Polyamides for Nonlinear Optics: Side-Chain All Donor-Attached NLO-phores versus Side-Chain Alternating Donor-Attached and Acceptor-Attached NLO-phores

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This article describes the syntheses and second-order nonlinear optical (NLO) properties of a novel type of polyamide with side-chain alternating donor-attached and acceptor attached NLO-phores as well as polyamide with side-chain all donor-attached NLO-phores. Two kinds of polyamides were prepared by condensation polymerization between 5-[2-(*N*-methyl-4-nitroanilino)ethoxy]isophthaloyl chloride and 3-{[4-(dihexylamino)phenyl]sulfonyl}propyl 3,5-diaminobenzoate (**P3**) or 2-[*N*-methyl-4-(octylsulfonyl)anilino]ethyl 3,5-diaminobenzoate (**P4**). In the side chain of **P3**, electron-donating and electron-withdrawing groups of the NLO-phores were alternatingly attached. The obtained polyamides exhibited good solubility in common organic solvents and provided optical-quality films by spin-coating. The 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 at various temperatures, indicating that **P3** and **P4** exhibited the optimum second-order NLO coefficient, d_{33}, of 6.4 and 7.1 pm/V, respectively. There were no significant differences in the temperature dependence of orientational behavior between two kinds of polyamides. The preliminary measurements of the short-term temporal SHG decay suggested that it is possible for the relaxation of the NLO-phore orientation in **P3** to be somewhat restricted, as far as deduced from the values of time coefficient obtained by curve-fitting to the SHG decay curves.

Introduction

The development of polymeric materials with second-order nonlinear optical (NLO) properties has been required because of the NLO applications such as a fast waveguide and electrooptic modulation by taking advantage of their high NLO activity, chemical resistance, and good processability. 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 have been bonded to polymeric matrixes with the high glass transition temperature (T_g). High-T_g polymeric matrixes are considered to be effective in restraining the relaxation of the noncentrosymmetric NLO-phore alignment induced by an electric field.[1] In general, aromatic polyamides, which are easily prepared from the corresponding dicarboxylic- and the diamino-functionalized monomers, exhibit the relatively high T_g's. Indeed, the preparation of the second-order NLO active main-chain- and side-chain-type polyamides[2] has been reported. Our primary interest is to investigate the NLO properties of easily processable polyamides attributed to the alternate alignment of the same or different functionalities, which can be realized by providing the same or different functionalities for each comonomer.[3] But, there have been very few reports where the functionalities are introduced into both comonomers. Our research group has reported the preparation and the second-order NLO properties of polyamides[3] and polyesters[4] obtained by the condensa-

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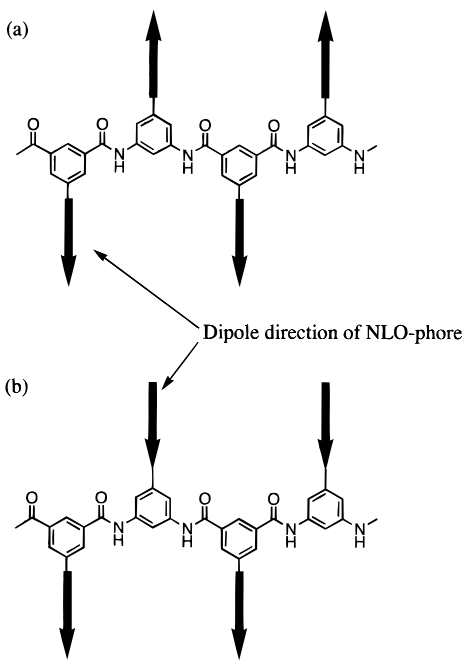
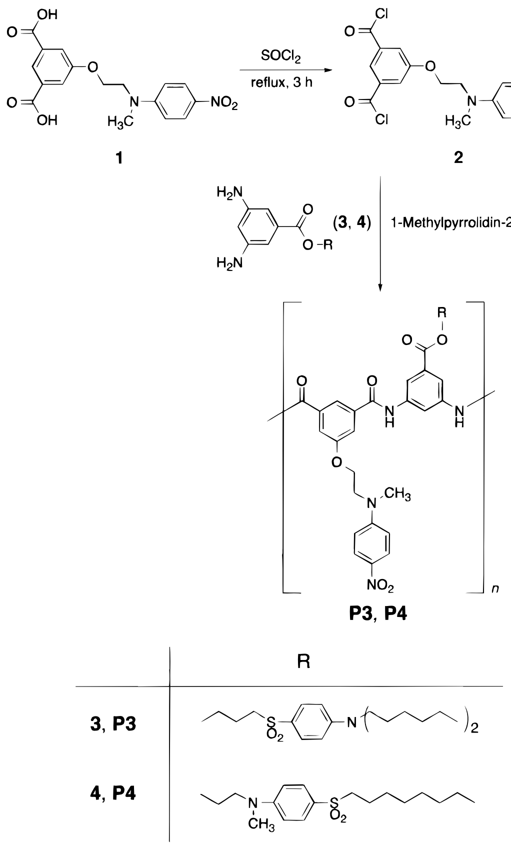


Figure 1. Schematic drawing of the dipole direction of NLO-phores in polyamides.

Scheme 1



tion 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 high second-order NLO susceptibility.[3,4]

On the other hand, as shown in Figure 1a, the dipole moments of NLO-phores are usually directed to the same direction as regards polymeric backbone. We have been interested in the effects of the dipole direction of the NLO-phores involved in each comonomer unit. Namely, we have intended to prepare the polyamide with side-chain alternating donor attached and acceptor attached NLO-phores, as shown in Figure 1b. We consider that the conformations formed by the polyamide backbone may take some advantages to the noncentrosymmetric alignment of NLO-phores.

From these points of view, we report here the syntheses of polyamide with side-chain alternating donor-attached and acceptor-attached NLO-phores as well as polyamide with side-chain all donor-attached NLO-phores, as shown in Scheme 1. **P3** and **P4** correspond to a type of polyamide described in Figure 1b,a, respectively. Both polyamides incorporate NLO-phores with an electron-withdrawing group at the side-chain terminal sites, which are derived from dicarboxylic acid comonomer. **P4** also contains NLO-phores with an electron-withdrawing group at the side-chain terminal sites derived from diamine comonomer; however, **P3** has NLO-phores with an electron-donating group at the side-chain terminal sites derived from diamine comonomer. The thermal, linear optical and second-order NLO properties of the obtained polyamides are also described.

Experimental Section

Materials. Dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), and 1-methylpyrrolidin-2-one (NMP) were distilled over CaH$_2$ under reduced pressure. Tetrahydrofuran (THF) was distilled twice (over CaH$_2$ and sodium) for the removal of traces of water. 4-Fluorothiophenol (Aldrich Chemical Co., Inc.), 3-chloropropan-1-ol, dihexylamine, 3,5-dinitrobenzoyl chloride, 4-(dimethylamino)pyridine (Tokyo Kasei Kogyo Co., Inc.), sodium tetrahydroborate (Kishida Chemical Co., Ltd.), SnCl$_2$·2H$_2$O, and thionyl chloride (Wako Pure Chemical Industries, Ltd.) were commercially available and used as received. 5-[2-(*N*-Methyl-4-nitroanilino)ethoxy]isophthalic acid (**1**)[4a] and 2-[*N*-methyl-4-(octylsulfonyl)anilino]ethanol (**10**)[4b] were prepared by the method reported earlier.

3-[(4-Fluorophenyl)thio]propan-1-ol (6). Under an argon atmosphere, 6.78 g (52.9 mmol) of 4-fluorothiophenol (**5**) in 10 mL of dry DMF was added dropwise to 3.20 g (80.0 mmol) of sodium hydride (60% in mineral oil) suspended in 30 mL of dry DMF in an ice bath. The reaction mixture was stirred at ambient temperature for 1 h, and 5.00 g (52.9 mmol) of 3-chloropropan-1-ol was added dropwise. After the reaction mixture was stirred at ambient temperature for 3 h, DMF was evaporated under reduced pressure. Water and ethyl acetate were added to the residue, and the organic layer was washed with water. The organic layer was dried on anhydrous sodium sulfate, and the solvent was evaporated. The crude product was purified on column chromatography packed with silica gel in chloroform/methanol (volume ratio 40/1) eluent. The product yield was 9.02 g (92%) as a colorless liquid. ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.54 (br s, 1H, −OH), 1.85 (dt, $J = 6.4, 7.2$, 2H, $-CH_2-\mathit{CH_2}-CH_2-$), 2.99 (t, $J = 7.2$, 2H, $-S-CH_2-$), 3.76 (t, $J = 6.4$, 2H, $-\mathit{CH_2}-OH$), 7.0−7.3 (m, 2H, phenylene protons), 7.3−7.7 (m, 2H, phenylene protons). IR (neat, cm^{-1}) 3360 (−OH), 2940, 2880, 1590, 1490, 1440, 1395, 1350, 1290, 1265, 1225, 1155, 1090, 1050, 905, 825, 630. Mass (*m*/*e*) 186 (M$^+$), 141 ($F-Ph-S^+{=}CH_2$), 128 ($F-Ph-SH$), 127 ($F-Ph-S^+$), 108, 95 ($F-Ph^+$), 83, 69, 57, 45, 31.

3-[(4-Fluorophenyl)thio]propyl Acetate (7). Acetic anhydride (10 mL) and 4-(dimethylamino)pyridine (0.061 g, 0.50 mmol) were added to 1.862 g (10.0 mmol) of **6**. After the reaction mixture was stirred at ambient temperature for 1 h, the reaction mixture was poured into 200 mL of saturated sodium hydrogen carbonate aqueous solution. The crude product was extracted by ethyl acetate. The residue resulting from the evaporation of solvent was purified by column chromatography packed with silica gel in chloroform/methanol (volume ratio 100/1) eluent. The evaporation of solvent afforded **7** as a colorless liquid with the yield of 2.170 g (95%). ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.8−2.1 (m, 2H, $-CH_2-\mathit{CH_2}-CH_2-$, overlapped by a singlet signal at 2.03 ppm), 2.03 (s, 3H, CH_3COO-), 2.92 (t, *J* = 7.2, 2H, $-S-CH_2-$), 4.16 (t, *J* = 6.3, 2H, $-COO-CH_2-$), 6.9−7.2 (m, 2H, phenylene protons), 7.3−7.6 (m, 2H, phenylene protons). IR (neat, cm^{-1}) 3065, 2960, 1740 ($-C{=}O$), 1590, 1490, 1440, 1385, 1365, 1240, 1155, 1090, 1040, 950, 830, 630, 605, 515. Mass (*m/e*) 228 (M^+), 168 ($F-Ph-S-CH_2-CH{=}CH_2$), 153, 141 ($F-Ph-S^+{=}CH_2$), 128 ($F-Ph-SH$), 127 ($F-Ph-S^+$),101 ($CH_3COO(CH_2)_3{}^+$), 83, 73 ($CH_3COO(CH_2)_2{}^+$), 43 (acetyl$^+$).

3-[(4-Fluorophenyl)sulfonyl]propyl Acetate (8). A mixture of 2.170 g (9.51 mmol) of **7**, 25 mL of acetic acid, and 3.40 g (30.0 mmol) of 30% hydrogen peroxide aqueous solution was refluxed for 2 h. The reaction mixture was poured into 200 mL of saturated sodium hydrogen carbonate aqueous solution. The crude product was extracted with ethyl acetate, and the combined ethyl acetate solution was dried on anhydrous sodium sulfate. The residue resulting from evaporation of ethyl acetate was purified on column chromatography packed with silica gel in chloroform eluent. The evaporation of solvent afforded **8** as a colorless liquid with the yield of 2.034 g (82%). ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.9−2.3 (m, 2H, $-CH_2-\mathit{CH_2}-CH_2-$, overlapped by a singlet signal at 2.03 ppm), 2.03 (s, 3H, CH_3COO-), 3.1−3.4 (m, 2H, $-SO_2-CH_2-$), 4.13 (t, *J* = 6.4, 2H, $-COO-CH_2-$), 7.2−7.5 (m, 2H, phenylene protons), 7.9−8.2 (m, 2H, phenylene protons). IR (neat, cm^{-1}) 3105, 3075, 2965, 1740 ($-C{=}O$), 1590, 1495, 1445, 1405, 1385, 1370, 1320, 1290, 1240, 1175, 1145 ($-SO_2-$), 1090, 1040, 950, 900, 845, 820, 780, 730, 695, 675, 635, 605, 570, 525. Mass (*m/e*) 217 (M^+ − Acetyl), 200, 187 ($F-Ph-SO_2CH_2CH_2{}^+$), 161, 159 ($F-Ph-SO_2{}^+$) 143, 101, 95 ($F-Ph^+$), 75, 43 (acetyl$^+$); [CI] 261 ($M^+ + 1$).

3-{[4-(Dihexylamino)phenyl]sulfonyl}propan-1-ol (9). Under an argon atmosphere, 5 mL of dry DMSO was added to a mixture of 4.078 g (22.0 mmol) of dihexylamine and 2.764 g (20.0 mmol) of anhydrous potassium carbonate. To this mixture was added 5.206 g (20.0 mmol) of **8**. The reaction mixture was stirred at 150 °C for 3 h and poured into 300 mL of water. The crude product was extracted by ethyl acetate, and the combined ethyl acetate solution was dried on anhydrous sodium sulfate. Then, 1.60 g (40.0 mmol) of sodium hydroxide, 20 mL of water, 20 mL of methanol, and 20 mL of THF were added to the residue resulting from evaporation of ethyl acetate. The reaction mixture was refluxed for 1 h, and the solvent was evaporated. To the residue was added 100 mL of chloroform, and the solution was washed with water. The organic layer was dried on anhydrous sodium sulfate. The residue resulting from evaporation of chloroform was purified on column chromatography packed with silica gel in ethyl acetate/hexane (volume ratio 1/1) eluent. The evaporation of solvent afforded **9** as a pale yellow liquid with the yield of 5.200 g (61%). ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.90 (t, *J* = 5.4, 6H, $\mathit{CH_3}-(CH_2)_5-N-$), 1.1−2.1 (m, 17H, $(CH_3-\mathit{(CH_2)_4}-CH_2)_2-N-$ and $-OH$), 2.1−2.3 (m, 2H, $-SO_2-CH_2-\mathit{CH_2}-$), 3.0−3.5 (m, 6H, $-SO_2-CH_2-$ and $(CH_3-(CH_2)_4-\mathit{CH_2})_2-N-$), 3.6−3.9 (m, 2H, $HO-\mathit{CH_2}-$), 6.62 (t, *J* = 9.0, 2H, phenylene protons), 7.64 (t, *J* = 9.0, 2H, phenylene protons). IR (neat, cm^{-1}) 3500 ($-OH$), 2960, 2930, 2860, 1595, 1555, 1515, 1465, 1405, 1370, 1300, 1255, 1210, 1135, 1095, 1065, 1000, 905, 815, 800, 725, 700, 665, 565, 535. Mass (*m/e*) 312 ($M^+-C_5H_{11}$), 224, 212, 198, 185, 170, 156, 142, 128, 114, 83, 72, 44, 43, 30; [CI]: 384 ($M^+ + 1$).

3-{[4-(Dihexylamino)phenyl]sulfonyl}propyl 3,5-Dinitrobenzoate (11). Under an argon atmosphere, 3,5-dinitrobenzoyl chloride (0.902 g, 3.91 mmol) in 20 mL of dry THF was added to 1.25 g (3.26 mmol) of **9** in 10 mL of dry THF in the presence of 1 mL of triethylamine. The reaction mixture was stirred at ambient temperature for 1 h, and poured into 50 mL of saturated sodium hydrogen carbonate aqueous solution. The crude product was extracted with chloroform (20 mL × 5), and the solvent was evaporated. The product was purified by column chromatography packed with silica gel in ethyl acetate/chloroform (volume ratio 1/4) eluent. Finally, the evaporation of solvent afforded **11** with the yield of 1.88 g (100%) as orange-colored crystals. ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.90 (t, *J* = 5.4, 6H, $\mathit{CH_3}-(CH_2)_5-$), 1.1−2.1 (m, 16H, $(CH_3-\mathit{(CH_2)_4}-CH_2)_2-N-$), 2.1−2.5 (m, 2H, $-SO_2-CH_2-\mathit{CH_2}-$), 3.0−3.5 (m, 6H, $-SO_2-CH_2-$ and $(CH_3-(CH_2)_4-\mathit{CH_2})_2-N-$), 4.55 (t, *J* = 6.4, 2H, $-O-CH_2-$), 6.63 (d, *J* = 9.0, 2H, phenyl (anilino) protons), 7.65 (d, *J* = 9.0, 2H, phenyl (anilino) protons), 9.10 (d, *J* = 2.0, 2H, dinitrophenyl protons), 9.22 (t, *J* = 2.0, 1H, dinitrophenyl proton). IR (KBr, cm^{-1}) 3110, 2950, 2930, 2855, 1735 ($-C{=}O$), 1630, 1595, 1545 ($-NO_2$), 1515, 1465, 1410, 1345 ($-NO_2$), 1285, 1235, 1180, 1155, 1135, 1090, 1075, 1050, 995, 930, 915, 860, 820, 790, 775, 720, 640, 570, 530. Mass (*m/e*) 577 (M^+), 547 ($M^+-(NO)$), 506 ($M^+-C_5H_{11}$), 476, 436, 406, 383 ($HO-(CH_2)_3-SO_2-Ph-N\text{-}(C_6H_{13})_2{}^+$), 354 ($HO-(CH_2)_3-SO_2-Ph-N-(C_6H_{13})C_4H_8{}^+$), 312 ($HO-(CH_2)_3-SO_2-Ph-N-(C_6H_{13})CH_2{}^+$), 195 ($(O_2N)_2-Ph-CO^+$), 179, 165, 149, 135, 119, 105, 91, 75, 55, 43. Anal. Calcd for $C_{28}H_{39}N_3O_8S$: C, 58.22; H, 6.80; N, 7.27; S, 5.55. Found: C, 58.17; H, 6.89; N, 7.16; S, 5.61.

12 was prepared by the same method as the preparation of **11** using 2-[*N*-methyl-4-(octylsulfonyl)anilino]ethanol (**10**) as a raw material. The product was obtained with the yield of 96% as an orange-colored solid. ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.85 (t, *J* = 5.5, 3H, $\mathit{CH_3}-(CH_2)_7-$), 1.1−2.0 (m, 12H, $(CH_3-\mathit{(CH_2)_6}-CH_2-SO_2-$), 3.0−3.2 (m, 2H, $-CH_2-SO_2-$), 3.14 (s, 3H, CH_3-N-), 3.90 (t, *J* = 5.9, 2H, $-N-CH_2-$), 4.67 (t, *J* = 5.9, 2H, $-O-CH_2-$), 6.81 (d, *J* = 9.2, 2H, phenyl (anilino) protons), 7.64 (d, *J* = 9.2, 2H, phenyl (anilino) protons), 9.02 (d, *J* = 2.0, 2H, dinitrophenyl protons), 9.19 (t, *J* = 2.0, 1H, dinitrophenyl proton). IR (KBr, cm^{-1}) 3105, 2950, 2930, 2855, 1735 ($-C{=}O$), 1630, 1595, 1545 ($-NO_2$), 1515, 1460, 1380, 1345 ($-NO_2$), 1275, 1215, 1170, 1130, 1090, 1075, 1025, 1000, 920, 820, 775, 720, 700, 650, 615, 565, 535. Mass (*m/e*) 521 (M^+), 491 ($M^+-(NO)$), 325, 309 ($CH_2{=}CH-N(CH_3)-Ph-SO_2-C_8H_{17}$), 296 ($^+CH_2-N(CH_3)-Ph-SO_2-C_8H_{17}$), 184, 133, 119, 107, 41.

3-{[4-(Dihexylamino)phenyl]sulfonyl}propyl 3,5-Diaminobenzoate (3). Under an argon atmosphere, 1.733 g (3.00 mmol) of **11** in 20 mL of THF was added to 6.771 g (30.0 mmol) of SnCl$_2$·2H$_2$O[5] in 20 mL of ethanol, and the mixture was stirred at 70 °C. To this solution, was added dropwise 0.226 g (6.00 mmol) of sodium tetrahydroborate in 20 mL of ethanol. The reaction mixture was stirred at 70 °C for 3 h. After the evaporation of solvent, 1000 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/hexane (volume ratio 3/1) eluent. Finally, the recrystallization from ethanol afforded **3** with the yield of 1.180 g (76%) as pale yellow crystals. ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.90 (t, *J* = 5.4, 6H, $\mathit{CH_3}-(CH_2)_5-$), 1.1−2.1 (m, 16H, $(CH_3-\mathit{(CH_2)_4}-CH_2)_2-N-$), 2.1−2.5 (m, 2H, $-SO_2-CH_2-\mathit{CH_2}-$), 3.0−3.5 (m, 6H, $-SO_2-CH_2-$ and $(CH_3-(CH_2)_4-\mathit{CH_2})_2-N-$), 3.5−3.8 (br s, 4H, $-NH_2$), 4.30 (t, *J* = 6.2, 2H, $-COO-CH_2-$), 6.18 (t, *J* = 2.0, 1H, diaminophenyl proton), 6.61 (d, *J* = 9.0, 1H, phenylene (anilino) protons), 6.72 (d, *J* = 2.0, 2H, diaminophenyl protons), 7.65 (d, *J* = 9.0, 2H, phenylene (anilino) protons). IR (KBr, cm^{-1}) 3425 ($-NH_2$), 3360 ($-NH_2$), 3340 ($-NH_2$), 3220, 2955, 2930, 2860, 1705 ($-C{=}O$), 1645, 1595, 1560, 1510, 1470, 1440, 1400, 1390, 1370, 1350, 1310, 1280, 1260, 1235, 1190, 1130, 1100, 1090, 1080, 1065, 1020, 995, 955, 905, 880, 855, 820, 790, 765, 740, 725, 675, 590, 565, 530. Mass (*m/e*) 517 (M^+), 446 ($M^+-C_5H_{11}$), 376, 312 ($HO-(CH_2)_3-SO_2-Ph-N-(C_6H_{13})CH_2{}^+$), 188, 152 ($(H_2N)_2-Ph-COOH$), 135, 107, 79, 43. Anal. Calcd for $C_{28}H_{43}N_3O_4S$: C, 64.96; H, 8.37; N, 8.12; S, 6.19. Found: C, 64.75; H, 8.42; N, 8.03; S, 6.19.

4 was prepared by the same method as the preparation of **3** using **12** as a raw material. The product was obtained with the yield of 87% as pale yellow crystals. ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.86 (t, *J* = 5.5, 3H, $\mathit{CH_3}-(CH_2)_7-$), 1.1−2.0 (m, 12H, $CH_3-\mathit{(CH_2)_6}-CH_2-SO_2-$), 3.0−3.2 (m, 2H, $-SO_2-CH_2-$), 3.09 (s, 3H, CH_3-N-), 3.6−3.8 (br s, 4H, $-NH_2$), 3.79 (t, *J* = 5.7, 2H, $-N-CH_2-$, overlapped by a broad singlet signal around 3.6−3.8 ppm)), 4.44 (t, *J* = 5.7, 2H, $-COO-CH_2-$), 6.14 (t, *J* = 2.2, 1H, diaminophenyl proton), 6.59 (d, *J* = 2.2, 2H, diaminophenyl protons), 6.82 (t, $J = 9.0$, 1H, phenylene (anilino) protons), 7.70 (d, $J = 9.0$, 2H, phenylene(anilino) protons). IR (KBr, cm^{-1}) 3480 ($-NH_2$), 3380 ($-NH_2$), 3230, 2930, 2855, 1700 ($-C{=}O$), 1625, 1595, 1560, 1515, 1455, 1440, 1385, 1355, 1290, 1250, 1200, 1125, 1090, 1025, 1000, 955, 900, 845, 815, 770, 725, 675, 650, 620, 565, 535. Mass (*m*/*e*) 461 (M^+), 309 ($CH_2{=}CH-N(CH_3)-Ph-SO_2-C_8H_{17}$), 296 ($^+CH_2-N(CH_3)-Ph-SO_2-C_8H_{17}$), 184, 167, 152 ($(H_2N)_2-Ph-COOH$), 133, 119, 107, 91, 80, 55, 41. Anal. Calcd for $C_{24}H_{35}N_3O_4S$: C, 62.45; H, 7.64; N, 9.10; S, 6.95. Found: C, 62.59; H, 7.72; N, 9.14; S, 6.98.

3-[(4-Fluorophenyl)thio]propyl 3,5-Dinitrobenzoate (13). Under an argon atmosphere, **6** (2.79 g, 15.0 mmol) in 20 mL of dry THF with triethylamine (1.82 g, 18.0 mmol) was added to 3,5-dinitrobenzoyl chloride (3.46 g, 15.0 mmol) in 20 mL of dry THF. The reaction mixture was stirred at ambient temperature for 2 h and poured into 50 mL of saturated sodium hydrogen carbonate aqueous solution. The crude product was extracted with ethyl acetate, and the solvent was evaporated. The residue was purified by recrystallization from methanol. The product yield was 5.37 g (94%) as yellow crystals. ^1H NMR ($CDCl_3$, 90 MHz) δ 2.16 (dt, $J = 6.4, 6.8$, 2H, $-CH_2-\mathit{CH_2}-CH_2-$), 3.03 (t, $J = 6.8$, 2H, $-S-CH_2-$), 4.57 (t, $J = 6.4$, 2H, $-COO-CH_2-$), 7.01 (t, $J = 8.7$, 2H, fluorophenyl protons), 7.3−7.4 (m, 2H, fluorophenyl protons), 9.13 (d, $J = 2.0$, 2H, dinitrophenyl protons), 9.23 (t, $J = 2.0$, 1H, dinitrophenyl proton). IR (KBr, cm^{-1}) 3030, 2965, 2930, 1730 ($-C{=}O$), 1630, 1590, 1545 ($-NO_2$), 1485, 1465, 1440, 1390, 1345 ($-NO_2$), 1330, 1285, 1220, 1175, 1090, 1075, 1055, 1010, 920, 875, 835, 815, 775, 720, 625, 515. Mass (*m*/*e*) 380 (M^+), 350 ($M^+-(NO)$), 253 ($(O_2N)_2-Ph-COO(CH_2)_3{}^+$), 223 ($[(O_2N)_2-Ph-COO(CH_2)_3{}^+]-(NO)$), 195 ($(O_2N)_2-Ph-CO^+$), 168, 153, 141 ($F-Ph-S-CH_2{}^+$), 128 ($F-Ph-SH$), 127 ($F-Ph-S^+$), 95 ($F-Ph^+$). Anal. Calcd for $C_{16}H_{13}N_2O_6SF$: C, 50.53; H, 3.45; N, 7.37. Found: C, 50.39; H, 3.18; N, 7.17.

3-[(4-Fluorophenyl)sulfonyl]propyl 3,5-Dinitrobenzoate (14). A mixture of 0.761 g (2.00 mmol) of **13**, 5 mL of acetic acid, and 0.680 g (30.0 mmol) of hydrogen peroxide (30% aqueous solution) was refluxed for 3 h. The reaction mixture was poured into 200 mL of saturated sodium hydrogen carbonate aqueous solution. The crude product was extracted with chloroform, and the combined chloroform solution was dried on anhydrous sodium sulfate. A concentration of this chloroform solution recrystallize **12** as colorless crystals with the yield of 0.751 g (91%). ^1H NMR ($CDCl_3$, 90 MHz) δ 2.1−2.5 (m, 2H, $-CH_2-\mathit{CH_2}-CH_2-$), 3.2−3.4 (m, 2H, $-SO_2-CH_2-$), 4.57 (t, $J = 6.4$, 2H, $-COO-\mathit{CH_2}-$), 7.28 (t, $J = 9.0$, 2H, fluorophenyl protons), 7.9−8.1 (m, 2H, fluorophenyl protons), 9.11 (d, $J = 2.0$, 2H, dinitrophenyl protons), 9.23 (t, $J = 2.0$, 1H, dinitrophenyl proton). IR (neat, cm^{-1}) 3115, 3070, 2960, 2930, 1735 ($-C{=}O$), 1635, 1600, 1545 ($-NO_2$), 1495, 1465, 1405, 1350 ($-NO_2$), 1330, 1280, 1230 ($-SO_2-$), 1175, 1160, 1140, 1080, 1050, 1005, 935, 865, 850, 835, 820, 775, 750, 730, 720, 640, 570, 520. Mass (*m*/*e*) 412 (M^+), 382 ($M^+-(NO)$), 253 ($(O_2N)_2-Ph-COO(CH_2)_3{}^+$), 217, 195 ($(O_2N)_2-Ph-CO^+$), 159 ($F-Ph-SO_2{}^+$), 143 ($F-Ph-SO^+$), 95 ($F-Ph^+$). Anal. Calcd for $C_{16}H_{13}N_2O_8SF$: C, 46.61; H, 3.18; N, 6.79. Found: C, 46.63; H, 3.17; N, 6.64.

General Procedure of Polymerization. The preparation of **P3** is given as a representative example. Under an argon atmosphere, 5 mL of thionyl chloride was added to 0.720 g (2.00 mmol) of 5-[2-(*N*-methyl-4-nitroanilino)ethoxy]isophthalic acid (**1**), and the mixture was refluxed for 2 h. To 5-[2-(*N*-methyl-4-nitroanilino)ethoxy]isophthaloyl chloride (**2**) resulting from a removal of excess thionyl chloride under reduced pressure was added 2 mL of NMP. This NMP solution was added to 1.035 g (2.00 mmol) of **3** dissolved in 2 mL of NMP, which had been cooled in a dry ice−acetone bath. The mixture was stirred at ambient temperature for 30 min and stirred at 40 °C for 5 min. Pouring the reaction mixture into 300 mL of methanol provided the yellow 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 0.946 g (55%). ^1H NMR ($CDCl_3$ + DMSO-d_6, 90 MHz) δ 0.8−0.9 (m, 6H), 1.2−1.4 (m, 16H), 1.5−1.6 (m, 4H), 2.1−2.3 (m, 2H), 3.1−3.3 (m, 5H), 3.8−4.1 (m, 2H), 4.2−4.5 (m, 4H), 6.5−6.8 (m, 4H), 7.5−8.4 (m, 9H), 8.7−8.8 (m, 1H), 10.0−10.4 (br s, 2H). IR (KBr, cm^{-1}): 3085 ($-NH$), 1720 (esteric $-C{=}O$), 1680 ($-C{=}O$ of amide), 1130 ($-SO_2-$).

P4 was prepared by the similar procedures as the preparation of **P3**. ^1H NMR and IR spectral data and the yields for the obtained polyamides are given as follows.

P4. Yield 89%. ^1H NMR ($CDCl_3$ + DMSO-d_6, 90 MHz) δ 0.8−0.9 (m, 3H), 1.1−1.4 (m, 12H), 1.5−1.7 (m, 2H), 3.1−3.3 (m, 6H), 3.7−4.1 (m, 4H), 4.2−4.6 (m, 4H), 6.6−6.9 (m, 4H), 7.5−8.4 (m, 9H), 8.6−8.7 (m, 1H), 9.9−10.3 (br s, 2H). IR (KBr, cm^{-1}) 3085 ($-NH$), 1720 (esteric $-C{=}O$), 1680 ($-C{=}O$ of amide), 1130 ($-SO_2-$).

Characterization. UV−vis absorption spectra were measured by transmission on a Shimadzu Model U-2100 spectrophotometer. ^1H 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 M-80B mass spectrometer 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. **P3** or **P4** 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 the set temperatures, was cooled a spin-coated film 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.[6] An experimental apparatus for the Maker fringe measurement has been shown in our previous report.[7] 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 **P3** and **P4** were evaluated by applying a mean-square method to the relationship of SH light intensity and an incident angle of an exciting beam measured by the Maker fringe method using eq 1 proposed by Jerphagnon et al.:[6]

$$I_{2\omega} = [512\pi^2/(cw^2)]I_\omega{}^2 d_{33}{}^2 t_\omega{}^4 T_{2\omega} R(\theta) p^2(\theta) B(\theta) \times I_\omega{}^2 \sin^2 \Psi(\theta)/(n_\omega{}^2 - n_{2\omega}{}^2)^2 \quad (1)$$

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, $B(\theta)$ is the beam size correction, and $\Psi(\theta)$ is the angular dependence

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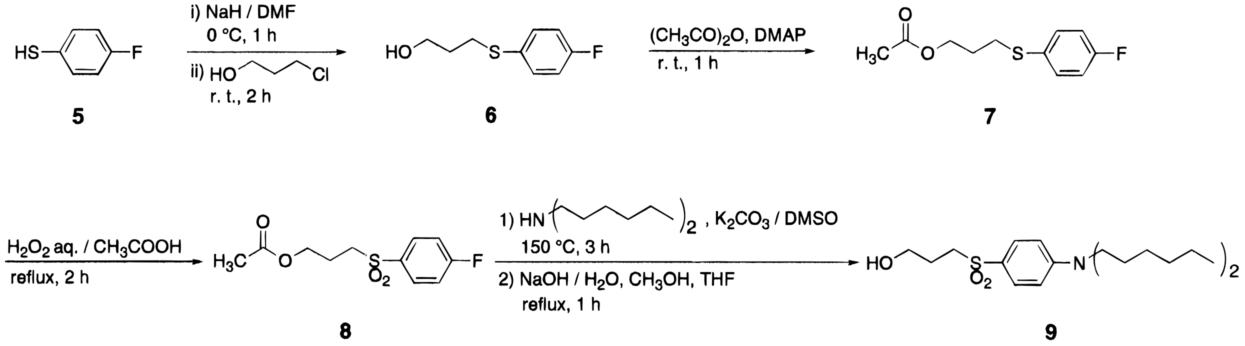
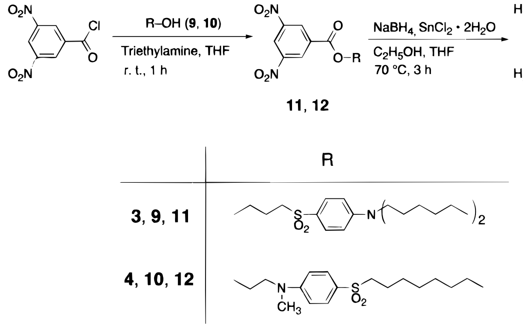
(6) Jerphagnon, J; Kurtz, S. K. *J. Appl. Phys.* **1970**, *41*, 1667.

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

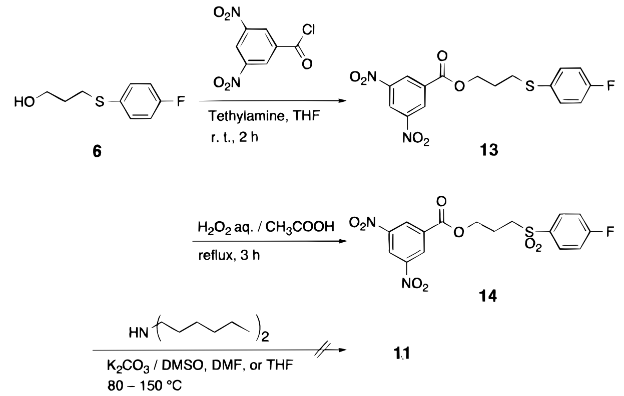
Scheme 2



Scheme 3



Scheme 4



of the second harmonic power. 1-mm-thick y-cut quartz (d_{11} = 0.46 pm/V) was used as a reference sample.

Measurement of SHG Decay. First, **P3** or **P4** was deposited on an indium tin oxide (ITO) slide glass by spin-coating at a rate of 2000 rpm from the 10 wt % THF solution. The spin-coated film was poled at 130 °C. Then the temperature was set at 50 °C with the poling field being applied. After the SH light intensity reached a constant value for these conditions, the poling field was turned off. The SHG signal was monitored in real time. During the SHG signal relaxation experiments, the sample was kept under isothermal conditions equipped with specially designed heater with optic windows.[8]

Results and Discussion

Synthesis and General Properties of Polyamides. Scheme 2 shows the pathways for the preparation of hydroxyl-functionalized NLO-phore **9**. 4-Fluorothiophenol was used as the starting material, and five-step reactions, i.e., alkylation, protection of hydroxyl group, oxidation, condensation, and deprotection, provided the desired hydroxyl-functionalized NLO-phore **9**. Scheme 3 describes the preparation of 3,5-diaminobenzoate derivatives **3** and **4** as the comonomers 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 **9** and **10**, followed by the reduction of the corresponding 3,5-dinitrobenzoate derivatives **11** and **12** with sodium tetrahydroborate in the presence of $SnCl_2 \cdot 2H_2O$ in ethanolic medium. We obtained 3,5-dinitrobenzoate **11** by the esterification reaction between 3,5-dinitrobenzoyl chloride and hydroxyl-functionalized NLO-phore **9**. At first, we tried to obtain 3,5-dinitrobenzoate **11** via the pathways shown in Scheme 4. In the pathways shown in Scheme 4, 3,5-dinitrobenzoyloxy group could also be used as the protecting group for hydroxyl group. Therefore, the pathways shown in Scheme 4 could decrease the two-step reactions, i.e., the protection of hydroxyl group by acetyl function and the deprotection, compared with that shown in Schemes 2 and 3. Unfortunately, the condensation reaction between 3-[(4-fluorophenyl)sulfonyl]propyl 3,5-dinitrobenzoate (**14**) and dihexylamine did not provide 3,5-dinitrobenzoate **11**. The variation of solvents and reaction temperature and the application of metal catalysts[9] were confirmed not to afford 3,5-dinitrobenzoate **11**, possibly due to the side reaction such as the substitution reaction of nitro group by nucleophilic amine.[10]

Scheme 1, which was described above, shows the preparation of polyamides. Both polyamides were prepared by solution polycondensation between 5-[2-(*N*-methyl-4-nitroanilino)ethoxy]isophthaloyl chloride (**2**) and 3,5-diaminobenzoate **3** or **4** in NMP. The reaction temperature was raised from −78 °C, where the solutions of each comonomer were mixed, to 40 °C, where the polymerization reactions proceeded in homogeneous systems. Pouring the reaction solution into methanol afforded the polyamides as yellow powder solids. The average molecular weights, which were determined by the light scattering measurements, and the solubilities of the obtained polyamides are summarized in Table 1. The obtained polyamides **P3** and **P4** are soluble in common polar organic solvents, such as THF, DMF, DMSO, and NMP at room temperature. The tail alkyl component in the side chain would inhibit the aggregation of the main chain and improve the solubility of

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(8) Wang, H.; Jarnagin, R. C.; Samulski, E. T. *Macromolecules* **1994**, *27*, 4705.

(9) (a) Gauthier, S; Fréchet, J. M. *Synthesis* **1987**, 383. (b) Hager, F. D. *Org. Synth.* **1941**, *I*, 544. (c) Allen, C. F. H.; McKee, G. H. W. *Org. Synth.* **1943**, *II*, 15.

(10) *The Chemistry of The Nitro and Nitroso Groups*; Feuer, H., Ed.; Interscience Publishers: New York, 1969; Part 1, Chapter 8.

Table 1. Characterization of Polyamides

polymer	10^{-4} M_w[a]	T_g,[b] °C	λ_{max}, nm	λ_{cutoff}, nm	solubility[c]						
					THF	DMF	NMP	DMSO	acetone	$CHCl_3$	ethanol
P3	4.80	118	394	490	S	S	S	S	PS	PS	I
P4	3.13	114	397	484	S	S	S	S	PS	PS	I

[a] Determined by light scattering measurements in THF. [b] Determined from DSC thermograms on a second heating scan. [c] S, soluble at room temperature; PS, partially soluble; I, insoluble.

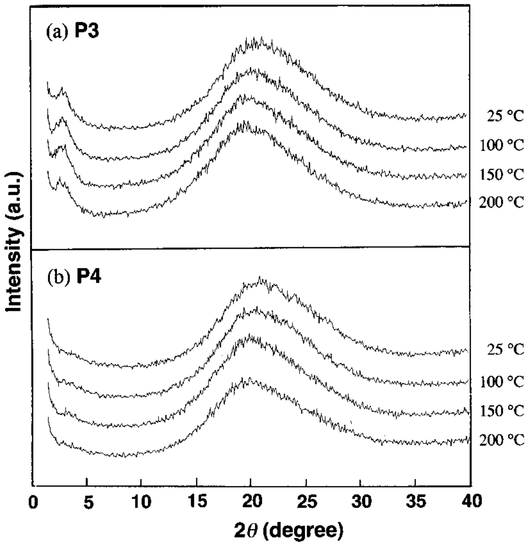

Figure 2. X-ray diffraction patterns of **P3** and **P4** obtained by a powder method.

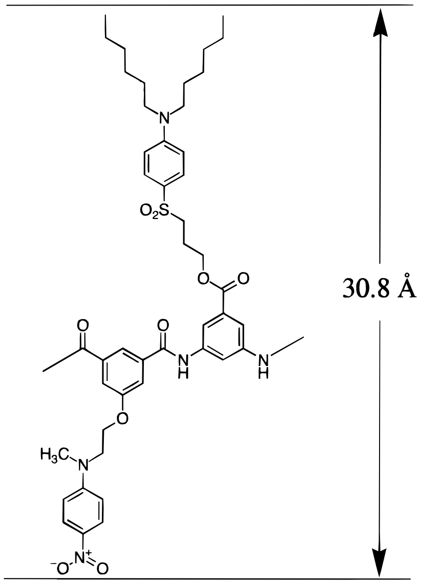

Figure 3. Estimated molecular size of monomeric unit of **P3**.

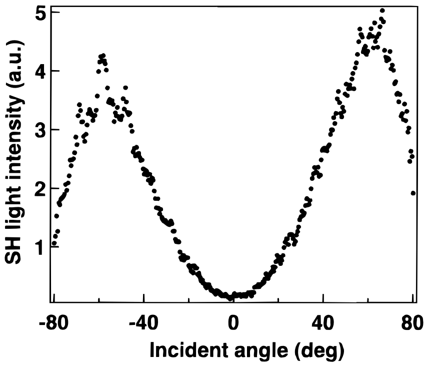

Figure 4. Relationship between SH light intensity and the incident angle of an exciting beam for a spin-coated film of **P3** after corona poling at 130 °C.

these polyamides. Therefore, the optical-quality thin film of **P3** and **P4** can be easily obtained by spin-coating from the THF solutions. The average molecular weights of the obtained polyamides were determined by the light scattering measurements and are the magnitude of 10^4. Table 1 also gives the T_g of the obtained polyamides determined from a second heating scan of DSC measurements. There seem to be no significant differences in T_g's of **P3** and **P4**, which were 118 and 114 °C, respectively. These relatively low T_g's are detrimental to the stabilization of noncentrosymmetric NLO-phore alignment, and are attributed to the incorporated side-chain alkyl group, which would increase the free volume around the polymer linkage. No other endothermic or exothermic peaks appeared in the temperature range from ambient temperature to 220 °C.

Figure 2 describes X-ray diffraction patterns of the polyamides carried out by the powder method at various temperatures. There were no diffraction peaks except for a broad halo around 22° in the diffraction pattern of **P4**; however, the broad and weak diffraction peak around 2.8°, the *d* spacing of which was calculated to be ca. 30 Å, was observed besides a broad halo around 22° in the diffraction pattern of **P3**. Figure 3 shows the molecular size of the monomeric unit of **P3**, which was estimated from the molecular model of the monomer unit optimized by MOPAC calculation (PM3 method).[11] The distance between the side-chain tail and another tail was estimated to be 30.8 Å, which may correspond to the X-ray diffraction peak around 2.8°. These findings would indicate that the polymeric conformations as shown in Figure 3 are relatively stable. But, the lack of optical anisotropy of the present polyamides was confirmed by polarized microscopic observations at various temperatures.

UV−vis spectroscopy was carried out using a spin-coated film on a glass substrate. We defined the cutoff wavelength (λ_{cutoff}) as the wavelength where the value of the first deviation for the absorbance becomes 0. There were no significant differences in the values of λ_{max} and λ_{cutoff} among the present polyamides, because the λ_{max} and λ_{cutoff} were dependent on 4-nitroanilino moieties involved.

SHG Measurements by the Maker Fringe Method. As a typical example, Figure 4 describes the relationship between SH light intensity and the incident angle of an exciting beam for a spin-coated film of **P3** after corona poling at 130 °C. It was confirmed that the similar Maker fringe patterns were obtained for spin-coated films of **P4** after corona poling. Figure 5 describes the dependence of the d_{33} values on the poling temperatures. The d_{33} values of **P3** and **P4** were 6.4

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(11) Stewart, J. J. P. *MOPAC Ver. 6, QPCE Bull.* **1989**, *9*, 10.

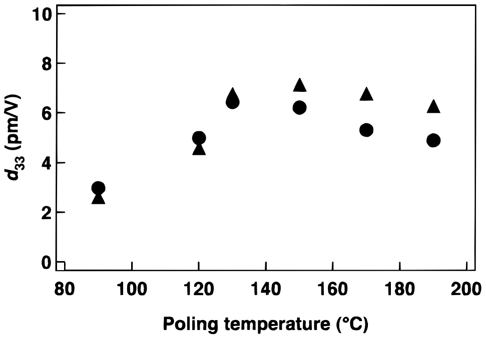


Figure 5. Dependence of d_{33} values on poling temperature: (●) **P3**; (▲) **P4**.

and 7.1 pm/V, respectively, after poling treatment at the corresponding optimum poling temperatures. Considering the comparable T_g's of **P3** and **P4**, Figure 5 would indicate that there are no significant differences in the statistical orientational behaviors of the NLO-phores between **P3** and **P4**. The orientational behaviors of the present polyamides fit a general tendency that poling treatment around or above T_g is most effective. We have expected the enhanced NLO activity of **P3** over **P4**. But no significant differences in their NLO activities were observed, as mentioned above. We could consider two reasons for these results. One reason is that the $\mu\beta$ value of nitroanilino moiety (e.g., $\mu\beta$ value of 4-nitro-*N*,*N*-dimethylaniline has been reported[12] to be 143 × 10^{-48} esu) is much larger than that of alkylsulfonylanilino moiety (e.g., $\mu\beta$ value of 4-methylsulfonyl-*N*,*N*-dimethylaniline has been reported[12] to be 26 × 10^{-48} esu). The $\mu\beta$ value of alkylsulfonylanilino moiety would be too small to clarify the effects of the alternate alignment of different NLO-phores with different dipole direction as regards polymer backbone. Another reason is that the ethylene or propylene group between the side-chain NLO-phore and the polymer backbone makes the NLO-phores mobile. The flexible alkylene groups would take disadvantage to restricting the motion of NLO-phores by the conformations formed by polyamide backbone.

SHG Decay. The short-term temporal behavior of the SH light intensity at 50 °C was preliminarily investigated as described in Figure 6. In the analysis of SHG decay, two functions are often used for fitting SHG decay data after removal of the poling field, i.e., the Kohlrausch–Williams–Watts (KWW) stretched exponential function:[13]

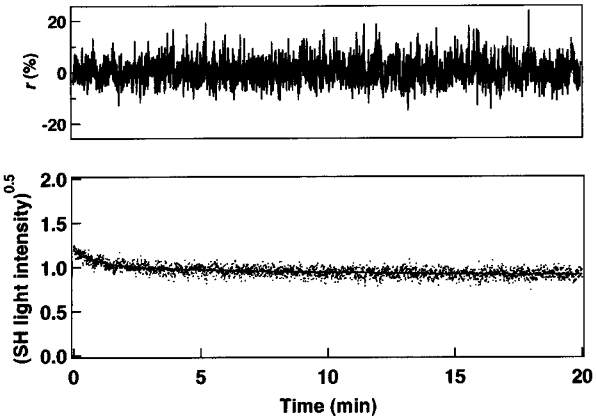
$$f(t) = A \exp[-(t/\tau)^{\beta}] + C \qquad (2)$$

or a biexponential function:

$$f(t) = A \exp(-t/\tau_A) + B \exp(-t/\tau_B) + C \qquad (3)$$

In the present system, a biexponential function (eq 3) was fit to the SHG decay by the mean-square method. The calculated parameters obtained by curve-fitting are given in Table 2. Both τ_A and τ_B values obtained for **P3** were larger than those for **P4**. As mentioned above, there were no significant differences in the statistically orientational behavior of NLO-phores between **P3** and **P4**, however, some differences would exist in the dynamically relaxational behavior between **P3** and **P4**. Our speculations for the interpretation of these results are as follows. As far as being estimated by these coefficients, the alternatingly attaching electron-donating and electron-withdrawing groups to the polymer backbone may be effective in restraining the relaxation of the noncentrosymmetric NLO-phore alignment induced by an electric field. As deduced from the X-ray diffraction measurements, a part of segments in **P3** would form the conformations which align the dipole direction of NLO-phores (Figure 3) even at 200 °C. These segments are not considered to contribute to the SHG decay because their conformations are stable. The SHG decay rate is considered to increase with the increase in concentration of noncentrosymmetrically aligned NLO-phores, which are induced by an electrical poling. In the case of **P3**, the existence of the segments which would not contribute to the SHG decay lowered the concentration of NLO-phores inducing the SHG decay. As a result, the apparent SHG decay rate for

(a) **P3**



(b) **P4**

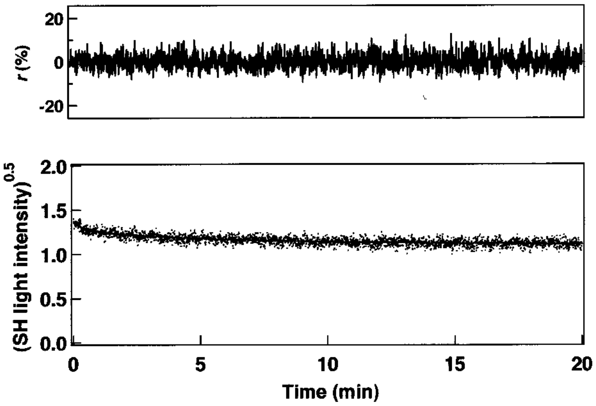


Figure 6. SHG decay measured at 50 °C; (●) measured signal; (—) fitting curve using a biexponential function.

Table 2. Parameters Obtained by Fitting the Square Root of the SHG Decay Curves at 50 °C in Figure 6 to Eq 3

polymer	A	τ_A, min	B	τ_B, min	C
P3	0.171 (58%)[a]	0.808	0.126 (42%)[a]	8.52	0.900
P4	0.111 (42%)[a]	0.389	0.153 (58%)[a]	6.25	1.11

[a] The values in parentheses were obtained by {A or $B/(A + B)$} × 100 (%).

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(12) Reference 1a, Chapter 10.

(13) (a) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80. (b) Williams, G. *Adv. Polym. Sci.* **1979**, *33*, 461.

P3 should be slow. Therefore, both τ_A and τ_B values for **P3** were estimated to be larger than those for **P4**. We would conclude that the alternatingly attaching electron-donating and electron-withdrawing groups of NLO-phores to the polymer backbone is effective in restraining the relaxation of the noncentrosymmetric NLO-phore alignment induced by an electric field. But, at the present stage, it would be undeniable that the differences in decay behavior are within an experimental error. The long-term temporal SHG decay measurements are needed for the detailed discussions, which are the subject of the future.

Conclusions

The syntheses of a novel type of polyamide with side-chain alternating donor-attached and acceptor-attached NLO-phores as well as polyamide with side-chain all donor-attached NLO-phores have been achieved. Spin-coating from a THF solution gave the optical-quality thin films of **P3**, where electron-donating and electron-withdrawing groups of the side-chain NLO-phores were alternatingly attached to their backbone, and **P4**, where electron-donating group of all side-chain NLO-phores were attached to their backbone. The optimum second-order NLO coefficients, d_{33}, for **P3** and **P4** were 6.4 and 7.1 pm/V, respectively, evaluated from the SHG measurements using an exciting beam at 1064 nm. No significant differences were observed in the temperature dependence of orientational behavior of side-chain NLO-phores between two kinds of polyamides. The time coefficients, which were obtained by curve-fitting to the short-time temporal SHG decay curves, indicates that the alternatingly attaching electron-donating and electron-withdrawing groups of NLO-phore to the polymer backbone could be somewhat effective in restraining the relaxation of the noncentrosymmetric NLO-phore alignment induced by an electric field.

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