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Polycondensation Catalyzed by Palladium Complex III. Syntheses of Linear Polyamines and Cyclic Oligoamines *via* π-Allyl Palladium Intermediates

Masato SUZUKI, Jong-Chan LIM, Masahiro OGUNI, Anke EBERHARDT, and Takeo SAEGUSA*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

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ABSTRACT: A new polymerization reaction with a Pd (0) catalyst has been explored, in which polyamines (linear and cyclic) having amino groups in the main chains are produced. Two components of monomeric compounds are employed; the one is a bifunctional allylic compound and the other is amine. As the amine components, tosylated amines are employed, too, to produce the corresponding tosylated derivatives of polyamine. A kind of polycondensation proceeded *via* a π-allyl palladium intermediate. The monomer structure and the character of the catalyst influence the proportion between linear and cyclic products.

KEY WORDS Polyamine / Cyclic Oligoamine / Polycondensation / Palladium Catalyst / π-Allyl Palladium Complex /

It is very interesting to contemplate useful synthetic reactions from the viewpoint of polymer synthesis. Our attention has been directed to palladium catalyzed synthetic reactions which have actively been explored in these two decades.[1] Then, we have recently reported a novel polycondensation by using the Heck reaction[2] and a quite new type of ring-opening polymerization which proceeds *via* a π-allyl palladium complex.[3] This paper deals with a new polycondensation *via* a π-allyl palladium intermediate to produce polyamines having amino groups in the main chains, cyclic oligoamines, and their *N*-tosylated derivatives.

Polymeric amines have actively been studied due to their characteristic properties and potentials of various applications.[4] As to the synthetic methods for polyamines, there have been several reports.[4] The ordinary method is the reaction between a dihalo compound and a diamine, which, however, is accompanied by extensive branching and crosslinking. Polyamine synthesis described here by using a Pd catalyzed substitution reaction at an allylic position does not involve such kind of undesirable reactions, which offers a new synthetic way for linear polyamines. Cyclic oligoamines also have attracted much attention due to their remarkable characters.[5] This paper presents also a new method for the synthesis of cyclic oligoamines having vinylidene groups, which are able to react with some reagents to be modified or converted to other functional groups.

It is well-known that allylic compounds having functional groups such as acetate, carbonate, and ether react with nucleophiles such as amines and active methylene compounds (enolates) in the presence of a palladium complex to give the substituted products.[6] Accordingly, for the polymer synthe-

* To whom all correspondence should be addressed.

sis on the basis of this synthetic methodology, the reactions of some bifunctional allylic acetate or carbonate with primary amines, secondary diamines, and tosylamide derivatives have been attempted with an intention of the synthesis of polyamines and *N*-tosylated polyamines.

EXPERIMENTAL

A bifunctional allylic compound of 2-methylene-1,3-propanedily diacetate (**1a**) was prepared by a substitution reaction of 3-chloro-2-chloromethyl-1-propene with potassium acetate with the aid of a phase-transfer catalyst, tetrabutylammonium bromide, in a two-phase (xylene/water) system. Dimethyl 2-methylene-1,3-propanedily dicarbonate (**1b**, bp 84°C/1.5 mmHg) was prepared by the reaction of 2-methylene-1,3-propanediol (**1c**), which was prepared from **1a** according to the reported method,[7] with methyl chloroformate. The commercially available amines and diamines were distilled over CaH_2. Tosylamide was recrystallized from ethanol. The *N,N'*-ditosylated diamines were prepared by the treatment of the related diamines with tosyl chloride. $Pd_2(dba)_3 \cdot CHCl_3$ (dba: dibenzylideneacetone) was prepared according to the reported method.[8] The commercially available other Pd compounds and phosphorous ligands were used without further purification. Solvents for reactions were dried and distilled according to ordinary methods. All reactions described below were carried out under N_2.

A Typical Procedure for the Polycondensation between **1** *and Piperazine*

A mixture of **1a** (344 mg, 2 mmol), Pd(acac)$_2$ (6.1 mg, 0.02 mmol), dppe (1,2-bis(diphenylphosphino)ethane, 15.9 mg, 0.04 mmol), and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 913 mg, 6 mmol) in THF (1 ml) was stirred at 50°C to produce a homogeneous mixture. Then, piperazine (172 mg, 2 mmol) in THF (4 ml) was added. After 5 h at 50°C, the reaction mixture was poured into CH_3OH (50 ml). The precipitated polyamine **PA1** was collected by filtration, which was purified by reprecipitation from $CHCl_3$ into CH_3OH and dried *in vacuo* (273 mg, 86%): ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 8H NCH_2CH_2N), 2.93 (s, 4H $NCH_2C{=}C$), 5.07 (s, 2H, $CH_2{=}C$); ^{13}C NMR ($CDCl_3$, ppm) 53.45 (NCH_2CH_2N), 62.35 ($NCH_2C{=}C$), 114.17 ($CH_2{=}C$), 143.03 ($CH_2{=}C$); IR (KBr, cm^{-1}) 3060, 2975, 2780, 1645, 1450, 1330, 1297, 1260, 1150, 1130, 1050, 914, 835.

A Typical Procedure for the Reaction of **1a** *with n-Butylamine*

A mixture of **1a** (344 mg, 2 mmol), Pd(acac)$_2$ (12.2 mg, 0.04 mmol), dppe (31.9 mg, 0.08 mmol), and Et_3N (486 mg, 4.8 mmol) in THF (5 ml) was stirred at 50°C to produce a homogeneous mixture. Then, *n*-butylamine (146 mg, 2 mmol) was added and heated at 50°C for additional 20 h. To pour the reaction mixture into hexane (50 ml) gave no precipitate, so that the solution was washed several times with aq. 1*N* NaOH. The organic layer was dried over $MgSO_4$ and evaporated to give viscous liquid, which was fractionated by using a Kugelrohr apparatus to give the cyclic oligoamines **2** (100°C, 0.5 mmHg) and **3** (150°C, 0.5 mmHg). **2**: MS (70 eV); *m/z* (rel. intensity) 250 (M^+, 27), 193 ($M^+ - n$-Bu, 53), 178 (52), 164 (100), 126 (74); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 6H, J=6.0 Hz, CH_3), 1.43 (m, 8H, $CH_2CH_2CH_3$), 2.42 (t, 4H, J=5.0 Hz, NCH_2CH_2), 3.24 (s, 8H, $NCH_2C{=}C$), 4.85 (s, 4H, $CH_2{=}C$); ^{13}C NMR ($CDCl_3$, ppm) 14.06 (CH_3), 20.58 (CH_2CH_3), 29.88 (NCH_2CH_2), 54.11 (NCH_2CH_2), 59.15 ($NCH_2C{=}C$), 113.36 ($CH_2{=}C$), 146.04 ($CH_2{=}C$). **3**: MS (70 eV) *m/z* (rel. intensity) 375 (M^+, 7.7), 318 (77), 249 (100), 209 (47), 178 (99), 136 (89), 126 (74); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 9H, J=6.0 Hz, CH_3), 1.39 (m, 12H, $CH_2CH_2CH_3$), 2.41 (t, 6H, J=5.0 Hz, NCH_2CH_2), 3.15 (s, 12H, $NCH_2C{=}C$), 4.97 (s, 6H, $CH_2{=}C$); ^{13}C NMR ($CDCl_3$, ppm) 14.06 (CH_3), 20.58

(CH_2CH_3), 29.66 (NCH_2CH_2), 52.98 (NCH_2-CH_2), 56.78 ($NCH_2C=C$), 114.07 ($CH_2=C$), 147.06 ($CH_2=C$).

A Typical Procedure for the Reaction of **1a** *with Aniline*

To a solution of $Pd_2(dba)_3 \cdot CHCl_3$ (41.4 mg, 0.04 mmol) and Ph_3P (42.0 mg, 0.16 mmol) in THF (2 ml) were added **1a** (344 mg, 2 mmol), aniline (186 mg, 2 mmol), and Et_3N (607 mg, 6 mmol). After 5 h at 50°C, the reaction mixture was poured into CH_3OH (50 ml) to precipitate the polymer, which was collected by filtration. The product polyamine **PA2** was purified by reprecipitation from $CHCl_3$ into CH_3OH, and dried *in vacuo* (267 mg, 78%). The CH_3OH soluble portion was subjected to preparative TLC (hexane–EtOAc = 4 : 1, v/v) to give the cyclic amine **4** (Rf = 0.7, 37.8 mg, 13%). **PA2**: ^1H NMR ($CDCl_3$) δ 3.82 (s, 4H, $NCH_2C=C$), 4.95 (s, 2H, $CH_2=C$), 6.57—7.30 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$, ppm) 53.76 ($NCH_2C=C$), 111.93 ($CH_2=C$), 112.87 (Ph), 116.92 (Ph), 129.01 (Ph), 140.65 ($CH_2=C$), 148.61 (Ph); IR (KBr, cm^{-1}) 3050, 2875, 2830, 1640, 1585, 1495, 1380, 1225, 895, 735, 665. **4**: mp 210—212°C; MS (70 eV) m/z (rel. intensity) 290 (M^+, 69), 198 (100), 184 (59), 144 (61), 106 (22); ^1H NMR ($CDCl_3$) δ 3.97 (s, 8H, $NCH_2C=C$), 5.24 (s, 4H, $CH_2=C$), 6.67—7.36 (m 10H, Ph); ^{13}C NMR ($CDCl_3$, ppm) 57.99 ($NCH_2C=C$), 110.89 (Ph), 111.25 ($CH_2=C$), 116.90 (Ph), 129.01 (Ph), 140.65 ($CH_2=C$), 148.96 (Ph).

A Typical Procedure for the Reaction of **1a** *with N,N'-Dimethylethylenediamine (DMEDA)*

A mixture of **1a** (344 mg, 2 mmol), $Pd(acac)_2$ (6.1 mg, 0.02 mmol), dppe (15.9 mg, 0.04 mmol), Et_3N (607 mg, 6 mmol), and THF (2 ml) was heated at 50°C to give a homogeneous mixture, to which DMEDA (176 mg, 2 mmol) was added. After 24 h at 50°C, the reaction mixture was poured into diethyl ether (20 ml) and the insoluble catalyst was filtered off. The diethyl ether soluble part was evaporated and subjected to Kugelrohr distillation to give the acetic acid salt of **5** (50°C, 0.3 mmHg). Acetic acid was removed by treating the CH_2Cl_2 solution of the salt with aq. 1*N* NaOH. The organic layer was dried over $MgSO_4$ and evaporated to give **5** (203 mg, 70%). The distillation residue of the diethyl ether soluble part was also washed with aq. 1*N* NaOH and distilled again by using a Kugelrohr apparatus (120°C, 0.3 mmHg) to give **6** (12.8 mg, 4.4%). **5**: MS (70 eV) m/z (rel. intensity) 140 (M^+, 16), 125 (2), 110 (4), 96 (100), 84 (33), 82 (30), 57 (38); ^1H NMR ($CDCl_3$) δ 2.38 (s, 6H, CH_3), 2.64 (s, 4H, NCH_2CH_2N), 3.28 (s, 4H, $NCH_2C=C$), 4.95 (s, 2H, $CH_2=C$); ^{13}C NMR ($CDCl_3$, ppm) 45.63 (NCH_3), 57.94 (NCH_2CH_2N), 62.48 ($NCH_2C=C$), 113.50 ($CH_2=C$), 145.46 ($CH_2=C$). **6**: MS (70 eV) m/z (rel. intensity) 280 (M^+, 0.96), 265 (0.43), 198 (2.6), 139 (16), 110 (46), 96 (95), 84 (51), 58 (100); ^1H NMR ($CDCl_3$) δ 2.11 (s, 12H, CH_3), 2.48 (s, 8H, NCH_2CH_2N), 3.01 (s, 8H, $NCH_2C=C$), 4.95 (s, 4H, $CH_2=C$); ^{13}C NMR ($CDCl_3$, ppm) 42.29 (NCH_3), 54.45 (NCH_2CH_2N), 61.26 ($NCH_2C=C$), 115.50 ($CH_2=C$), 146.04 ($CH_2=C$).

(E,E)-1,4-Bis(3-acetoxy-1-propenyl)benzene (**7**)

The monomer **7** was prepared according to the following three steps:

(1) To a solution of 1,4-dibromobenzene (9.4 g, 40 mmol), Pd $(OAc)_2$ (0.18 g, 0.8 mmol), and tri-*o*-tolyphosphine (0.97 g, 3.2 mmol) in DMF (100 ml) were added tri-*n*-butylamine (42 ml, 176 mmol) and methyl acrylate (7.9 ml, 88 mmol). After 10 h at 110°C, the mixture was poured into water to precipitate the product, (*E,E*)-1,4-bis[2-(methoxycabonyl)ethenyl]-benzence, which was collected by filtration and recrystallized from ethyl acetate (3.47 g, 35%, mp 156—159°C).

(2) A hexane solution of diisobutylaluminum hydride (1.04 M, 50 ml, 52 mmol) was added dropwise to (*E,E*)-1,4-bis[2-(methoxycarbonyl)ethenyl]-benzene (3.2 g, 13 mmol) in benzene

(50 ml) at 40°C for 1 h. After further 2 h, CH_3OH (6.4 ml, 157 mmol) and then aq. NaOH were slowly added with ice cooling. The precipitate, (*E,E*)-1,4-bis(3-hydroxy-1-propenyl)benzene, was collected by filtration, washed with diluted aq. HCl, and dried *in vacuo* (2.1 g, 86%).

(3) Acetyl chloride (2.4 ml, 34 mmol) was added to a solution of (*E,E*)-1,4-bis(3-hydroxy-1-propenyl)benzene (1.8 g, 9.4 mmol) and pyridine (3.3 ml, 41 mmol) in CH_2Cl_2 (50 ml) at 0°C and stirred at room temperature for 3 h. The reaction mixture was poured into water to precipitate the product, which was collected and purified with a silicagel column (hexane–EtOAc = 3 : 2, v/v) to give **7** (0.64 g, 25%): ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 6H, $CH_3C{=}O$), 4.70 (d, 4H, J = 5.2 Hz, $CH_2CH{=}C$), 6.15—6.85 (m, 4H, $CH{=}CH$), 7.25 (s, 4H, C_6H_4); IR (KBr, cm^{-1}) 1720, 1600, 1220.

1,4-Bis(1-acetoxy-2-propenyl)benzene (**8**)

The monomer **8** was prepared according to the following two steps:

(1) A THF solution of vinyl magnesium bromide (1 M, 120 ml, 0.12 mmol) was added dropwise to terephthalaldehyde (6.71 g, 50 mmol) in THF (400 ml) at 0°C for 30 min. After 2 h at room temperature, ammonium chloride (6.4 g) in water (100 ml) was carefully added to the reaction mixture with ice cooling. The separated organic layer was concentrated to give the residue, which was dissolved in diethyl ether and dried over $MgSO_4$. Removal of the solvent gave an oily crude product which was crystallized slowly in a refrigerator to give pure 1,4-bis(1-hydroxy-3-propenyl)benzene (2.1 g, 22%). mp 120—122°C; ^{1}H NMR ($CDCl_3$) δ 1.98 (s, 2H, O*H*), 4.9—5.5 (m, 6H, $CHCH{=}CH_2$), 5.7—6.3 (m, 2H, $CH{=}CH_2$). 7.35 (s, 4H, C_6H_4).

(2) A solution of acetyl chloride (1.3 g, 16.6 mmol) in THF (20 ml) was added to 1,4-bis(1-hydroxyl-2-propenyl)benzene (1.3 g, 6.9 mmol) and pyridine (1.57 g, 19.9 mmol) in THF (20 ml) at 0°C and stirred at room temperature for 1 h. After additional 1 h at 40°C, the work-up was carried out in the usual manner. The crude product was purified with a silicagel column (hexane–EtOAc = 3 : 2, v/v) to give **8** (1.46 g, 78%): mp 40—42°C; ^{1}H NMR ($CDCl_3$) δ 2.09 (s, 6H, $CH_3C{=}O$), 5.01—5.40 (m, 4H, $CH{=}CH_2$), 5.75—6.30 (m, 2H, $CH{=}CH_2$), 6.28 (d, 2H, J = 4.8 Hz, $CHCH{=}C$), 7.36 (s, 4H, C_6H_4).

A Typical Procedure for the Polycondensation between **7** *(or* **8***) and Amines*

To a solution of $Pd_2(dba)_3 \cdot CHCl_3$ (20.7 mg, 0.02 mmol), Ph_3P (21.0 mg, 0.08 mmol) and **8** (273 mg, 1 mmol) in THF (1 ml) were added DMEDA (88 mg, 1 mmol) and Et_3N (304 mg, 3 mmol). After 17 h at 25°C, the reaction mixture was poured into diethyl ether to precipitate the polymer **PA3** (223 mg, 91%). Further purification was carried out by reprecipitation from $CHCl_3$ to CH_3OH. **PA3**: ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 6H, CH_3), 2.58 (s, 4H, NCH_2CH_2N), 3.19 (d, 4H, J = 4.2 Hz, $NCH_2C{=}C$), 6.3—6.7 (m, 4H, $CH{=}CH$), 7.34 (s, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$, ppm) 42.61 (*N*CH3), 55.06 (NCH_2CH_2N), 60.70 ($NCH_2C{=}C$), 126.57 (benzene ring), 127.25 (vinylene group), 132.23 (vinylene group), 136.33 (benzene ring); IR (KBr, cm^{-1}) 3020, 2940, 2830, 2765, 1670, 1510, 1360, 1020, 960, 850, 740. **PA4**: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3H, J = 6.0 Hz, CH_3), 1.43 (br, 4H, $CH_2CH_2CH_3$), 2.52 (br, 2H, NCH_2CH_2), 3.28 (d, 4H, J = 4.2 Hz, $NCH_2C{=}C$), 6.3—6.7 (m, 4H, $CH{=}CH$), 7.34 (s, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$, ppm) 13.70 (CH_3), 20.30 (CH_2CH_3), 28.49 (NCH_2CH_2), 52.74 (NCH_2CH_2), 55.84 ($NCH_2C{=}C$), 127.21 (benzene ring), 129.00 (vinylene group), 133.69 (vinylene group), 137.07 (benzene ring); IR (KBr, cm^{-1}) 3020, 2940, 2850, 2785, 1675, 1600, 1505, 1450, 1355, 1100, 960, 850, 740.

A Typical Procedure for the Reaction of **1b** *with Tosylamide*

A solution of **1b** (204 mg, 1 mmol), tosyl-

amide (171 mg, 1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (5.2 mg, 0.005 mmol), and Ph_3P (10.5 mg, 0.04 mmol) in THF (1.6 ml) was stirred at 25°C for 15 h. The reaction mixture was poured into diethyl ether (50 ml) to precipitate the product polymer **PA5**, which was collected by centrifugation and dried *in vacuo* (110 mg, 49%): ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H, CH_3), 3.62 (s, 4H, $NCH_2C{=}C$), 4.99 (s, 2H, $C{=}CH_2$), 7.27 (d, 2H, J=8.4 Hz, *ortho* protons for the CH_3 group), 7.66 (d, 2H, J=8.4 Hz, *ortho* protons for the SO_2 group).

The diethyl ether soluble portion was subjected to preparative TLC (CH_2Cl_2–EtOAc=30:1, v/v; Rf=0.54) to give the mixture of the cyclic oligomers **9** and **10** (**9**:**10**=64:36, 28 mg, 13%): MS (70 eV) *m/z* (rel. intensity) 446 (M^+ of **9**, 4.5), 291 (100), 277 (31), 149 (45), 135 (50), 91 (100), 57 (85), 44 (87); ^{1}H NMR ($CDCl_3$) δ 2.43 (s, CH_3 of **9** and **10**), 3.76 (s, $NCH_2C{=}C$ of **10**), 3.82 (s, $NCH_2{=}C$ of **9**), 5.04 (s, $C{=}CH_2$ of **10**), 5.19 (s, $C{=}CH_2$ of **9**), 7.31 (d, J=8.02 Hz, *ortho* protons for the CH_3 group of **9** and **10**), 7.67 (m, *ortho* protons for the SO_2 group).

The Reaction of **1b** *with N,N'-Ditosylethylene(or trimethylene)diamine*

A solution of **1b** (204 mg, 1 mmol), *N,N'*-ditosylethylenediamine (368 mg, 1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (5.2 mg, 0.005 mmol), and Ph_3P (10.5 mg, 0.04 mmol) in THF (2 ml) was stirred at 25°C for 24 h. GPC analysis of the diethyl ether insoluble portion of the reaction mixture indicated that a very small amount of the linear polymer was contained, so that both of the diethyl ether insoluble and soluble portions were subjected to preparative TLC (CH_2Cl_2–EtOAc=50:1, v/v). Then, the cyclic oligomers **11a** (Rf=0.53, 223 mg, 53%) and **12a** (Rf=0.44, 67 mg, 16%) were isolated.

According to the same procedure (the eluent for TLC: CH_2Cl_2–EtOAc=30:1, v/v), the reaction of **1b** with *N,N'*-ditosyltrimethylenediamine gave **11b** (Rf= 0.53, 182 mg, 42%) and **12b** (Rf=0.34, 18 mg, 4%). **11a**: mp 158—159°C; MS (20 eV) *m/z* (rel. intensity) 420 (M^+, 0.6), 265 (M^+–Ts, 100), 110 (10), 109 (10), 91 (9), 82 (10); ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 6H, CH_3), 3.39 (s, 4H, NCH_2CH_2N), 3.89 (s, 4H, $NCH_2C{=}C$), 5.13 (s, 2H, $C{=}CH_2$), 7.29 (d, 4H, J=8.4 Hz, *ortho* protons for the CH_3 group), 7.66 (d, 4H, J=8.4 Hz, *ortho* protons for the SO_2 group). **12a**: mp 230—231°C; MS (20 eV) *m/z* (rel. intensity) 685 (M^+–Ts, 100), 375 (51), 279 (20), 91 (47); ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 12H, CH_3), 3.13 (s, 8H, NCH_2CH_2N), 3.56 (s, 8H, $NCH_2C{=}C$), 5.26 (s, 4H, $C{=}CH_2$), 7.39 (d, 8H, J=8.4 Hz, *ortho* protons for the CH_3 group), 7.80 (d, 8H, J=8.4 Hz, *ortho* protons for the SO_2 group). **11b**: mp 199—200°C; MS

Table I. Polycondensation between **1** and piperazine catalyzed by a palladium complex[a]

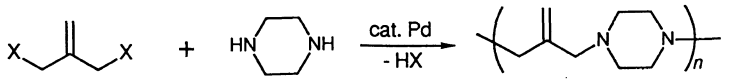
Run	1	Base[b]	Catalyst (mol%)[c]	Solvent	Time / h	Yield[d] / %	$\bar{M}_n$[e]
1	**1a**	Et_3N	Pd (acac)$_2$/2dppe (1)	THF	5	13	680
2	**1a**	DBU	Pd (acac)$_2$/2dppe (1)	THF	5	86	2100
3	**1b**	none	Pd_2 (dba)$_3 \cdot CHCl_3$/2dppe (1)	THF	5	62	3800
4	**1b**	none	Pd_2 (dba)$_3 \cdot CHCl_3$/2dppe (1)	$CHCl_3$	50	47	780
5	**1c**	none	Pd (acac)$_2$/2dppe (2)	THF	20	0	

[a] [**1**]=[piperazine]=0.4—0.5 mol l^{-1}; reaction temperature, 50°C.
[b] 3 equiv. for **1**.
[c] Mol% for **1**; acac=acetylacetonate; dba=dibenzylideneacetone; dppe=bis(diphenylphosphino)ethane.
[d] Insoluble polymer in CH_3OH (Run 1, 2, and 4) or in Et_2O (Run 3).
[e] VPO at 40°C in $CHCl_3$.

(20 eV) *m/z* (rel. intensity) 434 (M^+, 0.5), 279 ($M^+ - Ts$, 100), 155 (7), 108 (11), 96 (12), 82 (12), 44 (13); ^1H NMR ($CDCl_3$) δ 1.97 (quin, 2H, J=6.0 Hz, $CH_2CH_2CH_2$), 2.42 (s, 6H, CH_3), 3.32 (t, 4H, J=6.0 Hz $CH_2CH_2CH_2$), 3.78 (s, 4H, $NCH_2C{=}C$), 5.32 (s, 2H, $C{=}CH_2$), 7.35 (d, 4H, J=8.4 Hz, *ortho* protons for the CH_3 group), 7.72 (d, 4H, J=8.4 Hz, *ortho* protons for the SO_2 group). **12b**: mp 250—251°C; MS (20 eV) *m/z* (rel. intensity) 713 ($M^+ - Ts$, 29), 504 (60), 450 (24), 238 (30), 155 (85), 91 (100); ^1H NMR ($CDCl_3$) δ 1.8 (m, 4H, $CH_2CH_2CH_2$), 2.44 (s, 12H, CH_3), 3.11 (br t, 8H, J=6.6 Hz, CH_2CH_2-CH_2), 3.66 (s, 8H, $NCH_2C{=}C$), 5.28 (s, 4H, $C{=}CH_2$), 7.35 (d, 4H, J=8.4 Hz, *ortho* protons for the CH_3 group), 7.70 (d, 4H, J=8.4 Hz, *ortho* protons for the SO_2 group).

RESULTS AND DISCUSSION

Polycondensation between **1** *and Piperazine*



1a, X = $OCOCH_3$
1b, X = OCO_2CH_3
1c, X = OH

PA 1

The polymerization took place in THF at 50°C in the presence of a catalytic amount of a palladium complex with dppe ligand (Table I). The reaction of the diacetate **1a** required a base to trap liberated acetic acid. When Et_3N was employed, the AcOH salt of piperazine was precipitated to retard the polymerization. Thus, the stronger base, *i.e.*, DBU was required to produce the polyamine **PA1**. On the other hand, the dicarbonate **1b** was polymerized with piperazine without base, since the liberated products were methanol and carbon dioxide. An attempt of the polycondensation of the diol **1c** with piperazine resulted in recovering the starting materials, though allylic alcohol has been known to function as the substrates for the palladium catalyzed amination.[9] The molecular weight of the product polyamine was not high owing probably to the precipitation of the polymer during the reaction. The reaction in $CHCl_3$, in which the polymer was soluble, was very slow.

The Reaction of **1a** *with Primary Amines and Acyclic Secondary Diamines*

When the amine monomer was a primary

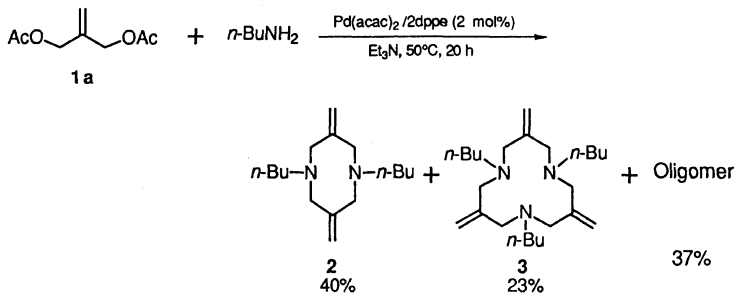
Table II. Effect of a catalyst on the reaction of **1a** with aniline[a]

Run	Catalyst (mol%[b])	Time	Polymer		4
			Yield[c]	$\bar{M}_n$[d]	Yield[e]
		h	%		%
1	Pd $(acac)_2$/2dppe (4)	55	48	1200	20
2	Pd $(acac)_2$/dppe (4)	55	7		
3	$Pd_2(dba)_3 \cdot CHCl_3$/4dppe (2)	55	7		27
4	$Pd_2(dba)_3 \cdot CHCl_3$/2dppe (2)	55	66	1200	20
5	$Pd_2(dba)_3 \cdot CHCl_3/4Ph_3P$ (2)	20	75	1700	
6	$Pd_2(dba)_3 \cdot CHCl_3/4Ph_3P$ (2)	55	78	2300	13

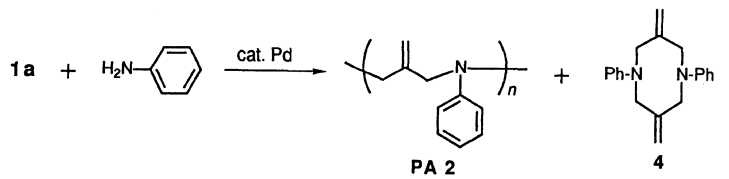
[a] In THF (2 mmol of the each monomer in 2 ml) at 50°C; base, Et_3N (3 equiv. for **1a**).
[b] Mol% for **1a**.
[c] Insoluble part in CH_3OH.
[d] VPO at 40°C in $CHCl_3$.
[e] The content in the rection mixture on the basis of the ^1H NMR spectra.

amine or an acyclic secondary amine in the place of piperazine, cyclic oligomers were produced along with linear oligomers.

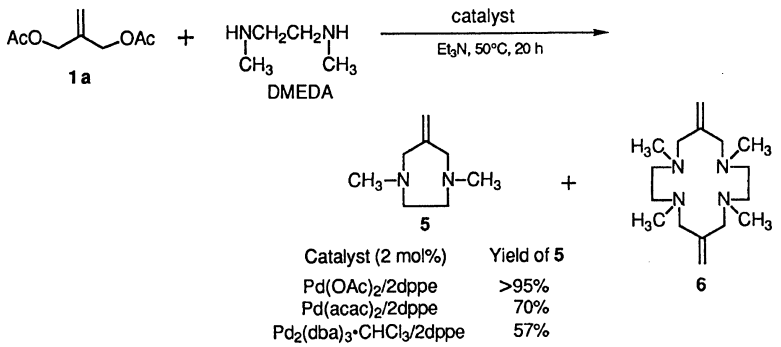
The ^{1}H NMR spectrum of the reaction mixture of **1a** with *n*-butylamine showed three peaks at δ 3.24, 3.15, and 2.89, which were assignable to methylene protons between the nitrogen atom and the C=C double bond. To pour the reaction mixture into hexane gave no precipitation of a polymeric material. On the other hand, distillation of the hexane soluble portion gave cyclic oligomers, the eight-membered cyclic diamine **2** and the twelve-membered cyclic triamine **3**, whose structures were established by the ^{1}H and ^{13}C NMR spectra as well as by mass spectra. The original contents of three species in the reaction mixture were respectively 40% for **2**, 23% for **3**, and 37% for other oligomers (cyclic and linear) on the basis of the relative intensity among the above three peaks in the ^{1}H NMR spectrum of the reaction mixture.



The catalyst influences the reaction rate and the products proportion. Table II shows the results of the reaction of **1a** with aniline with some different catalysts. The ratio of dppe as a ligand to a Pd atom had an opposite effect on the catalytic activity of $Pd(acac)_2$ and $Pd_2(dba)_3 \cdot CHCl_3$. The addition of two molar equivalents of dppe to saturate the four coordination sites of a Pd atom made the reaction faster as for $Pd(acac)_2$ but slower as for $Pd_2(dba)_3 \cdot CHCl_3$. It is assumed that two molar equivalents of dppe is required for the reduction of $Pd(acac)_2$ to a Pd(0) complex that actually works as the catalyst. A monodentate ligand, Ph_3P, enhances the catalyst activity more than a bidentate ligand, dppe, when $Pd_2(dba)_3 \cdot CHCl_3$ is employed. However, the degree of polymerization of the methanol insoluble polymers **PA2** was not high, while GPC curve was unimodal showing no contamination with cyclic oligomers. A cyclic diamine **4** was isolated from the methanol soluble portion. The ^{1}H NMR spectroscopy indicated that the terminal groups of the precipitated **PA2** were occupied predominantly with the aniline residues rather than with the acetate ones.



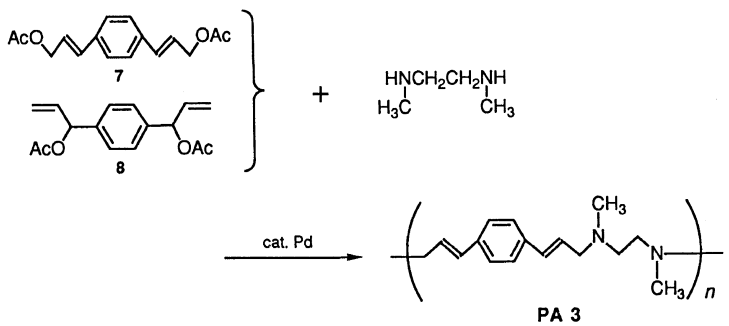
The nature of catalyst exerts a significant influence also on the products proportion of the reaction of **1a** with *N*,*N*′-dimethylethylenediamine (DMEDA).



$Pd(OAc)_2$/2dppe as the catalyst gave rise to a quantitative yield of a seven-membered cyclic diamine **5**, whereas the reactions catalyzed with $Pd(acac)_2$/2dppe and $Pd_2(dba)_3 \cdot CHCl_3$/2dppe gave **5** in lower yields along with some amount of linear oligomers and small amount (3—4%) of a fourteen-membered cyclic triamine **6**. The difference of the starting Pd(II) catalyst which is reduced *in situ* to an actual catalyst Pd(0) complex, assumably varies a structure of the active center of the π-ally palladium intermediate to change the products proportion. On the other hand, when the amine monomer was *N*,*N*′-dimethyltrimethylenediamine, cyclic products were not detected but hexane soluble linear oligomer was produced.

Polycondensation between Allylic Diacetate **7** *(or* **8***) Consisting of a 1,4-Phenylene Skeleton and Amines*

To exclude the preceding cyclization, the allylic diacetate **7** and **8** incorporating a 1,4-phenylene skeleton were employed. The polymerization of **7** (or **8**) with DMEDA were carried out at 25°C and at 50°C to produce a linear polyamine in high yields (Table III).



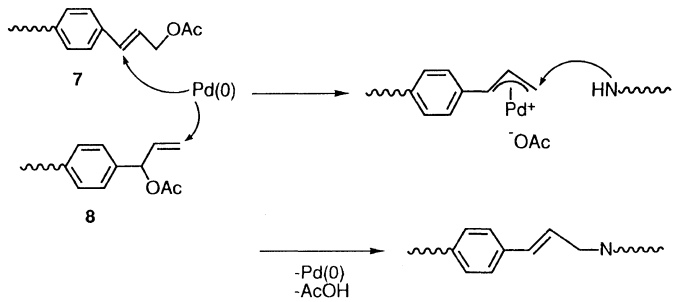
The spectroscopic data indicated that the polyamine **PA3** prepared from **7** consisted of the same units as that from its regio-isomer **8**. For example, the IR spectra of the both polymers from **7** and **8** with DMEDA showed an strong absorption band at 960 cm^{-1} due to an out-of-plane C–H bending vibration of *trans*-1,2-disubstituted olefin. This observation is taken to assume that the oxidative additions of a Pd (0) complex to **7** and to **8** generated the common π-allyl palladium intermediate, subsequently, in which less hindered carbon atom was attacked by the amine moiety (*vide infra*). However, **8** was more reactive than **7** to produce higher molecular weight polymer, which was partially soluble in $CHCl_3$, within shorter time (Run 1, 2). This is due to the faster generation of the π-allyl palladium inter-

Table III. Polycondansation between **7** (or **8**) and amines catalyzed by a palladium complex[a]

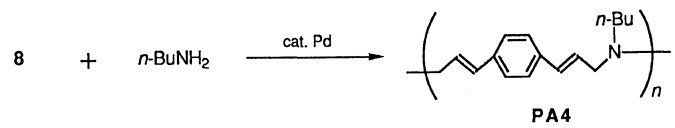
Run	Monomers	Catalyst (mol%[b])	Temp / °C	Time / h	Yield[c] / %	$\bar{M}_n$[d]
1	**7**, DMEDA	$Pd_2(dba)_3 \cdot CHCl_3/4Ph_3P$ (2)	25	25	85	3400
2	**8**, DMEDA	$Pd_2(dba)_3 \cdot CHCl_3/4Ph_3P$ (2)	25	17	91	4700[e]
3	**8**, DMEDA	$Pd_2(dba)_3 \cdot CHCl_3/4Ph_3P$ (2)	50	20	88	6300[e]
4	**8**, *n*-$BuNH_2$	$Pd(acac)_2$/2dppe (4)	50	20	78	4100[e]

[a] In THF (1 mmol of the each momoner in 1 ml); base, Et_3N (3 equiv. for **7** (or **8**)).
[b] Mol % for **7** (or **8**).
[c] Insoluble polymer in CH_3OH.
[d] VPO at 40°C in $CHCl_3$.
[e] $CHCl_3$ soluble polymer, which was 56% (Run 2), 73% (Run 3), and 76% (Run 4) of the product polymer, respectively.

mediate from **8** than from **7**. It has been reported that the oxidative addition of Pd (0) to an allylic compound proceeds via a S_N2' type reaction.[10] Accordingly, **8** is favorable for the oxidative addition at the less hindered vinylic carbon.



As expected, the polymerization of **8** with *n*-butylamine also produced the polyamine **PA4** in a good yield.



PA4

The polyamines **PA3** and **PA4** prepared from **8** contained a $CHCl_3$ insoluble part of higher molecular weight polymer, which was completely soluble in an acidic solvent, *e.g.*, acetic acid and showed the identical IR spectra with the $CHCl_3$ soluble part.

Reaction of **1b** *with Tosylamide and N,N'-Ditosylated Diamine*

It has been known that tosylamide reacts with an allylic epoxide with the aid of a palladium catalyst under mild and neutral comditions without base.[11] In the present study, the reaction of **1b** with tosylamide and with *N,N'*-ditosylethylene(or trimethylene)diamine were carried out.[12] As compared with the

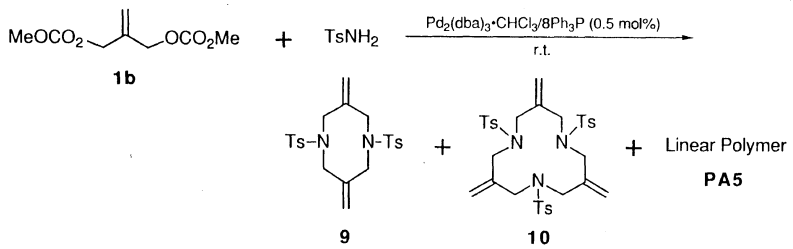
Table IV. Reaction of **1b** with tosylamide catalyzed by a palladium complex[a]

Run	Solvent	Mol% of Cat.[b]	Time / h	Polymer[c] Yield / %	Polymer[c] $\bar{M}_n$[d]	**9** and **10** Yield[e] / %	(**9**:**10**)[f]
1	THF	0.5	15	49	4400	13	(64:36)
2	THF	1.5	44	47	3200	32	(66:36)
3	CH_3CN	0.5	48	3		28	(72:28)

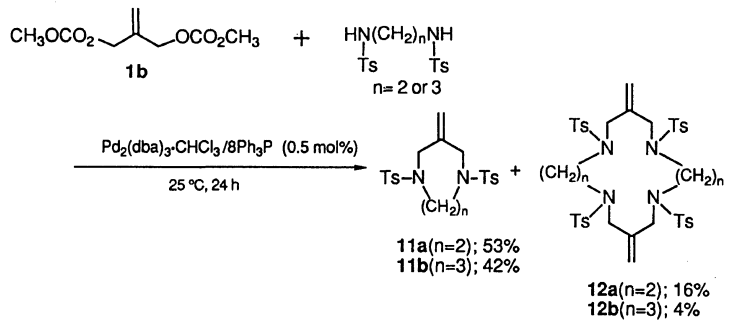
[a] In THR (1 mmol of monomers in 1.6 ml) at room temperature; cat., $Pd_2(dba)_3 \cdot CHCl_3/8Ph_3P$.
[b] For tosylamide.
[c] Et_2O insoluble polymer.
[d] VPO at 40°C in $CHCl_3$.
[e] Separated by TLC.
[f] Based on the ^1H NMR spectra of the mixture of **9** and **10**.

reaction of **1a** with the related amines, the reaction proceeded at room temperature without base and gave the different products proportion of linear polymers and cyclic oligomers, which is partly due to the structural difference of sulfonamide monomers from amine monomers: the former molecules are planar around the N atom, whereas the latter molecules are tetrahedral.

As shown in Table IV, **1b** reacted with tosylamide to produce the linear polymer **PA5** along with the cyclic oligomers **9** and **10**. The proportion of the cyclic products is rather smaller than that given by the reaction of **1a** with primary amines, while the product polymer had the higher degrees of polymerization. The cyclic products **9** and **10** were isolated by preparative TLC as the mixture, in which the ratio of **9** and **10** was determined by the ^1H NMR spectrum. Although the mass spectrum detected only the parent peak due to **9** but not due to **10**, the GPC analysis showed two clear peaks which were assignable to **9** and **10**, respectively. THF was a better solvent than CH_3CN to promote the reaction. Increase of the amount of the catalyst increased the yield of the cyclic products.



The reaction of *N,N'*-ditosylethylene(or trimethylene)diamine with **1b** produced cyclic oligomers much predominantly. The GPC analysis of the diethyl ether insoluble portion indicated that the production of a polymeric material was minor, whereas that cyclic oligomers, which were properly contained also in the diethyl ether soluble portion, were mainly produced. Then, the cyclic oligomers, **11a**, **12a**, **11b**, and **12b**, were isolated, respectively.



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