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Polyamides for Nonlinear Optics Containing Second-Order NLO-phores with High Density

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This article describes the syntheses and second-order nonlinear optical (NLO) properties of novel types of optically transparent polyamides containing second-order NLO-active chromophores with high density. The chromophore used in this study contained a perfluorooctylsulfonyl or cyano moiety as an electron-withdrawing group at the π-conjugating sites. The polyamides were prepared by condensation polymerization between 5-substituted isophthaloyl chloride derivatives and novel 3,5-diaminobenzoates. When the terminal groups in the side chain of each comonomer unit were different, amorphous polyamides exhibited good solubility in common organic solvents and provided optical-quality films by spin-coating. The optical transparency of the obtained polyamides was down to 400 nm. Second-harmonic generation (SHG) measurements of the obtained polyamides were carried out by the Maker fringe method using a Q-switched Nd:YAG laser as an exciting beam after corona-poling. One of the polyamides, which was prepared from 5-{2-[*N*-(4-cyanophenyl)-*N*-methylamino]-ethoxy}isophthaloyl chloride and 2-{*N*-methyl-*N*-[4-(perfluorooctylsulfonyl)phenyl]amino}-ethyl 3,5-diaminobenzoate, exhibited the desired optical-transparency and the second-order NLO coefficient, d_{33}, of 4.4 ± 1.3 pm/V, retaining 94% of its original d_{33} after storage for 2 weeks at ambient temperature.

Introduction

The study of polymeric materials with second-order nonlinear optical (NLO) properties has been the subject of intense interest because their high NLO activity, chemical resistance, and easy processability are available for NLO applications such as a fast waveguide and electrooptic modulation. As for the architecture of second-order NLO materials, it is generally established that the aromatic molecules having both electron-donor and electron-acceptor groups at the π-conjugate sites can be bonded to polymeric matrixes with the high glass transition temperatures (T_g). High-T_g polymers are considered effective in restraining the relaxation of the noncentrosymmetric NLO-phore alignment induced by an electric field.[1,2] Indeed, the synthesis and NLO properties of high-T_g aromatic polymers such as polyesters,[3−5] polyamides,[6] polyurethanes,[7] polyureas,[8] and polyimides[9] functionalized with NLO-phores have been reported. If condensation polymerization was carried out using two comonomers containing the same or different functionalities, the polymers obtained have alternate alignment of the same or different functionalities. However, there have been very few reports where the functionalities were introduced into both comonomers. Our research group has reported[4,5] the preparation and the second-order NLO properties of

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polyesters obtained by the condensation polymerization using two comonomers, both of which contain the second-order NLO-phores. These types of materials would increase the NLO-phore contents in polymer matrixes. It is expected that high concentration of NLO-phore in polymer matrixes should result in higher second-order NLO susceptibility, because 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 NLO-phores in polymeric matrixes:

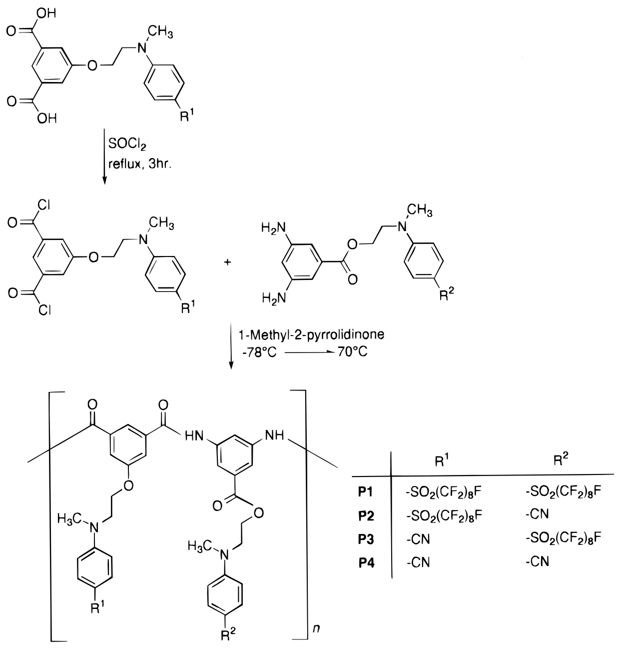
$$\chi^{(2)}{}_{333} = NF\beta_{zzz}\langle\cos^3\theta\rangle \qquad (1)$$

where N is the number of NLO-phores, 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.

Aromatic-containing polyamide matrixes, which are generally prepared from the corresponding dicarboxylic- and diamino-functionalized comonomers, are well-known to exhibit high T_g. Thus the preparation of second-order NLO active main-chain- and side-chain-type polyamides have been reported as mentioned above. One of the problems with aromatic-containing polyamides would be the difficulty in processability, e.g., poor solubility in common organic solvents. Our primary interest is to investigate the NLO properties of easily processable polyamides due to the alternate alignment of same or different functionalities. This can be easily realized by providing the same or different functionalities for each comonomer.

It is normally accepted that the value of the microscopic optical nonlinearity, β, is enlarged by a high degree of delocalization at the π-conjugate.[10] As a result, an intramolecular charge-transfer absorption is caused in the visible region. In contrast, a short cutoff wavelength of second-order NLO materials is desired for practical applications, because intolerable damage would be brought to the material by the absorption of second harmonic wave generated by the near-infrared wave of diode lasers. In other words, there should be a tradeoff relationship between optical nonlinearity and cutoff wavelength. Several research groups have made some efforts to prepare second-order NLO materials with blue shifted cutoff wavelengths.[8,11]

Scheme 1



	R^1	R^2
P1	$-SO_2(CF_2)_8F$	$-SO_2(CF_2)_8F$
P2	$-SO_2(CF_2)_8F$	-CN
P3	-CN	$-SO_2(CF_2)_8F$
P4	-CN	-CN

From these points of view, we report here the synthesis of the polyamides prepared by polycondensation using two comonomers, both of which contain the second-order NLO-phores with short cutoff wavelength, as shown in Scheme 1. We select a perfluorooctylsulfonyl or cyano moiety as an electron-withdrawing group in the NLO-phores attached to these polyamides so that the optical transparency below 400 nm would be achieved. The thermal, linear optical and second-order NLO properties of the obtained polyamides are described.

Experimental Section

Materials. Dimethyl sulfoxide (DMSO) and 1-methylpyrrolidin-2-one (NMP) used as solvent were distilled over CaH_2 under reduced pressure, and tetrahydrofuran (THF) was distilled twice (over CaH_2 and sodium) for the removal of traces of water. 4-Fluorobenzonitrile, *N*-methylethanolamine, 3,5-dinitrobenzoic acid, diethyl azodicarboxylate (Tokyo Kasei Kogyo Co., Inc.), sodium tetrahydroborate (Kishida Chemical Co., Ltd.), $SnCl_2\cdot 2H_2O$, 5% palladium on charcoal, and thionyl chloride (Wako Pure Chemical Industries, Ltd.) 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. Dimethyl 5-hydroxyisophthalate,[4] 2-{*N*-[4-(perfluorooctylsulfonyl)phenyl]-*N*-methylamino}ethanol (**1**),[5] and 5-(2-{*N*-[4-(perfluorooctylsulfonyl)phenyl]-*N*-methylamino}ethoxy)isophthalic acid (**11**)[5] were prepared by methods reported earlier.

2-[*N*-(4-Cyanophenyl)-*N*-methylamino]ethanol (2). Under an argon atmosphere, 30 mL of dry DMSO was added to the mixture of 22.53 g (300 mmol) of *N*-methylethanolamine and 55.28 g (400 mmol) of anhydrous potassium carbonate. To this mixture, was added 24.22 g (200 mmol) of 4-fluoroben-

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zonitrile. After the reaction mixture was stirred at 70 °C for 24 h, the reaction mixture was poured into 1000 mL of water. The crude product was extracted by ethyl acetate, and the solvent was evaporated. The residue was purified by column chromatography packed with silica gel in ethyl acetate/hexane (volume ratio 2/1). The evaporation of solvent afforded **2** as colorless crystals. The yield of product was 27.98 g (79%), mp 56 °C (determined by differential scanning calorimetry (DSC)). ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.60 (t, J = 5.7, 1H, $-$OH), 3.07 (s, 3H, $-$N$-$CH$_3$), 3.57 (t, J = 5.2, 2H, $-$N$-$CH$_2$$-$), 3.82 (t, J = 5.5, 2H, $-$O$-$CH$_2$$-$), 6.71 (d, 2H, J = 9.0, phenylene protons), 7.45 (d, 2H, J = 9.0, phenylene protons). IR (KBr, cm^{-1}) 3400 ($-$OH), 2210 ($-$CN). Mass (*m/e*) 176 (M$^+$), 157, 145 (NC$-$Ph$-$N(CH$_3$)CH$_2$$^+$), 129, 116, 102 ($^+Ph-$CN), 75, 51, 42, 31. Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90. Found: C, 68.34; H, 6.94; N, 15.98.

2-{*N*-[4-(Perfluorooctylsulfonyl)phenyl]-*N*-methylamino}ethyl 3,5-Dinitrobenzoate (3). Under an argon atmosphere, 10 mL of thionyl chloride was added to 1.06 g (5.00 mmol) of 3,5-dinitrobenzoic acid, and the mixture was refluxed for 3 h. After the evaporation of excess thionyl chloride, 20 mL of dry THF was added to the residue. To this solution, was added dropwise 3.17 g (5.00 mmol) of **1** in 30 mL of dry THF together with 1 mL of triethylamine. The reaction mixture was stirred at ambient temperature for 3 h and poured into 300 mL of saturated sodium hydrogen carbonate aqueous solution. The crude product was extracted with chloroform (100 mL × 5), and the solvent was evaporated. The product was purified by column chromatography packed with silica gel in ethyl acetate/chloroform (volume ratio 1/2) eluent. Finally, the recrystallization from chloroform afforded **3** with the yield of 3.58 g (86.5%) as pale yellow crystals, mp 166 °C. ^{1}H NMR (CDCl$_3$, 90 MHz) δ 3.21 (s, 3H, $-$N$-$CH$_3$), 3.95 (t, J = 5.9, 2H, $-$N$-$CH$_2$$-$), 4.70 (t, J = 5.9, 2H, $-$O$-$CH$_2$$-$), 6.87 (d, J = 9.5, 2H, phenyl (anilino) protons), 7.77 (d, J = 9.5, 2H, phenyl (anilino) protons), 9.05 (d, J = 2.0, 2H, dinitrophenyl protons), 9.21 (t, J = 2.0, 1H, dinitrophenyl proton). IR (KBr, cm^{-1}) 1735 ($-$C=O), 1545 ($-$NO$_2$), 1350 ($-$NO$_2$), 1240 and 1205 (perfluoroalkyl), 1155 ($-$SO$_2$$-$). Mass (*m/e*) 827 (M$^+$), 808 (M$^+$$-$F), 602 (F(CF$_2$)$_8SO_2$$-Ph-$N(CH$_3$)CH$_2$$^+$), 408 (M$^+$$-$(C$_8F_{17}$)), 344 (M$^+$$-$(SO$_2C_8F_{17}$)), 195 ((O$_2$N)$_2$PhCO$^+$), 169 (CF$_3$(CF$_2$)$_2$$^+$), 119 (CF$_3CF_2$$^+$ or Ph$-$N(CH$_3$)CH$_2$$^+$), 105, 91, 75, 69 (CF$_3$$^+$). Anal. Calcd for $C_{24}H_{14}N_3O_8F_{17}S$: C, 34.84; H, 1.71; N, 5.08. Found: C, 34.76; H, 1.53; N, 4.87.

4 was prepared by the same method as the preparation of **3** using **2** as a raw material. The product was obtained with the yield of 93% as orange-colored crystals, mp 180 °C. ^{1}H NMR (CDCl$_3$, 90 MHz) δ 3.12 (s, 3H, $-$N$-$CH$_3$), 3.87 (t, J = 5.9, 2H, $-$N$-$CH$_2$$-$), 4.67 (t, J = 5.8, 2H, $-$O$-$CH$_2$$-$), 6.76 (d, J = 9.2, 2H, phenyl (anilino) protons), 7.48 (d, J = 9.2, 2H, phenyl (anilino) protons), 9.04 (d, J = 2.0, 2H, dinitrophenyl protons), 9.22 (t, J = 2.0, 1H, dinitrophenyl proton). IR (KBr, cm^{-1}) 2220 ($-$CN), 1730 ($-$C=O), 1540 ($-$NO$_2$), 1340 ($-$NO$_2$). Mass (*m/e*) 370 (M$^+$), 195 ((O$_2$N)$_2$PhCO$^+$), 149, 145 (NC$-$Ph$-$N(CH$_3$)CH$_2$$^+$), 129, 102 ($^+Ph-$CN), 91, 75. Anal. Calcd for $C_{17}H_{14}N_4O_6$: C, 55.14; H, 3.81; N, 15.13. Found: C, 55.36; H, 3.77; N, 15.22.

2-{*N*-[4-(Perfluorooctylsulfonyl)phenyl]-*N*-methylamino}ethyl 3,5-Diaminobenzoate (5). Under an argon atmosphere, 50 mL of ethanol was added to 3.31 g (4.00 mmol) of **3** and 9.03 g (40.0 mmol) of SnCl$_2$·2H$_2$O, and the mixture was stirred at 60 °C. To this solution, was added dropwise 0.303 g (8.00 mmol) of sodium tetrahydroborate in 50 mL of ethanol, and the reaction mixture was stirred at 60 °C for 3h. After the evaporation of solvent, 500 mL of 0.5 mol/L of sodium hydroxide aqueous solution was added to the residue in an ice bath. The crude product was extracted with ethyl acetate (100 mL × 5), and the solvent was evaporated. The product was purified by column chromatography packed with silica gel in ethyl acetate eluent. Finally, the recrystallization from ethyl acetate afforded **5** with the yield of 2.50 g (81%) as pale yellow crystals, mp 145 °C. ^{1}H NMR (CDCl$_3$ + DMSO-d_6, 90 MHz) δ 3.18 (s, 3H, -N-CH$_3$), 3.8$-$4.2 (m, 6H, $-$N$-$CH$_2$$-$ and $-$NH$_2$), 4.46 (t, J = 5.7, 2H, $-$O$-$CH$_2$$-$), 6.22 (t, J = 2.2, 1H, diaminophenyl proton), 6.62 (d, J = 2.2, 2H, diaminophenyl protons), 6.89 (d, J = 9.3, 2H, phenyl (anilino) protons), 7.78 (d, J = 9.3, 2H, phenyl (anilino) protons). IR (KBr, cm^{-1}) 3375 ($-$NH$_2$), 1715 ($-$C=O), 1235 and 1215 (perfluoroalkyl), 1155 ($-$SO$_2$$-$). Mass (*m/e*) 767 (M$^+$), 602 (F(CF$_2$)$_8SO_2$$-Ph-$N(CH$_3$)CH$_2$$^+$), 348 (M$^+$$-$(C$_8F_{17}$)), 284 (M$^+$$-$(SO$_2C_8F_{17}$)), 196, 169 (CF$_3$(CF$_2$)$_2$$^+$), 152 ((H$_2$N)$_2$PhCOOH), 119 (CF$_3CF_2$$^+$ or Ph$-$N(CH$_3$)CH$_2$$^+$), 69 (CF$_3$$^+$). Anal. Calcd for $C_{24}H_{18}N_3O_8F_{17}S$: C, 37.56; H, 2.36; N, 5.48. Found: C, 37.58; H, 2.16; N, 5.41.

6 was prepared in the mixed solvent of ethanol/THF (volume ratio 1/1) by the similar method as the preparation of **5** using **4** as a raw material. The yield of the product was 83%, mp 117 °C. ^{1}H NMR (CDCl$_3$, 90 MHz) δ 3.07 (s, 3H, $-$N$-$CH$_3$), 3.6$-$3.7 (m, 4H, $-$NH$_2$), 3.75 (t, J = 5.9, 2H, $-$N$-$CH$_2$$-$), 4.43 (t, J = 5.9, 2H, $-$O$-$CH$_2$$-$), 6.17 (t, J = 2.1, 1H, diaminophenyl proton), 6.63 (d, J = 2.1, 2H, diaminophenyl protons), 6.73 (d, J = 9.3, 2H, phenyl (anilino) protons), 7.47 (d, J = 9.3, 2H, phenyl (anilino) protons). IR (KBr, cm^{-1}) 3470 and 3435 ($-$NH$_2$), 2210 ($-$CN), 1710 ($-$C=O). Mass (*m/e*) 310 (M$^+$), 158 (NC$-$Ph$-$N(CH$_3$)CH=CH$_2$), 152 ((H$_2$N)$_2$PhCOOH), 145 (NC$-$Ph$-$N(CH$_3$)CH$_2$$^+$), 129, 102 ($^+Ph-$CN), 80, 53, 42.

Dimethyl 5-{2-[*N*-(4-Cyanophenyl)-*N*-methylamino]ethoxy}isophthalate (8). Under an argon atmosphere, 5.29 g (30.0 mmol) of **2**, 7.57 g (36.0 mmol) of dimethyl 5-hydroxyisophthalate, and 9.44 g (36.0 mmol) of triphenylphosphine were dissolved in 40 mL of dry THF in an ice bath. To this solution, was added dropwise 6.13 g (36.0 mmol) of diethyl azodicarboxylate,[12] and the mixture was stirred at ambient temperature for 1 h. The residue resulting from the evaporation of solvent purified by column chromatography packed with silica gel in chloroform eluent. Finally, the recrystallization from chloroform afforded **8** with the yield of 9.26 g (84%), mp 146 °C. ^{1}H NMR (CDCl$_3$, 90 MHz) δ 3.13 (s, 3H, $-$N$-$CH$_3$), 3.83 (t, J = 5.1, 2H, $-$N$-$CH$_2$$-$), 3.93 (s, 6H, $-$COOCH$_3$), 4.24 (t, J = 5.1, 2H, $-$O$-$CH$_2$$-$), 6.77 (d, J = 9.2, 2H, phenyl (anilino) protons), 7.49 (d, J = 9.2, 2H, phenyl (anilino) protons), 7.70 (d, J = 1.1, 2H, phenyl (isophthalate) protons), 8.28 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}) 2210 ($-$CN), 1730 ($-$C=O). Mass (*m/e*) 368 (M$^+$), 337 (M$^+$$-$(OCH$_3$)), 179, 159 (NC$-Ph-$N(CH$_3$)CH$_2CH_2$$^+$), 145 (NC$-Ph-$N(CH$_3$)CH$_2$$^+$), 129, 102 ($^+Ph-$CN), 83, 63, 43, 28. Anal. Calcd for $C_{20}H_{20}N_2O_5$: C, 65.19; H, 5.48; N, 7.61. Found: C, 64.95; H, 5.35 N, 7.55. UV$-$vis (CHCl$_3$) λ_{max}/nm (ϵ/(L/mol cm)), 294 (32 380); λ_{cutoff}/nm, 344.

5-{2-[*N*-(4-Cyanophenyl)-*N*-methylamino]ethoxy}isophthalic Acid (10). Sodium hydroxide (2.71 g, 67.9 mmol) and 5.00 g (13.6 mmol) of **8** were dissolved in the mixed solvent of 20 mL of methanol, 20 mL of THF, and 10 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/water. The yield of the product was quantitative, mp 254 °C. ^{1}H NMR (CDCl$_3$ + DMSO-d_6, 90 MHz) δ 3.13 (s, 3H, $-$N$-$CH$_3$), 3.86 (t, J = 5.2, 2H, $-$N$-$CH$_2$$-$), 4.25 (t, J = 5.2, 2H, $-$O$-$CH$_2$$-$), 6.75 (d, J = 9.0, 2H, phenyl (anilino) protons), 7.47 (d, J = 9.0, 2H, phenyl (anilino) protons), 7.67 (d, J = 1.1, 2H, phenyl (isophthalate) protons), 8.27 (s, 1H, phenyl (isophthalate) proton). IR (KBr, cm^{-1}) 3435 (carboxylic $-$OH), 2210 ($-$CN), 1700 ($-$C=O). Mass (*m/e*) 340 (M$^+$), 182 ((HOOC)$_2$PhOH), 158 (NC$-$Ph$-$N(CH$_3$)CH=CH$_2$), 145 (NC$-$Ph$-$N(CH$_3$)CH$_2$$^+$), 129, 102 ($^+Ph-$CN), 91, 42, 28. Anal. Calcd for $C_{18}H_{16}N_2O_5$: C, 63.53; H, 4.74; N, 8.23. Found: C, 63.56; H, 4.61 N, 8.14.

Reduction of 3 with Hydrogen in the Presence of Pd on Charcoal. **3** (414 mg, 0.500 mmol) was added to 21.0 mg (0.010 mmol by Pd) of 5% Pd on charcoal powder suspended in 20 mL of the mixed solvent of ethanol and THF (volume ratio 1:1). The reaction mixture was stirred at ambient temperature for 16 h with bubbling of hydrogen gas. The complete consumption of **3** was confirmed by thin-layer chromatography, but the reaction did not proceed further by bubbling hydrogen gas. Then, the Pd on charcoal was filtered off, and the solvent was distilled off under reduced pressure. The product was purified by column chromatography packed

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(12) Mitsunobu, O. *Synthesis* **1981**, 1.

with silica gel in the eluent of chloroform/ethyl acetate (volume ratio 4/1). Finally, the recrystallization from ethyl acetate/hexane provided yellow crystals. The product was found to be 2-{*N*-[4-(perfluorooctylsulfonyl)phenyl]-*N*-methylamino}ethyl 3-amino-5-nitrobenzoate, which was obtained by the monoreduction of nitro groups of **3**, as deduced from the following spectral data. The yield was 0.356 g (89%), mp 166 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.19 (s, 3H, $-N-CH_3$), 3.92 (t, $J = 5.4$, 2H, $-N-CH_2-$), 4.60 (t, $J = 5.4$, 2H, $-O-CH_2-$), 6.88 (dt, $J = 9.4$, 2.0, 2H, phenyl (anilino) protons), 7.72 (dd, $J = 2.1$, 1.4, 1H, 3-amino-5-nitrophenyl proton), 7.78 (dt, $J = 9.4$, 2.0, 2H, phenyl (anilino) protons), 8.00 (t, $J = 2.2$, 1H, 3-amino-5-nitrophenyl proton), 8.33 (dd, $J = 2.1$, 1.4, 1H, 3-amino-5-nitrophenyl proton). IR (KBr, cm^{-1}) 3285 ($-NH_2$), 1710 ($-C{=}O$), 1535 ($-NO_2$), 1355 ($-NO_2$), 1215 (perfluoroalkyl), 1155 ($-SO_2-$). Mass (*m/e*) 797 (M^+), 615 ($F(CF_2)_8SO_2-Ph-N(CH_3)CH{=}CH_2$), 602 ($F(CF_2)_8SO_2-Ph-N(CH_3)CH_2^+$), 378 ($M^+-(C_8F_{17})$), 362, 330, 314 ($M^+-(SO_2C_8F_{17})$), 196, 169 ($CF_3(CF_2)_2^+$), 119 ($CF_3CF_2^+$ or $Ph-N(CH_3)CH_2^+$), 69 (CF_3^+).

Reduction of 2-{*N*-[4-(perfluorooctylsulfonyl)phenyl]-*N*-methylamino}ethyl 3-Amino-5-nitrobenzoate. Under an argon atmosphere, 5 mL of ethanol was added to 0.200 g (0.25 mmol) of 2-{*N*-[4-(perfluorooctylsulfonyl)phenyl]-*N*-methylamino}ethyl 3-amino-5-nitrobenzoate and 0.282 g (1.25 mmol) of $SnCl_2 \cdot 2H_2O$, and the mixture was stirred at 60 °C. To this solution was added dropwise 0.010 g (0.25 mmol) of sodium tetrahydroborate in 2 mL of ethanol, and the reaction mixture was stirred at 60 °C for 2 h. The similar working-up procedures as the reduction of **3** provided **5** with the yield of 0.160 g (83%).

General Procedure of Polymerization. The preparation of **P2** is given as a representative example. Under an argon atmosphere, 5 mL of thionyl chloride was added to 1.196 g (1.50 mmol) of **9**, and the mixture was refluxed for 2 h. After excess thionyl chloride was removed under reduced pressure, 3 mL of dry NMP was added to the residue. This NMP solution was added to 0.466 g (1.50 mmol) of **6** dissolved in 3 mL of dry NMP, which had been cooled in a dry ice–acetone bath. The mixture was stirred at ambient temperature for 30 min and stirred at 70 °C for 30 min. Pouring the reaction mixture into 300 mL of methanol provided the colorless precipitate, which was collected by filtration and purified by reprecipitation in a THF/methanol system. Finally, the product was dried in vacuo. The product yield was 1.323 g (82%). ^{1}H NMR ($CDCl_3$ + DMSO-d_6, 90 MHz) δ 3.0–3.4 (m, 6H), 3.7–4.1 (m, 4H), 4.3–4.6 (m, 4H), 6.7–6.9 (m, 2H), 6.9–7.1 (m, 2H), 7.3–7.5 (m, 2H), 7.6–7.9 (m, 4H), 8.1–8.3 (m, 2H), 8.3–8.4 (m, 1H), 8.6–8.7 (m, 1H), 10.3–10.7 (br s, 2H). IR (KBr, cm^{-1}) 3120 ($-NH$), 2215 ($-CN$), 1720 (esteric $-C{=}O$), 1670 ($-C{=}O$ of amide), 1250 (perfluoroalkyl), 1160 ($-SO_2-$).

P3 was prepared by the similar procedures of the preparation of **P2**. **P1** and **P4** were purified in an NMP/methanol system. ^{1}H NMR and IR spectral data and the yields for the obtained polyamides are given as follows.

P1. Yield 83%. ^{1}H NMR ($CDCl_3$ + DMSO-d_6, 90 MHz) δ 3.1–3.4 (m, 6H), 3.6–4.0 (m, 4H), 4.2–4.6 (m, 4H), 6.8–7.0 (m, 4H), 7.0–7.2 (m, 2H), 7.4–7.6 (m, 2H), 7.6–7.8 (m, 5H), 7.9–8.1 (m, 1H), 10.3–10.7 (br s, 2H). IR (KBr, cm^{-1}) 3100 ($-NH$), 1720 (esteric $-C{=}O$), 1675 ($-C{=}O$ of amide), 1250 (perfluoroalkyl), 1160 ($-SO_2-$).

P3. Yield 76%. ^{1}H NMR ($CDCl_3$ + DMSO-d_6, 90 MHz) δ 3.0–3.4 (m, 6H), 3.7–4.1 (m, 4H), 4.2–4.7 (m, 4H), 6.7–6.9 (m, 2H), 6.9–7.1 (m, 2H), 7.4–7.5 (m, 2H), 7.6–7.9 (m, 4H), 8.1–8.4 (m, 3H), 8.6–8.8 (m, 1H), 10.3–10.7 (br s, 2H). IR (KBr, cm^{-1}) 3130 ($-NH$), 2215 ($-CN$), 1720 (esteric $-C{=}O$), 1675 ($-C{=}O$ of amide), 1250 (perfluoroalkyl), 1155 ($-SO_2-$).

P4. Yield 61%. ^{1}H NMR ($CDCl_3$ + DMSO-d_6, 90 MHz) δ 3.0–3.4 (m, 6H), 3.6–4.0 (m, 4H), 4.1–4.7 (m, 4H), 6.8–7.0 (m, 4H), 7.4–7.6 (m, 4H), 7.6–7.9 (m, 2H), 8.0–8.4 (m, 3H), 8.5–8.8 (m, 1H), 10.0–10.7 (br s, 2H). IR (KBr, cm^{-1}) 3110 ($-NH$), 2215 ($-CN$), 1720 (esteric $-C{=}O$), 1675 ($-C{=}O$ of amide).

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. IR spectra were measured by transmission on a Jasco A-202 IR spectrometer. Mass spectrometry was conducted on a Hitachi Mass Spectrometer M-80B by electron ionization method. Differential scanning calorimetry (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. X-ray diffraction patterns were recorded on a MAC Science MXP^3 X-ray diffractometer, equipped with a thermal controller Model 5310. Light-scattering measurements were performed on a Tosoh LS-8000 instrument equipped with gel permeation chromatography (Tosoh HLC-802A) in THF eluent. Average molecular weights were evaluated by a polystyrene standard.

Film Preparation. **P2** or **P3** was deposited on an ordinary cover glass by spin-coating at a rate of 2000 rpm from a 10 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 at 190 °C for **P2** and at 200 °C for **P3**, a spin-coated film was cooled to the ambient temperature with continuous corona poling.

SHG Measurement. The second harmonic generation (SHG) of polyamides at 532 nm was measured in transmission by means of the Maker fringe method.[13] An experimental apparatus for the Maker fringe measurement has been shown in our previous report.[14] An outline is as follows. A Q-switched Nd:YAG laser (Spectron SL404G, $\lambda = 1064$ nm, 10-Hz repetition rate, 6-ns pulse duration) was used for the exciting light source after its pulse energy was decreased 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 $\lambda/4$ wave plate and a linear polarizer.

Determination of Nonlinear Optical Coefficient. The second-order NLO coefficients, d_{33}, of **P2** and **P3** were evaluated by applying a mean-square method[4] to the relationship of SH light intensity and an incident angle of an exciting beam measured by the Maker fringe method using eq 2 proposed by Jerphagnon et al.:[13]

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

where $I_{2\omega}$ is the intensity of SH wave in a uniaxial poled material generated by p-polarized exciting wave, the intensity of which is represented by I_ω, 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 indexes, $R(\theta)$ is the multiple reflection correction, $p(\theta)$ is a projection factor,[2a] $B(\theta)$ is the beam size correction, and $\Psi(\theta)$ is the angular dependence of the second harmonic power. A 1 mm thick y-cut quartz ($d_{11} = 0.46$ pm/V) was used as a reference sample.

Results and Discussion

Synthesis of Polyamides. Scheme 2 shows the pathways for the preparations of the 3,5-diaminobenzoate derivatives **5** and **6** as the precursors for the preparation of polyamides. 3,5-Diaminobenzoate derivatives were prepared by the esterification reaction between 3,5-dinitrobenzoyl chloride and hydroxyl-functionalized NLO-phores followed by reduction of the corresponding 3,5-dinitrobenzoate derivatives with sodium tetrahydroborate in the presence of $SnCl_2 \cdot 2H_2O$

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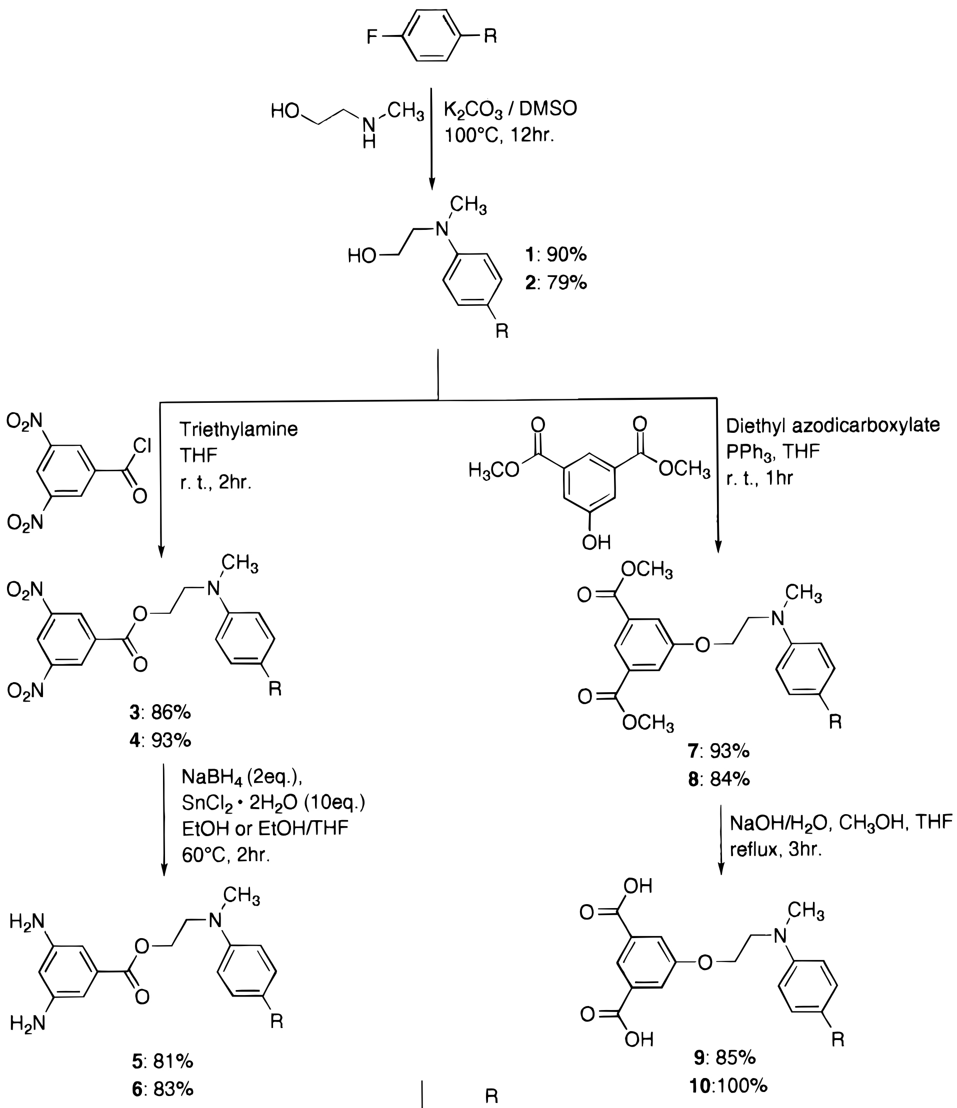
(13) Jerphagnon, J.; Kurtz, S. K. *J. Appl. Phys.* **1970**, *41*, 1667.

(14) Nemoto, N.; Nagase, Y.; Abe, J.; Matsushima, H.; Shirai, Y.; Takamiya, N. *Macromol. Chem. Phys.* **1995**, *196*, 2237.

Scheme 2



	R
1, 3, 5, 7, 9	$-SO_2(CF_2)_8F$
2, 4, 6, 8, 10	-CN

in ethanolic medium. Hydroxyl-functionalized NLO-phores **1** and **2** were prepared from the corresponding 4-substituted fluorobenzene and *N*-methylethanolamine.[15] The esterification reaction between 3,5-dinitrobenzoyl chloride and the hydroxyl-functionalized NLO-phores proceeded with favorable yields.

The reduction of nitro groups to amines required a rather extensive study. At first, we tried to reduce the two nitro groups in 3,5-dinitrobenzoate derivatives **3** and **4** by hydrogen in the presence of 5% Pd on charcoal under the ambient pressure. It has been reported by Chien et al.[16] that the similar types of 3,5-diaminobenzoate derivatives are obtained by the reduction of the corresponding 3,5-dinitrobenzoate derivatives using hydrogen in the presence of 5% Pd on charcoal at the hydrogen pressure of 3.8 atm, although the yield and selectivity of the reduction have not been described. However, the reduction of **3** by hydrogen in the presence of 5% Pd on charcoal at the ambient hydrogen pressure provided the corresponding 3-amino-5-nitrobenzoate compound as shown in Scheme 3. The complete consumption of **3** was confirmed by thin-layer chromatography; however, the reaction did not proceed further by bubbling hydrogen gas nor by the addition of 5% Pd on charcoal. The present reaction conditions are not able to reduce the nitro group in 3-amino-5-nitrobenzoate derivatives. In other words, the present reaction conditions allow us to obtain aminonitroarene derivatives selectively by the monoreduction of the two nitro groups in 3,5-dinitrobenzoate derivative. Sodium tetrahydroborate–stannous chloride in alcoholic medium reported by Sato et al.[17] was applied as a reductant for the two nitro groups in 3,5-dinitrobenzoate derivatives. This reaction proceeds in a homogeneous system. As shown in Scheme 3, the treatment of 2-{*N*-[4-(perfluorooctylsulfonyl)phenyl]-*N*-methylamino}ethyl 3-amino-5-nitrobenzoate with sodium tetrahydroborate–stannous chloride in ethanolic medium afforded the corresponding 3,5-diaminobenzoate derivative **5** with good yield.

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(15) Parker, R. E. *Adv. Fluorine Chem.* **1963**, *3*, 63.

(16) Chien, L.-C.; Lin, C.; Fredley, D. S.; McCarger, J. W. *Macromolecules* **1992**, *25*, 133.

(17) Sato, T.; Mitsuo, N.; Nishiki, M.; Inoue, Y.; Ooi, Y. *Chem. Pharm. Bull.* **1981**, *29*, 1443.

Scheme 3

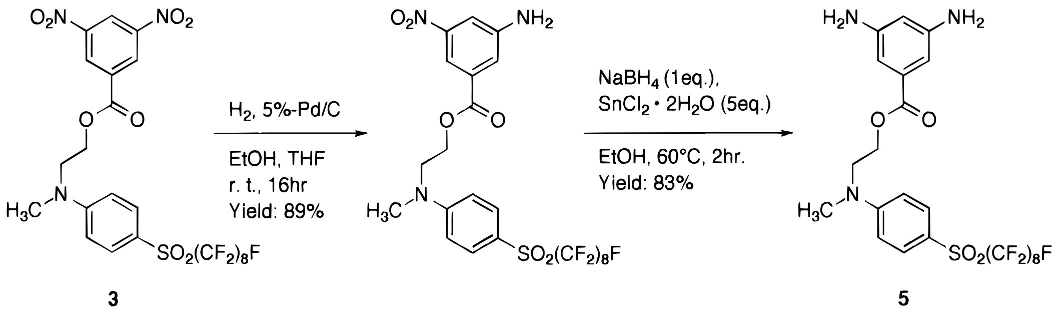

Table 1. Characterization of Polyamides

			solubility[c]						
polymer	M_w[a]	T_g (°C)[b]	THF	DMF	DMSO	NMP	$CHCl_3$	acetone	ethanol
P1	8 170		△	○	○	○	×	×	×
P2	64 100	157	□	□	□	□	△	×	×
P3	28 300	165	□	□	□	□	△	×	×
P4		167	×	○	○	○	×	×	×

[a] Determined by light-scattering measurements in THF. [b] Determined from DSC thermograms on a second heating scan. [c] □: soluble at room temperature. ○: soluble at 70 °C. △: partially soluble. ×: insoluble.

Namely, this system is able to reduce the remaining nitro group in 3-amino-5-nitrobenzoate derivatives. The reduction of **3** or **4** with sodium tetrahydroborate–stannous chloride system was found to provide the corresponding 3,5-diaminobenzoate derivatives **5** or **6** in favorable yields as shown in Scheme 2. The perfluorooctylsulfonyl, the cyano group or the ester moiety were not affected by the present reductant. In addition, it is confirmed that this reductant can be applied for the reduction of the similar 3,5-dinitrobenzoate derivatives containing an octylsulfonyl or an acetyl moiety with yields of 74% or 87%, respectively.[18]

Scheme 1, which was described above, shows the preparation of polyamides containing NLO-phores with high density. All the polyamides were prepared by solution polycondensation between isophthaloyl chloride derivatives, obtained by the reaction between isophthalic acid derivatives and thionyl chloride, and 3,5-diaminobenzoate derivatives in 1-methylpyrrolidin-2-one (NMP). The reaction temperature was raised from −78 °C, at which temperature the solutions of the comonomers were mixed, to 70 °C, where the polymerization reactions proceeded in homogeneous systems. Pouring the reaction solution into methanol afforded the polyamides as powder solid. The yields of polyamides were in the range 61−83%.

Solubility of Polyamides. The solubilities in some common organic solvents and the average molecular weights determined by the light-scattering measurements of the obtained polyamides are summarized in Table 1. Interestingly, polyamides **P2** and **P3**, prepared from comonomers containing the different electron-withdrawing groups, are superior in solubility to **P1** and **P4**, which were prepared from the comonomers containing the same electron-withdrawing group. For instance, **P1** is partially soluble in THF, **P2** and **P3**, however, exhibit the good solubility in THF at ambient temperature. Probably, the low molecular weight parts of **P1** are soluble in THF at ambient temperature. Thus, the average molecular weight of **P1** determined from the light scattering measurement in THF was lower than those of **P2** and **P3**. The average molecular weight of **P4** could not be estimated due to the insolubility in THF. In addition, **P1** and **P4** are partially soluble in polar solvents such as DMF, DMSO, and NMP at ambient temperature, whereas **P2** and **P3** are soluble. These findings may result from the para-crystalline aggregation of side-chain terminal groups in the case of **P1** and **P4**. Optical-quality thin films of **P1** and **P4** could not be obtained by spin-coating from common organic solvents as listed in Table 1. In contrast, optical-quality thin films of **P2** and **P3** could be easily obtained by spin-coating from their THF solutions.

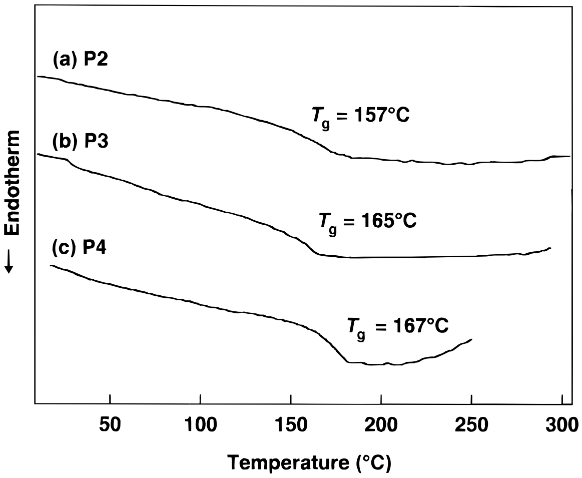

Figure 1. Typical example of DSC traces on a second heating scan at a rate of 10 °C/min and a helium flow rate of 20 mL/min: (a) **P2**, (b) **P3**, (c) **P4**.

Thermal Properties of Polyamides. Typical examples of DSC thermograms are shown in Figure 1. On the DSC thermograms of **P2**−**P4**, the glass transitions were observed, but no other endothermic or exothermic peaks appeared. **P2** and **P3** are thermally stable to 280 °C; however, the thermolysis of **P4** seemed to occur around 220 °C as deduced from their DSC thermograms. It was confirmed that the same T_g's were observed repeatedly on heating−cooling cycles below the temperature mentioned above. On the DSC thermogram of **P1**, glass transition was not detected and no other endo-

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(18) Unpublished results.

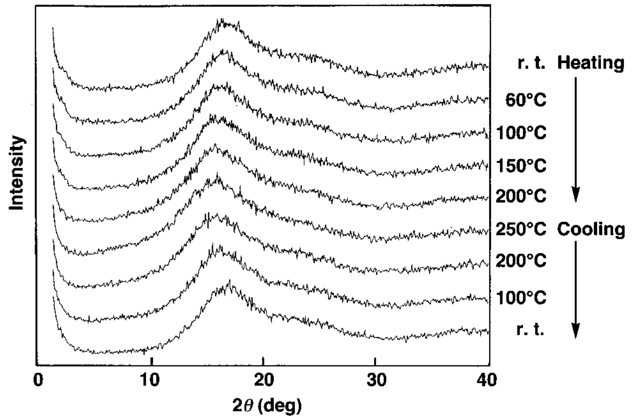

Figure 2. X-ray diffraction patterns of **P2** obtained by a powder method.

Table 2. X-ray Diffraction Angle and *d* Spacing for Polyamides P1−P4 at Room Temperature

polymer	diffraction angle, deg	*d* spacing, nm
P1	16.9	0.524
P2	17.0	0.520
P3	17.1	0.518
P4	21.4	0.414

thermic or exothermic peaks appeared in the temperature range from ambient temperature to 280 °C. Therefore, polyamides containing perfluoroalkyl side chains seem to have superior thermal stability. The T_g's of polyamides, which were determined from a second heating scan of DSC measurements, were in the range of 157−167 °C as provided in Table 1. The kind of chromophore does not seem to affect T_g in the present series of polyamides.

X-ray diffraction measurements of polyamides, a typical example of which is shown in Figure 2, were also carried out by a powder method at various temperatures and exhibited no diffraction peaks except for the broad halo. It was confirmed that the similar X-ray diffraction patterns were obtained for the present polyamides. These findings indicate that the obtained polyamides are amorphous. Table 2 summarizes the diffraction angles around the broad halo and the *d* spacing calculated from the angles. **P1**−**P3**, which have perfluoroalkyl side chain, exhibited the broad halo around 17° and **P4**, which does not have perfluoroalkyl side chain, around 21°, meaning the statistically average distances between the molecules for **P1**−**P3** are longer than those for **P4**. In other words, the statistically average distances are mainly dependent on the presence of perfluoroalkyl side chains.

Optical Properties. UV−vis spectroscopy and SHG measurement were carried out for **P2** and **P3**, from which the thin films could be obtained by spin-coating. Figure 3 shows the UV−vis absorption spectrum of **P2** using a spin-coated film, the thickness of which was <1 μm, on a quartz glass substrate. The data obtained by UV−vis spectroscopy are summarized in Table 3. We defined the cutoff wavelength (λ_{cutoff}) as the wavelength where the value of the first deviation for the absorbance becomes 0. The λ_{cutoff} of the present polyamides **P2** and **P3** were 372 and 386 nm, respectively, which indicates that the present polyamides are desirable for practical uses. **P2** and **P3** contain similar chromophores, therefore, there was no significant difference in the cutoff wavelength.

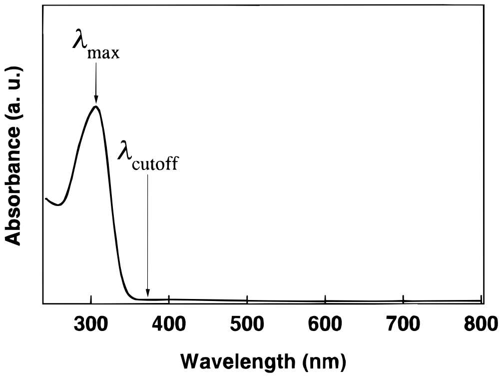

Figure 3. Typical example of UV−vis absorption spectra of a spin-coated film of **P2**.

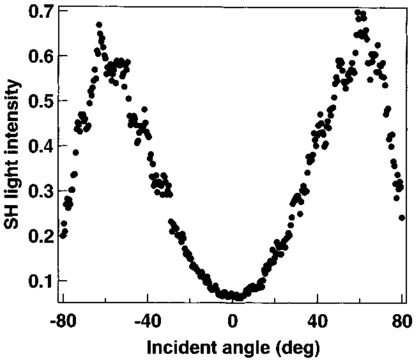

Figure 4. Relationship between SH light intensity and incident angle of an exciting beam using a spin-coated film of **P2** after corona poling.

Table 3. Optical Properties of Polyamides P2 and P3

polymer	λ_{max}, nm	λ_{cutoff}, nm	poling temp, °C	d_{33}, pm/V
P2	306	372	190	3.6 ± 0.6
P3	306	386	200	4.4 ± 1.3

As a typical example of the relationship between SH light intensity and incident angle of an exciting beam for a spin-coated film of **P2** after corona poling is shown in Figure 4. The poling temperature was set at a temperature ca. 35 °C higher than T_g as shown in Table 2. Below these temperatures even though higher than T_g, the effects of a corona-poling treatment were not remarkable, probably due to the high viscosity of the obtained polyamides. The obtained second-order NLO coefficients, d_{33}, are also summarized in Table 2. **P2** and **P3** exhibited the d_{33} values of 3.6 ± 0.6 and 4.4 ± 1.3 pm/V, respectively. Tripathy et al. reported[11g] that the polymeric NLO material based on bisphenol-A structure with (*N*,*N*-dialkylamino)-4-cyanophenyl moiety exhibits the d_{33} value of 4.2 pm/V with the λ_{cutoff} of 340 nm for an exciting wave at 1064 nm. The d_{33} values in the present system are of the same magnitude as that of Tripathy's polymer. On the other hand, Clays et al.[11e] have reported that the second-order NLO susceptibility, $\chi^{(2)}{}_{zzz}$, of a Langmuir−Blodgett (LB) film composed of an acrylate polymer containing the similar chromophore, (*N*,*N*-dialkylamino)-4-(perfluorodecyl)phenyl moiety ($\beta = 9 \times 10^{-30}$ esu), is estimated to be 3 pm V^{-1} for an exciting wave at 1907 nm using the free gas approximation. On using a relationship[19] of $\chi^{(2)}{}_{zzz} = 2d_{33}$, the $\chi^{(2)}{}_{zzz}$ values of the present polyamides can be estimated for 7.2 ± 1.2 and 8.8 ± 2.6 pm V^{-1} for an exciting wave at 1064 nm. The difference in wavelength of a fundamental light has been known to result in different $\chi^{(2)}_{zzz}$ value. Therefore, the $\chi^{(2)}_{zzz}$ values in both cases cannot be directly compared; however, the $\chi^{(2)}_{zzz}$ values in the present system may be of the same magnitude as that of a highly ordered LB film composed of an acrylate polymer estimated by Clays et al. It is considered that the high NLO-phore density results in the d_{33} values equivalent to that of the highly ordered LB film. Additionally, **P2** and **P3** retained 86% and 94% of the original d_{33} values after storage at ambient temperature for 2 weeks, respectively, indicating the relatively good temporal stability of the second-order NLO activity.

Conclusions

We have successfully prepared novel types of polyamides containing second-order NLO-phores with high density by means of polycondensation between isophthaloyl chloride derivatives and novel 3,5-diaminobenzoates, obtained by reduction of the corresponding 3,5-dinitrobenzoates. Alternate alignment of different side-chain functional groups was found to improve the solubility. **P2** and **P3** exhibited good thermal stability as well as the good solubility in common polar organic solvents and provided optical-quality films by spin-coating. The present polyamides **P2** and **P3** turned out to be second-order NLO materials exhibiting the relatively high and stable second-order NLO activity, due to the high NLO-phore density, with the desired transparency.

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