

Facile Synthesis of Unsaturated Polyamines having Hydroxyl Groups by Pd(0)-Catalyzed Polyaddition of Bifunctional Vinylepoxyde and Aliphatic Amines

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ABSTRACT: Unsaturated polyamines having hydroxyl groups were synthesized by polymerization of a bifunctional vinylepoxyde, **1,4-bis(1-methyl-2-vinylepoxyethyl)-benzene (1)**, and aliphatic amines in the presence of a Pd(0) catalyst. The polyaddition was carried out for 24 h at 90°C in dioxane. Among the phosphine ligands employed, bis(2-diphenylphosphinophenyl)ether (DPEphos) was most effective and gave polyamines with high molecular weight. Benzylamine and piperazine were appropriate nucleo-

philes and the corresponding polyamines were obtained in moderate to high yields, the number-average molecular weights (M_n) of which were high ($M_n = 29,000$ – $33,000$). The polyaddition between **1** and anilines was not successful. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2274–2279, 2008

Key words: polyaddition; polyamines; catalysts; synthesis; gel permeation chromatography (GPC)

INTRODUCTION

Although the palladium-catalyzed allylic substitution reaction (Tsuji-Trost reaction) of allylic compounds and nucleophiles are widely used in organic synthesis,¹ application of the Tsuji-Trost type reaction to polymer synthesis is still limited. Suzuki et al. reported the Pd(0)-catalyzed ring-opening polymerization of cyclic monomers such as vinylcyclopropanes via π -allylpalladium intermediates.² They also reported that the Pd(0)-catalyzed polycondensation of allylic monomers and aliphatic amines afforded the corresponding polyamines. However, the number-average molecular weights (M_n) of the polyamines were not high ($M_n = 2000$ – 4000).³ More recently, Nomura and coworkers reported the Pd(0)-catalyzed polycondensation between allylic acetates and malonic esters as carbon nucleophiles, which offers a new method of Csp³-Csp³ bond-forming polymerization of the monomers.^{4–6} One of the unique characteristics is that the polycondensation can proceed under stoichiometrically imbalanced conditions.

The nucleophiles employed are limited to carbon and nitrogen nucleophiles in the Pd(0)-catalyzed polycondensation using allylic monomers as described earlier. There is no report on the polycondensation with other kind of nucleophile. We recently reported that the palladium(0)-catalyzed polyaddition of

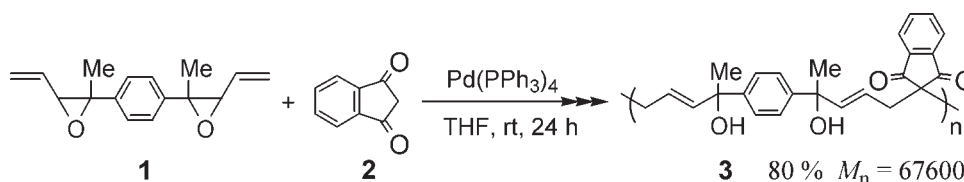
bifunctional vinylepoxyde **1** with carbon nucleophiles such as 1,3-indandione could afford new polymers having an allyl alcohol moiety in the main chain accompanying carbon–oxygen bond cleavage of the oxirane ring (Scheme 1).^{7,8} Various nucleophiles such as bisphenols and diacids could be used in the polyaddition.^{9–11} The stereochemistry of the obtained polymers was *E*-configuration.

There are many reports on the Pd(0)-catalyzed addition reaction of vinylepoxydes with carbon nucleophiles.¹ On the other hand, only a few studies on the addition reaction of vinylepoxydes with nitrogen nucleophiles have been reported.^{12–14} From the viewpoint of polymer synthesis, it is important to contemplate carbon–nitrogen bond formation by palladium-catalyzed reaction to obtain various functional polymers. We already reported that benzenesulfonamides could be used as nitrogen nucleophiles in the Pd(0)-catalyzed polyaddition with **1** and the desired nitrogen-containing polymers were formed in good yields.¹⁰

It is well known that epoxides react with aliphatic amines to give β -amino alcohols. To our knowledge, however, there is no report that the Pd(0)-catalyzed addition reaction of vinylepoxydes and aliphatic amines gives 1,4-adducts (Scheme 2). Tsuda et al. reported that a Pd(0)-catalyzed addition reaction of a vinylepoxyde, methyl γ,δ -epoxysorbate, and diethylamine gave a 1,2-adduct in 19%.¹² However, the corresponding 1,4-adduct was not produced.

In this article, we report the Pd(0)-catalyzed polyaddition of bifunctional vinylepoxyde **1** and aliphatic

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Scheme 1

amines as nitrogen nucleophiles to synthesize new polyamines containing an allyl amine moiety in the main chain and pendant hydroxyl groups. Unsaturated polymers are of importance for synthesizing crosslinked polymers, and polymers having hydroxyl groups are also significant in functional polymers such as polymeric reagents.¹⁵ Generally, it is difficult to synthesize unsaturated polymers with hydroxyl groups by conventional polymerization methods.^{16,17} Therefore, the Pd(0)-catalyzed polyaddition of bifunctional vinyloxyepoxide **1** and aliphatic amines was investigated to offer a new synthetic method for unsaturated polyamines with hydroxyl groups.

EXPERIMENTAL SECTION

Materials

All reagent-grade commercial chemicals were used without further purification, unless otherwise stated. Pd(PPh₃)₄ and Pd₂(dba)₃·CHCl₃ were commercially available and were used as received. 1,4-Bis(1-methyl-2-vinyloxyethyl)benzene¹ was synthesized by the reported method.⁷ Tetrahydrofuran (THF) and dioxane as solvents were distilled from sodium/benzophenone ketyl under argon.

Measurement

¹H and ¹³C-NMR spectra were recorded on a JEOL-AL300 or a Bruker-DMX 500 with CDCl₃ or dimethyl-*d*₆ sulfoxide (DMSO-*d*₆) as a solvent and Me₄Si as an internal standard. IR spectra were recorded on a JASCO FT-IR 460 Plus. Gel permeation chromatography (GPC) was performed on a Shimadzu HPLC-LC 10vp system equipped with three columns (Shim-pack GPC 80MD, Shim-pack GPC 804D, and Shim-pack GPC 802D), and dimethylformamide (DMF) was used as an eluent at 40°C. The GPC was calibrated against standard poly(methyl methacrylate) samples. Elemental analyses were performed on a ThermoFinnigan Flash EA1112 CHN-O Analyzer.

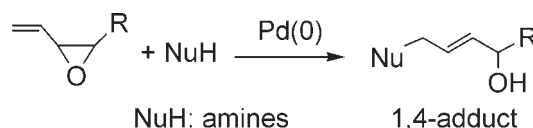
Pd(0)-catalyzed addition reaction of vinyloxyepoxide **4** and benzylamine **5**

To a yellow solution of Pd₂(dba)₃·CHCl₃ (where dba is dibenzylideneacetone) (0.026 g, 2.5 μmol) and bis(2-diphenylphosphinophenyl)ether (DPEphos; 0.054 g,

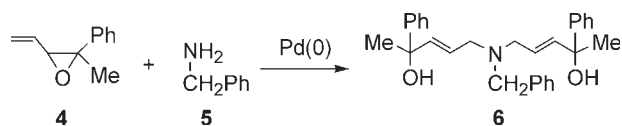
10 μmol) in THF (2 mL) **5** (0.107 g, 1.0 mmol) was added. To the mixture a solution of vinyloxyepoxide **4** (0.160 g, 1.0 mmol) in THF (1 mL) was added. After being stirred for 24 h at 60°C under an Ar atmosphere, the reaction mixture was evaporated to dryness. The residue was subjected to flash column chromatography on silica gel (1 : 1 hexane/ethyl acetate) to give the desired **2** : **1** product **6** (0.194 g, 91%). IR (neat): 3395, 3085, 3060, 3028, 2977, 2927, 2878, 2805, 1600, 1493, 1446, 1366, 1066, 975, 908, 735, 699 cm⁻¹. ¹H-NMR (CDCl₃) δ: 1.60 (6H, s, CH₃), 2.13 (2H, s, OH), 3.10 (4H, d, *J* = 6.3 Hz, CH₂), 3.56 (2H, s, NCH₂Ph), 5.68–5.77 (2H, m, CH₂CH=CH), 5.86 (2H, d, *J* = 15.6 Hz, CH₂CH=CH), 7.20–7.42 (15H, m, ArH). ¹³C-NMR (CDCl₃) δ: 29.64(CH₃), 55.65(CH₂), 55.66 (CH₂), 58.30(CH₂), 58.32 (CH₂), 74.29(C—OH), 125.07, 125.55, 125.58, 126.85, 126.87, 128.16, 128.17, 128.94, 139.28, 139.93, 146.77. Anal. Calcd for C₂₉H₃₃NO₂: C, 81.46; H, 7.78; N, 3.28. Found: C, 81.14; H, 7.95; N, 3.20.

Pd(0)-catalyzed polyaddition of bifunctional vinyloxyepoxide **1** and benzylamine **5**: A typical procedure

To a yellow solution of Pd₂(dba)₃·CHCl₃ (0.026 g, 2.5 μmol) and DPEphos (0.054 g, 10 μmol) in dioxane (2 mL) **5** (0.107 g, 1.0 mmol) was added. To the mixture a solution of vinyloxyepoxide **1** (0.242 g, 1.0 mmol) in dioxane (1 mL) was added. After being stirred for 24 h at 90°C under an Ar atmosphere, the reaction mixture was poured into toluene (100 mL) to precipitate the polymer (run 6 in Table II). The resulting polymer was filtered off, washed with toluene, and dried *in vacuo* (0.158 g, 45%) giving polymer **7**: IR (KBr): 3402, 3027, 2972, 2924, 2856, 2802, 1451, 1402, 1364, 1119, 1076, 973, 871, 838, 740, 699 cm⁻¹. ¹H-NMR (CDCl₃) δ: 1.51 (6H, br s, CH₃), 3.03 (4H, br s, CH₂), 3.52 (2H, br s, NCH₂Ph), 5.68–5.76 (4H, m, CH=CH), 7.22–7.26 (9H, m, ArH). ¹³C-NMR (CDCl₃)



Scheme 2



δ : 29.45(CH₃), 55.35(CH₂), 58.28(CH₂), 74.07(C—OH), 125.02, 126.94, 128.16, 129.10, 138.78, 140.20, 145.36.

Polymer **9**: IR (KBr) 3362, 2968, 2927, 2860, 2820, 1604, 1365, 1074, 974, 838, 730 cm⁻¹. ¹H-NMR (DMSO-*d*₆) δ : 1.45 (8H, br s, CH₃ and CH₂), 2.40 (2H, br s, NCH₂), 2.97 (4H, br s, NCH₂CH=CH), 3.38 (2H, br s, HOCH₂), 5.17 (2H, s, OH), 5.53–5.65 (2H, m, CH₂CH=CH), 5.77 (2H, d, *J* = 15.0 Hz, CH₂CH=CH), 7.31 (4H, br s, ArH). ¹³C-NMR (DMSO-*d*₆) δ : 29.73 (CH₂), 29.87 (CH₃), 50.00 (CH₂), 54.79 (CH₂), 59.64 (CH₂), 72.66 (C—OH), 123.20, 124.58, 140.97, 146.09.

Polymer **11**: IR (KBr) 3402, 2974, 2932, 2816, 1458, 1402, 1347, 1288, 1133, 1077, 978, 839 cm⁻¹. ¹H-NMR (DMSO-*d*₆) δ : 1.45 (6H, s, CH₃), 2.29 (8H, br s, CH₂N), 2.85 (4H, d, *J* = 4.8 Hz, CH₂NCH=CH), 5.24 (2H, s, OH), 5.49–5.58 (2H, m, CH₂CH=CH), 5.79 (2H, d, *J* = 15.3 Hz, CH₂CH=CH), 7.30 (4H, s, ArH). ¹³C-NMR (DMSO-*d*₆) δ : 30.00 (CH₃), 52.64 (CH₂), 59.80 (CH₂), 72.81 (C—OH), 123.13, 124.74, 141.23, 146.19. Anal. Calcd for C₂₀H₂₈N₂O₂: C, 73.13; H, 8.59; N, 8.53. Found: C, 71.88; H, 8.39; N, 7.61.

RESULTS AND DISCUSSION

Pd(0)-catalyzed addition reaction of vinyl epoxide **4** and benzylamine **5**

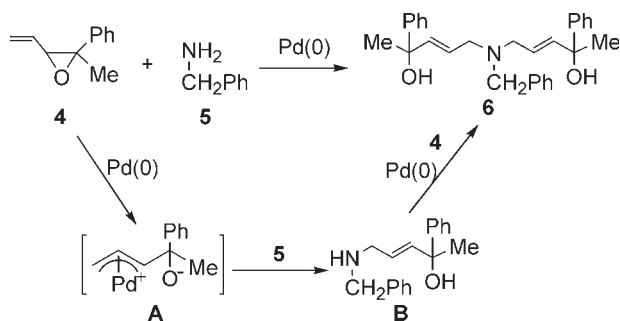
We first studied whether vinyl epoxide **4** gives the desired 1,4-adduct **6** predominantly by reaction with **5** in the presence of Pd(0) catalyst (Scheme 3). The Pd(0)-catalyzed addition reaction of **4** and **5** (1 equiv)

TABLE I
Pd(0)-Catalyzed Addition Reaction of **4** and **5**^a

Entry	Pd(0)	Yield of 6 (%) ^b
1	Pd(PPh ₃) ₄	12
2	Pd ₂ (dba) ₃ ·CHCl ₃ /dppe	84
3	Pd ₂ (dba) ₃ ·CHCl ₃ /dppp	75
4	Pd ₂ (dba) ₃ ·CHCl ₃ /dppb	78
5	Pd ₂ (dba) ₃ ·CHCl ₃ /dpppent	82
6	Pd ₂ (dba) ₃ ·CHCl ₃ /dppf	81
7	Pd ₂ (dba) ₃ ·CHCl ₃ /DPEphos	96

^a 1 equiv of **5** to **4** was used.

^b Determined by ¹H-NMR using CH₃NO₂ as an internal standard.



was carried out at 60°C for 20 h in THF in the presence of various phosphine ligands. The results are summarized in Table I. The obtained product was the 1,4-adduct **6** and the 1,2-adduct **6'** was not formed (Scheme 5), contrary to the reaction of methyl γ,δ -epoxysorbate and diethylamine reported by Tsuda et al. The yield of **6** was very low when Pd(PPh₃)₄ was used as a catalyst (entry 1). On the other hand, bidentate phosphine ligands gave **6** in high yields. Especially, Pd₂(dba)₃·CHCl₃/DPEphos afforded **6** quantitatively (entry 7). Other bidentate ligands such as dppe and dppf were also effective. The structure of **6** was determined by NMR, IR, and elemental analysis. The stereochemistry was *E*-configuration (*J* = 15.6 Hz). Interestingly, despite the use of one equiv of **5** to **4**, the desired 2 : 1 addition product **6** was mainly obtained in all cases. This result suggests that the 1 : 1 product **B** obtained from **4** and **5**, which is a secondary amine, is more reactive than **5** toward the π -allylpalladium intermediate **A** generated from **4** (Scheme 4).

It is well known that β -amino alcohols are formed by direct attack of amines on epoxides without Pd(0) catalyst. The reaction of **5** and **4** may afford aminoalcohol **6'** in a similar manner (Scheme 5). In the Pd(0)-catalyzed addition reaction of **4** and **5**, however, the formation of aminoalcohol **6'** was not observed. In addition, the reaction of **4** and **5** did not take place in the absence of Pd(0) and **4** was recovered. These results indicate that the direct attack of **5** on the epoxy ring of **4** did not occur.

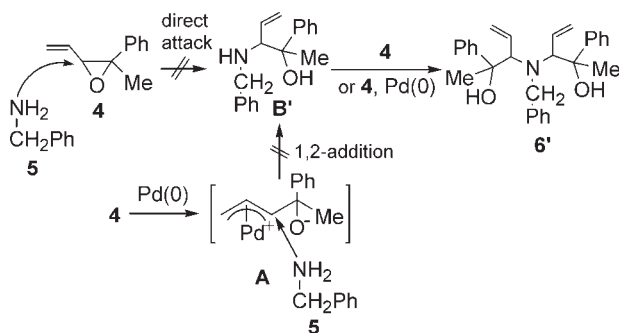


TABLE II
Pd(0)-Catalyzed Polyaddition of 1 and 5



Entry	Equiv of 5	Pd(0)	Solvent	Temp. (°C)	Yield of 7 (%) ^a	M_n ^b	M_w/M_n ^b
1	1.0	Pd(PPh ₃) ₄	THF	60	0		
2	1.0	Pd ₂ (dba) ₃ ·CHCl ₃ /dppe	THF	60	0		
3	1.0	Pd ₂ (dba) ₃ ·CHCl ₃ /DPEphos	THF	60	58	14,400	1.19
4	1.0	Pd(PPh ₃) ₄	Dioxane	90	0		
5	1.0	Pd ₂ (dba) ₃ ·CHCl ₃ /dppe	Dioxane	90	62	19,700	1.22
6	1.0	Pd ₂ (dba) ₃ ·CHCl ₃ /DPEphos	Dioxane	90	45	29,000	1.59
7	1.5	Pd ₂ (dba) ₃ ·CHCl ₃ /DPEphos	Dioxane	90	26	8,500	1.27
8	0.5	Pd ₂ (dba) ₃ ·CHCl ₃ /DPEphos	Dioxane	90	0		

^a Insoluble in toluene.

^b Estimated by GPC (based on PMMA).

The methyl group on the epoxy ring of 4 was necessary to obtain the desired 1,4-adduct. 2-Phenyl-3-vinylepoxide, which has a hydrogen atom instead of a methyl group on the epoxy ring, was also used in the Pd(0)-catalyzed addition reaction with aliphatic amines. Although the starting epoxide was completely consumed, the corresponding 1,4-adduct was not formed at all. It seems that β -hydrogen elimination of the intermediate occurred in this case because the π -allylpalladium intermediate generated by oxidative addition of Pd(0) to 2-phenyl-3-vinylepoxide has a β -hydrogen at the benzylic position.⁷ On the other hand, vinyl epoxide 4 gives a π -allylpalladium intermediate with no β -hydrogen.

Thus, we found that the Pd(0)-catalyzed addition reaction of 4 and 5 could lead to the formation of the desired 1,4-adduct 6 in excellent yield when Pd₂(dba)₃·CHCl₃/DPEphos was employed as the catalyst.

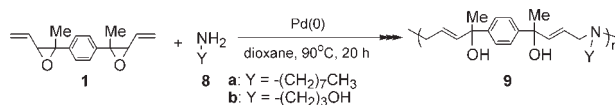
Pd(0)-catalyzed polyaddition of bifunctional vinyl epoxide 1 and aliphatic amines

Based on the results of the model reaction of 4 and 5, the Pd(0)-catalyzed polyaddition of 1 and 5 was

first examined under the same conditions. The resulting polymer was isolated by pouring the reaction mixture into toluene. Table II shows the results. The expected polyamine 7 was not obtained by polymerization using Pd(PPh₃)₄ and Pd₂(dba)₃·CHCl₃/dppe as catalysts (entries 1 and 2). On the other hand, the polyaddition of 1 and 5 gave polyamine 7 with high number-average molecular weight (M_n) when Pd₂(dba)₃·CHCl₃/DPEphos was used (entry 3). The molecular weight of 7 was increased by polymerization at elevated temperature (90°C). Although Pd(PPh₃)₄ was not effective even at 90°C (entry 4), the polyaddition using Pd₂(dba)₃·CHCl₃/dppe gave 7 in good yield, the M_n of which increased to 19,700 (entry 5). The M_n of 7 reached 29,000 when the polyaddition was carried out using DPEphos as the ligand (entry 6). The M_n value was about twice that of 7 obtained at 60°C under the same conditions. The structure of 7 was determined by NMR and IR. The stereochemistry could not be confirmed to be *E*-configuration because the signals of the vinyl protons were multiplet.

In the Pd(0)-catalyzed addition reaction of 4 and 5, 2 : 1 adduct 6 instead of 1 : 1 adduct B was obtained

TABLE III
Pd(0)-Catalyzed Polyaddition of 1 and 8

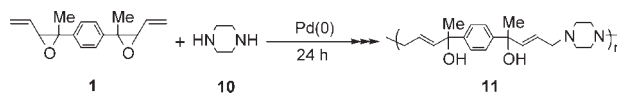


Entry	Amine 8	Pd(0)	Yield of 9 (%) ^a	M_n ^b	M_w/M_n ^b
3	a	Pd ₂ (dba) ₃ ·CHCl ₃ /dppe	0		
4	a	Pd ₂ (dba) ₃ ·CHCl ₃ /DPEphos	0		
1	b	Pd ₂ (dba) ₃ ·CHCl ₃ /dppe	86	9,400	1.38
2	b	Pd ₂ (dba) ₃ ·CHCl ₃ /DPEphos	92	14,600	1.30

^a Insoluble in toluene.

^b Estimated by GPC (based on PMMA).

TABLE IV
Pd(0)-Catalyzed Polyaddition of **1** and **10**



Entry	Pd(0)	Solvent	Temp. (°C)	Yield of 11 (%) ^a	M_n ^b	M_w/M_n ^b
1	Pd(PPh ₃) ₄	THF	60	0		
2	Pd ₂ (dba) ₃ ·CHCl ₃ /dppe	THF	60	96	18,700	1.58
3	Pd ₂ (dba) ₃ ·CHCl ₃ /DPEphos	THF	60	85	18,200	1.60
4	Pd(PPh ₃) ₄	Dioxane	90	0		
5	Pd ₂ (dba) ₃ ·CHCl ₃ /dppe	Dioxane	90	100	18,900	1.57
6	Pd ₂ (dba) ₃ ·CHCl ₃ /DPEphos	Dioxane	90	92	33,200	1.30

^a Insoluble in toluene.

^b Estimated by GPC (based on PMMA).

in an excellent yield (Scheme 4) even when 1 equiv of **5** to **4** was used (entry 7 in Table I). Consequently, the polyaddition of **1** and an excess of **5** was expected to give polymer **7**. Actually, the polyaddition of **1** and 1.5 equiv of **5** gave the desired polyamine **7** as expected. However the yield and M_n were largely diminished (entry 7). On the other hand, **7** was not obtained by polymerization using 0.5 equiv of **5** (entry 8).

The polyaddition of **1** and **5** was also conducted at 90°C in dioxane without Pd(0) catalyst. In this case, **7** was not isolated and vinyl epoxide **1** was recovered.

n-Octylamine (**8a**) and 3-amino-1-propanol (**8b**) were next tested as primary amines. Table III shows the results. In the polyaddition of **1** and **8a**, **1** was completely consumed and the ¹H-NMR of the reaction mixture showed the formation of **9a**. However toluene-insoluble **9a** was not obtained (entries 1 and 2). Although **8a** did not give the corresponding polyamine **9a** with high molecular weight, **8b** did. The Pd(0)-catalyzed polyaddition of **1** and **8b** using dppe as a ligand gave the desired polyamine **9b** in 86%, M_n of which was 9400 (entry 3). DPEphos was more effective than dppe in the polyaddition of **1** and **8b** and the M_n of **9b** became higher (entry 4), similarly to that of **1** and **5**.

Aromatic amines were not appropriate for the polyaddition with **1**. We attempted the polyaddition of **1** using anilines, but the corresponding polyamines could not be obtained at all.

We finally examined the Pd(0)-catalyzed polyaddition of **1** with piperazine (**10**) as a secondary amine. The results are showed in Table IV. The corresponding polyamine **11** was not formed by polymerization at 60°C in the presence of Pd(PPh₃)₄ (entry 1). Vinyl epoxide **1** remained in the reaction mixture. Bidentate ligands, dppe and DPEphos, were effective and the M_n values of the obtained polyamine **11** were more than 18,000 (entries 2 and 3). The M_n of **11** reached 33,200 when the polyaddition was conducted at

elevated temperature (90°C) in dioxane by use of DPEphos as a ligand (entry 6). On the other hand, the M_n of **11** obtained by polymerization using dppe at 90°C was almost identical to that of **11** obtained by polymerization at 60°C (entry 5). Pd(PPh₃)₄ was not efficient in the polyaddition at 90°C (entry 4) and **1** was recovered. Thus, polyamine **11** with high M_n was obtained when the polyaddition was conducted at 90°C using DPEphos as the ligand. The structure of **11** was confirmed by NMR and IR. The stereochemistry was *E*-configuration ($J = 15.0$ Hz). The polyaddition of **1** and **10** was also attempted in the absence of a Pd(0) catalyst, but any polymeric products were not formed and **1** was recovered over 85%.

CONCLUSIONS

We found that the Pd(0)-catalyzed polyaddition of bifunctional vinyl epoxide **1** and aliphatic amines proceeded successfully under the conditions of 90°C in dioxane by use of DPEphos as the ligand and gave unsaturated polyamines having hydroxyl groups. The M_n values of the obtained polyamines were about 30,000 when benzylamine and piperazine were used. Thus, we could obtain unsaturated polyamines having hydroxyl groups in moderate to good yields which were difficult to synthesize by conventional methods.

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