimental section). The stereochemistries were *E* configurations; both the *J* values of **3bc** and **3bd** were 15.3 Hz.

In the polyaddition of **1b** with **2c** and **2d**, the M_n values of the obtained polyethers **3bc** and **3bd** were much higher than those of polyethers **3ac** and **3ad** obtained from **1a**. The main reason why **1a** gave polyethers with lower M_n values seems to be the occurrence of β -hydrogen elimination as a termination because the π -allylpalladium intermediate generated by the oxidative addition of Pd(0) to **1a** has a β -hydrogen atom at the benzylic position.^{8,12,13}

The Pd(0)-catalyzed polyaddition of **1b** was next examined by use of **2e** and **2f**, which have a carbonyl and sulfonyl groups as an electron-withdrawing group, respectively. The corresponding polyethers were not obtained by polymerization using Pd₂(dba)₃·CHCl₃/dppe as a catalyst, and the starting vinyloxirane **1b** was recovered (runs 6 and 8). The polyaddition of **1b** and **2e** in the presence of Pd(PPh₃)₄ produced the expected polyether (**3be**), the M_n value of which was not high ($M_n = 2500$; run 5). The M_n value of the polyether (**3bf**) obtained from **1b** and **2f** was lower than that of polyether **3be** (run 7). The low M_n values of **3be** and **3bf** are probably due to slow nucleophilic attack of the phenoxide ions generated from **2e** and **2f** onto the π -allylpalladium intermediate generated from **1b**, similar to the polyaddition of **1a** with **2e** and **2f**. From these results using **1b** and **2c–f**, the Pd(0)-catalyzed polyaddition was found to be largely affected by the kinds of bisphenol analogues employed; the M_n values of the obtained polyethers decreased in the following order: **3bc** > **3bd** > **3be** > **3bf**.

CONCLUSIONS

We found that the Pd(0)-catalyzed polyaddition of **1b** and bisphenol analogues **2c** and **2d**, which have an electron-donating group, afforded the corresponding unsaturated polyethers **3bc** and **3bd** with high M_n values. On the other hand, when **2e** and **2f**, which have an electron-withdrawing group, were used, the M_n values of the obtained polymers **3be** and **3bf** were very low. In the polyaddition using **2c** and **2d**, the M_n values of **3bc** and **3bd** were much higher than those of the polyethers **3ac** and **3ad** obtained by polymerization with **1a**. Therefore, the combination of bifunc-

tional vinyloxirane **1b** and bisphenol analogues with an electron-donating group was found to be a better way for the synthesis of unsaturated polyethers with high M_n values.

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