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The synthesis of polyesters with a biphenyl skeleton by palladium catalyzed carbonylation–polycondensation

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Abstract

For synthesizing heat-resistant polyesters, the one step synthesis of biphenyl-containing polyesters was developed from palladium-catalyzed carbonylation–polycondensation of dihalobiphenyls and bisphenols. Reaction parameters, such as base, solvent, palladium–phosphine catalyst and CO pressure in the reaction of 2,7-dibromo-9,10-dihydrophenanthrene and 4,4′-(1-methylethylidene)bisphenol (bisphenol A), were found to affect the molecular weight of poly[oxy-1,4-phenylene(1-methylethylidene)-1,4-phenyleneoxycarbonyl-(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (**2**). The solution after the reaction was homogeneous when high molecular weight polyester was formed. The use of strong base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) yielded high molecular weight polyesters. Key step for the reaction is considered the alcoholysis step. High nucleophilicity of phenoxide anion formed from the phenol moiety and DBU enhanced the step to increase the rate of the carbonylation–polycondensation. The use of palladium catalyst with PPh_3 gave higher molecular weight polyester than that with $Ph_2P(CH_2)_3PPh_2$ in spite of higher catalytic activity of the latter catalyst. This is due to higher termination rate caused by the carbonylation of chlorobenzene for the latter catalyst. Under optimum conditions, polyester **2** was obtained in 95% yield with high molecular weight (polystyrene equivalent $M_w = 102\,600$). Bisphenols with sufficiently bulky alkyl spacers, such as 4,4′-cyclohexylidenebisphenol, 4,4′-(*s*-butylidene)bisphenol, 4,4′-(1-phenylethylidene) bisphenol, 4,4′-ethylidenebisphenol, 4,4′-methylidenebis(2,6-dimethylphenol) and 4,4′-(1-methylethylidene)bis(2,6-dimethylphenol) gave polyesters with high to moderately high molecular weight. On the basis of a thermal analysis, 5% weight loss temperature (T_5) and 10% weight loss temperature (T_{10}) of **2** in air was 394 and 414°C, respectively.

Keywords: Synthesis; Polyester; Biphenyl skeleton; Palladium catalysis; Carbonylation–polycondensation

1. Introduction

Polymers with a skeleton of polynuclear aromatics are expected to be candidates for producing materials with high degrees of molecular orientation and order that should result in superior mechanical strength and high heat resistance [1–3]. Biphenyl derivatives are promising components for advanced materials such as heat-resistant polymers and liquid crystalline polymers. Co-polyesters based on terephthalic acid, isophthalic acid and bisphenol A have been used in practice because they are heat-resistant and transparent [3]. Wholly aromatic polyesters containing a biphenyl-4,4′-di-

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carboxylate moiety in place of terephthalate and isophthalate moieties must have a high potential for heat-resistance. For this reason, we tried to synthesize biphenyl-containing polyesters. Among several synthetic methods, the carbonylation–polycondensation method developed originally by Imai and co-workers [4,5], and subsequently by Perry and co-workers [6–8] based on the Heck reaction [5] is the most straightforward way to reach the target polyesters.

In this paper, we report first the efficient phenoxycarbonylation of 4-bromobiphenyl (BBP) to demonstrate the applicability of the carbonylation–polycondensation. Then, we describe the successful synthesis of polyesters with a biphenyl skeleton by palladium-catalyzed carbonylation–polycondensation of dihalobiphenyls and bisphenols. Especially, the introduction of 9,10-dihydrophenanthrene moiety was found to afford highly soluble polyesters in organic solvent. This is advantageous for polyester formation by carbonylation–polycondensation in solution and for molding the resulting polyesters.

2. Experimental

2.1. Materials

2,7-Dibromo-9,10-dihydrophenanthrene (DBDHP) and 2,7-diiodo-9,10-dihydrophenanthrene (DIDHP) were prepared from 9,10-dihydrophenanthrene by reported methods [10,11]. 4-Bromobiphenyl (BBP), 4,4′-dibromobiphenyl (DBBP) and 4,4′-diiodobiphenyl (DIBP) were obtained from Aldrich Japan, Tokyo, Japan, and purified by recrystallization from toluene. Triphenylphosphine (PPh_3), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), 1,5-bis(diphenylphosphino)pentane (dpppe) and 1,6-bis(diphenylphosphino)hexane (dpph) were obtained from Strem Chemicals, USA and used without further purification. All other materials were purchased commercially and were used with the appropriate purification.

2.2. Measurements

Gas chromatographic analysis was performed on a Shimadzu GC-14A instrument, equipped with a flame ionization-detector, using a capillary column of Hewlett Packard Ultra-1 (0.2 mm × 12 m). Mass spectra were recorded on a Hewlett-Packard model 5890 series II equipped with a 5971A mass selective detector system, using a capillary column of GL Science Neutrabond-1 (0.25 mm × 25 m). IR spectra were recorded on a Perkin-Elmer 1720X FT-IR spectrometer. NMR spectra were obtained on a Bruker AC200 FT-NMR spectrometer. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) were determined by means of gel permeation chromatography (GPC) based on a polystyrene calibration on a Yokogawa HPLC model LC100 System (column, TOSOH TSK-GEL G4000HHR; eluent, chloroform or chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) = 3/1 (v/v); detection, UV (254 nm)). Thermal characteristics were studied with a Mettler FP800 thermal analysis system and a MAC Science TG-DTA 2000 apparatus.

2.3. Phenoxycarbonylation of BBP

In a 50-ml stainless-steel autoclave were placed 582.8 mg (2.5 mmol) of BBP, 282.3 mg (3.0 mmol) of phenol, 8.9 mg (0.05 mmol) of $PdCl_2$, 41.2 mg (0.1 mmol) of dppp, 388.3 mg (1.25 mmol) of docosane (internal standard), 5 ml of benzene, and 0.41 ml (2.75 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Carbon monoxide was introduced at an initial pressure of 0.6 MPa and then heated with stirring at 100°C in an oil bath for 2 h. After excess carbon monoxide was purged, the mixture was diluted with chloroform. Phenyl biphenyl-4-carboxylate (**1a**) and BBP were found in the mixture by GC analysis. They were separated by column chromatography on silica gel (eluent: hexane–chloroform followed by chloroform) to give 54 mg (9%) of BBP and 620 mg (90%) of **1a**. **1a** was recrystallized from benzene–hexane and obtained as colorless pillars: mp 161.0–161.5°C. *Anal.* Found: C, 83.44; H, 5.02%. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14%. MS *m/z*: 274 (M^+), 181 ($M^+ - OPh$). IR (KBr): 1730 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.22–7.32 (3 H, m), 7.37–7.53 (5 H, m), 7.63–7.68 (2 H, m), 7.73 (2 H, dt, $J = 8.4$, 1.7 Hz), 8.27 (2 H, dt, $J = 8.4$ Hz, 1.7 Hz). ^{13}C NMR ($CDCl_3$) δ: 121.72 (2 CH), 125.86 (CH), 127.21 (2 CH), 127.31 (2 CH), 128.28 (C), 128.28 (CH), 128.97 (2 CH), 129.48 (2 CH), 130.69 (2 CH), 139.86 (C), 146.31 (C), 150.99 (C), 165.05 (C = O).

Phenoxycarbonylation of BBP with *o*-methylphenols, 2,3- and 2,5-dimethylphenols and 2,4,6-trimethylphenol was carried out by a similar procedure and the products afforded satisfactory analytical and spectral data.

2.4. Typical procedure for the carbonylation–polycondensation

In a 50-ml stainless steel autoclave equipped with a magnetic stirrer were placed 845.1 mg (2.5 mmol) of DBDHP, 570.7 mg (2.5 mmol) of 4,4′-(1-methylethylidene)bisphenol (bisphenol A), 17.7 mg (0.1 mmol) of $PdCl_2$, 104.9 mg (0.4 mmol) of PPh_3, 10 ml of chlorobenzene, and 0.82 ml (5.5 mmol) of DBU. Carbon monoxide was introduced at an initial pressure of 1.1 MPa and then heated with vigorous stirring at 130°C in an oil bath for 3 h. After excess carbon monoxide was purged, the mixture was poured into 100 ml of methanol. The precipitated polymer was separated from methanol by decantation, dissolved in 50 ml of chloroform, and then poured into 100 ml of methanol again with stirring. The resulting polymer was filtered, washed with 100 ml of methanol, and dried in vacuo to afford poly[oxy-1,4-phenylene(1-methylethylidene)-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (**2**) as a white or pale green–yellow solid. The yield was 1.09 g (95%). M_w and M_w/M_n determined by GPC were 102600 and 2.5, respectively. The 10% weight loss temperature (T_{10}) was 414°C and the 5% weight loss temperature (T_5) was 394°C in air. *Anal.* Found: C, 79.93; H, 5.09; Br, 1.35%. Calcd for $(C_{31}H_{24}O_4)_n$: C, 80.85; H, 5.25%. IR (KBr) 1733, 1612, 1505, 1278, 1259, 1206, 1175, 1158, 1073, 1016, 752 cm^{-1}. ^1H NMR ($CDCl_3$) δ = 1.74 (m, CH_3), 3.02 (br s, CH_2), 7.16 and 7.33 (2 d, $J = 8.7$ Hz, O-Ar-*H*), 7.94 and 8.17 (2 d, $J = 8.2$ Hz, C*H* = C*H*-C-C = O), and 8.12 (s, CH_2-C-C*H*); intensity ratio: 6:4:8:4:2. ^{13}C NMR ($CDCl_3$) δ = 28.62 (CH_2), 31.00 (CH_3), 42.58 (*C*-CH_3), 121.07 (*C*H = C-O), 124.57 (*C*H = CH-C-C = O), 127.95 (*C*-C = O), 129.01 (*C*H-C-C = O), 129.20 (*C* = C-CH_2), 130.02 (*C*H-C-CH_2), 138.22 and 138.35 (*C*-CH = *C*-C = O), 148.03 (*C*-C-CH_3), 148.80 (*C*-O-C = O), and 165.00 (*C* = O).

Pertinent analytical and spectral data are shown below.

2.4.1. Poly[oxy-1,4-phenylene(1-methylethylidene)-1,4-phenyleneoxycarbonyl(4,4′-biphenylylene)carbonyl] (3)

$M_w = 11600$ ($M_w/M_n = 2.5$). T_5 (air) = 415°C. T_{10} (air) = 434°C. *Anal.* Found: C, 79.14; H, 4.81; I, 4.00%. Calcd for $(C_{29}H_{22}O_4)_n$: C, 80.17; H, 5.10%. IR (KBr): 2969, 1735, 1607, 1505, 1263, 1206, 1069, 1016, 1006, 752 cm^{-1}.

2.4.2. *Poly[oxy-1,4-phenylene(1-methylethylidene)-1,4-phenyleneoxyterephthaloyl]* (**4**)

$M_w = 2600$ ($M_w/M_n = 2.5$). T_5 (air) = 394°C. T_{10} (air) = 429°C. *Anal.* Found: C, 76.07; H, 5.04; Br, 1.65%. Calcd for $(C_{23}H_{18}O_4)_n$: C, 77.08; H, 5.06%. IR (KBr) 2970, 1741, 1503, 1411, 1268, 1248, 1202, 1171, 1071, 1017, 876, 811, 728 cm^{-1}.

2.4.3. *Poly[oxy-1,4-phenylenecyclohexylidene-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl]* (**5**)

$M_w = 20200$ ($M_w/M_n = 3.1$). T_5 (air) = 375°C. T_{10} (air) = 389°C. *Anal.* Found: C, 80.21; H, 5.51; Br, 1.49%. Calcd for $(C_{34}H_{28}O_4)_n$: C, 81.58; H, 5.64%. IR (KBr) 2936, 2858, 1735, 1611, 1505, 1407, 1279, 1259, 1208, 1175, 1158, 1078, 753 cm^{-1}.

2.4.4. *Poly[oxy-1,4-phenylene-s-butylidene-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl]* (**6**)

$M_w = 25100$ ($M_w/M_n = 3.7$). T_5 (air) = 410°C. T_{10} (air) = 440°C. *Anal.* Found: C, 79.82; H, 5.45; Br, 1.51%. Calcd for $(C_{32}H_{26}O_4)_n$: C, 80.99; H, 5.52. IR (KBr) 1732, 1609, 1505, 1259, 1207, 1175, 1072, 1015, 752 cm^{-1}.

2.4.5. *Poly[oxy-1,4-phenylene(1-phenylethylidene)-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl]* (**7**)

$M_w = 12800$ ($M_w/M_n = 3.0$). T_5 (air) = 392°C. T_{10} (air) = 441°C. *Anal.* Found: C, 79.99; H, 4.88; Br, 2.39%. Calcd. for $(C_{36}H_{26}O_4)_n$: C, 82.74; H, 5.01%.IR (KBr) 1733, 1609, 1505, 1436, 1259, 1209, 1171, 1073, 1014, 752, 699 cm^{-1}.

2.4.6. *Poly[oxy-1,4-phenyleneethylidene-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl]* (**8**)

$M_w = 12200$ ($M_w/M_n = 2.7$). T_5 (air) = 365°C. T_{10} (air) = 393°C. *Anal.* Found: C, 79.07. H, 4.82; Br, 2.01%. Calcd for $(C_{30}H_{22}O_4)_n$: C, 80.70; H, 4.97%. IR (KBr) 1732, 1610, 1506, 1436, 1406, 1278, 1260, 1202, 1174, 1079, 1016, 1005, 839, 753 cm^{-1}.

2.4.7. *Poly[oxy-1,4-phenylene(1-trifluoromethyl-2,2,2-trifluoroethylidene)-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl]* (**9**)

$M_w = 3100$ ($M_w/M_n = 2.4$). T_5 (air) = 418°C. T_{10} (air) = 444°C.

2.4.8. *Poly[oxy-1,4-phenyleneisopropylidene-1,4-phenyleneisopropylidene-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl]* (**10**)

$M_w = 4400$ ($M_w/M_n = 2.4$). T_5 (air) = 363°C. T_{10} (air) = 398°C. *Anal.* Found: C, 81.48; H, 5.89; Br, 4.14%. Calcd for $(C_{40}H_{34}O_4)_n$: C, 83.02; H, 5.92%. IR (KBr) 2967, 1732, 1611, 1506, 1406, 1279, 1260, 1207, 1176, 1075, 1016, 1006, 836, 754 cm^{-1}.

2.4.9. *Poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl]* (**11**)

$M_w = 1,200$ ($M_w/M_n = 2.0$). T_5 (air) = 356°C. T_{10} (air) = 418°C. *Anal.* Found: C, 67.92; H, 3.71; Br, 3.35%. Calcd for $(C_{28}H_{18}O_6S)_n$: C, 69.70; H, 3.76%. IR (KBr) 1735, 1585, 1490, 1407, 1279, 1259, 1205, 1152, 1107, 1068, 1005, 838, 751, 716, 696, 663, 583, 557 cm^{-1}.

2.4.10. Poly[oxy-1,4-phenylenethio-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (12)

M_w was not determined because this product was insoluble. T_5 (air) = 382°C. T_{10} (air) = 413°C. *Anal.* Found: C, 73.05; H, 3.92; Br, 4.30%. Calcd for $(C_{28}H_{18}O_4S)_n$: C, 74.65; H, 4.03%. IR (KBr) 1730, 1610, 1584, 1488, 1436, 1405, 1279, 1259, 1201, 1173, 1072, 1014, 837, 753 cm^{-1}.

2.4.11. Poly[oxy-1,4-phenyleneoxy-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (13)

M_w was not determined because this product was insoluble. T_5 (air) = 380°C. T_{10} (air) = 424°C. *Anal.* Found: C, 76.63; H, 4.10; Br, 2.05%. Calcd for $(C_{28}H_{18}O_5)_n$: C, 77.41; H, 4.18%. IR (KBr) 1732, 1611, 1495, 1280, 1258, 1207, 1184, 1078, 1005, 839, 753 cm^{-1}.

2.4.12. Poly[oxy-1,4-(2,6-dimethyl)phenylenemethylidene-1,4-(3,5-dimethyl)phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (14)

$M_w = 15900 (M_w/M_n = 2.3)$. T_{10} (air) = 359°C. T_5 (air) = 340°C. *Anal.* Found: C, 79.56; H, 5.78; Br, 1.34%. Calcd for $(C_{33}H_{28}O_4)_n$: C, 81.13; H, 5.78%. IR (KBr) 1734, 1611, 1485, 1437, 1280, 1259, 1191, 1174, 1158, 1135, 1077, 754 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 2.20$ (t, $J = 7.3$ Hz, CH_3-Ar), 3.05 (s, CH_2-CH_2), 3.89 (br s, Ar-CH_2-Ar), 6.83, 6.93 (small peaks), 6.97 (s, O-Ar-H), 7.96 and 8.22 (2 d, $J = 8.1$ Hz, $CH = CH$-C-C = O), and 8.16 (s, CH_2-C-CH-C-C = O); Intensity ratio: 12:4:2:4:4:2. ^{13}C NMR ($CDCl_3$) $\delta = 16.68$ (6CH_3), 15.91 (CH_3, small peak), 28.63 (2 CH_2), 40.77 (CH_2), 124.64 (2 CH), 128.95 (2 CH), 129.04 (2 C), 129.16 (4 CH), 130.03 (2 CH), 130.21 (4 C), 138.31 (2 C), 138.40 (2 C), 138.58 (2 C), 146.65 (2 C), and 164.26 (2 $C = O$).

2.4.13. Poly[oxy-1,4-(2,6-dimethyl)phenylene(1-methylethylidene)-1,4-(3,5-dimethyl)phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (15)

$M_w = 26600 (M_w/M_n = 1.8)$. T_{10} (air) = 376°C. T_5 (air) = 360°C. *Anal.* Found: C, 80.05; H, 6.15; Br, 1.52%. Calcd for $(C_{35}H_{32}O_4)_n$: C, 81.37; H, 6.24%. IR (KBr) 1736, 1611, 1487, 1280, 1259, 1156, 1110, 1077, 754 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 1.68$ (s, CH_3-C-CH_3), 2.19 (t, $J = 7.4$ Hz, CH_3-Ar), 3.04 (s, CH_2-CH_2), 7.01 (s, O-Ar-H), 7.96 and 8.22 (2 d, $J = 8.3$ Hz, $CH = CH$-C-C = O), and 8.16 (s, CH_2-C-CH-C-C = O); Intensity ratio: 6:12:4:4:4:2. ^{13}C NMR ($CDCl_3$) $\delta = 16.68$ (6 CH_3), 28.66 (2 CH_2), 31.09 (2 CH_3), 42.19 (C-CH_3), 124.64 (2 CH), 127.17 (4 CH), 129.02 (2 CH, 2 C), 129.45 (4 C), 130.03 (2 CH), 138.31 (2 C), 138.40 (2 C), 146.22 (2 C), 148.01 (2 C), and 164.26 (2 $C = O$).

2.5. Phenoxycarbonylation of DBBP with palladium–PPh_3 catalyst

In a 50-ml stainless steel autoclave equipped with a stirrer were placed 780.1 mg (2.5 mmol) of DBBP, 564.7 mg (6.0 mmol) of phenol, 17.7 mg (0.1 mmol) of $PdCl_2$, 104.9 mg (0.4 mmol) of PPh_3, 0.82 ml (5.5 mmol) of DBU, and 10 ml of chlorobenzene. Carbon monoxide was introduced at 1.1 MPa and then heated with vigorous stirring at 120°C in an oil bath for 3 h. After excess carbon monoxide was purged, the mixture was diluted with chloroform. Diphenyl biphenyl-4,4′-dicarboxylate (**19**) and phenyl benzoate (**20**) were detected as carbonylation products by GC analysis. **19** (2.48 mmol, 99%) and **20** (0.044 mmol) were found by analysis using docosane as an internal standard.

2.5.1. Diphenyl biphenyl-4,4′-dicarboxylate (19)

mp 214.5–215.0°C. *Anal.* Found: C, 79.06; H, 4.57%. M^+, 394. Calcd. for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60%. M, 394. IR (KBr) 1730, 1592, 1495, 1289, 1211, 1160, 1090, 843, 749, 693 cm^{-1}. ^1H

NMR ($CDCl_3$) δ = 7.23–7.34 (6 H, m), 7.43–7.50 (4 H, m), 7.80 and 8.33 (each 4 H, dt, J = 8.4 Hz, 1.7 Hz). ^{13}C NMR ($CDCl_3$) δ = 121.68 (4 CH), 125.99 (2 CH), 127.49 (4 CH), 129.20 (2 C), 129.54 (4 CH), 130.85 (4 CH), 144.86 (2 C), 150.86 (2 C), 164.67 (2 C = O).

2.6. Phenoxycarbonylation of DBBP with palladium–dppp catalyst

780.1 mg, (2.5 mmol) of DBBP, 564.7 mg (6.0 mmol) of phenol, 17.7 mg (0.1 mmol) of $PdCl_2$, 82.5 mg, (0.2 mmol) of dppp, 0.82 ml (5.5 mmol) of DBU, and 10 ml of chlorobenzene were reacted in the same manner. **19** (2.40 mmol, 96%) and **20** (0.115 mmol) were found in the mixture.

3. Results and discussion

3.1. Effect of base on the phenoxycarbonylation of 4-bromobiphenyl

The phenoxycarbonylation of BBP was examined to investigate the applicability of the carbonylation–polycondensation of dihalobiphenyls with bisphenols.

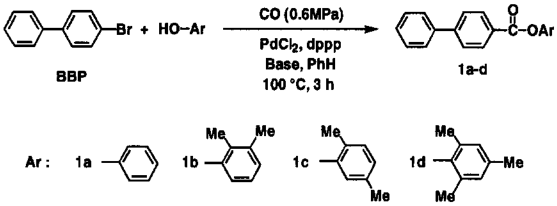

Table 1 summarizes the effect of base on the phenoxycarbonylation of BBP by the catalyst with dppp as a ligand with benzene as solvent. Phenyl 4-biphenylcarboxylate (**1a**) was obtained in low yields with tertiary amines (Et_3N, n-Bu_3N, (c-C_6H_{12})$_2$NEt, etc.), which were described as effective base for the carbonylation with aliphatic alcohols [9]. Even the reaction with 1,8-bis(dimethylamino)naphthalene (Proton Sponge®) which was reported as the best base in the methoxycarbonylation of benzyl chloride gave **1a** in a poor yield [12]. A weak base such as 2,6-lutidine and pyridine, which does not work well for the reaction [12], gave no carbonylation products. On the other hand, when a cyclic amidine such as DBU or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) [13–15] was used, the rate of the carbonylation drastically increased, and the yield of **1a** was moderate to high. With a cyclic guanidine such as 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) [16], **1a** was obtained in higher yield than with a cyclic amidine. Thus, ester **1a** was obtained in 95, 91 and 77% yield with MTBD (pK_a = 13.0), DBU (pK_a = 11.9) and DBN (pK_a = 11.0), respectively. Carbonylation with 2-t-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) [16,17], which is about 2000 times more basic than DBU, also gave **1a** in high yield. These results showed that the reaction in the presence of a strong base gave **1a** in high yield. However, there was an exception. The pK_a of 1,4-diazabicyclo[2.2.2]octane (DABCO) (pK_a = 8.2) is considerably smaller than that of Et_3N (pK_a = 10.75), but the yield of **1a** with DABCO was two times higher than that of Et_3N. The steric factor is one possible explanation for this exception. When a phenol and a base form an ion-pair, the phenoxide anion is considered to make a nucleophilic attack on an acyl palladium intermediate. A bulky counter cation might prevent this

Table 1
Palladium catalyzed phenoxycarbonylation of BBP [a]

Base	pK_a [b]	Conv. (%)	Yield (%)
BEMP [c]		91	90
MTBD [d]	13.0	95	95
DBU [e]	11.9	91	91
DBU [f]	11.9	70	68
DBN [g]	11.0	81	77
$(c\text{-}C_6H_{12})_2NEt$		26	14
$n\text{-}Bu_3N$	10.9	11	10
$i\text{-}Pr_2NEt$		9	9
Et_3N	10.75	8	8
Proton Sponge® [h]		1	1
DMAP [i]	9.7	0	0
TMEDA [j]	9.15	2	2
DABCO [k]	8.2	17	17
2,6-Lutidine	6.6	0	0
Pyridine	5.2	0	0
NaOAc		7	7
K_2CO_3		0	0

[a] Reaction conditions: BBP 2.5 mmol, phenol 3.0 mmol, $PdCl_2$ 0.05 mmol, dppp 0.1 mmol, base 2.75 mmol, docosane (internal standard for GC analysis) 1.25 mmol, solvent benzene 5 ml, CO pressure 0.6 MPa, temperature 100°C, period 2 h. [b] pK_a values for aqueous solutions of the corresponding conjugate acids. See [18–20]. [c] 2-*t*-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine. [d] 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene. [e] 1,8-Diazabicyclo[5.4.0]undec-7-ene. [f] 0.2 mmol of PPh_3 was used in place of dppp. [g] 1,5-Diazabicyclo[4.3.0]non-5-ene. [h] 1,8-Bis(dimethylamino)naphthalene. [i] 4-Dimethylaminopyridine. [j] *N,N,N′,N′*-Tetramethylethylenediamine. [k] 1,4-Diazabicyclo[2.2.2]octane.

attack. DABCO is particularly effective, probably because its bridge-head nitrogen makes the phenoxide anion less hindered than other phenoxide anions paired with acyclic tertiary amines. Moreover, its bridge-head nitrogen could form an acyl ammonium intermediate to assist the nucleophilic substitution by a phenoxide anion. NaOAc and K_2CO_3 do not work well because of heterogenous reaction systems and their weak basicities.

We also examined the phenoxycarbonylation of BBP with *o*-methylphenols in the presence of DBU as a base at 120°C as shown in Table 2. Ester products (**1b**–**1d**) were obtained over 94% yields with 2,3- and 2,6-dimethylphenols and 2,4,6-trimethylphenol.

The results shown above suggest that the carbonylation–polycondensation is possible from dihalobiphenyls and bisphenols as the substrates in the presence of a strong base such as DBU.

Table 2
The phenoxycarbonylation of BBP with *o*-methylphenols in the presence of DBU [a]

Phenol	Product	Conv. (%)	Yield [b] (%)
Phenol [c]	**1a**	91	90
2,3-Dimethylphenol	**1b**	100	98
2,5-Dimethylphenol	**1c**	100	97
2,4,6-Trimethylphenol	**1d**	100	94

[a] Reaction conditions: BBP 2.5 mmol, phenols 3.0 mmol, $PdCl_2$ 0.05 mmol, dppp 0.1 mmol, DBU 2.75 mmol, docosane (internal standard for GC analysis) 1.25 mmol, benzene 5 ml, CO pressure 0.6 MPa, temperature 120°C, period 3 h. [b] Isolated yield. [c] Temperature 100°C, period 2 h.

3.2. *Effect of reaction parameters on the carbonylation–polycondensation*

The synthesis of polyesters by the carbonylation–polycondensation is shown below. The efficiency of the synthesis is affected not only by catalytic activity, but by other parameters such as temperature, CO pressure, solvent and base. The influences on the reaction were studied for polyester **2** from DBDHP and bisphenol A.

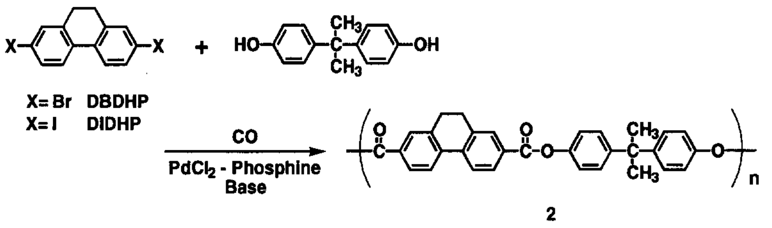

Fig. 1 summarizes the effect of temperature on the molecular weight of **2** in the presence of Pd–PPh_3 catalyst and DBU. The carbonylation–polycondensation was dependent on temperature, and the molecular weight was the highest at 120–130°C. The low molecular weight is due to low reaction rate at low temperatures, and to side reactions at high temperatures. It has been reported that a reaction temperature above 110°C was enough for the carbonylation–polycondensation of bis(4-bromophenyl)ether with bisphenol A and that the preferable reaction temperature was 115°C [4].

The effect of solvent on molecular weight of **2** in the presence of Pd–dppp catalyst and DBU is shown in Table 3. The solubility of the product is considered as a more important factor than the polarity of solvent for the carbonylation–polycondensation, although the alcoholysis of the acyl-palladium intermediate with phenol is favorable in a polar solvent. Polyester **2** dissolves easily in chlorobenzene, nitrobenzene, dichloromethane and chloroform. Among them, only chlorobenzene and anisole effectively mediated the carbonylation–polycondensation. Consequently, we chose chlorobenzene as a standard solvent.

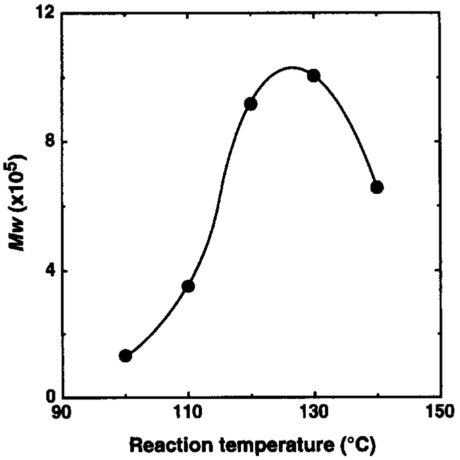

Fig. 1. Effect of reaction temperature on the molecular weight of **2**. Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, PPh_3 0.2 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 1.1 MPa, period 3 h.

Table 3
Effect of solvent on the carbonylation–polycondensation in the presence of DBU [a]

Solvent	Yield (%)	M_w ($\times 10^3$)	M_w/M_n
Chlorobenzene	99	35	3.6
Anisole	99	25	4.0
Flurobenzene	98	6.7	2.3
Benzene	94	5.8	2.1
Toluene	93	5.8	2.1
Nitrobenzene	0	–	–
NMP [b]	92	0.8	8.0
DMA [c]	96	1.7	4.8
Dichloromethane	0	–	–

[a] Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, dppp 0.2 mmol, DBU 5.5 mmol, solvent 10 ml, CO pressure 2.1 MPa, temperature 120°C, period 3 h. [b] 1-Methyl-2-pyrrolidinone. [c] *N,N*-Dimethylacetamide.

Table 4 shows the effect of base on the carbonylation–polycondensation by Pd–PPh_3 catalyst in chlorobenzene. The highest molecular weight was obtained for DBU. TMEDA and DABCO gave relatively high molecular weight polyesters. However, conventional amines such as Et_3N and *i*-Pr_2NEt did not yield high molecular weight polymers. The effectiveness of DBU was quite similar as in the phenoxycarbonylation of BBP. DBU was an efficient base under the variety of conditions used because it swells the resulting polymers well, and because the salt from DBU and HBr liberated by the carbonylation is highly soluble in organic solvents. It is easier to remove as its hydrogen bromide salt from solution than the salts of other bases such as Et_3N and *i*-Pr_2NEt. From these results, we chose DBU as a standard base for the carbonylation–polycondensation. Under the optimum conditions, **2** was obtained in 95% yield with a high molecular weight of 1.0×10^5 (M_w) as described in the Experimental section.

The catalytic activity of the palladium–phosphine complex on the carbonylation–polycondensation is an important factor for the molecular weight of polyesters. The effect of the L/Pd ratio (L:phosphine moiety) on the molecular weight of **2** is summarized in Table 5. The use of 4 moles of PPh_3 per mole of palladium was necessary to prevent catalyst decomposition, probably due to a cluster formation discussed in several papers [20–24]. Bidentate phosphines such as dppp were reported to be more effective ligands for various carbonylations than a monodentate phosphine such as PPh_3 [25–29]. In our previous work [25], high catalytic activities were observed for bidentate phosphines, α,ω-bis(diphenylphosphino)alkanes ($Ph_2P(CH_2)_nPPh_2$ ($n = 2$–6)), especially for dppp

Table 4
Effect of base on the carbonylation–polycondensation in chlorobenzene [a]

Base	Yield (%)	M_w ($\times 10^3$)	M_w/M_n
DBU	97 [b]	92	2.3
TMEDA	99	16	3.3
DABCO	96 [b]	12	4.1
Et_3N	92 [b]	4.5	3.0
i-Pr_2NEt	22	0.9	1.4
Proton sponge®	17	0.9	1.5
DMAP	7	0.8	1.4
2,6-Lutidine	trace	0.1	1.2
K_2CO_3	trace [c]	0.8	1.7

[a] Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, dppp 0.2 mmol, base 5.5 mmol, chlorobenzene 10 ml, CO pressure 2.1 MPa, temperature 120°C, period 3 h. [b] PPh_3 0.4 mol, was used as a ligand. [c] Palladium precipitate was observed.

Table 5
Effect of palladium catalyst on the carbonylation–polycondensation [a]

Catalyst	Yield (%)	M_w ($\times 10^3$)	M_w/M_n
$PdCl_2/2PPh_3$	39	1.2	1.6
$PdCl_2/4PPh_3$	92	37	3.0
$Pd(PPh_3)_4$ [b]	96	19	3.8
$PdCl_2$/2dppe	94	12	3.6
$PdCl_2$/dppp	97	6.2	2.5
$PdCl_2$/2dppp	99	35	3.6
$PdCl_2$/5dppp	39	1.2	1.6
$PdCl_2$/2dppb	95	21	3.4
$PdCl_2$/2dpppe	91	17	3.2

[a] Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, phosphine 0.1–0.5 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 2.1 MPa, temperature 120°C, period 3 h. [b] $Pd(PPh_3)_4$, 0.1 mmol.

($n = 3$) and dppb ($n = 4$), in palladium catalyzed ethoxycarbonylation of DBBP and DBDHP. The catalysts with these ligands were much more active than those with PPh_3. The effectiveness of the bidentate ligand was explained by the formation of a chelate complex with palladium, such as a six-membered ring for dppp. Differences among bidentate phosphines were ascribed to the differences of the coordination ability and the flexibility of the chelate. In the carbonylation–polycondensation, dppp gave the highest molecular weight of **2** among these bidentate phosphines. A two-fold excess of dppp for palladium was also required for the carbonylation and for a higher molecular weight. However, much lower yields and molecular weights were observed with a large excess of dppp.

Fig. 2 shows the effect of CO pressure on the molecular weight of **2** in the presence of the catalysts with PPh_3 and dppp. The molecular weight was the highest under a CO pressure of around 1 MPa, and then gradually decreased with further increase of CO pressure. Both PPh_3 and dppp were effective ligands in the carbonylation–polycondensation, especially under a low pressure of 0.6–1.5 MPa. However, PPh_3 was more superior to dppp for the formation of high molecular weight polyester **2** under these conditions. A high CO pressure was considered to change the coordination of ligand and to affect the rate-determining oxidative addition step of aryl bromide. As shown in Fig. 2, the molecular weight of **2** for DIDHP was low under every pressure. This shows that the effect of CO

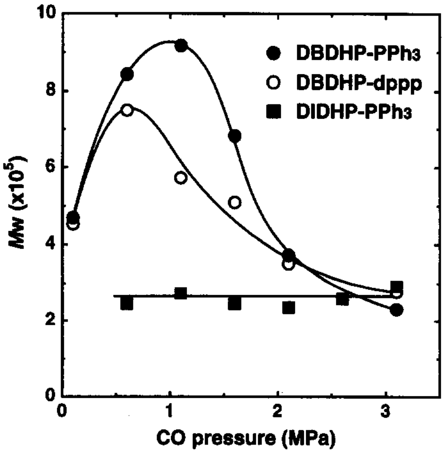

Fig. 2. Effect of CO pressure on the molecular weight on the formation of **2**. Reaction conditions: dihalide 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, PPh_3 0.2 mmol or dppp 0.1 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, temperature 120°C, period 3 h.

Table 6
Effect of dihalobiphenyls on the formation of polyesters from bisphenol A[a]

Dihalobiphenyl	Polyester	Yield (%)	M_w ($\times 10^3$)	M_w / M_n
DBDHP	**2**	99	35	3.6
DIDHP	**2**	98	24	2.8
DBBP	**3**	94	5.6	6.3
DIBP	**3**	98	12	2.5
p-Dibromobenzene	**4**	96	2.6	2.5

[a] Reaction conditions: dihalide 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, dppp 0.2 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 2.1 MPa, temperature 120°C, period 3 h.

pressure on the molecular weight of **2** for DIDHP was different from the case for DBDHP.

The structure of dihalides and bisphenols affected the carbonylation–polycondensation. Table 6 shows the effect of dihalides with bisphenol A on the molecular weight of the polyesters in the presence of the catalyst with dppp. Polyester **2** from DBDHP or DIDHP has higher solubility than polyester **3** from DBBP or DIBP. Such an increase of solubility is due to the effect of the bulkiness of the 9,10-dihydrophenanthrene moiety. Highly soluble polyester **2** should grow more rapidly resulting in a high molecular weight. The molecular weight of **2** from DBDHP was higher than that from DIDHP. This is ascribed to the difference of the contribution of oxidative addition and alcoholysis steps as discussed below. Higher molecular weight of **3** was observed with DIBP instead of DBBP. High reactivity of the iodobenzene moiety of the intermediate polyester from DIBP should overcome the negative effect of the low solubility of the resulting polymer. When *p*-dibromobenzene was used as a dihalide, polyester **4** was obtained with low molecular weight due to the low solubility of the resulting polyester.

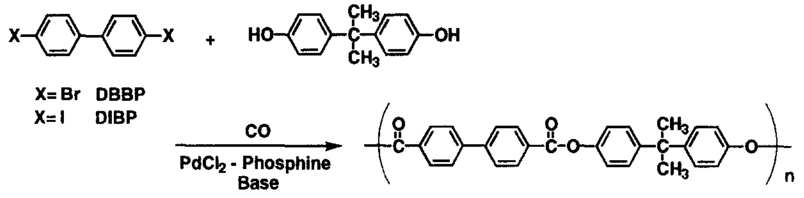

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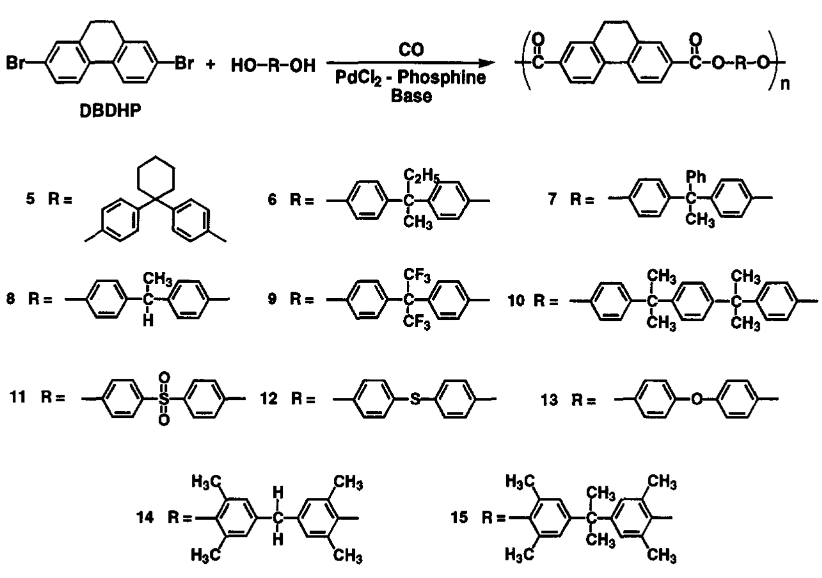
Table 7 summarizes the effect of bisphenols on the molecular weight of polyesters in the reaction with DBDHP in the presence of the catalyst with dppp. Bisphenols having sufficiently bulky alkyl spacers, such as 4,4′-cyclohexylidenebisphenol, 4,4′-(*s*-butylidene)bisphenol, 4,4′-(1-phenylethylidene)bisphenol and 4,4′-ethylidenebisphenol, gave the corresponding polyesters with high to moderately high molecular weight. Especially, bisphenol A gave the best results among them. 4,4′-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bisphenol gave a product soluble in the reaction solvent. However, the NMR spectrum of the product did not show the typical pattern of this series of polyesters, indicating that carbonylation–polycondensation of DBDHP did not occur sufficiently. The polyesters from 4,4′-[1,4-phenylenebis(1-metylethylidene)]bisphenol and 4,4′-sulfonylbisphenol were also obtained with low molecular weight. This is due to the low solubility of the resulting polyesters. The products from 4,4′-thiobisphenol and 4,4′-oxybisphenol were quite insoluble in the solvents tested.



The carbonylation–polycondensation of DBDHP and bisphenols with *o*-methyl groups was examined to determine if the solubility of the polyesters improves by increasing the bulkiness at the *o*-positions. The reaction with 2,2′,6,6′,-tetramethylbisphenols, **14** and **15**, occurred smoothly to give relatively high molecular weight polyesters as shown also in Table 7.

3.3. Mechanistic aspects of the carbonylation–polycondensation

According to previous papers, a possible mechanism for the carbonylation of aromatic halide is shown in Fig. 3 [9,12,30–34]. Active species is expected to be Pd(0)L_2 complex (**16**), which is formed in situ from Pd(II)Cl_2 and phosphine or from Pd(II)L_2Cl_2 complex with phosphine [9,31]. The complex **16** is in an equilibrium with PdL_n (L: phosphine moiety; *n*: 1–4). Oxidative addition of aryl halide to Pd(0)L_2 species gives Aryl-PdL_2X (**17**), and CO insertion to **17** forms Acyl-PdL_2X

Table 7
Effect of bisphenols on the formation of polyesters from DBDHP [a]

Bisphenol	Polyester	Yield (%)	M_w ($\times 10^3$)	M_w/M_n	T_5 (°C)	T_{10} (°C)	Remarks [b]
Bisphenol A	**2**	99	35	3.6	394	414	–
4,4′-Cyclohexylidenebisphenol	**5**	93	20	3.1	375	389	–
4,4′-(*s*-Butylidene)bisphenol [c]	**6**	99	25	3.7	410	440	–
4,4′-(1-Phenylethylidene)bisphenol	**7**	97	13	3.0	392	441	–
4,4′-Ethylidenebisphenol	**8**	98	12	2.7	365	393	+
4,4′-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bisphenol	**9**	78	3.1	2.4	418	444	–
4,4′-[1,4-Phenylenebis(1-methylethylidene)bisphenol	**10**	98	4.4	2.4	363	398	+ +
4,4′-Sulfonylbisphenol	**11**	77	1.2	2.0	356	418	+ +
4,4′-Thiobisphenol	**12**	99	– [d]	–	382	413	+ +
4,4′-Oxybisphenol	**13**	95	– [d]	–	380	424	+ +
4,4′-Methylidenebis(2,6-dimethylphenol)	**14**	92	16	2.3	340	359	–
4,4′-(1-Methylethylidene)bis(2,6-dimethylphenol)	**15**	96	27	1.8	360	376	–

[a] Reaction conditions: DBHDP 2.5 mmol, bisphenol 2.5 mmol, $PdCl_2$ 0.1 mmol, dppp 0.4 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 2.1 MPa, temperature 120°C, period 3–5 h. [b] Reaction mixture just after the reaction: –, homogeneous; +, slightly suspended; + +, suspended. [c] CO pressure 1.1 MPa. [d] M_w could not be determined because of lack of solubility in organic solvent.

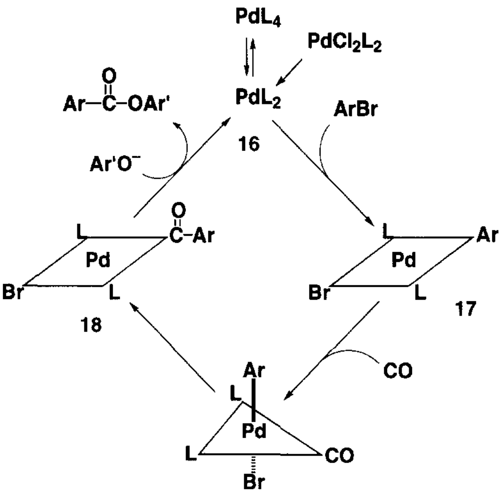


Fig. 3. A possible mechanism of the alkoxycarbonylation of aryl halide.

(**18**). The base mediated the alcoholysis of **18** to yield the ester with the regeneration of **16**. This mechanism is plausible and applicable to the carbonylation–polycondensation.

We found several characteristic features in the carbonylation–polycondensation that support the mechanism. The molecular weight of **2** in the carbonylation–polycondensation was dependent on the type of base. Strong organic bases such as DBU and TMEDA performed better than conventional amines such as Et_3N and i-Pr_2NEt. Catalytic activity of the phenoxycarbonylation of BBP was also enhanced by these strong bases. These results suggest that the strong base participates in the key steps of both reactions, and enhances the catalytic activity. Judging from our results, the alcoholysis step is the key step for both reactions. This is a different feature from usual carbonylation reactions between aryl bromide and aliphatic alcohol [9,12,30–34]. The formation of phenoxide anion in the presence of a strong base such as DBU is considered to promote the carbonylation because the phenoxide anion is more nucleophilic than phenol itself. The enhancement of the catalytic activity of the carbonylation–polycondensation with DBU resulted in a higher molecular weight polyester **2**. The molecular weight of polyester decreases with the increase of CO pressure, because the oxidative addition step is retarded by strong CO coordination to the Pd(0) complex. These results suggest that the harmonization of the rates of oxidative addition, CO insertion and alcoholysis reactions is important for the formation of high molecular weight polyesters.

The molecular weight of **2** for DIDHP was inferior to that for DBDHP as shown in Fig. 2. Terminal halobenzene and phenol moieties of polyester intermediate should be important for high molecular weight of polyesters. The rate of the carbonylation–polycondensation for DIDHP should be controlled by the alcoholysis step because of rapid oxidative addition of the iodobenzene moiety in the intermediate polyester to the palladium. Under these conditions, the dependence of molecular weight of the phenol moieties on the reactivity of the alcoholysis step is considered as an important factor. Because the acyl complex from DIDHP reacts easily with the low molecular weight phenol moiety, the resulting polyester does not have a high molecular weight. However, the carbonylation–polycondensation with DBDHP is controlled by both the oxidative addition and the alcoholysis steps because of its lower reactivity. Therefore, the alcoholysis step is not always dependent on molecular weight of the phenol moiety, and the phenol moiety with high molecular weight participates in the reactions to increase the molecular weight. The effect of CO pressure on the molecular weight of **2** for

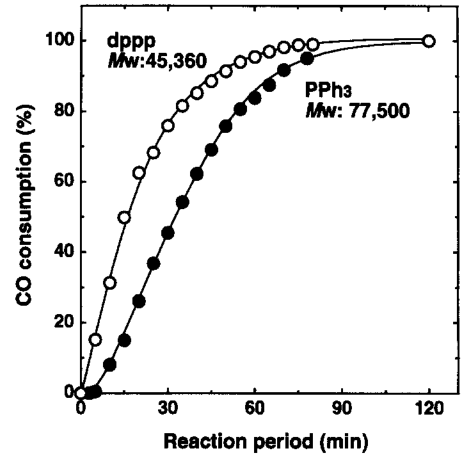


Fig. 4. CO consumption during the carbonylation–polycondensation. Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, PPh_3 0.4 mmol or dppp 0.2 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 0.1 MPa.

DIDHP was quite different from the case for DBDHP. Because oxidative addition for DIDHP is rapid even under high CO pressure, the acyl complex reacts easily with low molecular weight phenol moiety. These results suggest that the harmonization of every step is essential for high molecular weight polyester, and the reactivity of intermediate polyester is important for the growth of the resulting polyester.

Fig. 4 shows time dependence curves on CO consumption with dppp and PPh_3, respectively, under atmospheric pressure. The periods for which half the amount of carbon monoxide was consumed for the reaction were 16 min and 32 min for dppp and PPh_3, respectively. This means that the catalytic activity for dppp is apparently higher than that for PPh_3. Fig. 5 shows the time dependence on M_w by use of dppp and PPh_3, respectively, under the same conditions as in Fig. 4. The initial rate of the increase of M_w for dppp is obviously faster than that for PPh_3, whereas the final molecular weight for PPh_3 is higher than that for dppp. The catalytic activity is not parallel to the final molecular weight of the resulting polyesters. This means that some inhibitory side reactions occur during the growth of the polyester with dppp because the rate of polyester formation did not affect the final molecular weight of the polyester.

To find out what type of side reaction occurs, phenoxycarbonylation of DBBP using the catalysts with dppp and PPh_3 was examined. Diphenyl biphenyl-4,4′-dicarboxylate (**19**) was observed as the

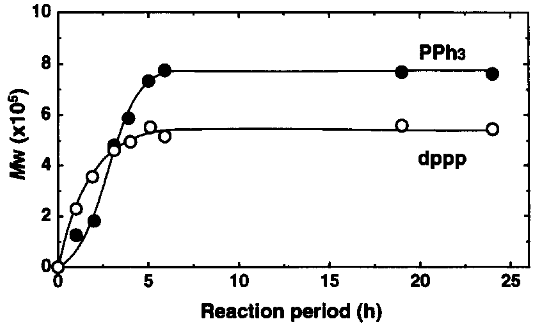
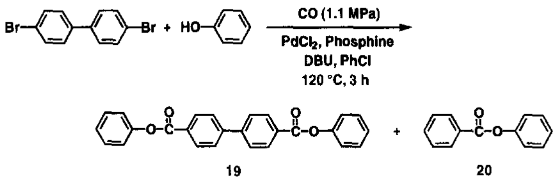


Fig. 5. Time dependence of molecular weight during the synthesis of **2**. Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, PPh_3 0.4 mmol or dppp 0.2 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, CO pressure 0.1 MPa.

sole product from DBBP in high yields in both cases. The only detectable product except **19** was phenyl benzoate (**20**) from GC analysis. Ester **20** should be formed via the carbonylation of chlorobenzene used as the reaction solvent. The amount of **20** was 0.115 mmol with dppp and 0.044 mmol with PPh_3, respectively, from phenol (6.0 mmol) and chlorobenzene (10 ml) in the presence of DBBP (2.5 mmol). These results showed that the carbonylation–polycondensation with dppp formed **20** about three times faster than that with PPh_3. The benzoyl complex as an intermediate of the carbonylation of chlorobenzene can act as a terminator of the carbonylation–polycondensation. This is a possible reason why the molecular weight of **2** with dppp was lower than that with PPh_3 in spite of the higher catalytic activity of the palladium–dppp complex. The selectivity of the catalyst for the carbonylation is a more important factor than the catalytic activity to obtain high molecular weight polyesters.



3.4. Thermal properties of polyesters

Wholly aromatic polyesters (**2**–**15**) did not have a glass transition temperature (T_m) up to 400°C. Representative TG patterns of the wholly aromatic polyesters **2**–**4** are shown in Fig. 6. Biphenyl-containing polyesters **2** and **3** were more stable than **4** at 300–390°C, although weight loss of **2** and **3** were faster than **4** above 400°C. The 10% weight-loss temperature (T_{10}) of the polyesters were above 380°C in an air stream as shown in Table 7. **2** and **7** were soluble in chloroform and dichloromethane, whereas **3**, **4**, **5**, **6**, **8**, **10**, and **11** were not soluble in chloroform but soluble in 25% HFIP/chloroform (v/v). Soluble polyesters with M_w higher than 10000 formed transparent casting films. They are expected to be easily molded.

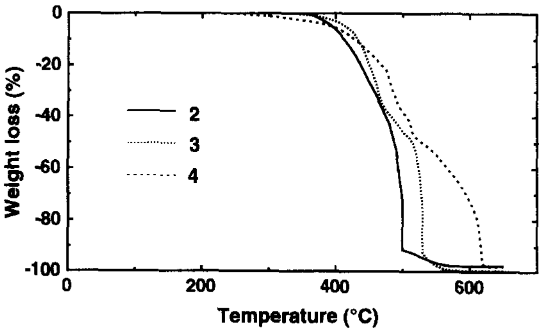


Fig. 6. TG profiles of the polyesters **2**, **3** and **4**. Analyzing conditions: polyester 10 mg, programmed rate 10°C/min under an air stream.

4. Conclusions

The one step synthesis of biphenyl-containing wholly aromatic polyesters was developed from palladium-catalyzed carbonylation–polycondensation of dihalobiphenyls and bisphenols. Reaction parameters, such as base, solvent, palladium–phosphine catalyst, CO pressure and reaction temperature in the carbonylation–polycondensation of 2,7-dibromo-9,10-dihydrophenanthrene and bisphenol A, were found to significantly affect the molecular weight of the resulting polyester, poly[oxy-1,4-phenylene(1-methylethylidene)-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (**2**). The high solubility of the resulting polymers is also essential for the synthesis of high molecular weight polyesters. A strong base such as DBU also enhanced the carbonylation–polycondensation to yield high molecular weight polyesters. The key step for the reaction is considered to be the alcoholysis step. The high nucleophilicity of the phenoxide anion formed from the phenol and DBU promotes the step to increase the rate of the reaction. Palladium catalyst with PPh_3 gave higher molecular weight polyester than the catalyst with $Ph_2P(CH_2)_3PPh_2$ in spite of the higher catalytic activity of the latter catalyst. This is due to the termination reaction yielding phenyl benzoate by the carbonylation of chlorobenzene solvent. Under the optimum conditions with DBU as a base, palladium–PPh_3 as catalyst, and chlorobenzene as solvent, **2** was obtained in 95% yield with high molecular weight (polystyrene equivalent $M_w = 102\,600$) under 0.6 MPa of CO pressure and at a reaction temperature of 130°C. Bisphenols with sufficiently bulky alkyl spacers, such as 4,4′-cyclohexylidene-bisphenol, 4,4′-(*s*-butylidene)bisphenol, 4,4′-(1-phenylethylidene)bisphenol and 4,4′-ethylidenebisphenol, 4,4′-methylidenebis(2,6-dimethylphenol) and 4,4′-(1-methylethylidene)bis(2,6-dimethylphenol) gave polyesters with high to moderately high molecular weight. From thermal analysis, 5% weight loss temperature (T_5) and 10% weight loss temperature (T_{10}) of **2** in air were 394 and 414°C, respectively. Polyesters soluble in organic solvent and having M_w higher than 10 000 easily formed transparent casting films.

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