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Novel Types of Polyesters Containing Second-Order Nonlinear Optically Active Chromophores with High Density

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ABSTRACT: This article describes the syntheses and second-order nonlinear optical (NLO) properties of novel types of polyesters containing second-order NLO active chromophores with high density, which were obtained by condensation polymerization using two comonomers with the *N*,*N*-dialkyl-4-nitroaniline or *N*,*N*-dialkyl-4-((4-cyanophenyl)azo)aniline moiety. The polyesters were synthesized by condensation polymerization between isophthalic acid derivatives and N-substituted diethanolamines using triphenylphosphine and diethyl azodicarboxylate as the condensation reagents in dimethyl sulfoxide (DMSO) or 1-methyl-2-pyrrolidinone (NMP). The obtained amorphous polyesters exhibited good solubility in common organic solvents and provided optical-quality films by spin-coating. The SHG measurements of the spin-coated films of the resulting polyesters were carried out by the Maker fringe method using a Q-switched Nd:YAG laser (1064 nm) as an exciting beam after corona-poling. One of the polyesters, which was prepared from 5-[2-(*N*-methyl-4-nitroanilino)ethoxy]isophthalic acid and *N*-[4-((4-cyanophenyl)azo)phenyl]diethanolamine, exhibited the large second-order NLO coefficient, d_{33}, of 202 pm/V. On the other hand, a polyester containing chromophore moieties with the highest density, which was prepared from 5-{[1,3-bis[4-((4-cyanophenyl)azo)-*N*-methylanilino]-2-propyl]oxy}isophthalic acid and *N*-[4-((4-cyanophenyl)azo)phenyl]diethanolamine, exhibited good temporal stability of the second-order nonlinearity at ambient temperature.

Introduction

Polymeric materials with second-order nonlinear optical (NLO) properties have been the subject of intense studies because of nonlinear optical applications such as high-speed electro-optic modulation by taking advantage of their high NLO activity, chemical resistance, and good processability. In many cases, such aromatic molecules that contain both electron-donor and electron-acceptor groups at the conjugate sites have been dispersed in polymeric matrices with high glass transition temperatures (T_g), which is considered to be effective in restraining the relaxation of the noncentrosymmetric alignment of chromophores induced by an electric field.[1−9] However, chromophore-dispersed polymers suffer from the limited solubility of a chromophore in a host polymer or from the loss of a chromophore by sublimation. For the purpose of the solution of these problems, the syntheses and NLO properties of high T_g polymers functionalized with NLO active molecules have been studied.[10−25]

In general, aromatic-containing polyester matrices, which are easily prepared from the corresponding dicarboxylic-functionalized monomers and the dihydroxyl-functionalized ones, exhibit relatively high T_g's and optical transparency and form high-quality films. In fact, the preparation of the second-order NLO active main-chain-[26−33] and side-chain-type[34,35] polyesters has been reported. Our primary interest is to investigate the NLO properties of good-processable polyesters attributed to the alternate alignment of the same or different functionalities, which can be easily realized by providing the same or different functionalities for each comonomer.

From these points of view, we report here the syntheses of the polyesters obtained by the condensation polymerization using two comonomers, both of which contain the same functional moieties, i.e. the second-order NLO active chromophore shown in Figure 1. The aromatic components and the aliphatic ones in the main chain contribute to the high T_g and the improvement of the solubility, respectively. The present types of polyesters give increased NLO-chromophore concentration in polymer matrices. We have expected that the high concentration of chromophore in polymer matrices should result in the high second-order NLO susceptibility, because the second-order NLO susceptibility, $\chi^{(2)}{}_{333}$, which is expressed as eq 1 using the free gas approximation, is known to increase with the increase in the number of chromophores in polymeric matrices.

$$\chi^{(2)}{}_{333} = NF\beta_{zzz}\langle\cos^3\theta\rangle \qquad (1)$$

where N is the number of chromophores, F is a dimensionless combined field factor of the electric and electromagnetic fields, and β_{zzz} is a tensor element of molecular hyperpolarizability along the dipole axis. The thermal, linear optical, and second-order NLO properties of the obtained polyesters containing chromophores with high density are also described.

Experimental Section

Materials. Organic solvents for synthesis were purified by distillation on the suitable dehydrating reagents before use. 4-Aminobenzonitrile, 2-(*N*-methylanilino)ethanol, 1,3-dichloro-2-propanol, *N*-methylaniline, *N*-phenyldiethanolamine, diethanolamine, 4-fluoronitrobenzene, 5-hydroxyisophthalic acid, and diethyl azodicarboxylate (Tokyo Kasei Kogyo Co., Inc.) were commercially available and used as received. Triphenylphosphine was purchased from Tokyo Kasei Kogyo Co., Inc. and purified by recrystallization from ethanol prior to use. 4-[*N*-

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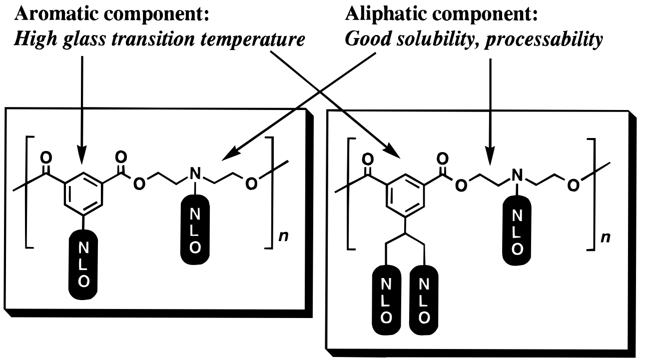


Figure 1. General structure of polyesters containing NLO-active chromophores with high density.

(2-Hydroxyethyl)-*N*-methylanilino]nitrobenzene (**3**), 4-(4-hydroxypiperidino)nitrobenzene (**4**), and 4-[4-(2-hydroxyethyl)-piperidino]nitrobenzene (**5**) were prepared by the method reported elsewhere.[36]

2-[4-((4-Cyanophenyl)azo)-*N*-methylanilino]ethanol (1). Sodium nitrite (7.01 g, 101.6 mmol) in 50 mL of water was slowly added dropwise to 10.0 g (84.7 mmol) of 4-aminobenzonitrile suspended in the mixture of 40 mL of hydrochloric acid and 120 mL of water, and the reaction mixture was stirred for 30 min below 5 °C. To this mixture was added 19.22 g (127.1 mmol) of 2-(*N*-methylanilino)ethanol below 5 °C, and the reaction mixture was stirred for 1 h. Sodium hydrogen carbonate was added to the reaction mixture till the supernatant solution was neutralized. The resulting dark red precipitate was collected by filtration and the crude product was purified by recrystallization from methanol. The product yield was 11.6 g (49%). ^{1}H NMR ($CDCl_3$): δ 3.14 (s, 3H, −N−CH_3), 3.6−4.1 (m, 4H, −N−CH_2− and −CH_2−OH), 6.80 (d, J = 9.2, 2H, phenyl (anilino) protons), 7.6−8.2 (m, 6H, phenyl (anilino) and cyanophenyl protons). Anal. Calcd for $C_{16}H_{16}N_4O$: C, 68.55; H, 5.75; N, 19.99. Found: C, 68.71; H, 5.78; N, 20.07.

6-[4-((4-Cyanophenyl)azo)-*N*-methylanilino]-1-hexanol (2). **2** was prepared by the same method as the preparation of **1** using 6-(*N*-methylanilino)-1-hexanol[37] as a raw material. The crude product was purified by recrystallization from ethanol. The product yield was 56%. ^{1}H NMR ($CDCl_3$): δ 1.1−1.8 (m, 9H, −$(CH_2)_4$− and −OH), 3.6−4.1 (m, 4H, −N−CH_2− and −CH_2−OH), 6.72 (d, J = 9.2, 2H, phenyl (anilino) protons), 7.6−8.2 (m, 6H, phenyl (anilino) and cyanophenyl protons). Anal. Calcd for $C_{20}H_{24}N_4O$: C, 71.40; H, 7.19; N, 16.65. Found: C, 71.46; H, 7.18; N, 16.68.

Dimethyl 5-Hydroxyisophthalate (6). To 50 mL of a methanol solution of 5.40 g (29.6 mmol) of 5-hydroxyisophthalic acid was added 0.5 mL of concentrated sulfuric acid. After this solution was refluxed overnight, excess methanol was evaporated. The residue was dissolved in ethyl acetate, and the solution was washed with saturated sodium hydrogen carbonate aqueous solution. The organic layer was dried on anhydrous sodium sulfate, and the concentration of the organic layer gave **6** as white crystals with 94% yield. ^{1}H NMR ($CDCl_3$): δ 3.94 (s, 6H, −$COOCH_3$), 5.52 (s, 1H, −OH), 7.73 (d, 2H, J = 1.1, phenyl protons), 8.26 (s, 1H, phenyl proton). Anal. Calcd for $C_{10}H_{10}O_5$: C, 57.14; H, 4.80. Found: C, 57.04; H, 4.76.

Dimethyl 5-{2-[4-((4-Cyanophenyl)azo)-*N*-methylanilino]ethoxy}isophthalate (7). Under an argon atmosphere, 2.80 g (10.0 mmol) of **1**, 3.16 g (15.0 mmol) of **6**, and 3.16 g (12.0 mmol) of triphenylphosphine were dissolved in 20 mL of dry tetrahydrofuran (THF) in an ice bath. To this solution was added dropwise 2.55 g (15.0 mmol) of diethyl azodicarboxylate[38] in 10 mL of dry THF, and the mixture was stirred at ambient temperature for 1 h. The residue resulting from the evaporation of solvent was recrystallized from ethyl acetate. The yield of the product was 91%. Mp: 165 °C. ^{1}H NMR ($CDCl_3$): δ 3.22 (s, 3H, −N−CH_3), 3.8−4.1 (m, 2H, −N−CH_2−), 3.92 (s, 6H, −$COOCH_3$), 4.29 (t, J = 5.1, 2H, −O−CH_2−), 6.82 (d, J = 9.2, 2H, phenyl (anilino) protons), 7.6−8.0 (m, 8H, phenyl (anilino and isophthalate) protons), 8.28 (s, 1H, phenyl(isophthalate) proton). IR (KBr, cm^{-1}): 2220 (−CN), 1740 (−C=O). Mass (m/e): 472 (M^+), 263 (M^+ − (OPh-$(COOCH_3)_2$)), 249 (NC−Ph−N=N−Ph−N(CH_3)CH_2^+), 179, 135, 119 (Ph−N(CH_3)CH_2^+), 77 (phenyl$^+$). Anal. Calcd for $C_{26}H_{24}N_4O_5$: C, 66.09; H, 5.12; N, 11.86. Found: C, 65.95; H, 5.04; N, 11.87. UV−vis (DMSO): λ_{max}/nm (ϵ/(L/mol cm)), 464 (35 510); λ_{cutoff}/nm, 592.

Compounds 8−11. **8−11** were prepared by the same method as the preparation of **7** using **2−5** as raw materials, respectively.

8. Yield: 91%. Mp: 134 °C. ^{1}H NMR ($CDCl_3$): δ 1.3−2.0 (m, 8H, −N−CH_2−$(CH_2)_4$−CH_2OH), 3.09 (s, 3H, −N−CH_3), 3.3−3.6 (m, 2H, −N−CH_2−), 3.93 (s, 6H, −$COOCH_3$), 3.9−4.2 (m, 2H, −O−CH_2−), 6.73 (d, J = 9.2, 2H, phenyl (anilino) protons), 7.6−8.1 (m, 8H, phenyl (anilino and isophthalate) protons), 8.26 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}): 2220 (−CN), 1720 (−C=O). Mass (m/e): 528 (M^+), 319 (M^+ − (OPh($COOCH_3)_2$)), 249 (NC−Ph−N=N−Ph−N(CH_3)-CH_2^+), 179, 119 (Ph−N(CH_3)CH_2^+), 77 (phenyl$^+$). Anal. Calcd for $C_{30}H_{32}N_4O_5$: C, 68.16; H, 6.10; N, 10.60. Found: C, 68.28; H, 6.05; N, 10.62. UV−vis (DMSO): λ_{max}/nm (ϵ/(L/mol cm)), 477 (37 530); λ_{cutoff}/nm, 590.

9. Yield: 91%. Mp: 162 °C. ^{1}H NMR ($CDCl_3$): δ 3.20 (s, 3H, −N−CH_3), 3.8−4.1 (m, 2H, −N−CH_2−), 3.93 (s, 6H, −$COOCH_3$), 4.27 (t, J = 5.1, 2H, −O−CH_2−), 6.70 (d, J = 9.5, 2H, phenyl (anilino) protons), 7.70 (d, J = 1.1, 2H, phenyl (isophthalate) protons), 8.14 (d, J = 9.5, 2H, phenyl (anilino) protons), 8.28 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}): 1720 (−C=O), 1520 (−NO_2), 1340 (−NO_2). Mass (m/e): 388 (M^+), 179 (M^+ − (OPh($COOCH_3)_2$)), 119 (Ph−N(CH_3)-CH_2^+), 77 (phenyl$^+$). Anal. Calcd for $C_{19}H_{20}N_2O_7$: C, 58.76; H, 5.19; N, 7.21. Found: C, 58.83; H, 5.01; N, 7.17. UV−vis (DMSO): λ_{max}/nm (ϵ/(L/mol cm)), 403 (21 380); λ_{cutoff}/nm, 488.

10. Yield: 89%. Mp: 178 °C. ^{1}H NMR ($CDCl_3$): δ 2.04 (t, 4H, J = 5.3, piperidinyl protons), 3.4−3.8 (m, 4H, piperidinyl protons), 3.94 (s, 6H, −$COOCH_3$), 4.6−4.9 (m, 1H, piperidinyl proton), 6.85 (d, J = 9.5, 2H, phenyl (anilino) protons), 7.79 (d, J = 1.1, 2H, phenyl (isophthalate) protons), 8.13 (d, J = 9.5, 2H, phenyl(anilino) protons), 8.29 (s, 1H, phenyl(isophthalate) proton). IR (KBr, cm^{-1}): 1720 (−C=O), 1510 (−NO_2), 1340 (−NO_2). Mass (m/e): 414 (M^+), 205 (M^+ − (OPh-$(COOCH_3)_2$)), 179, 119 (Ph−N(CH_3)CH_2^+), 77 (phenyl$^+$). Anal. Calcd for $C_{21}H_{22}N_2O_7$: C, 60.86; H, 5.35; N, 6.76. Found: C, 60.93; H, 5.22; N, 6.73. UV−vis (DMSO): λ_{max}/nm (ϵ/(L/mol cm)), 408 (22 220); λ_{cutoff}/nm, 497.

11. Yield: 93%. Mp: 129 °C. ^{1}H NMR ($CDCl_3$): δ 1.2−1.7 (m, 3H, piperidinyl protons), 1.7−2.1 (m, 4H, piperidinyl protons), 2.97 (t, 2H, J = 13.5, −CH_2−piperidine), 4.0−4.3 (m, 4H, piperidinyl protons), 3.94 (s, 6H, −$COOCH_3$), 6.85 (d, J = 9.5, 2H, phenyl (anilino) protons), 7.79 (d, J = 1.1, 2H, phenyl (isophthalate) protons), 8.13 (d, J = 9.5, 2H, phenyl (anilino) protons), 8.29 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}): 1720 (−C=O), 1510 (−NO_2), 1340 (−NO_2). Mass (m/e): 442 (M^+), 233 (M^+ − (OPh($COOCH_3)_2$)), 179, 119 (Ph−N-(CH_3)CH_2^+), 77 (phenyl$^+$). Anal. Calcd for $C_{23}H_{26}N_2O_7$: C, 62.43; H, 5.92; N, 6.33. Found: C, 62.37; H, 5.99; N, 6.35. UV−vis(DMSO): λ_{max}/nm (ϵ/(L/mol cm)), 402 (24 170); λ_{cutoff}/nm, 493.

5-{2-[4-((4-Cyanophenyl)azo)-*N*-methylanilino]ethoxy}-isophthalic Acid (12). **7** (0.30 g, 0.63 mmol) and 0.24 g (6.0 mmol) of sodium hydroxide were dissolved in the mixed solvent of 24 mL of methanol, 10 mL of THF, and 6 mL of water. The mixture was refluxed for 3 h and cooled. Hydrochloric acid was added to the reaction mixture till the supernatant solution was slightly acidic. The precipitate was collected by filtration and purified by the recrystallization from acetone. The yield of the product was 89%. Mp: >230 °C dec. ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 3.22 (s, 3H, −N−CH_3), 3.8−4.1 (m, 2H, −N−CH_2−), 4.29 (t, J = 4.4, 2H, −O−CH_2−), 6.83 (d, J = 9.2, 2H, phenyl (anilino) protons), 7.7−8.1 (m, 8H, phenyl (anilino and isophthalate) protons), 8.31 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}): 3410 (carboxylic −OH), 2220 (−CN), 1700 (−C=O). Mass (m/e): 444 (M^+), 249 (NC−Ph−N=N−Ph−N(CH_3)CH_2^+), 182, 165, 77 (phenyl$^+$).

Compounds 13−16. **13−16** were prepared by the same method as the preparation of **12** using **8−11** as raw materials, respectively.

13. Yield: 81%. Mp: >230 °C dec. ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 1.2−2.1 (m, 8H, $-N-CH_2-(CH_2)_4-CH_2-O-$), 3.09 (s, 3H, $-N-CH_3$), 3.2−3.6 (m, 2H, $-N-CH_2-$), 4.05 (t, J = 6.1, 2H, $-O-CH_2-$), 6.74 (d, J = 9.2, 2H, phenyl (anilino) protons), 7.6−8.2 (m, 8H, phenyl (anilino and isophthalate) and cyanophenyl protons), 8.29 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}): 3450 (carboxylic −OH), 2220 (−CN), 1700 (−C=O). Mass (m/e): 500 (M^+), 249 ($NC-Ph-N=N-Ph-N(CH_3)CH_2^+$), 182, 165, 77 (phenyl$^+$).

14. Yield: 84%. Mp: >240 °C dec. ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 3.20 (s, 3H, $-N-CH_3$), 3.8−4.1 (m, 2H, $-N-CH_2-$), 4.23 (t, J = 5.5, 2H, $-O-CH_2-$), 6.73 (d, J = 9.5, 2H, phenylene (anilino) protons), 7.70 (d, J = 1.1, 2H, phenyl (isophthalate) protons), 8.10 (d, 2H, J = 9.5, phenyl (anilino) protons), 8.28 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}): 3420 (carboxylic −OH), 1700 (−C=O), 1340 ($-NO_2$). Mass (m/e): 360 (M^+), 182, 165, 77 (phenyl$^+$).

15. Yield: 85%. Mp: >280 °C dec. ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 1.9−2.2 (m, 4H, piperidinyl protons), 3.4−3.8 (m, 4H, piperidinyl protons), 4.6-4.9 (m, 1H, piperidinyl proton), 6.87 (d, J = 9.5, 2H, phenyl (anilino) protons), 7.77 (d, J = 1.1, 2H, phenyl (isophthalate) protons), 8.11 (d, 2H, J = 9.5, phenyl (anilino) protons), 8.31 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}): 3430 (carboxylic −OH), 1690 (−C=O), 1310 ($-NO_2$). Mass (m/e): 386 (M^+), 205 ($M^+ - (OPh(COOH)_2)$), 182, 165, 77 (phenyl$^+$).

16. Yield: 92%. Mp: >240 °C dec. ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 1.2−2.7 (m, 3H, piperidinyl protons), 1.7−2.1 (m, 4H, piperidinyl protons), 2.98 (t, J = 13.8, 2H, $-CH_2$-piperidine), 4.0−4.2 (m, 4H, piperidinyl protons and $-CH_2-O-$), 6.81 (d, J = 9.5, 2H, phenyl (anilino) protons), 7.74 (d, J = 1.1, 2H, phenyl (isophthalate) protons), 8.09 (d, J = 9.5, 2H, phenyl (anilino) protons), 8.32 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}): 3410 (carboxylic −OH), 1725 and 1695 (−C=O), 1320 ($-NO_2$). Mass (m/e): 414 (M^+), 233 ($M^+ - (OPh(COOH)_2)$), 182, 165, 77 (phenyl$^+$).

***N*-[4-((4-Cyanophenyl)azo)phenyl]diethanolamine (17).** **17** was prepared by the same method as the preparation of **1** using *N*-phenyldiethanolamine instead of 2-(*N*-methylanilino)-ethanol as a raw material. The yield of product was 62%. Mp: 176 °C. ^{1}H NMR ($CDCl_3$): δ 2.7−2.9 (bs, 2H, −OH), 3.7−4.2 (m, 8H, $-N-CH_2-$), 6.78 (d, J = 9.2, 2H, phenyl (anilino) protons), 7.7−8.1 (m, 6H, phenyl (anilino) and cyanophenyl protons). IR (KBr, cm^{-1}): 3420 (−OH), 2225 (−CN). Anal. Calcd for $C_{17}H_{18}N_4O_2$: C, 65.79; H, 5.85; N, 18.05. Found: C, 65.58; H, 5.75; N, 17.97. UV−vis (DMSO): λ_{max}/nm (ϵ/(L/mol cm)), 478 (36 400); λ_{cutoff}/nm, 596.

***N*-(4-Nitrophenyl)diethanolamine (18).** **18** was prepared by the same method as the preparation of **3** using diethanolamine and 4-fluoronitrobenzene as raw materials. The yield of product was 55%. Mp: 106 °C. ^{1}H NMR ($CDCl_3$): δ 2.7−2.9 (bs, 2H, −OH), 3.7−4.2 (m, 8H, $-N-CH_2-$), 6.66 (d, J = 9.5, 2H, phenyl protons), 8.10 (d, J = 9.5, 2H, phenyl protons). IR (KBr, cm^{-1}): 3360 (−OH), 1520 and 1325 ($-NO_2$). Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.38. Found: C, 53.11; H, 6.27; N, 12.26. UV−vis (DMSO): λ_{max}/nm (ϵ/(L/mol cm)), 409 (17 800); λ_{cutoff}/nm, 496.

1,3-Bis(*N*-methylanilino)-2-propanol (19). To the mixture of 150 mL of 1-butanol, 97.0 g (812 mmol) of *N*-methylaniline, 9.0 g of potassium iodide, and 67.4 g (488 mmol) of anhydrous potassium carbonate, 25.4 g (198 mmol) of 1,3-dichloro-2-propanol was added. The reaction mixture was refluxed for 40 h. Ethyl acetate was added to the residue resulting from the evaporation of 1-butanol, and the solution was washed with water several times. The organic layer was dried on anhydrous sodium sulfate, and the solvent was evaporated. The crude product was purified by column chromatography packed with silica gel in ethyl acetate/hexane (volume ratio 1/9, which was changed to the ratio of 1/3 after the *N*-methylaniline was eluted). Finally, the recrystallization of the product from acetone/hexane afforded 29.6 g (55%) of **19** as a colorless crystal. ^{1}H NMR ($CDCl_3$): δ 2.42 (d, J = 2.2, 2H, −OH), 2.96 (s, 6H, $-N-CH_3$), 3.36 (t, J = 6.2, 4H, $-N-CH_2-$), 4.0−4.3 (m, 1H, $HO-CH-(CH_2)_2-$), 6.6−6.9 (m, 6H, phenyl protons), 7.1−7.4 (m, 4H, phenyl protons). IR (KBr, cm^{-1}): 3440 (−OH). Mass (m/e): 270 (M^+), 150 ($M^+ - (Ph-N(CH_3)CH_2)$), 120 ($Ph-N(CH_3)CH_2^+$), 77 (phenyl$^+$). Anal. Calcd for $C_{17}H_{22}N_2O$: C, 75.52; H, 8.20; N, 10.36. Found: C, 75.71; H, 8.37; N, 10.33.

Dimethyl 5-{[1,3-[Bis(*N*-methylanilino)]-2-propyl]oxy}-isophthalate (20). Under an argon atmosphere, 2.703 g (10.0 mmol) of **19**, 3.155 g (15.0 mmol) of **6**, and 3.155 g (12.0 mmol) of triphenylphosphine were dissolved in 50 mL of dry THF in an ice bath. To this solution was added dropwise 2.550 g (15.0 mmol) of diethyl azodicarboxylate, and the mixture was stirred overnight at ambient temperature. The residue from the evaporation of THF was purified by column chromatography packed with silica gel in ethyl acetate/hexane (volume ratio 1/5). The concentration of the eluted solution recrystallized 2.45 g (53%) of **20** as white crystals. ^{1}H NMR($CDCl_3$): δ 2.94 (s, 6H, $-N-CH_3$), 3.6−3.8 (m, 4H, $-N-CH_2-$), 3.83 (m, 6H, $-COOCH_3$), 4.9−5.1 (m, 1H, $-O-CH-(CH_2)_2-$), 6.6−6.9 (m, 6H, phenyl (anilino) protons), 7.1−7.4 (m, 4H, phenyl (anilino) protons), 7.59 (d, J = 1.1, 2H phenyl (isophthalate) protons), 8.19 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}): 1720 (−C=O). Mass (m/e): 462 (M^+), 179, 120 ($Ph-N(CH_3)$-CH_2^+), 77 (phenyl$^+$). Anal. Calcd for $C_{27}H_{30}N_2O_5$: C, 70.11; H, 6.54; N, 6.06. Found: C, 69.92; H, 6.50; N, 6.14.

Dimethyl 5-{[1,3-Bis[4-((4-cyanophenyl)azo)-*N*-methylanilino]-2-propyl]oxy}isophthalate (21). Under an argon atmosphere, 5 mL of dry DMF was added to the mixture of 1.45 g (3.13 mmol) of **20** and 0.95 g (6.89 mmol) of anhydrous potassium carbonate. To this mixture was added dropwise in an ice bath 1.90 g (6.89 mmol) of 4-cyanobenzenediazonium hexafluorophosphate, which was prepared by modifying the method of Katz *et al.*[39] The reaction mixture was stirred at ambient temperature for 1 h and poured into 200 mL of water. The produced precipitate was collected by filtration and dissolved in chloroform. The chloroform solution was washed with water several times. The organic layer was dried on anhydrous sodium sulfate and concentrated. The crude product was purified by column chromatography packed with silica gel in chloroform eluent. The concentration of the eluted solution recrystallized 1.72 g (76%) of **21** as dark red crystals. Mp: 214 °C. ^{1}H NMR ($CDCl_3$): δ 3.11 (s, 6H, $-N-CH_3$), 3.7−3.9 (m, 4H, $-N-CH_2-$), 3.83 (m, 6H, $-COOCH_3$), 4.9−5.1 (m, 1H, $-O-CH-(CH_2)_2-$), 6.76 (d, J = 9.2, 4H, phenyl (anilino) protons), 7.55 (d, J = 1.3, 2H, phenyl (isophthalate) protons), 7.6−8.0 (m, 12H, phenyl (anilino) and cyanophenyl protons), 8.21 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}): 2220 (−CN), 1720 (−C=O). Mass (m/e): 720 (M^+), 179, 120 ($Ph-N(CH_3)CH_2^+$), 77 (phenyl$^+$). Anal. Calcd for $C_{41}H_{36}N_8O_5$: C, 68.32; H, 5.03; N, 15.55. Found: C, 68.28; H, 4.82; N, 15.43. UV−vis (DMSO): λ_{max}/nm (ϵ/(L/mol cm)), 469 (65 500); λ_{cutoff}/nm, 592.

5-{[1,3-Bis[4-((4-cyanophenyl)azo)-*N*-methylanilino]-2-propyl]oxy}isophthalic Acid (22). **22** was prepared by the same method as the preparation of **12** using **21** as a raw material. ^{1}H NMR ($CDCl_3$ + DMSO-d_6): δ 3.14 (s, 6H, $-N-CH_3$), 3.7−4.1 (m, 4H, $-N-CH_2-$), 5.0−5.3 (m, 1H, $-O-CH-(CH_2)_2-$), 6.84 (d, J = 9.7, 4H, phenyl (anilino) protons), 7.5−8.3 (m, 15H, phenyl (anilino and isophthalate) and cyanophenyl protons). IR (KBr, cm^{-1}): 3470 (carboxylic −OH), 2230 (−CN), 1700 (−C=O).

General Procedure of Polymerization. All polyesters were prepared by the same procedure. The preparation of **P1** is given as a representative example. Under an argon atmosphere, 0.444 g (1.00 mmol) of **12**, 0.310 g (1.00 mmol) of **17**, and 0.577 g (2.20 mmol) of triphenylphosphine were dissolved in 2.0 mL of dry DMSO and maintained at 50 °C. To this solution was added 0.374 g (2.20 mmol) of diethyl azodicarboxylate. The reaction mixture was stirred at 100°C for 12 h and poured into 200 mL of methanol. The produced precipitate was collected by filtration and reprecipitated in a THF/methanol system. Finally, the product was dried in vacuo. The product yield was 0.538 g (75%). ^{1}H NMR ($CDCl_3$): δ 3.09 (s, 3H), 3.5−4.0 (m, 6H), 4.0−4.2 (m, 2H), 4.2−4.8 (m, 4H), 6.6−7.1 (m, 4H), 7.4−8.3 (m, 15H). IR (KBr, cm^{-1}): 2220 (−CN), 1720 (−C=O).

^{1}H NMR and IR spectral data and the yields for the obtained polyesters are given as follows.

P2. Yield: 61%. ^{1}H NMR ($CDCl_3$): δ 1.1−1.9 (m, 8H), 3.04 (s, 3H), 3.2−3.6 (m, 2H), 3.6−4.3 (m, 6H), 4.4−4.8 (m, 4H), 6.6−7.1 (m, 4H), 7.4−8.3 (m, 15H). IR (KBr, cm^{-1}): 2220 (−CN), 1720 (−C═O).

P3. Yield: 56%. ^{1}H NMR (CDCl$_3$): δ 3.18 (s, 3H), 3.7−4.1 (m, 6H), 4.1−4.4 (m, 2H), 4.4−4.9 (m, 4H), 6.6−7.1 (m, 4H), 7.3−7.6 (m, 2H), 7.9−8.4 (m, 5H). IR (KBr, cm^{-1}): 1720 (−C═O), 1520 and 1320 (−NO$_2$).

P4. Yield: 56%. ^{1}H NMR (CDCl$_3$): δ 1.7−2.3 (m, 4H), 3.2−3.8 (m, 4H), 3.8−4.1 (m, 4H), 4.1−4.4 (m, 1H), 4.5−4.8 (m, 4H), 6.7−7.1 (m, 4H), 7.60 (s, 2H), 7.9−8.3 (m, 5H). IR (KBr, cm^{-1}): 1720 (−C═O), 1510 and 1320 (−NO$_2$).

P5. Yield: 46%. ^{1}H NMR (CDCl$_3$): δ 1.1−1.8 (m, 3H), 1.8−2.1 (m, 4H), 2.97 (t, J = 12.5, 2H), 3.8−4.4 (m, 8H), 4.5−4.8 (m, 4H), 6.7−7.1 (m, 4H), 7.56 (s, 2H), 7.9−8.3 (m, 5H). IR (KBr, cm^{-1}): 1720 (−C═O), 1510 and 1320 (−NO$_2$).

P6. Yield: 85%. ^{1}H NMR (CDCl$_3$ + DMSO-d_6): δ 2.7−3.1 (m, 6H), 3.4−4.5 (m, 12H), 5.0−5.3 (m, 1H), 6.5−7.2 (m, 6H), 7.2−8.2 (m, 21H). IR (KBr, cm^{-1}): 2230 (−CN), 1720 (−C═O).

P7. Yield: 54%. ^{1}H NMR (CDCl$_3$ + DMSO-d_6): δ 3.09 (s, 3H), 3.6−4.1 (m, 6H), 4.1−4.3 (m, 2H), 4.4−4.8 (m, 4H), 6.6−7.1 (m, 4H), 7.4−8.3 (m, 11H). IR (KBr, cm^{-1}): 2230 (-CN), 1720 (−C═O), 1540 and 1310 (−NO$_2$).

P8. Yield: 40%. ^{1}H NMR (CDCl$_3$ + DMSO-d_6): δ 3.11 (s, 3H), 3.6−4.1 (m, 6H), 4.1−4.3 (m, 2H), 4.3−4.7 (m, 4H), 6.5−7.1 (m, 4H), 7.4−8.2 (m, 11H). IR (KBr, cm^{-1}): 2230 (−CN), 1720 (−C═O), 1540 and 1310 (−NO$_2$).

P9. Yield: 45%. ^{1}H NMR (CDCl$_3$ + DMSO-d_6): δ 1.0−1.5 (m, 3H), 1.5−2.0 (m, 4H), 2.7−3.0 (m, 2H), 3.6−4.4 (m, 8H), 4.4−4.8 (m, 4H), 6.6−7.3 (m, 4H), 7.5−8.3 (m, 11H). IR (KBr, cm^{-1}): 2230 (−CN), 1720 (−C═O), 1510 and 1320 (−NO$_2$).

Characterization. UV−vis absorption spectra were measured by transmission on a Hitachi Model U-3200 spectrophotometer. ^{1}H NMR was conducted with a Hitachi R-90H FT NMR (90 MHz) spectrometer. DSC measurements were carried out on a Shimadzu Model DSC-50 under a helium flow rate of 20 mL/min and a heating rate of 10°C/min. Gel permeation chromatography (GPC) was performed on a Tosoh HLC-802A instrument equipped with TSK gels G5000H$_6$, G4000H$_6$, G3000H$_6$, and G2000H$_6$ using polystyrene standards in THF eluent. X-ray diffraction patterns were recorded on a MAC Science MXP^3 X-ray diffractometer, equipped with a thermal controller Model 5310.

Film Preparation. Polymer was deposited on an ordinary cover glass by spin-coating at a rate of 2000 rpm from a 5 wt % THF solution.

Heating and Poling Procedures. The poling procedure of a spin-coated film was achieved by poling normal to the surface by corona discharge. The distance of the tungsten needle from the surface is 25 mm. The needle side was set to 10 kV negative to an aluminum heating plate. After 20 min of poling around T_g, a spin-coated film was cooled to the ambient temperature with continuous corona poling.

SHG Measurement. The second harmonic generation (SHG) of polyesters at 532 nm was measured in transmission by means of the Maker fringe method.[40] An experimental apparatus for the Maker fringe measurement has been shown in our previous report.[36] An outline is as follows. A Q-switched Nd:YAG laser (Spectron SL404G, λ = 1064 nm, 10-Hz repetition rate, 6-ns pulse duration) was used for the exciting light source after its pulse energy was decreased to less than 1 mJ through neutral density filters. The polymer sample was placed on a rotating stage and rotated around a horizontal axis from an incident angle of −80° to +80°. SHG signals were detected by a photomultiplier tube. The signal from the photomultiplier tube was integrated with a boxcar integrator (Stanford Research SR-250). The p-polarized laser beam was chosen using a λ/4 wave plate and a linear polarizer.

Determination of Nonlinear Optical Coefficient. The second-order NLO coefficients, d_{33}, of the obtained polyesters were determined from the relationship of SH light intensity and an incident angle of an exciting beam measured by the Maker fringe method. According to Jerphagnon *et al.*,[40] the intensity of the SH wave, $I_{2\omega}$, in a uniaxial poled material generated by p-polarized exciting wave, the intensity of which is represented by I_ω, is given by

$$I_{2\omega} = [512\pi^2/(cw^2)]I_\omega{}^2 d_{33}{}^2 t_\omega{}^4 T_{2\omega} R(\theta) p^2(\theta) B(\theta) I_\omega{}^2 \times \sin^2 \Psi(\theta)/(n_\omega{}^2 - n_{2\omega}{}^2)^2 \quad (2)$$

where c is the light velocity, w is the spot radius of the Gaussian beam, θ is the incident angle of an exciting wave, t_ω and $T_{2\omega}$ are Fresnel-like transmission factors, n_ω and $n_{2\omega}$ are the refractive indices, $R(\theta)$ is the multiple reflection correction, $p(\theta)$ is a projection factor[9], $B(\theta)$ is the beam size correction, and $\Psi(\theta)$ is the angular dependence of the second harmonic power. These functions are given by

$$t_\omega = 2\cos\theta(n_\omega \cos\theta_\omega + \cos\theta) \quad (3)$$

$$T_{2\omega} = 2n_{2\omega}\cos\theta_{2\omega}(n_\omega\cos\theta_\omega + \cos\theta)(n_\omega\cos\theta_\omega + n_{2\omega}\cos\theta_{2\omega})/(n_{2\omega}\cos\theta_{2\omega} + \cos\theta)^3 \quad (4)$$

$$p(\theta) = \cos\theta_\omega \sin\theta_\omega \cos\theta_{2\omega} + (\cos^2\theta_\omega/3 + \sin^2\theta_\omega)\sin\theta_{2\omega} \quad (5)$$

$$B(\theta) = \exp[-(L^2/w^2)\cos^2\theta(\tan\theta_\omega - \tan\theta_{2\omega})^2] \quad (6)$$

$$\Psi(\theta) = (2\pi L/\lambda)|(n_\omega\cos\theta_\omega - n_{2\omega}\cos\theta_{2\omega})| \quad (7)$$

$$\theta_\omega = \cos^{-1}[(n_\omega{}^2 - \sin^2\theta)^{1/2}/n_\omega] \quad (8)$$

$$\theta_{2\omega} = \cos^{-1}[(n_{2\omega}{}^2 - \sin^2\theta)^{1/2}/n_{2\omega}] \quad (9)$$

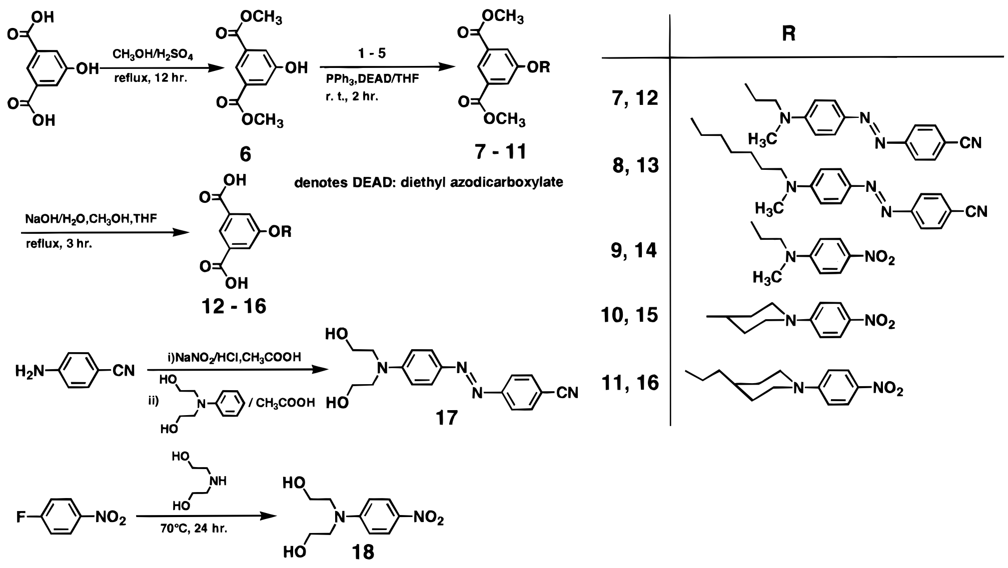
where L is the sample thickness. The d_{33} values of the resulting polyesters were determined by the mean square methods using eqs 2−9 and 1 mm thick y-cut quartz (d_{11} = 0.5 pm/V) as a reference sample.

Results and Discussion

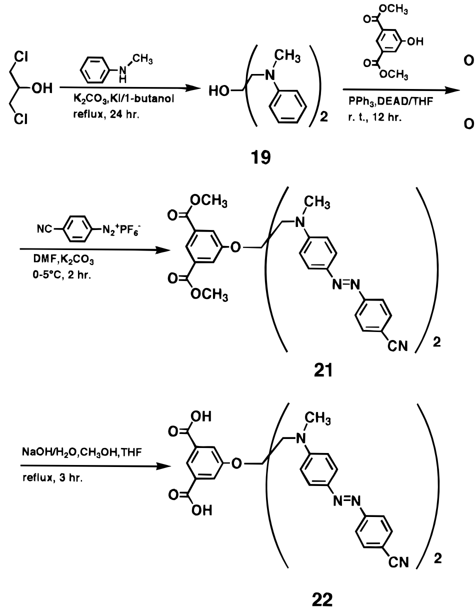
Synthesis and General Properties of Polyesters. Scheme 1 shows the pathways for the syntheses of 5-position-substituted isophthalic acid derivatives **12**−**16** as the precursors for the preparation of polyesters. 5-Position-substituted isophthalic acid derivatives were prepared by the Mitsunobu reaction between dimethyl 5-hydroxyisophthalate and hydroxyl-functionalized chromophores followed by hydrolyses of the dimethyl isophthalate derivatives. All these reactions provided the 5-position-substituted isophthalic acid derivatives with favorable yields. Isophthalic acid derivative **22**, which contains two chromophore moieties per molecule, was prepared for the purpose of the increase in the content of the chromophore moieties, as shown in Scheme 2. In this preparation, the Mitsunobu reaction between dimethyl 5-hydroxyisophthalate and 1,3-bis(N-methylanilino)-2-propanol was carried out followed by an azo-coupling reaction because the poor solubility of 1,3-bis[4-((4-cyanophenyl)azo)-N-methylanilino]-2-propanol, which also caused difficulty in the purification, is detrimental to the progress of the Mitsunobu reaction between dimethyl 5-hydroxyisophthalate and 1,3-bis[4-((4-cyanophenyl)azo)-N-methylanilino]-2-propanol. Their comonomers, namely N-substituted diethanolamines **17** and **18**, were also prepared as shown in Scheme 1.

Scheme 3 shows the preparation of polyesters containing NLO active chromophores with high density. All of the polyesters were prepared by solution polycondensation of the above isophthalic acid derivatives and N-substituted diethanolamines in dimethyl sulfoxide (DMSO) or 1-methyl-2-pyrrolidinone (NMP) at 100°C using triphenylphosphine and diethyl azodicarboxylate as the condensation reagents. Pouring the reaction solution into methanol provided the polyesters as a powder solid. The yields of polyesters were in the range

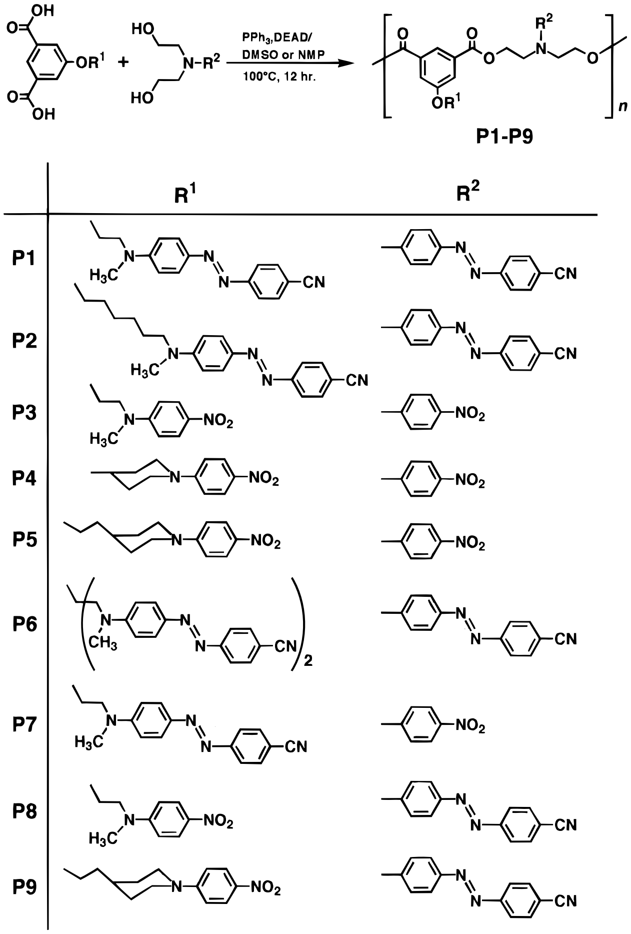
Scheme 1



Scheme 2



Scheme 3



40−75%. The obtained polyesters **P1**−**P9** are soluble in common polar organic solvents, such as tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), DMSO, and NMP at room temperature, and slightly soluble acetone or ethyl acetate but insoluble in methanol or ethanol. The aliphatic components in the backbone are expected to improve the solubility of these polyesters. Therefore, the optical-quality thin film can be easily obtained by spin-coating from THF solutions of all present polyesters. Table 1 summarizes the general characteristics of the resulting polyesters. The weight-average molecular weights of polyesters estimated from GPC were the magnitude of thousand, which indicates the degree of polymerization was ca. 10−15. NMR end-group analysis for molecular weight estimation could not be carried out owing to the very weak signals based on end groups and to the high viscosity of polymer solutions, which caused signal-broadening. Some efforts have been made for the purpose of increasing the molecular weight, e.g. variation in the reaction temperature, variation of concentrations of comonomers or condensation reagents, and variation of solvent. However, not only molecular weights were varied, but also it turned out that too high a reaction temperature resulted in very low yields of the polyester due to thermal decomposition of diethyl azodicarboxylate.

On the other hand, typical examples of DSC thermograms are shown in Figure 2. On each DSC thermogram, the glass transitions were observed; however, no other endothermic or exothermic peaks appeared in the temperature range from ambient temperature to 200 °C. The T_g's of polyesters, which were determined from a second heating scan of DSC measurements, were in the range 72−139 °C, as provided in Table 1. The bulkiness of the chromophore makes T_g higher, and the highest T_g in the present polyesters was 139 °C for **P6**

Table 1. General Properties of Polyesters P1−P9

polymer	monomer	M_w[a]	M_w/M_n[b]	T_g,[c] °C
P1	**12**, **17**	4450	1.42	118
P2	**13**, **17**	3260	1.31	105
P3	**14**, **18**	1220	1.20	87
P4	**15**, **18**	1630	1.19	85
P5	**16**, **18**	1640	1.21	72
P6	**22**, **17**	4830	1.34	139
P7	**12**, **18**	1870	1.41	114
P8	**14**, **17**	2210	1.48	109
P9	**16**, **17**	5940	1.69	89

[a] The values estimated from GPC using polystyrene standards. [b] Polydispersity index. [c] The values determined from DSC on a second heating scan.

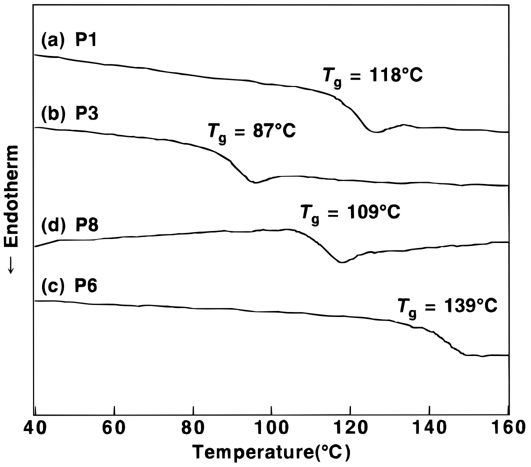


Figure 2. Typical examples of DSC traces on a second heating scan at a rate of 10°C/min and a helium flow rate of 20 mL/min: (a) **P1**; (b) **P3**; (c) **P8**; (d) **P6**.

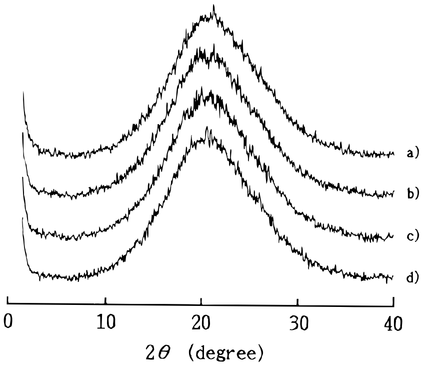


Figure 3. X-ray diffraction patterns of **P1** obtained by a powder method: (a) 25 °C; (b) 80 °C; (c) 100 °C; (d) 120 °C.

which contains the bulky chromophores with the highest density. In addition, X-ray diffraction measurements of polyesters, a typical example of which is shown in Figure 3, were also carried out by a powder method and exhibited no diffraction peaks except for the broad halo around 20°. These findings indicate that the obtained polyesters are amorphous.

UV−Vis Spectroscopy and SHG Measurement. Figure 4 shows the UV−vis absorption spectra of **P1** received using a spin-coated film, the thickness of which was <1 μm, on a glass substrate before and after corona poling. The data obtained by UV−vis spectroscopy are summarized in Table 2. In the UV−vis absorption spectrum of **P1** after corona poling, a decrease in the absorbance in the visible region was observed. Taking into account that the UV−vis spectra were measured by the transmission method, this result indicates the promotion of chromophore orientation by electric poling.

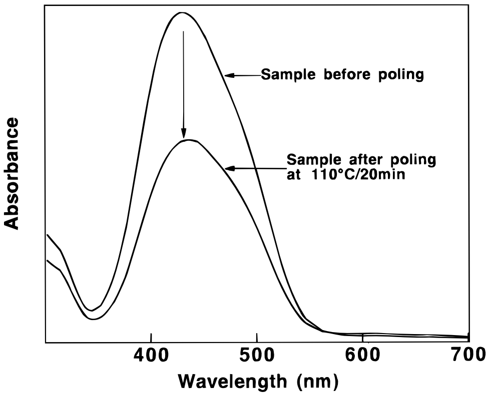


Figure 4. Typical example of UV−vis absorption spectra of a spin-coated film of **P1** before and after heating with corona poling.

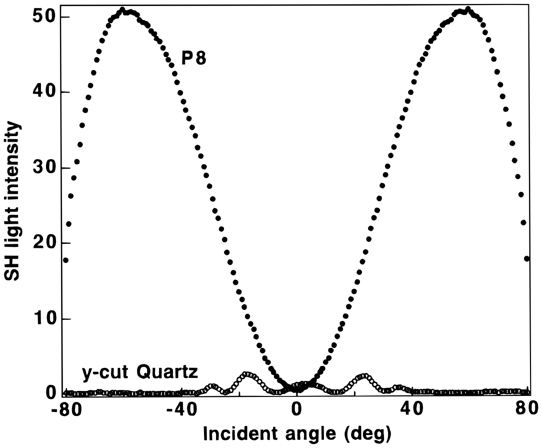


Figure 5. Relationship between SH light intensity and the incident angle of an exciting beam: (●) spin-coated film of **P8** after heating with corona poling; (○) 1 mm thickness of *y*-cut quartz.

Table 2. Optical Properties of Polyesters P1−P9

polymer	λ_{max},[a] nm	λ_{cutoff},[a] nm	poling temp, °C	d_{33}, pm/V
P1	433	606	130	110
P2	434	606	115	84
P3	391	492	80	29
P4	391	515	90	27
P5	392	505	90	17
P6	427	577	150	32
P7	389	589	120	55
P8	407	617	120	202
P9	410	615	100	36

[a] The values in the visible region.

This trend is observed for all resulting polyesters in the present system.

On the other hand, as a typical example, Figure 5 describes the relationship between SH light intensity and the incident angle of an exciting beam for a spin-coated film of **P8** after corona poling. It was confirmed that the similar Maker-fringe patterns were obtained for spin-coated films of the present polyesters after corona poling. The obtained second-order NLO coefficients, d_{33}, are summarized in Table 2. Polyesters **P1** and **P2**, which consist of two comonomers containing *N*,*N*-dialkyl-4-[(4-cyanophenyl)azo]anilino moieties, exhibited 84 and 110 pm/V of d_{33}, respectively. Polyesters **P3**−**P5**, which consist of two comonomers containing *N*,*N*-dialkyl-4-(nitrophenyl)anilino moieties, exhibited the d_{33} range 17−29 pm/V. Such a difference between a series of **P1** and **P2** and that of **P3**−**P5** in the magnitude of the d_{33} values is attributed to the differ-

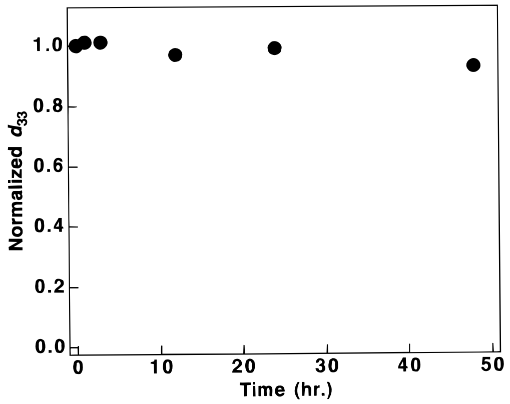


Figure 6. Temporal stability of the second harmonic generation signal of **P6** at ambient temperature.

ence in the microscopic optical nonlinearity of the chromophore involved. However, polyester **P6**, which contains *N*,*N*-dialkyl-4-[(4-cyanophenyl)azo]anilino moieties with the highest density in the present polyesters, exhibited the d_{33} value of 32 pm/V, which was smaller than that of **P1** containing the similar chromophore. It would be because too high a density of the bulky chromophore inhibits the alignment of the dipole moments such that the d_{33} value of **P6** was smaller than that of **P1**. Figure 6 shows the temporal stability of the value of d_{33} for polyester **P6** at ambient temperature, which makes it clear that the value of d_{33} for polyester **P6** exhibited only a slight decay. On the other hand, polyester **P8**, which was prepared from 5-[2-(*N*-methyl-4-nitroanilino)ethoxy]isophthalic acid and *N*-[4-((4-cyanophenyl)azo)phenyl]diethanolamine, exhibited the largest d_{33} value in the present system. This may be because the combination of the bulky chromophore, i.e. *N*,*N*-dialkyl-4-[(4-cyanophenyl)azo]anilino moieties, and the compact chromophore, i.e. *N*,*N*-dialkyl-4-(4-nitrophenyl)anilino moieties, takes advantage of the alignment of the dipole moments. The detailed studies on the alignment of chromophores and the stability of the chromophore orientation including theoretical aspects are subjects of the future.

Conclusions

The novel types of polyesters containing second-order NLO active chromophores with high density were obtained by the condensation polymerization between the isophthalic acid derivatives and the N-substituted diethanolamines. The obtained amorphous polyesters exhibited good solubility in common organic solvents and provided optical-quality films by spin-coating. The SHG measurements of the spin-coated films of the resulting polyesters were carried out by the Maker fringe method after corona-poling. One of polyesters, which was prepared from 5-[2-(*N*-methyl-4-nitroanilino)ethoxy]isophthalic acid and *N*-[4-((4-cyanophenyl)azo)phenyl]diethanolamine, exhibited the large second-order NLO coefficient, d_{33}, of 202 pm/V. On the other hand, a polyester containing chromophore moieties with the highest density, which was prepared from 5-{[1,3-bis[4-((4-cyanophenyl)azo)-*N*-methylanilino]-2-propyl]oxy}isophthalic acid and *N*-[4-((4-cyanophenyl)azo)phenyl]diethanolamine, exhibited good temporal stability of the second-order optical nonlinearity at ambient temperature.

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