A New Synthetic Approach to Novel Polymers Exhibiting Large Electrooptic Coefficients and High Thermal Stability

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ABSTRACT: The Stille coupling reaction was explored to synthesize novel polymers with a pending NLO chromophore exhibiting a large $\mu\beta$ value but high chemical sensitivity. This approach enabled the synthesis of aromatic polyimides through the careful design of dibromo monomers bearing NLO chromophores. The resulting polyimide was shown to possess a glass transition temperature of 170 °C and a large electrooptic coefficient.

Polymeric second-order nonlinear optical (NLO) materials were envisioned to possess advantages over inorganic materials in photonic technologies, such as fast response time, good processability, and a low dielectric constant.[1−3] For practical applications, these polymers must meet the following requirements: (1) a large nonresonant second-order nonlinearity, (2) excellent chemical and thermal stability under both operating and fabrication conditions, and (3) low optical loss.[4,5] Numerous polymer systems have been developed to meet these requirements, and the performance of polymers thus developed has been enhanced.[4−14] However, after many years of research, it has become apparent that the synthesis of a second-order NLO polymer that possesses a combination of properties suitable for extensive device exploration remains a challenge.

Among the polymer systems developed, functionalized aromatic polyimides are promising for the investigation of second-order NLO materials because their high glass transition temperatures can be utilized to stabilize the dipole orientation of the NLO chromophore at high temperatures. Recently, we have developed a series of functionalized polyimides with second-order NLO properties.[7,12] Detailed physical and structural analyses have revealed their important features. It seems clear that the thermal stability of the functionalized polyimides is good enough for numerous device applications. The limiting factor is the NLO response, namely, small r_{33} values. To improve this, the incorporation of an NLO chromophore exhibiting a large $\mu\beta$ value is important.

However, the majority of the NLO chromophores exhibiting large $\mu\beta$ values are very sensitive to numerous chemical manipulations.[4,8] For example, a weak nucleophile, such as tributylamine, can cause the decomposition of these chromophores. To incorporate these chromophores into a polymer backbone, especially polyimide's backbone, mild reaction conditions are required. In the past few years, our group has been involved in exploring palladium-catalyzed reactions for polycondensation and gained extensive knowledge about these reactions.[14] We have demonstrated that the Stille coupling reaction is very versatile in the synthesis of NLO polymers, and due to its mild conditions, many functional groups can be tolerated.[11] A series of conjugated photorefractive polymers containing NLO chromophores have synthesized.[15] The question is how to utilize this reaction to prepare NLO polyimides that will maintain high thermal stability and processability. This paper describes the design, synthesis, and characterization of new polymers containing a unique chromophore (see Scheme 1). Two polymers were synthesized utilizing the Stille coupling reaction: polyphenylene thiophene (PPT) and a novel polyphenyleneimide thiophene. It was found that the latter polymer exhibited high optical nonlinearity and reasonably high glass transition temperatures.

Experimental Section

Tetrahydrofuran (THF) was purified by distillation over sodium chips and benzophenone. NMP was purified by distillation over phosphorus pentaoxide. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride was purified by recrystallization from acetic anhydride and dried in a vacuum at 150 °C. All other chemicals were purchased from Aldrich Chemical Co. and were used as received unless otherwise stated.

Synthesis of Monomers and Polymers. The synthetic approaches for the monomers and polymers are outlined in Schemes 1 and 2. The following compounds were synthesized according to the literature procedure: 4-[*N*-ethyl-*N*-[(benzoyloxy)ethyl]amino]benzaldehyde (**12**),[12] diethyl-2-thenyl phosphate (**6**),[16] 1,3-diethylbarbaturic acid (**9**),[17] and 2,5-bis(tributylstannyl)thiophene (**11**).[18]

Compound 2. A 5 mL aliquot of compound **1** (21.5 g, 127.7 mmol) was added to a suspension containing Mg (3.06 g, 127.7 mmol) in THF (50 mL). After stirring for a couple of minutes, the mixture started to reflux. The rest of compound **1** was then added to the mixture in such a rate to maintain the refluxing. After the addition was finished, the mixture was refluxed for another half an hour. The resulting Grignard reagent was transferred into an addition funnel and added dropwise into a mixture containing an excess of 1,5-dibromopentane (36.14 g, 157.0 mmol), Li_2CuCl_4 (15 mL of 0.1 M THF solution, 1.5 mmol), and 20 mL of THF at 5−10 °C. The resulting mixture was stirred overnight at room temperature and then poured into water. The mixture was extracted with methylene chloride. The organic layer was washed with water, aquaous $NaHCO_3$ solution, and water again. It was then dried with $MgSO_4$. After the removal of the solvent, the resulting liquid was distilled to give 17.2 g of product, a colorless liquid (57%, bp 111−113 °C/1.0 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 1.51 (m, $-CH_2-$, 2H), 1.66 (m, $-CH_2-$, 2H), 1.91 (m, $-CH_2-$, 2H), 2.35 (s, $-CH_3$, 3H), 2.61 (t, $ArCH_2-$, 2H), 3.43 (t, $-CH_2Br$, 2H), 7.1 (m, aromatic, 4 H). Anal. Calcd for $C_{12}H_{17}Br$: C, 59.76; H, 7.10. Found: C, 60.02; H, 7.01.

Compound 3. Bromine (24.0 g, 150.0 mmol, 2.1 equiv) was added quickly to a stirred solution of compound **2** (16.5 g, 68.5 mmol) and iodine (0.17 g, 0.69 mmol) in 100 mL of CH_2Cl_2.

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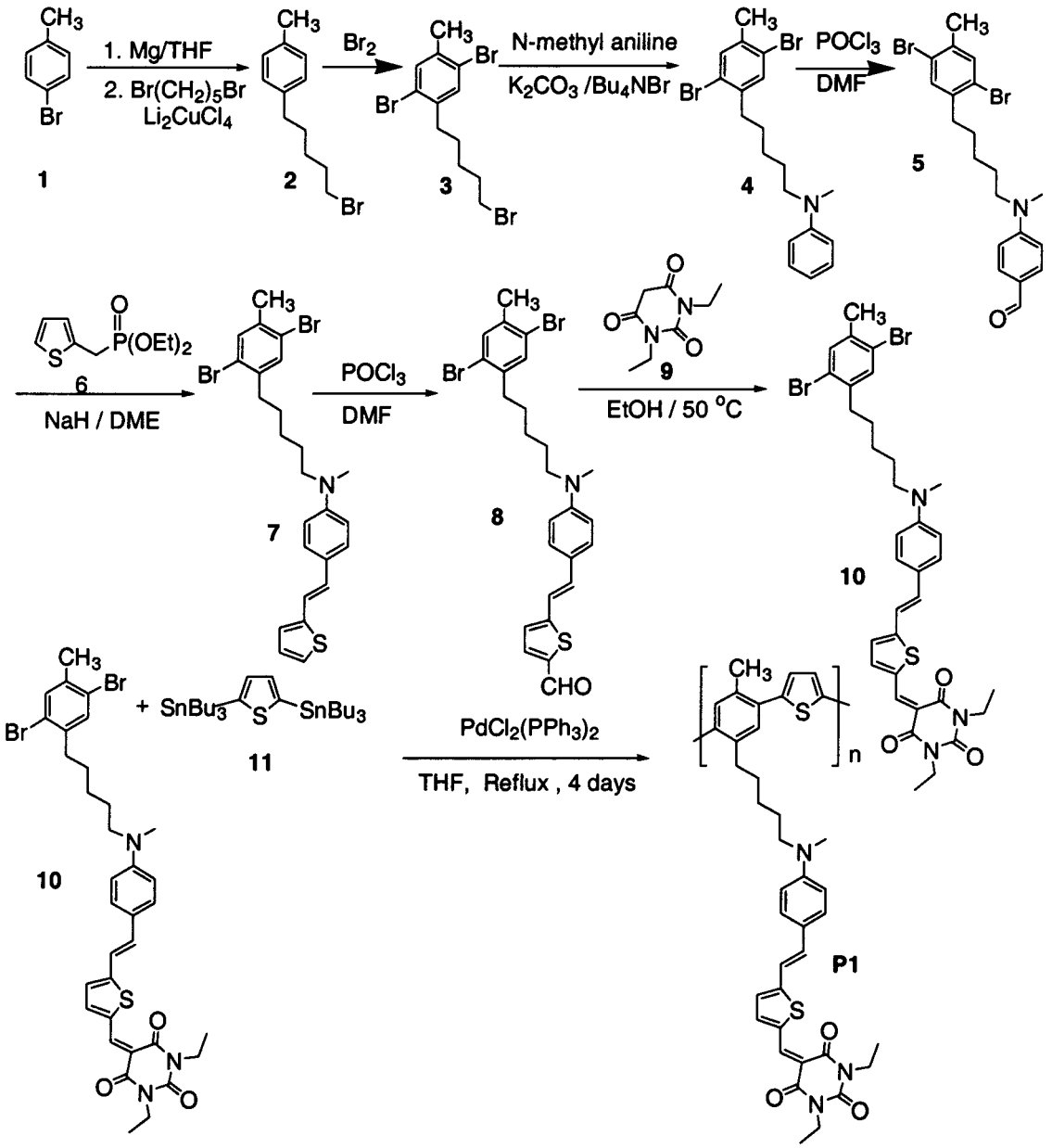
Scheme 1. Synthesis of Polymer 1



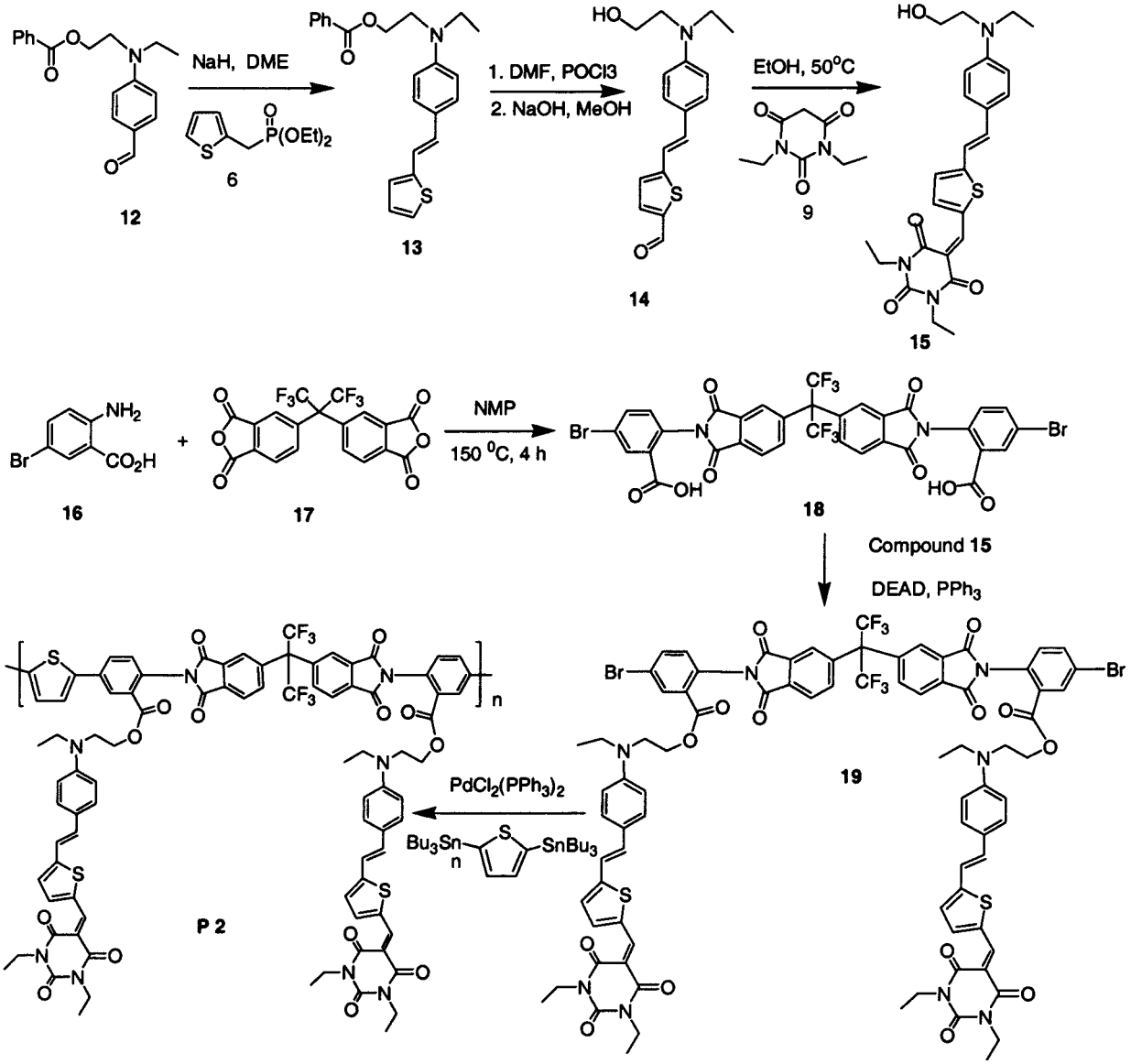
The resulting solution was stirred at room temperature under rigorous exclusion of light for 1 day. A 20% KOH solution (80 mL) was added until the until the color of the solution disappeared. The organic layer was separated and then dried over $MgSO_4$. After removing the solvent, the residue was distilled to give 22.0 g of the product, a colorless liquid (80%, bp 161−163 °C/1.0 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 1.53 (m, $-CH_2-$, 2H), 1.65 (m, $-CH_2-$, 2H), 1.93 (m, $-CH_2-$, 2H), 2.36 (s, $ArCH_3$, 3H), 2.69 (t, $ArCH_2-$, 2H), 3.44 (t, $-CH_2Br$, 2H), 7.38 (s, aromatic, 1H), 7.41 (s, aromatic, 1H). Anal. Calcd for $C_{12}H_{15}Br_3$: C, 36.13; H, 3.79. Found: C, 36.38; H, 3.75.

Compound 4. A solution of compound **3** (18.0 g, 45.0 mmol), *N*-methylaniline (5.79 g, 57.13 mmol), potassiun carbonate (12.5 g, 90.2 mmol), tetrabutylammonium bromide (1.45 g, 4.51 mmol), and sodium iodide (30 mg) in toluene (30 mL) was stirred under refluxing overnight. $CHCl_3$ (80 mL) and water (60 mL) were then added. The organic layer was separated and dried over magnesium sulfate. After the removal of the solvent, the residue was distilled to give 17.0 g of the product, a pale yellow oil (94%, bp 212−215 °C/0.70 mmHg). ^{1}H NMR ($CDCl_3$, ppm): δ 1.43 (m, $-CH_2-$, 2H), 1.65 (m, $-CH_2-$, 4 H), 2.37 (s, $ArCH_3$, 3H), 2.68 (t, $ArCH_2-$, 2H), 2.96 (s, $-NCH_3$, 3H), 3.34 (t, J = 7.4 Hz, $-NCH_2$, 2H), 6.72 (m, aromatic, 3H), 7.27 (m, aromatic, 2H), 7.37 (s, aromatic, 1H), 7.42 (s, aromatic, 1 H). Anal. Calcd for $C_{19}H_{23}Br_2N$: C, 53.67; H, 5.45; N, 3.30. Found: C, 53.38; H, 5.56; N, 3.40.

Compounds 5, 8, and 14: General Procedure. Compound 5. Phosphorus oxychloride (1.53 g, 10.0 mmol) was added dropwise to DMF (5 mL, 64.6 mmol) at 0 °C. The solution was stirred at 0 °C for 1 h and then at 25 °C for another 1 h. Compound **5** (4.25 g, 10 mmol) in 5 mL of DMF was then added dropwise to the mixture. The resulting solution was stirred at 80 °C for 4 h. After being cooled to room temperature, the solution was poured into cold water and neutralized with NaOAc. The mixture was extracted with methylene chloride. The organic layer was washed with water and then dried. After the removal of the solvent, the crude product was chromatographed using $CHCl_3$ to yield yellow solid (3.85 g, 85%, mp 80−82 °C). ^{1}H NMR ($CDCl_3$, ppm): δ 1.43 (m, $-CH_2-$, 2H), 1.67 (m, $-CH_2-$, 4H), 2.35 (s, $ArCH_3$, 3H), 2.69 (t, J = 7.5 Hz, $ArCH_2-$, 2H), 3.07 (s, $-NCH_3$, 3H), 3.44 (t, J = 7.4 Hz, $-NCH_2$, 2H), 6.70 (d, J = 8.7 Hz, aromatic, 3H), 7.37 (s, aromatic, 1H), 7.42 (s, aromatic, 1H), 7.75 (d, J = 8.7 Hz, aromatic, 2H), 9.75 (s, 1H, aldehyde proton). Anal. Calcd for $C_{20}H_{23}Br_2NO$: C, 53.00; H, 5.12; N, 3.09. Found: C, 53.17; H, 5.21; N, 3.10.

Compound 8. Yield, 31%, mp 71−73 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 1.42 (m, $-CH_2-$, 2H), 1.65 (m, $-CH_2-$, 4 H), 2.36 (s,

Scheme 2. Synthesis of Polymer 2



$ArCH_3$, 3H), 2.99 (t, J = 7.5 Hz, $ArCH_2-$, 2H), 3.01 (s, $-NCH_3$, 3H), 3.39 (t, J = 7.4 Hz, $-NCH_2$, 2H), 6.68 (d, J = 8.6 Hz, aromatic, 2H), 7.05 (d, J = 16.0 Hz, =CH, 1 H), 7.07 (m, J = 3.5 Hz, thienyl proton, 1H), 7.12 (d, J = 16.0 Hz, =CH, 1H), 7.37 (s, aromatic, 1H), 7.40 (d, J = 8.6 Hz, aromatic, 2H), 7.42 (s, aromatic, 1H), 7.65 (d, J = 3.5 Hz, thienyl proton, 1H), 9.84 (s, aldehyde proton, 1H). Anal. Calcd for $C_{26}H_{27}Br_2NOS$: C, 55.63; H, 4.85; N, 2.50. Found: C, 55.39; H, 4.69; N, 2.43.

Compound 14. The above procedure is followed. After removal of the solvent, the crude product was saponified by a sodium hydroxide solution (10%) to yield an orange solid which was recrystallized from chloroform/hexane (40%, mp 118−120 °C). The ^{1}H NMR ($CDCl_3$, ppm): δ 1.22 (t, J = 7.0 Hz, $-NCH_2CH_3$, 3H), 1.73 (t, J = 3.8 Hz, −OH, 1H), 3.48 (q, J = 7.1 Hz, $-NCH_2CH_3$, 2H), 3.55 (t, J = 5.8 Hz, $-OCH_2CH_2N-$, 2H), 3.86 (t, J = 5.8 Hz, $-OCH_2CH_2N-$, 2H), 6.75 (d, J = 8.8 Hz, ArH, 2H), 7.0 (d, J = 16.0 Hz, =CH, 1H), 7.06 (d, J = 3.3 Hz, thienyl proton, 1H), 7.10 (d, J = 16.0 Hz, =CH, 1H), 7.39 (d, J = 8.8 Hz, ArH, 2H), 7.65 (d, J = 3.3 Hz, thienyl proton, 1H), 9.83 (s, aldehyde proton, 1H). Anal. Calcd for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.68; H, 6.19; N, 4.32.

Compounds 7 and 13: **General Procedure. Compound 7**. To a dried, three-necked, 250 mL round-bottom flask were added 1,2-dimethoxyethane (20 mL) and sodium hydride (0.48 g, 20.0 mmol) under nitrogen. The mixture was stirred for 5 min, and compound **6** (4.53 g, 10.0 mol) in 1,2-dimethoxyethane (20 mL) was then added. The diethyl 2-thenylphosphonate[15] (2.35 g, 10.0 mmol) in 1,2-dimethoxyethane (10 mL) was added slowly to the reaction mixture. The resulting solution was heated to 60 °C for 4 h and then poured into crushed ice (80 g) under nitrogen. The mixture was extracted with dichloromethane (3 × 30 mL). The organic layer was washed with water (3 × 50 mL). After removing the solvent, the crude product was chromatographed using $CHCl_3$/Hex (9:1) to yield a yellow solid (5.2 g, 88%, mp 67−69 °C). ^{1}H NMR ($CDCl_3$, ppm): δ 1.42 (m, J = 7.0 Hz, $-CH_2CH_2CH_2-$, 2H), 1.65 (m, $-CH_2CH_2CH_2-$, 4H), 2.37 (s, $ArCH_3$, 3H), 2.67 (t, J = 7.7 Hz, $-CH_2Ar$, 2H), 2.97 (s, CH_3N-, 3H), 3.37 (t, J = 7.7 Hz, $-CH_2NCH_3$, 2H), 6.81 (d, J = 8.8 Hz, ArH, 2H), 6.88 (d, J = 16.0 Hz, =CH, 1H), 6.97 (d, J = 3.35 Hz, thienyl proton, 1H), 6.99 (d, J = 3.35 Hz, thienyl proton, 1H) 7.04 (d, J = 16.0 Hz, =CH, 1H), 714 (m, thienyl proton, 1H), 7.36 (d, J = 8.8 Hz, ArH, 2 H), 7.37 (s, ArH, 1H), 7.41 (s, ArH, 1H). Anal. Calcd for $C_{25}H_{27}Br_2NS$: C, 56.30; H, 5.10; N, 2.63. Found: C, 56.08; H, 5.26; N, 2.68.

Compound 13. 77%, mp 54−56 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 1.22 (t, J = 7.0 Hz, $-NCH_2CH_3$, 3H), 3.55 (q, J = 7.0 Hz, $-NCH_2CH_3$, 2H), 3.79 (t, J = 5.8 Hz, $-OCH_2CH_2N-$, 2H), 4.55 (t, J = 5.8 Hz, $-OCH_2CH_2N-$, 2H), 6.78 (d, J = 8.5 Hz, ArH, 2H), 6.90 (d, J = 16.0 Hz, =CH, 1H), 7.0 (d, J = 4.8 Hz, thienyl proton, 1H), 7.02 (d, J = 4.8 Hz, thienyl proton, 1H),

7.08 (d, J = 16.0 Hz, =CH, 1H), 7.14 (m, thienyl proton, 1H), 7.40 (d, J = 8.5 Hz, ArH, 2H), 7.48 (t, J = 7.7 Hz, ArH, 2H), 7.61 (t, J = 6.6 Hz, ArH, 1H), 8.05 (d, J = 7.9 Hz, ArH, 2H), Anal. Calcd for $C_{21}H_{23}NO_2S$: C, 73.18; H, 6.14; N, 3.71. Found: C, 72.90; H, 6.28; N, 3.47.

Compound 10 and 15. General Procedure. Monomer 10. To a mixture of compound **8** (0.40 g, 0.71 mmol) in EtOH (5.0 mL) was added compound **9** (0.16 g, 0.85 mmol). The reaction mixture was stirred overnight at 50 °C. After cooling, the purple solid was filtered and recrystallized from $CHCl_3$/Hex to give a pure product (0.42 g, 81%, mp 130−132 °C). ^{1}H NMR ($CDCl_3$, ppm): δ 1.30 (m, $-NCH_2CH_3$, 6H), 1.43 (m, $-CH_2-$, 2H), 1.67 (m, $-CH_2-$, 4 H), 2.36 (s, $ArCH_3$, 3H), 2.71 (t, J = 7.5 Hz, $ArCH_2-$, 2H), 3.01 (s, $-NCH_3$, 3H), 3.40 (t, J = 7.4 Hz, $-NCH_2$, 2H), 4.10 (q, J = 7.0 Hz, $-NCH_2CH_3$, 4H), 6.69 (d, J = 8.6 Hz, aromatic, 2H), 7.08 (d, J = 16.0 Hz, =CH, 1H), 7.20 (m, J = 3.5 Hz, thienyl proton, 1H), 7.37 (d, J = 16.0 Hz, =CH, 1H), 7.38 (s, aromatic, 1 H), 7.42 (s, aromatic, 1H), 7.45 (d, J = 8.6 Hz, aromatic, 2H), 7.76 (d, J = 3.5 Hz, thienyl proton, 1H), 8.61 (s, bridge proton, 1H). Anal. Calcd for $C_{34}H_{37}Br_2N_3O_3S$: C, 56.13; H, 5.12; N, 5.78. Found: C, 56.29; H, 5.19; N, 5.53.

Compound 15. 93%, mp 186−188 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 1.22 (t, J = 7.0 Hz, $-NCH_2CH_3$, 3 H), 1.30 (m, $-NCH_2CH_3$, 6H), 1.80 (s, −OH, 1H), 3.55 (m, $-CH_2NCH_2-$, 4H), 3.86 (t, J = 5.8 Hz, $-OCH_2CH_2N-$, 2H), 4.10 (m, CH_3-CH_2N-, 4H), 6.76 (d, J = 8.9 Hz, ArH, 2H), 7.06 (d, J = 16.0 Hz, =CH, 1H), 7.17 (d, J = 4.0 Hz, thienyl proton, 1H), 7.35 (d, J = 16.0 Hz, =CH, 1H), 7.43 (d, J = 8.9 Hz, Ar, 2H), 7.75 (d, J = 4.0 Hz, thienyl proton, 1H), 8.60 (s, bridge proton, 1H). Anal. Calcd for $C_{25}H_{29}N_3O_4S$: C, 64.22; H, 6.25; N, 8.99. Found: C, 64.01; H, 6.34; N, 8.93.

Compound 18. To a stirred solution of 2-amino-5-bromobenzoic acid (**16**) (3.88 g, 18.0 mmol) in 12 mL of anhydrous NMP was added anhydride **17** (4.0 g, 9.0 mmol) at room temperature under nitrogen. The mixture was stirred at 90 °C for 12 h. Then a solution of 16 mL of acetic anhydride and 8 mL of pyridine was added to the reaction mixture. After being heated at 90 °C for 12 h, the solution was cooled and poured into a 100 mL solution of H_2O/MeOH (9:1). The crude product was collected by filtration and purified by chromatography over deactivated silica gel (15% H_2O) using $CHCl_3$ as the eluent to give the title compound as a white solid (3.78 g, 50%, mp 164−166 °C). ^{1}H NMR (DMSO-d_6, ppm): δ 7.50 (d, J = 7.5 Hz, 2H), 7.77 (s, ArH, 2H), 7.98 (m, ArH, 4H), 8.12 (d, J = 3.0 Hz, ArH, 2H), 8.18 (d, J = 8.0 Hz, ArH, 2H). Anal. Calcd for $C_{33}H_{14}F_6N_2O_8$: C, 47.17; H, 1.68; N, 3.33. Found: C, 47.37; H, 1.54; N, 3.38.

Compound 19. Diethyl azodicarboxylate (0.21 g, 1.20 mmol) in THF (2 mL) was added dropwise to a solution of compound **18** (0.25 g, 0.30 mmol), compound **15** (0.28 g, 0.60 mmol), and triphenylphosphine (0.32 g, 1.20 mmol) in 8 mL of THF at 0 °C. After the addition was completed, the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was treated with MeOH (50 mL), and then the resulting solid was collected by filtration and recrystallized from chloroform/methanol to yield dark black crystals (0.35 g, 70%, mp 174−176 °C). ^{1}H NMR ($CDCl_3$, ppm): δ 1.15 (t, J = 7.0 Hz, $-CH_2NCH_2CH_3$, 6H), 1.25 (m, $-NCH_2CH_3$, 12H), 3.39 (t, J = 6 Hz, $-CH_2NCH_2CH_3$, 4H), 3.61 (m, $-CH_2NCH_2$-CH_3, 4H), 4.04 (m, $-NCH_2CH_3$, 8H), 4.35 (t, J = 6 Hz, $-OCH_2$-CH_2N-, 4H), 6.67 (d, J = 8.8 Hz, ArH, 2H), 7.01 (d, J = 16.0 Hz, =CH, 1H), 7.13 (d, J = 4.2 Hz, thienyl proton, 2H), 7.24 (d, J = 8.3, ArH, 2H), 7.28 (d, J = 16.0 Hz, =CH, 2H), 7.38 (d, J = 8.9 Hz, Ar, 4H), 7.72 (d, J = 4.6 Hz, thienyl proton, 2H), 7.79 (dd, J = 8.4, 2.5 Hz, ArH, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.94 (s, ArH, 2H), 7.97 (d, J = 8.2 Hz, ArH, 2H), 8.14 (d, J = 3.0 Hz, ArH, 2H), 8.56 (s, bridge proton, 1H). Anal. Calcd for $C_{83}H_{68}Br_2F_6N_8O_{14}S_2$: C, 57.31; H, 3.94; N, 6.44. Found: C, 57.47; H, 3.93; N, 6.31.

Polymerization. A general polymerization procedure is described here. A dibromo monomer (**10** or **19**) and a distannyl monomer (1 mmol each) were dissolved in 10 mL of dry THF, and $PdCl_2(PPh_3)_2$ (2 mol % equiv) was added as the catalyst. The solution was refluxed under nitrogen for 4 days for **P1** and 2 days for **P2**. The mixture was filtered to remove the metallic palladium, and the filtrate was then concentrated to about 10 mL and precipitated into MeOH. The precipitate was collected by filtration, redissolved, and precipitated into MeOH twice. The polymer was collected and washed with MeOH in a Soxhlet extractor for 2 days and then dried under a vacuum at 50 °C for 24 h.

P1. ^{1}H NMR ($CDCl_3$, ppm): δ 1.28 (m, $-NCH_2CH_3$, 6H), 1.39 (m, $-CH_2-$, 2 H), 1.65 (m, $-CH_2-$, 4H), 2.42 (s, $ArCH_3$, 3H), 2.75 (t, $ArCH_2-$, 2H), 3.01 (s, $-NCH_3$, 3H), 3.32 (t, $-NCH_2$, 2H), 4.07 (s, $-NCH_2CH_3$, 4H), 6.62 (s, Ar, 2H), 7.01 (s, ArH, 1H), 7.09 (s, thiophene,2H), 7.25 (s, ArH, 2H), 7.41 (s, aromatic, 4H), 7.72 (s, thienyl proton, 1H), 8.59 (s, bridge proton, 1H). Anal. Calcd for $(C_{38}H_{39}N_3O_3S_2)_n$: C, 70.23; H, 6.05; N, 6.46. Found: C, 67.14; H, 5.94; N, 5.79.

P2. ^{1}H NMR ($CDCl_3$, ppm): δ 1.18 (s, $-CH_2NCH_2CH_3$, 6H), 1.24 (s, $-NCH_2CH_3$, 12H), 3.42 (s, $-CH_2NCH_2CH_3$, 4H), 3.62 (s, $-CH_2NCH_2CH_3$, 4 H), 4.00 (s, $-NCH_2CH_3$, 8H), 4.37 (s, $-OCH_2CH_2N-$, 4H), 6.70 (d, J = 8.8 Hz, ArH, 2H), 6.87 (d, J = 16.0 Hz, =CH, 2H), 6.97 (s, ArH, 2H), 7.10 (s, thiophene protons, 2H), 7.24 (d, J = 16.0 Hz, =CH, 2H), 7.34 (s, Ar, 6H), 7.39−7.84 (m, ArH, 6H), 7.99−8.10 (m, ArH, 6H), 8.52 (s, bridge proton, 2H). Anal. Calcd for $(C_{87}H_{70}F_6N_8O_{14}S_3)_n$: C, 62.88; H, 4.24; N, 6.74. Found: C, 60.29; H, 4.16; N, 5.95.

Characterization. ^{1}H NMR spectra were recorded on a Bruker AM 400 spectrometer. UV−vis spectra were collected using a Shimadzu UV-2401PC spectrophotometer. The GPC measurements were performed on a Waters RI system equipped with a UV detector and a differential refractometer detector using THF as an eluent. The molecular weight distribution was calculated on the basis of monodispersed polystyrene standards. Thermal analyses were performed by using the DSC-10 and TGA-50 systems from TA instruments under a nitrogen atmosphere. The melting points were obtained with open capillary tubes on a Mel-Temp apparatus. Elemental analyses were performed by Atlantic Microlab, Inc.

Optical Measurement. We performed the Teng and Man ellipsometric technique for the electrooptic coefficient measurements.[20] For these measurements a casted polymer sample on an indium−tin oxide (ITO) substrate was poled under a corona discharge at 170 °C. While maintaining the corona discharge, the sample was cooled to room temperature. The 0.1 μm thick silver electrodes were evaporated on the polymer surface, and measurements were performed. The thickness and refractive index measurements were performed by a prizm−coupler from Metricon.

The second harmonic generation (SHG) of the poled polymeric films was measured using a model-locked Nd:YAG laser (Continuum-PY61C-10 with a pulse width of 25 ps and a repetition rate of 10 Hz) as a fundamental source (1.064 μm). A quartz crystal was used as the reference sample.

Results and Discussion

Monomer Synthesis. The central step is the syntheses of monomers **10** and **19**, both of which contain two bromo groups necessary for palladium-catalyzed reactions and two NLO chromophores with large $\mu\beta$ values. Monomer **10** was first synthesized to test the feasibility and tolerance of the Stille reaction. As shown in Scheme 1, the Grignard reagent of 4-bromotoluene was treated with 1,5-dibromopentane to yield compound **2**. Compound **2** was brominated in the absence of light to avoid any radical side reaction and then reacted with *N*-methylaniline to give compound **4**. Vilsmeier formylation gave aldehyde **5**, which then reacted with diethyl-2-thenyl phosphate (**6**) through the Horner−Emmons reaction to give compound **7**. Formylation of this material gave aldehyde **8**. A further Knoevenagle reaction of compound **8** with diethylbarbituric acid (**9**) afforded monomer **10** in a good yield.

The need to improve the thermal stability of the polymer directed our effort to synthesize a new class of

Table 1. Molecular Weights of Polymers

	M_w	M_n	polydispersity	degree of polymerization
P1	9600	5800	1.65	15
P2	21000	13100	1.59	13

monomers (**19**, see Scheme 2). Three advantages can be seen from this monomer structure: (1) the arrangement ensures a high NLO chromophore density in resulting polyimides; (2) the bromo groups will be activated by the electron-withdrawing imido and ester groups; (3) the two trifluoromethyl groups render the resulting polymers soluble in polar organic solvents. Chromophore **15** was synthesized according to the same reaction sequence used to synthesize monomer **10**. Compound **18** was synthesized by reacting 2-amino-5-bromobenzoic acid with dianhydride **17** in a high boiling point solvent such as NMP to give the corresponding amic acid which was cyclized through chemical imidization using Py/Ac_2O. Because of the chemical sensitivity of the chromophore, the Mitsunobu reaction[19] was utilized to attach it to compound **18**. The treatment of compound **18** and compound **15** with diethyl azidocarboxylate/triphenylphosphine in THF afforded monomer **19** in ca. 70%. All of the monomers were carefully purified and fully characterized.

Polymerization. The polymer was synthesized using a typical Stille coupling reaction in THF as a solvent and $PdCl_2(PPh_3)_2/PPh_3$ as a catalytic system.[14] Both polymers were soluble in common organic solvents (THF, $CHC1_3$, TCE, DMF). The molecular weights of these polymers, determined by GPC using THF as eluent, are shown in Table 1. Although the molecular weights of **P1** and **P2** were not high (M_w 9.6 and 21 kDa, respectively), optical quality films could be cast from tetrachloroethane (TCE) for NLO studies.

The structure of polymers **P1** and **P2** were characterized by different spectroscopic techniques. The ^{1}H NMR spectra show several typical aliphatic peaks; **P1** has seven peaks around 1.39, 1.60, 1.67, 2.75, 2.95, and 3.32 ppm due to the chemical shifts of methyl and methylene protons connected to the amino group of the NLO chromophore and the alkyl spacer. The methyl group attached to the benzene ring appears as a singlet at 2.52 ppm. **P2** has four aliphatic protons at 1.23, 3.42, 3.62, and 4.37 ppm that correspond to methyl and methylene protons connected to the amino group of the NLO chromophore. ^{1}H NMR spectra of **P1** and **P2** show two aliphatic peaks at around 4.05 and 1.25 ppm which correspond to the electron acceptor *N*-ethyl protons attached to the NLO chromophore. In the aromatic region, both polymers show two peaks at 6.65 and 7.45 ppm corresponding to benzenoid protons of the NLO chromophore. The chemical shift of thiophene protons on the backbone appears at 7.1 ppm in both polymers. The methyne proton at the carbon bridge appears at around 8.60 ppm for both **P1** and **P2**.

In FTIR spectra, both polymers have characteristic strong absorption peaks at 1660 and 1653 cm^{-1}, attributed to the imide carbonyls in the electron-accepting *N*,*N*-diethylbarbituric acid group. However, **P2** exhibited an extra strong absorption peak at 1725 cm^{-1} which is characteristic of imide carbonyls in the polymer backbone.

The UV−vis spectra of these polymers showed an absorption maximum at 540 nm due to the NLO chromophore (Figure 1). After the molecular dipoles

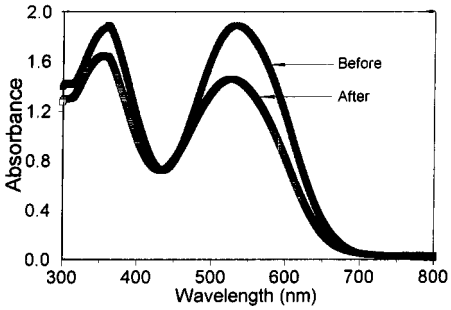


Figure 1. Uv/vis spectra of **P2** before and after electric poling.

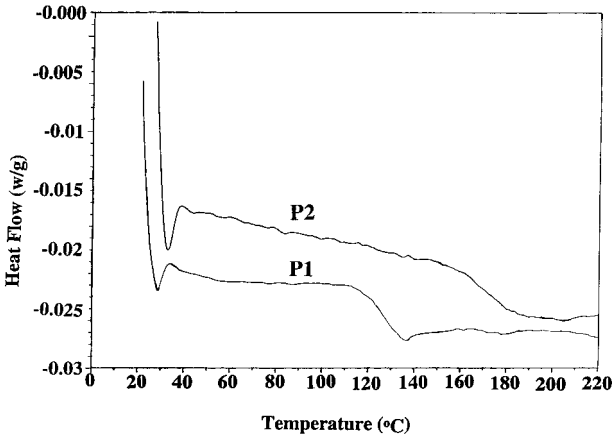


Figure 2. DSC Diagrams of polymers **P1** and **P2** with a heating rate of 10 °C/min under nitrogen atmosphere.

were aligned along the direction of the electric field by electric poling, the maximum absorbances were reduced. The poling efficiency is determined by using the order parameter ($\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after corona poling, respectively). The order parameter values for **P1** and **P2** were estimated to be 0.15 and 0.23, respectively. The poling was carried out by applying a voltage of 4 kV through a corona needle for 45 min at a temperature of 150 and 180 °C for **P1** and **P2**, respectively.

Thermal Properties. DSC traces of samples annealed at 120 °C for 2 h indicated that **P1** has a lower glass transition temperature (T_g) than **P2** (Figure 2). The difference in T_g between **P1** and **P2** is about 45 °C. This difference is due to the imide groups present in the **P2** backbone, which increase the T_g values, and the long spacer group between the NLO chromophore and the conjugated backbone in **P1,** which diminish the T_g values. The TGA traces (Figure 3) showed that these polymers have a decomposition temperature (T_d) at ca. 245 °C, which represents the decomposition of the NLO chromophore from the polymer backbone. However, the TGA trace of polymer **P2** showed a higher thermal stability. For example, **P1** loses 65% of its weight at 410 °C, while **P2** loses the same weight at 570 °C.

Nonlinear Optical Properties. The requirement for the second-order nonlinear optical process is that the material must be noncentrosymmetric, which can be easily achieved by corona poling at a temperature close to T_g. To gain insight into the poling process, we carried out in situ poling for both polymer samples. Figure 4 shows the SHG signal of **P2** as a function of temperature. As the voltage is turned on, an SHG signal can be observed, even at room temperature. By further heating, the SHG signal increases until it reaches close to T_g where it tends to decrease. The SHG signal is higher

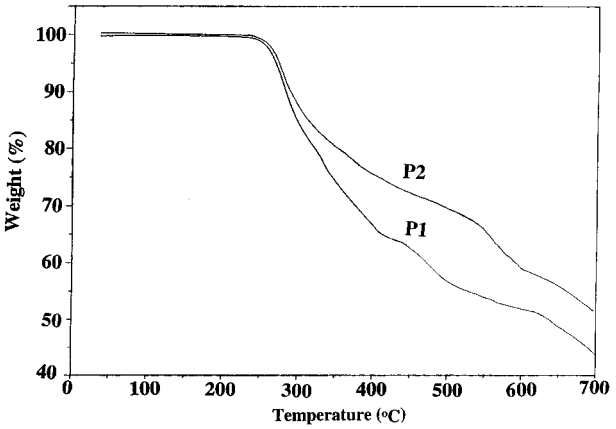


Figure 3. TGA traces of polymers **P1** and **P2** with a heating rate of 10 °C/min under nitrogen atmosphere.

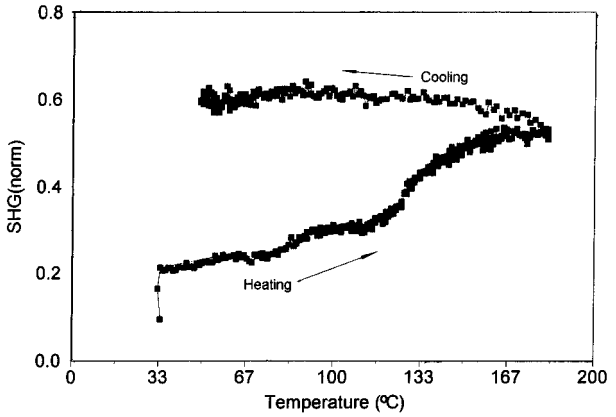


Figure 4. In situ poling dynamics of polymer **P2**.

Table 2. Physical Properties of Polymers

	chromophore (%)	T_g (°C)	T_d (°C)	Φ	r_{33} (pm/V)
P1	65.04	125	245	15	9
P2	50.85	170	245	23	35

during cooling stage, due to a decrease in thermal randomization. The films of **P1** cannot be effectively poled, and the SHG signal generated during the poling of the **P1** film was small. This is also reflected in the small r_{33} values. This result could be attributed to the high NLO chromophore loading density. The loading density for **P1** and **P2** is 65.04% and 50.85%, respectively (Table 2). As pointed out by Dalton et al., as the loading of the NLO chromophore increases, the average distance between chromophore dipoles decreases and the antiparallel chromophore−chromophore electrostatic dipole interaction becomes stronger. These strong interactions will cancel the nonlinear optical contributions of the chromophores; hence, the net alignment will decrease.[21]

The thermal relaxation process of dipole orientation is directly related to the glass transition temperature (T_g) of the polymer; a high T_g implies a higher orientational stability. To probe this stability, we monitored the temporal and thermal stability of the second harmonic generation signal for **P2**. At room temperature the SHG signal is stable and showed no decay. At 80 °C in air, after an initial decay to ca. 93% of the original signal, more than 82% of the SHG signal remained after 1500 h (Figure 5). A temperature-dependent SHG experiment was carried out in situ by monitoring the SHG signal for **P2** while heating at a rate of 2 °C /min.

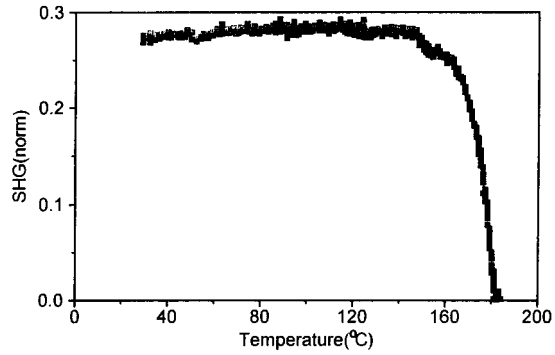


Figure 5. SHG signal of polymers **P2** as a function of temperature.

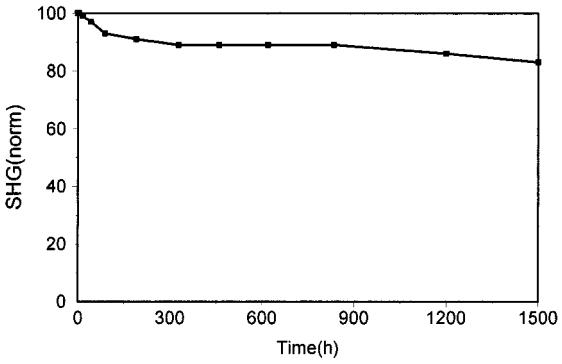


Figure 6. Temporal stability of the SHG signals of **P2** at 80 °C in the air.

Figure 6 shows that the SHG signal was stable until the temperature reached 150 °C. A fast decay of the SHG signal was observed when the temperature was close to the polymer's glass transition temperature (170 °C). It completely disappeared as the temperature went above T_g.

The electrooptic coefficients (r_{33}) were measured using a simple reflection technique at 1300 nm, which is beyond the absorption band of the NLO chromophore.[20] The r_{33} values for **P1** and **P2** are 9 and 35 pm/V, respectively. The low r_{33} value for **P1** is mainly due to the dipole−dipole interactions that oppose the poling field and make the net alignment difficult. It is also obvious that the chromophore density of **P2** is rather high. It may be possible to further enhance the r_{33} value by carefully adjusting the NLO chromophore density. Work along this line is in progress.

Conclusion

It was found that the Stille coupling reaction could be utilized to synthesize polymers bearing sensitive NLO chromophores. Careful design and synthesis of a dibromo monomer having imide groups led to the synthesis of a new functional NLO polyimide. The resulting polymer exhibits a large r_{33} value (35 pm/V at 1300 nm) and a good temporal stability at elevated temperatures (80 °C). This approach proves to be tolerable to some sensitive NLO chromophores.

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