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Synthesis of Heat-Resistant Polyester Containing Rigid Biphenyl Moiety by Palladium-Catalyzed Carbonylation-Polycondensation

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For the purpose of synthesizing heat-resistant polyesters, the one-step synthesis of a rigid biphenyl-containing polyester from dihalobiphenyl and diol by palladium-catalyzed carbonylation-polycondensation was examined. The reaction parameters, such as the 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 significantly affect the molecular weight of the resulting polyester. Under the optimum conditions, poly[oxy-1,4-phenylene(1-methylethylidene)-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (**1**) were obtained in 95% yield with high molecular weight (polystyrene equivalent $M_w=102600$). By choosing the phosphine ligands and controlling the pressure of carbon monoxide, polymer **1** was obtained with a M_w of 10000—100000. The procedure was applied to various dihalobiphenyls and diols. Polycondensation with 1,10-decanediol gave poly[oxydecamethyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (**15**) with a much lower molecular weight ($M_w=4900$) than polyester **1**. On the basis of a thermal analysis, a 5% weight-loss temperature (T_5) and a 10% weight-loss temperature (T_{10}) of **1** in air was 394 and 414 °C, respectively, whereas melting temperature (T_m), T_5, and T_{10} of **15** were 148, 369, and 383 °C, respectively.

Stiff macromolecules are expected, when properly processed, to produce materials with high degrees of molecular orientation and order, which should result in superior mechanical strength.[1—3] They are called liquid-crystalline polymers, and biphenyl is known to be one of the mesogenic units in the polymers. Very often, stiff-chain polymers do not melt and are insoluble in organic solvents. Biphenyl derivatives are therefore a promising component to construct advanced constitutional materials, such as heat-resistant polymers and liquid-crystalline polymers. Since copolyesters based on terephthalic acid, isophthalic acid, and bisphenol A have already been widely used for its heat-resistance and transparency, wholly aromatic polyesters containing the biphenyldicarboxylate moiety in place of the terephthalate and isophthalate moiety must have potential to be of higher heat-resistance. For this reason, we tried to synthesize biphenyl-containing polyesters. Among several synthetic methods to obtain the target polyesters, the carbonylation-polycondensation technique originally reported by Imai[4—7] seemed to be the most straightforward way. Although some relation to this method has also been reported by Perry et al.,[8,9] no attention has been paid to biphenyl skeletones as substrates of this carbonylation-polyesterification method, probably because the lack of solubility of the products in the reaction medium due to their promising molecular rigidity.

We report herein on the successful synthesis of polyesters which contain a rigid biphenyl skeleton by palladium-catalyzed carbonylation-polycondensation. The introduction of biphenyl moieties, especially the 9,10-dihydrophenanthrene moieties, was found to improve the solubility of the resulting polyesters in an organic solvent. This was advantageous for polymer formation during carbonylation-polycondensation in solution and for molding the resulting polyesters. Biphenyl-containing polyesters maintained a high heat-resistance. Control of the molecular weight by changing the pressure of carbon monoxide and by using palladium-α,ω-bis(diphenylphosphino)alkane catalyst is also described.

Experimental

Materials. 4,4′-Dibromobiphenyl (DBBP) was recrystallized from toluene. 2,7-Dibromo-9,10-dihydrophenanthrene (DBDHP) and 2,7-diiodo-9,10-dihydrophenanthrene (DIDHP) were prepared from 9,10-dihydrophenanthrene by known methods.[10,11] Bisphenol A was recrystallized from benzene. 1,2-Ethanediol was distilled from KOH under reduced pressure. Triethylamine was distilled from CaH_2 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was distilled under reduced pressure. 1-Methyl-2-pyrrolidinone (NMP) was distilled from CaH_2 under reduced pressure. All other materials were conmmercially available as special grade and used as received.

Measurements. The IR spectra were recorded on a Perkin–Elmer 1720X FT-IR spectrometer. The 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) on the basis of 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)). The thermal characteristics were studied with a Mettler FP800 Thermal Analysis System and a Mac Science TG-DTA 2000 apparatus. Gas chromatography 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). The peak areas were measured using a Shimadzu chromatopac C-R5A. The mass spectra were recorded on a Hewlett Packard Model 5890 series II, equipped with a 5971A Mass Detector System, using a capillary column of GL Science Neutrabond-1 (0.25 mm×25 m).

Typical Procedure for Polycondensation. In a 50 ml stainless-steel autoclave equipped with a stirrer were placed 845.1 mg (2.5 mmol) of DBDHP, 570.7 mg (2.5 mmol) of bisphenol A, 17.7 mg (0.1 mmol) of $\mathrm{PdCl_2}$, 104.9 mg (0.4 mmol) of $\mathrm{PPh_3}$, 10 ml of chlorobenzene, and 0.82 ml (5.5 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Carbon monoxide was introduced at 10 bar of an initial pressure and then heated with vigorous stirring at 130 °C in an oil bath for 3 h. After excess carbon monoxide was purged, the reaction 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 precipitated polymer was filtered, washed with 100 ml of methanol, and dried in vacuo to obtain poly[oxy-1,4-phenylene(1-methylethylidene)-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (**1**) as a white or pale green-yellow solid. The yield was 1.09 g (95%).

M_w and $M_\mathrm{w}/M_\mathrm{n}$ 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. Found: C, 79.93; H, 5.09; Br, 1.35%. Calcd for $(\mathrm{C_{31}H_{24}O_4})_n$: C, 80.85; H, 5.25%. IR (KBr) 1733, 1612, 1505, 1278, 1259, 1206, 1175, 1158, 1073, 1016, 752 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta=1.74$ (m, $\mathrm{C\underline{H}_3}$), 3.02 (br s, $\mathrm{C\underline{H}_2}$), 7.16 and 7.33 (two d, $J=8.7$ Hz, O–Ar–$\underline{\mathrm{H}}$), 7.94 and 8.17 (two d, $J=8.2$ Hz, $\mathrm{C\underline{H}{=}C\underline{H}{-}C{-}C{=}O}$), and 8.12 (s, $\mathrm{CH_2{-}C{-}C\underline{H}}$); Intensity ratio: 6:4:8:4:2; ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta=28.62$ ($\mathrm{\underline{C}H_2}$), 31.00 ($\mathrm{\underline{C}H_3}$), 42.58 ($\mathrm{\underline{C}{-}CH_3}$), 121.07 ($\mathrm{\underline{C}H{=}C{-}O}$), 124.57 ($\mathrm{\underline{C}H{=}CH{-}C{-}C{=}O}$), 127.95 ($\mathrm{\underline{C}{-}C{=}O}$), 129.01 ($\mathrm{\underline{C}H{-}C{-}C{=}O}$), 129.20 ($\mathrm{\underline{C}{=}C{-}CH_2}$), 130.02 ($\mathrm{\underline{C}H{-}C{-}CH_2}$), 138.22 and 138.35 ($\mathrm{\underline{C}{-}CH{=}\underline{C}{-}C{=}O}$), 148.03 ($\mathrm{\underline{C}{-}C{-}CH_3}$), 148.80 ($\mathrm{\underline{C}{-}O{-}C{=}O}$), and 165.00 ($\mathrm{\underline{C}{=}O}$).

Pertinent analytical and spectral data are shown below.

Poly[oxy-1,4-phenylene(1-methylethylidene)-1,4-phenyleneoxycarbonyl(4,4′-biphenylylene)carbonyl] (5): M_w=11600 ($M_\mathrm{w}/M_\mathrm{n}$=2.5); T_5(air)=415°C; T_{10}(air)=434°C; IR (KBr) 2969, 1735, 1607, 1505, 1263, 1206, 1069, 1016, 1006, 752 $\mathrm{cm^{-1}}$. Found: C, 79.14; H, 4.81; I, 4.00%. Calcd for $(\mathrm{C_{29}H_{22}O_4})_n$: C, 80.17; H, 5.10%.

Poly[oxy-1,4-phenylenecyclohexylidene-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (6): M_w=20200 ($M_\mathrm{w}/M_\mathrm{n}$=3.1); T_5(air)=375°C; T_{10}(air)=389°C; IR (KBr) 2936, 2858, 1735, 1611, 1505, 1407, 1279, 1259, 1208, 1175, 1158, 1078, 753 $\mathrm{cm^{-1}}$. Found: C, 80.21; H, 5.51; Br, 1.49%. Calcd for $(\mathrm{C_{34}H_{28}O_4})_n$: C, 81.58; H, 5.64%.

Poly[oxy-1,4-phenylene-*s*-butylidene-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (7): M_w=25100 ($M_\mathrm{w}/M_\mathrm{n}$=3.7); T_5(air)=410°C; T_{10}(air)=440°C; IR (KBr) 1732, 1609, 1505, 1259, 1207, 1175, 1072, 1015, 752 $\mathrm{cm^{-1}}$. Found: C, 79.82; H, 5.45; Br, 1.51%. Calcd for $(\mathrm{C_{32}H_{26}O_4})_n$: C, 80.99; H, 5.52%.

Poly[oxy-1,4-phenylene(1-phenylethylidene)-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (8): M_w = 12800 ($M_\mathrm{w}/M_\mathrm{n}$ = 3.0); T_5(air) = 392°C; T_{10}(air) = 441°C; IR (KBr) 1733, 1609, 1505, 1436, 1259, 1209, 1171, 1073, 1014, 752, 699 $\mathrm{cm^{-1}}$. Found: C, 79.99; H, 4.88; Br, 2.39%. Calcd for $(\mathrm{C_{36}H_{26}O_4})_n$: C, 82.74; H, 5.01%.

Poly[oxy-1,4-phenyleneethylidene-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (9): M_w=12200 ($M_\mathrm{w}/M_\mathrm{n}$=2.7); T_5(air)=365°C; T_{10}(air)=393°C; IR (KBr) 1732, 1610, 1506, 1436, 1406, 1278, 1260, 1202, 1174, 1079, 1016, 1005, 839, 753 $\mathrm{cm^{-1}}$. Found: C, 79.07; H, 4.82; Br, 2.01%. Calcd for $(\mathrm{C_{30}H_{22}O_4})_n$: C, 80.70; H, 4.97%.

Poly[oxy-1,4-phenylene(1-trifluoromethyl-2,2,2-trifluoroethylidene)-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (10): M_w=3100 ($M_\mathrm{w}/M_\mathrm{n}$=2.4); T_5(air)=418°C; T_{10}(air)=444°C.

Poly[oxy-1,4-phenyleneisopropylidene-1,4-phenyleneisopropylidene-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (11): M_w=4400 ($M_\mathrm{w}/M_\mathrm{n}$=2.4); T_5(air)=363°C; T_{10}(air)=398°C; IR (KBr) 2967, 1732, 1611, 1506, 1406, 1279, 1260, 1207, 1176, 1075, 1016, 1006, 836, 754 $\mathrm{cm^{-1}}$. Found: C, 81.48; H, 5.89; Br, 4.14%. Calcd for $(\mathrm{C_{40}H_{34}O_4})_n$: C, 83.02; H, 5.92%.

Poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (12): M_w=1200 ($M_\mathrm{w}/M_\mathrm{n}$=2.0); T_5(air)=356°C; T_{10}(air)=418°C; IR (KBr) 1735, 1585, 1490, 1407, 1279, 1259, 1205, 1152, 1107, 1068, 1005, 838, 751, 716, 696, 663, 583, 557 $\mathrm{cm^{-1}}$. Found: C, 67.92; H, 3.71; Br, 3.35%. Calcd for $(\mathrm{C_{28}H_{18}O_6S})_n$: C, 69.70; H, 3.76%.

Poly[oxy-1,4-phenylenethio-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (13): M_w was not determined because this product was insoluble. T_5(air)=382°C; T_{10}(air)=413°C; IR (KBr) 1730, 1610, 1584, 1488, 1436, 1405, 1279, 1259, 1201, 1173, 1072, 1014, 837, 753 $\mathrm{cm^{-1}}$. Found: C, 73.05; H, 3.92; Br, 4.30%. Calcd for $(\mathrm{C_{28}H_{18}O_4S})_n$: C, 74.65; H, 4.03%.

Poly[oxy-1,4-phenyleneoxy-1,4-phenyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (14): M_w was not determined because this product was insoluble. T_5(air)=380°C; T_{10}(air)=424°C; IR (KBr) 1732, 1611, 1495, 1280, 1258, 1207, 1184, 1078, 1005, 839, 753 $\mathrm{cm^{-1}}$. Found: C, 76.63; H, 4.10; Br, 2.05%. Calcd for $(\mathrm{C_{28}H_{18}O_5})_n$: C, 77.41; H, 4.18%.

Poly[oxydecamethyleneoxycarbonyl(9,10-dihydro-2,7-phenanthrenediyl)carbonyl] (15): M_w = 10200 ($M_\mathrm{w}/M_\mathrm{n}$ = 2.8); T_5(air) = 369°C; T_{10}(air) = 383°C; T_m = 148°C; IR (KBr) 2929, 2853, 1715, 1611, 1473, 1437, 1408, 1281, 1261, 1181, 1160, 1106, 761 $\mathrm{cm^{-1}}$. Found: C, 75.34; H, 7.39; Br, 1.52%. Calcd for $(\mathrm{C_{26}H_{30}O_4})_n$: C, 76.82; H, 7.44%.

Poly[oxydecamethyleneoxycarbonyl(4,4′-biphenylylene)carbonyl] (16): M_w = 14400 ($M_\mathrm{w}/M_\mathrm{n}$ = 3.4); T_5(air) = 373°C; T_{10}(air) = 384°C; T_m = 176°C; IR (KBr) 2918, 2850, 1716, 1608, 1473, 1398, 1278, 1176, 1110, 1005, 845, 758, 696 $\mathrm{cm^{-1}}$. Found: C, 72.83; H, 7.15; I, 4.23%. Calcd for $(\mathrm{C_{24}H_{28}O_4})_n$: C, 75.76; H, 7.42%.

Poly[oxyoctamethyleneoxycarbonyl(4,4′-biphenylylene)carbonyl] (17): M_w = 8600 ($M_\mathrm{w}/M_\mathrm{n}$ = 3.2); T_5(air) = 373°C; T_{10}(air) = 384°C; T_m = 191°C; IR (KBr) 2929, 2853, 1718, 1607, 1396, 1273, 1176, 1101, 1005, 846, 756, 696 $\mathrm{cm^{-1}}$. Found: C, 74.27; H, 6.86; I, 2.68%. Calcd for $(\mathrm{C_{22}H_{24}O_4})_n$: C, 74.98; H, 6.86%.

Poly[oxyhexamethyleneoxycarbonyl(4,4′-biphenylylene)carbonyl] (18): M_w = 5800 ($M_\mathrm{w}/M_\mathrm{n}$ = 3.9); T_5(air) = 372°C; T_{10}(air) = 382°C; T_m = 263°C; IR (KBr) 2937, 1706, 1608, 1397, 1277, 1177, 1123, 849, 757, 697 cm^{-1}; Found: C, 72.43; H, 5.73; I, 2.31%. Calcd for $(C_{20}H_{20}O_4)_n$: C, 74.06; H, 6.21%.

Poly[oxytetramethyleneoxycarbonyl(4, 4′-biphenylylene)carbonyl] (19): $M_w=1800$ ($M_w/M_n=1.8$); T_5(air)$=349$°C; T_{10}(air)$=367$°C; $T_m=293$°C; IR (KBr) 2960, 1715, 1608, 1398, 1268, 1178, 1110, 847, 756, 696 cm^{-1}. Found: C, 71.75; H, 5.42; I, 2.87%. Calcd for $(C_{18}H_{16}O_4)_n$: C, 72.96; H, 5.44%.

Poly[oxytrimethyleneoxycarbonyl(4, 4′-biphenylylene)carbonyl] (20): $M_w=2600$ ($M_w/M_n=4.3$); T_5(air)$=349$°C; T_{10}(air)$=365$°C; $T_m=260$°C; IR (KBr) 2964, 1715, 1608, 1396, 1267, 1180, 1101, 845, 755, 697 cm^{-1}. Found: C, 70.80; H, 4.92; I, 2.96%. Calcd for $(C_{17}H_{14}O_4)_n$: C, 72.33; H, 5.00%.

Poly[oxyethyleneoxycarbonyl(4,4′-biphenylylene)carbonyl] (21): $M_w=1000$ ($M_w/M_n=2.9$); T_5(air)$=354$°C; T_{10}(air)$=400$°C; $T_m=347$°C; IR (KBr) 1718, 1608, 1399, 1340, 1263, 1180, 1122, 1005, 848, 754, 697 cm^{-1}. Found: C, 69.68; H, 4.43; I, 2.59%. Calcd for $(C_{16}H_{12}O_4)_n$: C, 71.64; H, 4.51%.

Poly[oxy-1,4-phenylene(1-methylethylidene)-1,4-phenyleneoxyterephthaloyl] (22): $M_w=2600$ ($M_w/M_n=2.5$); T_5(air)$=394$°C; T_{10}(air)$=429$°C; IR (KBr) 2970, 1741, 1503, 1411, 1268, 1248, 1202, 1171, 1071, 1017, 876, 811, 728 cm^{-1}. 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%.

Phenoxycarbonylation of 4,4′-Dibromobiphenyl (DBBP). A. Isolation of Phenyl 4′-Bromobiphenyl-4-carboxylate and Diphenyl Biphenyl-4,4′-dicarboxylate: In a 50 ml 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 $PdCl_2$, 82.5 mg (0.2 mmol) of 1,3-bis(diphenylphosphino)propane (dppp), 10 ml of benzene, and 0.77 ml (5.5 mmol) of triethylamine. Carbon monoxide was introduced at 10 bar and then heated with vigorous stirring at 120 °C in an oil bath for 3 h. After excess carbon monoxide was purged, the reaction mixture was diluted with chloroform. Phenyl 4′-bromobiphenyl-4-carboxylate and diphenyl biphenyl-4,4′-dicarboxylate and unreacted DBBP were found in the mixture by a GC analysis. They were separated by column chromatography on silica gel (eluent: hexane–benzene followed by chloroform) to give 50 mg (6%) of DBBP, 245 mg (28%) of phenyl 4′-bromobiphenyl-4-carboxylate, and 606 mg (61%) of diphenyl biphenyl-4,4′-dicarboxylate. Each carbonylated product was recrystallized from benzene–hexane and obtained as colorless scales.

Phenyl 4′-Bromobiphenyl-4-carboxylate: Mp 182.5—184.0 °C. Found: C, 64.86; H, 3.42%; M^++2, 355, M^+, 353. Calcd for $C_{19}H_{13}O_2Br$: C, 64.61; H, 3.71%; M+2, 355; M, 353; ^{1}H NMR ($CDCl_3$) $\delta=7.22$—7.33 (3H, m, phenyl-H), 7.42—7.49 (2H, m, phenyl-H), 7.52 and 7.62 (each 2H, dt, $J=8.7$, 2.1 Hz), 7.70 and 8.27 (each 2H, $J=8.5$, 1.7 Hz); ^{13}C NMR ($CDCl_3$) $\delta=121.69$ (2CH), 122.74 (C–Br), 125.94 (CH), 127.02 (2CH), 128.60 (C), 128.87 (2CH), 129.52 (2CH), 130.81 (2CH), 132.12 (2CH), 138.73 (C), 145.20 (C), 150.88 (C), 164.94 (C=O); IR (KBr) 1723, 1279, 1193, 1161, 1083, 1001, 823, 763, 739, 698 cm^{-1}.

Diphenyl Biphenyl-4,4′-dicarboxylate: Mp 214.5—215.0 °C. 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; ^{1}H NMR ($CDCl_3$) $\delta=7.23$—7.34 (6H, m), 7.43—7.50 (4H, m), 7.80 and 8.33 (each 4H, dt, $J=8.4$, 1.7 Hz); ^{13}C NMR ($CDCl_3$) $\delta=121.68$ (4CH), 125.99 (2CH), 127.49 (4CH), 129.20 (2C), 129.54 (4CH), 130.85 (4CH), 144.86 (2C), 150.86 (2C), 164.67 (2C=O); IR (KBr) 1730, 1592, 1495, 1289, 1211, 1160, 1090, 843, 749, 963 cm^{-1}.

B. Phenoxycarbonylation of DBBP Using Palladium–PPh$_3$ Complex Catalyst and DBU: DBBP (780.1 mg, 2.5 mmol), phenol (564.7 mg, 6.0 mmol), $PdCl_2$ (17.7 mg, 0.1 mmol), PPh_3 (104.9 mg, 0.4 mmol), DBU (0.82 ml, 5.5 mmol), and chlorobenzene (10 ml) were subjected to react in the same manner as described in **A**.

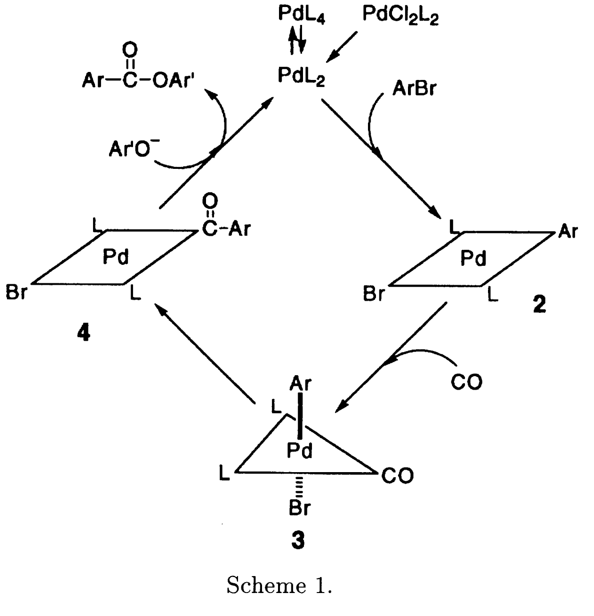
Diphenyl biphenyl-4,4′-dicarboxylate (2.48 mmol, 99%) and phenyl benzoate (0.044 mmol) were detected by GC analysis using docosane as an internal standard. The GC parameters employed for the analysis were as follows: injection port, 280 °C; detector, 280 °C; temperature program, 160 °C, 2 min, 10 °C min^{-1}, 280 °C, 20 min.

C. Phenoxycarbonylation of DBBP Using Palladium–dppp Complex Catalyst and DBU: DBBP (780.1 mg, 2.5 mmol), phenol (564.7 mg, 6.0 mmol), $PdCl_2$ (17.7 mg, 0.1 mmol), dppp (82.5 mg, 0.2 mmol), DBU (0.82 ml, 5.5 mmol), and chlorobenzene (10 ml) were subjected to react in the same manner as described in **A**.

Diphenyl biphenyl-4,4′-dicarboxylate (2.40 mmol, 96%) and phenyl benzoate (0.115 mmol) were detected by GC analysis.

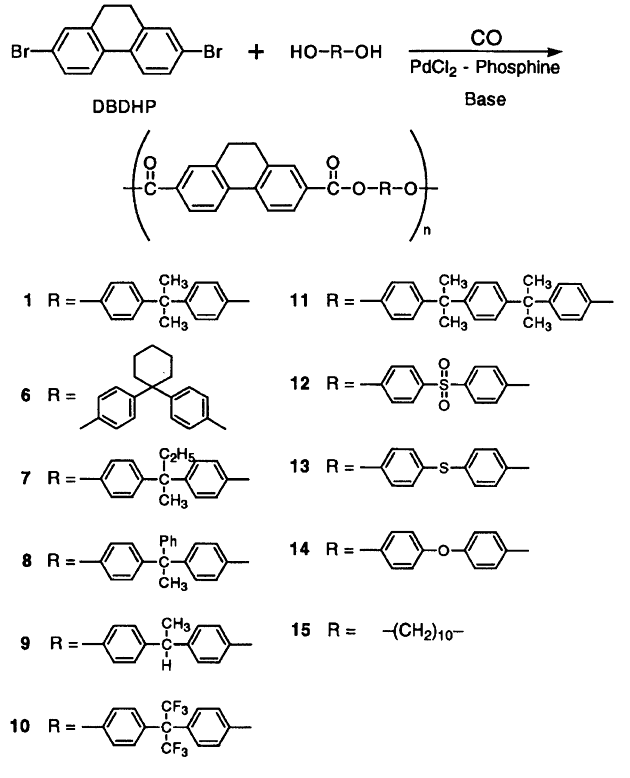
Results and Discussion

The synthesis of polyester is shown in Eq. 1. According to a number of studies,[12—19] particularly the recent study by Moser et al.,[20] the carbonylation of aromatic halide is considered to proceed through the mechanism shown in Scheme 1. The active catalyst in the carbonylation is expected to be the Pd(0)L$_n$ complex (L: phosphine moiety; n; 1—4), which is formed in situ from the Pd(II)Cl$_2$ and phosphines or from Pd(II)L$_2$Cl$_2$ complex[13,16] with or without phosphines. The oxidative addition of aryl halide to a Pd(0) species (forming **2**), followed by CO coordination, insertion (giving **4**),



Scheme 1.

and base mediated alcoholysis yielding an ester product as well as regenerating the palladium catalyst, is a plausible and applicable mechanism regarding the polycondensation study.



(1)

The efficiency of polymerization is affected not only by the catalytic activity, but also by other factors. In order to clarify the effect of the catalytic activity on the synthesis of polyester **1**, the effects of the reaction parameters, such as the temperature, solvent and base, on the carbonylation-polycondensation were studied.

Effect of Temperature. The effect of the temperature is summarized in Fig. 1. The results indicated that a reaction temperature of 120—130 °C was an asset. It was also reported that a temperature above 110 °C was sufficient for the carbonylation-polycondensation of bis(4-bromophenyl) ether with bisphenol A, and that the preferable reaction temperature was 115 °C.[6]

Effect of Solvent. The solvent effect is summarized in Table 1. A protic solvent, such as alcohols, cannot be employed in carbonylation-polycondensation. Although the alcoholysis of the acyl-palladium intermediate is expected to be favorable in polar solvents, the solubility of the product is a more important factor than the polarity in this case. The tested solvents in which the resulting polyesters dissolved was chlorobenzene, nitrobenzene, dichloromethane, and chloroform. Among them, only chlorobenzene mediated the carbonylation-polycondensation. The efficiency of chlorobenzene may be due to the good solubility of the resulting polyesters in it.

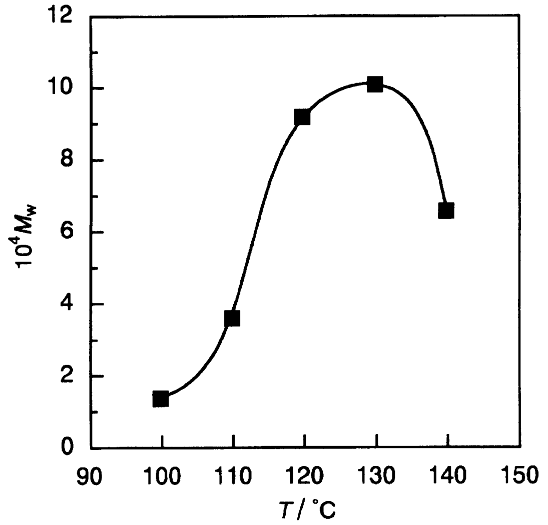


Fig. 1. Effect of the reaction temperature (T) on M_w of polymer **1**. Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, Ph_3P 0.2 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, P (CO) 10 bar, reaction time 3 h.

Table 1. Effect of the Reaction Medium in the Synthesis of Polymer **1**[a)]

Run	Solvent	Yield/%	$10^3 M_w$	(M_w/M_n)
1	Chlorobenzene	99	35	(3.6)
2	Anisole	99	25	(4.0)
3	Fluorobenzene	98	6.7	(2.3)
4	Benzene	94	5.9	(2.2)
5	Toluene	93	5.8	(2.1)
6	Nitrobenzene	0	—	—
7	1-Methyl-2-pyrrolidinone (NMP)	92	0.8	(8.0)
8	*N*,*N*-Dimethylacetamide (DMA)	96	1.7	(4.8)
9	Dichloromethane	0	—	—

a) Carbonylation-polycondensation was carried out with 2.5 mmol of DBDHP, 2.5 mmol of bisphenol A, 0.1 mmol of $PdCl_2$, 0.2 mmol of dppp, and 5.5 mmol of DBU in 10 ml of the solvent at 120 °C under 20 bar of CO for 3 h.

Effect of Base. Table 2 summarizes the effect of the base. DBU gave the best results. DBU is efficient under a wide variety of conditions, not only because it is a strong base ($pK_a=11.5$), but because it swells the resulting polymer well. Moreover, its salt liberated during the reaction was readily soluble in organic solvents and, therefore, easier to remove than the salt of the other bases tested. Under the optimum condition, polyester **1** was obtained in 95% yield with high molecular weight ($M_w=1.0\times10^5$), as described in the experimental part.

Table 2. Synthesis of **1** by the Use of Various Bases[a)]

Run	Base	Yield/%	10^3M_w	$(M_\mathrm{w}/M_\mathrm{n})$
10	DBU	95[b)]	92	(2.5)
11	TMEDA[d)]	99	16	(3.3)
12	DABCO[e)]	96[b)]	12	(4.1)
13	Et_3N	92[b)]	4.5	(3.0)
14	i-Pr_2NEt	22	0.9	(1.4)
15	Proton sponge[f)]	17	0.9	(1.5)
16	DMAP[g)]	7	0.8	(1.4)
17	2,6-Lutidine	Trace	0.1	(1.2)
18	K_2CO_3	Trace[c)]	0.8	(1.7)

a) Carbonylation-polycondensation was carried out with 2.5 mmol of DBDHP, 2.5 mmol of bisphenol A, 0.1 mmol of $PdCl_2$, 0.4 mmol of dppp, and 5.5 mmol of the base in 10 ml of chlorobenzene at 120 °C under 20 bar of CO for 3 h. b) The same scale reaction as above was carried out by use of 0.2 mmol of PPh_3 instead of dppp at 120 °C under 10 bar of carbon monoxide for 3 h. c) Precipitation of palladium black was observed. d) *N,N,N′,N′*-Tetramethylethylenediamine. e) 1,4-Diazabicyclo[2.2.2]octane. f) 1,8-Bis(dimethylamino)naphthalene. g) 4-Dimethylaminopyridine.

Effect of Ligand and CO Pressure. The influence of the catalytic activity on the molecular wight of the polymers was investigated. The effects of phosphine and the L/Pd ratio are summarized in Table 3. In our present study, the use of four moles of phosphine moiety per mole of palladium was necessary to prevent catalyst decomposition via the cluster formation referred in several reports.[20—27)] A large excess of the phosphine moiety (10 mol per 1 mole of palladium) inhibited polymer production because excess ligands coordinate to the metal center and reduce the coordination site of the substrate and carbon monoxide. This is quite a different feature from the ethoxycarbonylation of DBBP and DBDHP.

Table 3. Synthesis of **1** by the Use of Various Palladium Catalysts[a)]

Run	Catalyst	Yield/%	10^3M_w	$(M_\mathrm{w}/M_\mathrm{n})$
19	$Pd(PPh_3)_4$	96	19	(3.8)
20	$PdCl_2/4PPh_3$	92	37	(3.0)
21	$PdCl_2$/2dppe[c)]	94	12	(3.1)
22	$PdCl_2$/2dppp[c)]	99	35	(3.6)
23	$PdCl_2$/2dppb[c)]	95	21	(3.4)
24	$PdCl_2$/2dpppe[c)]	91	17	(3.2)
25	$PdCl_2$/dpph[c)]	84	7.2	(4.7)
26	$PdCl_2$/dppp	97[b)]	6.2	(2.5)
27	$PdCl_2/2PPh_3$	76	8.4	(2.9)
28	$PdCl_2$/5dppp	39	1.2	(1.6)

a) Carbonylation-polycondensation was carried out with 2.5 mmol of DBDHP, 2.5 mmol of bispehnol A, 0.1 mmol of $PdCl_2$, 0.1—0.5 mmol of phosphines, and 5.5 mmol of DBU in 10 ml of chlorobenzene at 120 °C under 20 bar of CO for 3 h. For run 19, 0.1 mmol of $Pd(PPh_3)_4$ was used as the catalyst. b) Precipitation of palladium black was observed. c) dppe: 1,2-Bis(diphenylphosphino)ethane. dppp: 1,3-Bis(diphenylphosphino)propane. dppb: 1,4-Bis(diphenylphosphino)butane. dpppe: 1,5-Bis(diphenylphosphino)pentane. dpph: 1,6-Bis(diphenylphosphino)hexane.

In our previous study,[28)] the effect of the chain length of α,ω-bis(diphenylphosphino)alkane ($Ph_2P(CH_2)_nPPh_2$ (n=2—5)) on the carbonylation of DBBP and DBDHP was studied. The maximum activities have been observed for 1,3-bis(diphenylphosphino)propane (dppp, $n=3$) and 1,4-bis(diphenylphosphino)butane (dppb, $n=4$). The catalysts with these ligands have been much more active than those with PPh_3. The difference in the activity has been ascribed to the coordination ability of the ligands. It should also be noted that the used bisphosphines to form a six-membered chelate, such as dppp, have been reported to have high catalytic activities in the carbonylation of aryl halide and triflates,[29,30)] and some reports describe that both the coordination ability and the flexibility of the chelating ligand are important factors in related reactions.[31,32)] The role of the pressure of carbon monoxide has been considered to change the coordination state of the ligands and to affect the rate-determining oxidative addition step of aryl bromide.

Considering these results, we investigated the effect of $Ph_2P(CH_2)_nPPh_2$ (n=2—6) and the pressure of carbon monoxide on the carbonylation-polycondensation. The result is shown in Fig. 2. The low pressure of carbon monoxide (5—10 bar) was most adequately employed in the synthesis of polymer **1**. The molecular weights gradually decreased with increasing the pressure of carbon monoxide above 5—10 bar. This suggests that the rate-determining step of the carbonylation-polycondensation is the oxidative addition, although the slightly inferior results at ordinary pressure are still unclear. Among the five bidentate phosphines, dppp was the most effective ligand, consistent with some reported results.[28—30)] However, PPh_3 was still more effective than dppp for the polycondensation.

Figure 3 shows that time-dependence curves for the consumption of carbon monoxide by the use of dppp and PPh_3, respectively, under ordinary pressure. The half-life period of the substrate in the case of dppp and of PPh_3 were 16 and 32 min, respectively. This means that the catalytic activity using dppp is apparently higher than that of PPh_3.

Figure 4 shows that time dependence on M_w by using dppp and PPh_3, respectively, under the same conditions as described in Fig. 3. The initial increase of M_w in the case of dppp is obviously larger than that of PPh_3, whereas the final M_w in the case of PPh_3 is higher than that of dppp. This means that the catalytic activity is not parallel to the final molecular weight of the resulting polymers, and that some inhibiting factors may occur during the development of the polymer in the case of dppp.

We should consider the side reaction, since the rate of polyester formation should not affect the final molecular

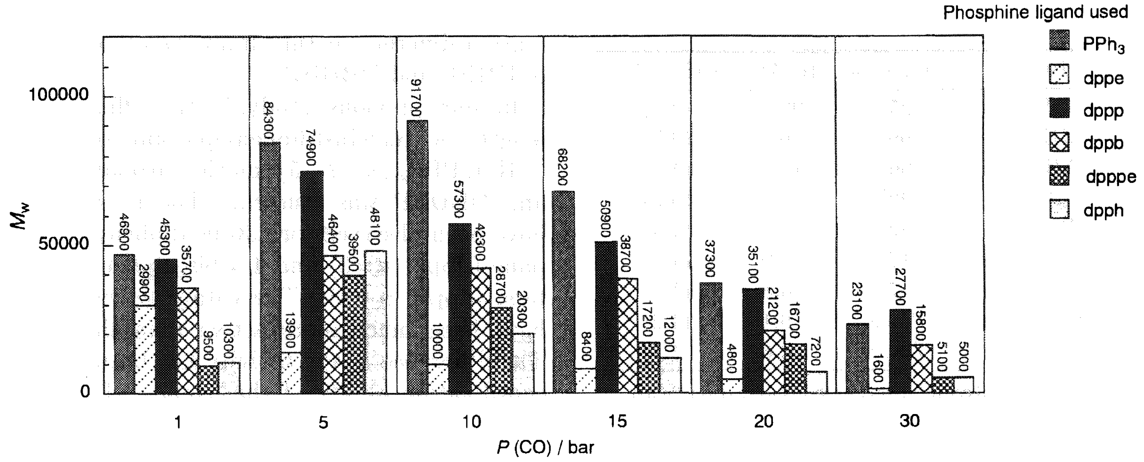
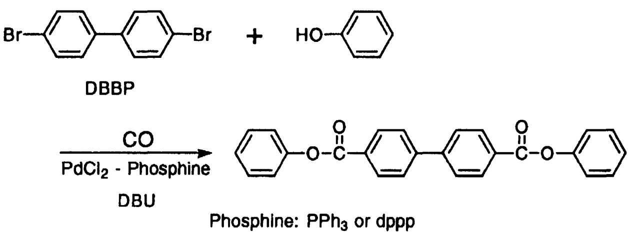


Fig. 2. M_w of **1** synthesized with various phosphine ligands under various pressures of CO. Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, 0.4 mmol of PPh_3 or 0.2 mmol of various bisphosphines, DBU 5.5 mmol, chlorobenzene 10 ml, reaction temperature 120 °C, reaction time 3 h.

weight of the polyester if the reaction can be carried to full conversion with sufficient selectivity. In order to know whether the side reactions take place or not, phenoxycarbonylation of DBBP using a catalyst with dppp or PPh_3 was examined as a model study (Eq. 2).



(2)

In both cases, only diphenyl biphenyl-4,4′-dicarboxylate was observed as a sole detectable product from DBBP by GC in high yield. The only other detectable product was phenyl benzoate. Since this was not observed when benzene was used as the reaction medium, this product should have occurred via carbonylation of the chlorobenzene used as the reaction medium. It is evident that the benzoyl complex as an intermediate in the carbonylation of chlorobenzene can be a terminator of polycondensation. The detected amount of phenyl benzoate was 0.115 mmol with dppp (0.2 mmol) and 0.044 mmol with PPh_3 (0.4 mmol), respectively, from phenol (6.0 mmol) and chlorobenzene (10 ml) in the presence of DBBP (2.5 mmol). Namely, the amount of phenyl benzoate arising during the carbonylation polycondensation with dppp was about three-times larger than that with PPh_3. This is a possible reason why the molecular weight is lower with dppp than with PPh_3 in spite of higher catalytic activity with the Pd–dppp complex.

Effect of Dihalides and Diols. The structures of the monomer and polymer greatly affected the polycondensation process. In order to determine the effects of the dihalides and diols on polycondensation, some other monomers were examined. Table 4 shows the effect of the dihalides. When tricyclic DBDHP or DIDHP was used as the dihalobiphenyl monomer and bisphenol A was used as the diol monomer, the solubility of the resulting polyester greatly increased compared with using DBBP as the dihalobiphenyl monomer, accompanying an enhancement of the molecular weight. Such an increase in the solubility is considered to be due to the effects of substitution and bulkiness. A significant increase in the molecular weight was effected by the

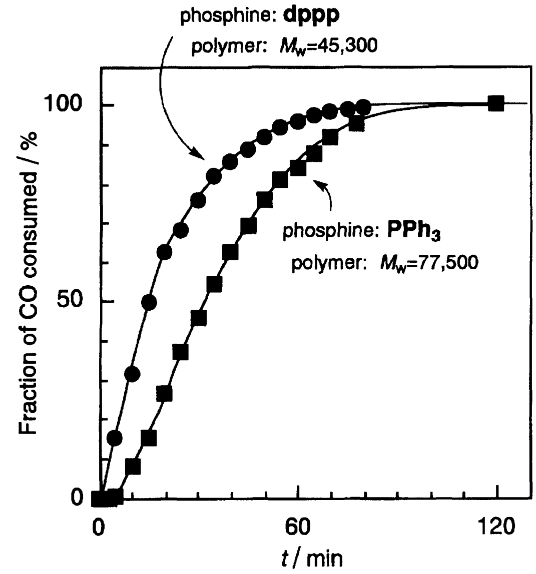


Fig. 3. CO consumption during the carbonylation-polycondensation forming **1**. Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, 0.4 mmol of PPh_3 or 0.2 mmol of dppp, DBU 5.5 mmol, chlorobenzene 10 ml, reaction temperature 120 °C, P (CO) 1 bar, reaction time 3 h.

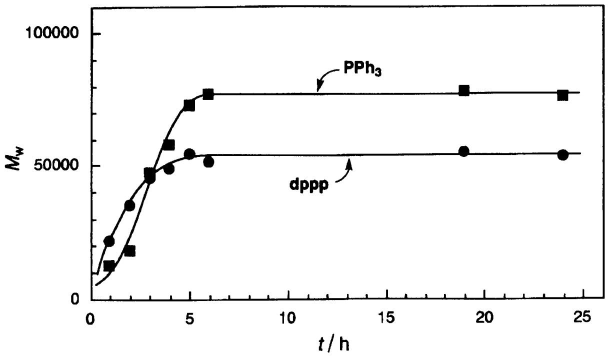


Fig. 4. Time dependence on M_w of polymer **1**. Reaction conditions: DBDHP 2.5 mmol, bisphenol A 2.5 mmol, $PdCl_2$ 0.1 mmol, 0.4 mmol of PPh_3 or 0.2 mmol of dppp, DBU 5.5 mmol, chlorobenzene 10 ml, reaction temperature 120 °C, P (CO) 1 bar, reaction time 24 h. The reaction mixture was partly sampled, worked up as usual, and subjected to GPC analysis.

Table 4. Effect of Dihalides[a)]

Run	Dihalobiphenyl	Product	Yield/%	10^3M_w	(M_w/M_n)
29	DBDHP	**1**	99	35	(3.6)
30	DIDHP	**1**	98	24	(2.8)
31	DBBP	**5**	94	5.6	(6.3)
32	DIBP	**5**	98	12	(2.5)
33	*p*-Dibromobenzene	**22**	96	2.6	(2.5)

a) Carbonylation-polycondensation was carried out with 2.5 mmol of dihalobiphenyl, 2.5 mmol of bisphenol A, 0.1 mmol of $PdCl_2$, 0.4 mmol of dppp, and 5.5 mmol of DBU in 10 ml of chlorobenzene at 120 °C under 20 bar of CO for 3 h.

use of DIBP instead of DBBP. This was due to the enhanced reactivity of diiodomonomer, which compensated for the negative factor of the insolubility. When monocyclic *p*-dibromobenzene was used as the dihalide monomer, product **22** was obtained with low molecular weight due to its low solubility.

Table 5 summarizes the effect of the diols. Bisphenols having sufficiently bulky alkyl spacers resulted in a moderately high molecular weight. However, 4,4′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bisphenol, 4,4′-[1,4-phenylenebis(1-metylethylidene)]bisphenol, and 4,4′-sulfonylbisphenol gave polyesters with low molecular weight. The NMR spectrum of the product from 4,4′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bisphenol did not show the typical pattern of this series of polyesters, indicating that carbonylation-polycondensation of DBDHP with 4,4′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bisphenol did not proceed sufficiently. Thus, a high polymer could not be obtained from 4,4′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-bisphenol, although the product showed good solubility. The polyester from 4,4′-[1,4-phenylenebis(1-metylethylidene)]bisphenol and bis(4-hydroxyphenyl)sulfone had low molecular weight due to their low solubility. The products from 4,4′-thiobisphenol and 4,4′-oxybisphenol were quite insoluble in the solvents tested.

Aliphatic diols, such as 1,10-decanediol, gave a much lower molecular weight than did the aromatic diols (Table 5, Run 44). Since the rate of CO consumption was rather higher with 1,10-decanediol than with bisphenol A (Fig. 5), the low molecular weight with 1,10-decanediol is ascribed to the low nucleophilicity of the terminal aliphatic hydroxyl groups, due to the shrunk conformation of the growing polymer in the medium.[33)] On the other hand, one reason for the superior molecular weight from bisphenol A could be the enhanced concentration of the phenoxide species. Because the phenol moieties are expected to expand in an aromatic medium, rather than shrink, and because of their acidity, the phenoxides could be readily formed. Thus, the result-

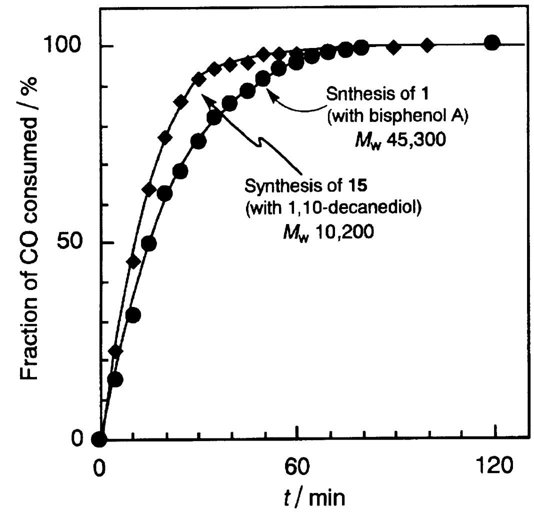


Fig. 5. CO consumption during the carbonylation-polycondensation forming **1** and **15**. Reaction conditions: DBDHP 2.5 mmol, bisphenol A or 1,10-decanediol 2.5 mmol, $PdCl_2$ 0.1 mmol, dppp 0.2 mmol, DBU 5.5 mmol, chlorobenzene 10 ml, reaction temperature 120 °C, P (CO) 1 bar, reaction time 3—5 h.

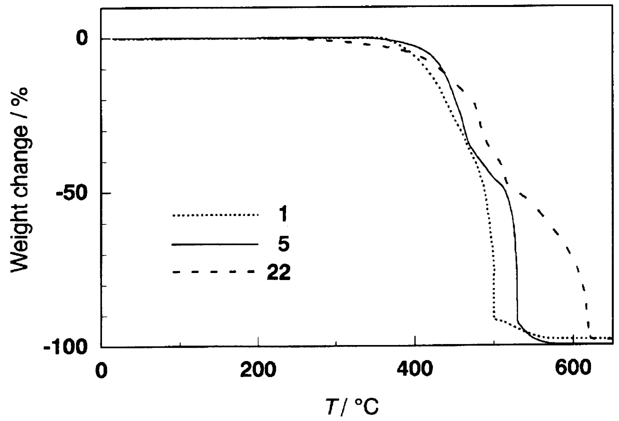


Fig. 6. TG curves for polymer **1**, **5**, and **22** at a heating rate of 10 $°C\,min^{-1}$ in air.

Table 5. Effect of Diols[a)]

Run	Dihalide	Diol	Product	Yield/%	10^3M_w	(M_w/M_n)	R.M.[c)]
34	DBDHP	Bisphenol A	**1**	99	35	(3.6)	−
35	DBDHP	4,4′-Cyclohexylidenebisphenol	**6**	93	20	(3.1)	−
36	DBDHP	4,4′-(*s*-Butylidene)bisphenol	**7**	99[b)]	25	(3.7)	−
37	DBDHP	4,4′-(1-Phenylethylidene)bisphenol	**8**	97	13	(3.0)	−
38	DBDHP	4,4′-Ethylidenebisphenol	**9**	98	12	(2.7)	+
39	DBDHP	4,4′-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bisphenol	**10**	78	3.1	(2.4)	−
40	DBDHP	4,4′-[1,4-Phenylenebis(1-methylethylidene)]bisphenol	**11**	98[b)]	4.4	(2.4)	++
41	DBDHP	4,4′-Sulfonylbisphenol	**12**	77	1.2	(2.0)	++
42	DBDHP	4,4′-Thiobisphenol	**13**	99	Insoluble		++
43	DBDHP	4,4′-Oxybisphenol	**14**	95	Insoluble		++
44	DBDHP	1,10-Decanediol	**15**	91	4.9	(2.7)	−
45	DIBP	1,10-Decanediol	**16**	91	14	(3.4)	−
46	DIBP	1,8-Octanediol	**17**	80	8.6	(3.2)	−
47	DIBP	1,6-Hexanediol	**18**	90	5.8	(3.9)	++
48	DIBP	1,4-Butanediol	**19**	96	1.8	(5.0)	++
49	DIBP	1,3-Propanediol	**20**	95	2.6	(4.3)	++
50	DIBP	1,2-Ethanediol	**21**	97	1.0	(2.9)	++

a) Carbonylation-polycondensation was carried out with 2.5 mmol of each monomer, 0.1 mmol of $PdCl_2$, 0.4 mmol of dppp, and 5.5 mmol of DBU in 10 ml of chlorobenzene at 120 °C under 20 bar of CO for 3—5 h. b) CO pressure was 10 bar. c) Outlook of the reaction mixture just after the reaction. −: homogeneous, +: slightly suspended, ++: suspended.

ing terminal phenoxides may be sufficiently nucleophilic in the ester formation step between polymers.

When more reactive DIBP was used as the dihalobiphenyl monomer instead of DBBP, a moderately high polymer was obtained, even from 1,10-decanediol. When other alkanediols, such as 1,8-octanediol, 1,6-hexanediol, 1,4-butanediol, 1,3-propanediol, and 1,2-ethanediol, were used, the molecular weight of the products gradually decreased with decreasing the length of the alkane chain.

Property of Products. T_m, T_5, and T_{10} of the obtained products are shown in the experimental part. Wholly aromatic polyesters (**1**, **6**—**14**) did not have a T_m and glass transition temperature up to 400 °C. Their T_{10} value was above 380 °C in air. The representative thermogravimetry (TG) patterns of the wholly aromatic polyester (e.g. polymer **1**, **5**) obtained in this study (compared with polyester **22**) are shown in Fig. 6. On the basis of the TG curves, biphenyl-containing polyesters **1** and **5** were more stable than **22** at 300—390 °C, although the weight loss of **1** and **5** were faster than **22** above 400 °C. Products **1** and **8** were found to be soluble in chloroform and dichloromethane. Products **5**, **6**, **7**, **9**, **11**, **12**, and **22** were not soluble in chloroform, but soluble in 25% HFIP/chloroform (v/v). Soluble products having an M_w larger than 10000 formed transparent casting films. They are expected to be readily molded.

In conclusion, the heat-resistance of wholly aromatic polyesters containing biphenyl moieties were as high as that of polyester **22**. In termes of molding, biphenyl-containing polyester **1** was more advantageous than polyester **22** because of the solubility. Aromatic–aliphatic polyesters containing biphenyl moieties, such as **15**—**21**, tend to be less stable to heat than wholly aromatic polyesters.

The other properties of the polymers obtained in this study are now under investigation and will be published elsewhere in the near future.

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