Macromolecules **1992,** *25,* 5609–5612 **5609**

Synthesis and Characterization of a Thermally Curable Second-Order Nonlinear Optical Polymer

Luping Yu,* Waikin Chan, and Zhenan Bao

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

Received December 20, 1991; Revised Manuscript Received July 7, 1992

ABSTRACT: To stabilize the dipole alignments induced by an electric field in a second-order nonlinear optical (NLO) polymer, especially at elevated temperatures, we have synthesized a thermally cross-linkable, second-order nonlinear optical polymer containing ethynyl groups. The ethynyl groups in the polymer backbone can undergo thermal intramolecular reactions with amide groups to form heterocyclic structures and/or undergo intermolecular reactions with amide groups on other polymer chains to form cross-linkages. The thermal curing of the polymer can be effected during electric poling and therefore the device elements (planar waveguide, channelized waveguide) can be easily prepared by using this polymer. Second harmonic generation measurements indicated that the cured polymer indeed exhibits a high stability in the dipole orientation: no obvious decay at room temperature for more than 1000 h. Long-term stability of second harmonic coefficients was observed even at 90 °C, at least for 500 h.

Introduction

It will not be unrealistic to envision the practical applications of second-order nonlinear optical (NLO) polymers in the near future. However, one of the critical problems in the development of second order NLO polymers is to stabilize the dipole alignments induced by an electric field, especially at elevated temperatures.[1–26] The advantage of the second order NLO polymers is the ease of the fabrication of waveguides onto semiconductor integrated circuits to form hybrid structures.[1–6] Some of these processes involve high temperatures, which adds a requirement for second order NLO polymers to withstand a high-temperature environment at least during the fabrication processes. Most of the current materials suffer from relaxation of the dipole alignments even at room temperature, such as the case of polymer composites and polymers with covalently attached chromophores.[1–26] Therefore, much research effort is needed to overcome this problem before these materials can be used in real devices.

Recently, several works focused on this issue have been published, where (chemically or photochemically) cross-linking reactions have been utilized to stabilize the dipole orientation after electrical poling. Eich et al. first described the preparation of epoxy oligomers containing NLO chromophores, these oligomers can be further thermally treated to effect cross-linking.[19] Chen et al. developed a new type of photo-cross-linkable second order NLO polymers containing cinnamic groups as cross-linking sites, and, also, they introduced diacetylene units into the polymer backbone to perform both the photo-cross-linking and thermal cross-linking.[22–24] Tripathy et al. utilized similar cinnamic chemistry to prepare photo-cross-linkable polymer composites.[25] Wu et al. reported a thermally treated polyimide composite systems doped with NLO molecules.[26] In all these systems, certain degrees of stabilization of dipole alignment have been realized, which encourage us to further explore new systems with improved processibility, stability, and optical nonlinearity.

Curable aromatic polyamides have been prepared by using monomers containing ethynyl groups,[27,28] which has been proven a useful approach to enhance the processibility and mechanical properties of aromatic polyamides. This approach can also be adopted to prepare curable second order NLO polymers. Recently, we have synthesized thermally cross-linkable, second order NLO polymers containing ethynyl groups, as shown in Schemes I and II. The ethynyl groups in the polymer backbone can undergo thermal intramolecular reaction with amide groups to form heterocyclic structures or undergo intermolecular reaction with amide groups on other polymer chain to form cross-linkages. Since this is a true polymer containing cross-linkable moieties (not oligomers or composite systems), and it is soluble in many common organic solvents, the thermal curing can be effected during electric poling; therefore, the device elements (planar waveguide, channelized waveguide) can be prepared by using these materials. Second harmonic generation measurements indicated that the cured material indeed showed high stability in dipole orientation; long-term stability of the second harmonic coefficient has been observed. In this paper, we report the synthesis and characterization of this new polymer.

Experimental Section

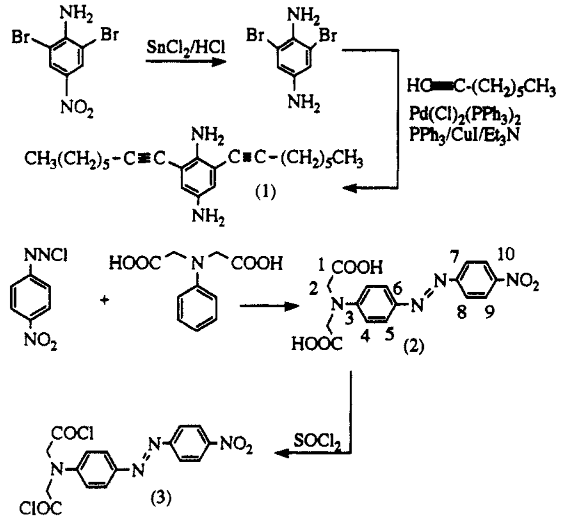
2,5-Dibromo-1,4-diaminobenzene. This compound is synthesized according to the following procedure, which is different from that of ref 27. Thus, 2,5-dibromo-4-nitroaniline (20 g) was added to a solution containing tin chloride (140 g) and hydrochloric acid (37%, 70 mL) and the resulting mixture was heated to reflux for 1 h. The solution was then cooled down to 0 °C and the white precipitate was collected. After it was dried in the air, the solid was then dissolved in a diluted hydrochloric acid (5%), hydrogen sulfide was bubbled through the solution, and the tin sulfide formed was removed by filtration. The product was separated by adding ammonia solution (30% NH_3) to the filtrate and crystallized from distilled water (yield 45%, mp 137 °C). ^{1}H NMR ($CDCl_3$) δ (ppm) 3.2 (s, 2 H, 4-NH_2), 4.1 (s, 2 H, 1-NH_2), 6.8 (s, 2 H, Ar H). Anal. Calcd for ($C_6H_6Br_2N_2$): C, 27.07; H, 2.26; N, 10.53. Found: C, 27.17; H, 2.25; N, 10.46.

Compound 1. This compound is prepared according to a known procedure.[27] By following the literature separation procedure, we always obtained a mixture. However, when a hexane/chloroform (80/20, v/v) mixture was used as eluent, pure monomer was obtained. ^{1}H NMR ($CDCl_3$) δ (ppm) 0.88 (t, J = 6.7 Hz, 6 H, CH_3), 1.27 (multiple, 8 H, CH_2CH_2C), 1.46 (multiple, 4 H, CH_2CCC), 1.54 (multiple, 4 H, $\equiv CCCH_2$), 2.41 (t, J = 6.8 Hz, 4 H, $\equiv CCH_2$), 3.8 (s, 4 H, NH_2), 6.6 (s, 2 H, Ar H); ^{13}C NMR δ (ppm) 13.9 (C_1), 19.5 (C_6), 22.4 (C_2), 28.5 (C_5), 28.7 (C_4), 31.2 (C_3), 76.9 (C_7), 95.5 (C_8), 109.1 (C_9), 119.5 (C_{10}), 136.8 (C_{11}), 142.0 (C_{12}). Anal. Calcd for ($C_{22}H_{32}N_2$): C, 81.48; H, 9.88; N, 8.05. Found: C, 81.21; H, 10.02; N, 8.45.

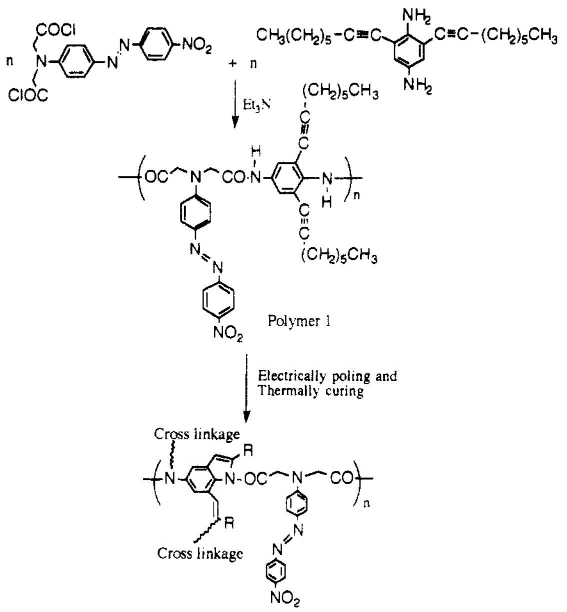
Compound 2. *p*-Nitroaniline (1.80 g, 0.017 mol) was dissolved in concentrated hydrochloric acid (10 mL) and the solution was

0024-9297/92/2225-5609$03.00/0

Scheme I
Synthesis of Monomers



Scheme II
Synthesis of Cross-Linkable Second-Order NLO Polymer



cooled to 0 °C in an ice bath. Sodium nitrite solution (1.17 g, in 5 mL of water) was added to the mixture while stirring. The resulting solution was then added to anilinediacetic acid (3.5 g, 0.017 mol) dissolved in concentrated hydrochloric acid (10 mL). The solution was stirred for 2 h in an ice bath, a saturated sodium acetate solution was added gradually to neutralize the solution. The precipitate was collected and washed with water. Recrystallization from acetic acid/water yield plate crystals (yield, 82% mp 170 °C, dec). ^{1}H NMR (DMSO-d_6) δ 3.34 (s, 2 H, COOH), 4.27 (s, CH_2), 6.74 (d, $J = 9.10$ Hz, 2 H, H_4), 7.85 (d, $J = 9.03$ Hz, 2 H, H_5), 7.95 (d, $J = 9.03$ Hz, 2 H, H_8), 8.37 (d, $J = 9.10$ Hz, 2 H, H_9); ^{13}C NMR (DMSO-d_6) δ (ppm) 58.0 (C_2), 110.2 (C_4), 120.3 (C_9), 120.5 (C_8), 120.7 (C_5), 140.3 (C_6), 140.7 (C_{10}), 150.1 (C_3), 150.6 (C_7), 170.3 (C_1). Anal. Calcd for ($C_{16}H_{14}N_4O_6$): C, 53.63; H, 3.91; N, 15.64. Found: C, 53.69; H, 3.96; N, 15.54.

Compound 3. The mixture of compound 2 (1.289 g, 3.600 mmol), thionyl chloride (20 mL), and benzene (5 mL) was heated to reflux until a clear solution was obtained. The thionyl chloride and benzene were removed by distillation and the residual thionyl chloride was pumped out. This compound was used directly in further polymerization. The structural information was obtained in the final analysis of the polymer.

Polymer 1. Compound 3 prepared above was dissolved in 1,2-dichloroethane (10 mL), to which were added compound 1 (1.166 g, 3.600 mmol) in 1,2-dichloroethane (5 mL) and triethylamine (1 mL). The resulting mixture was heated at 60 °C for 3 h and was then poured into methanol The precipitate was collected and washed with methanol. To further purify the polymer, the collected solid was then redissolved in chloroform and precipitated out from methanol (yield, 65%). ^{1}H NMR ($CDCl_3$) δ (ppm) 0.8 (s, 6 H, CH_3), 1.27 (s, 8 H, CH_2CH_2C), 1.46 (s, 4 H, CH_2CCC), 1.54 (shoulder, $=CCCH_2$), 2.41 (s, 4 H, $=CCH_2$), 4.5 (s, CONH?), 6.6–8.5 (br m, 10 H, Ar H). Anal. Calcd for $(C_{38}H_{42}N_6O_4{\cdot}HCl)_n$: C, 66.81; H, 6.30; N, 12.31. Found: C, 66.44; H, 6.03; N, 12.92.

Nonlinear Optical Measurements. To prepare thin films for the second harmonic generation measurements, the polymer was dissolved in chloroform. The solution was then filtered through a 0.2-μm filter and spin-cast onto transparent glass substrates with an ITO (indium tin oxide) conductive layer. The polymer films were dried either in a drybox or under vacuum for 2 days. The thickness of the film, varied from 0.5 to 3 μm, was measured with a Rudolph 43603-200E ellipsometer and a Dektak II profile. The dried film was poled by using a corona discharge apparatus. The poling conditions are as follows: temperature, 180–190 °C; high voltage, 12–14 kV at needle point; gap distance, ca. 1.5 cm; poling current <0.1 mA. After being thermally cured for 2 h, the polymer film was cooled down to room temperature in the presence of the electric field.

The second harmonic measurements were performed according to the procedure reported previously.[22-24] A Spectra-Physics DCR-11 Q-switched Nd:YAG laser with pulse width of <10 ns and a 10-Hz repetition rate was used as a fundamental source. The polymer sample was held at a 45° angle to the incident laser beam. A quartz crystal was used as a reference sample. The second harmonic coefficient, d_{33}, was determined according to the following equation:[29]

$$d_{33} = d^r_{11}\,[P_2/P^r_2]^{1/2}[F(0)_r/F(0)_p]^{1/2} \tag{1}$$

where P_2 and P^r_2 are the second harmonic powers of polymer film and quartz sample, respectively, and

$$F(0)_i = 32n^i_2/(n^i_1 + n^i_2)(n^i_1 + 1)^3(n^i_2 + 1)^3(n^i_1 - n^i_2)^2, \quad i = r, p \tag{2}$$

where n^i_1, n^i_2 are the indices of refraction of either polymer or quartz at fundamental and second harmonic frequency, respectively.

FTIR spectra were taken with a Perkin-Elmer FTIR spectrometer and thermal analyses were performed by using Perkin-Elmer DSC-7 and TGA-7 systems with a heating rate of 20 °C/min. NMR spectra were recorded on a GE, Omega, 500-MHz NMR spectrometer. Viscosity measurements were performed employing a Ubbelohde viscometer at 30 °C.

Results and Discussion

Synthesis and Characterization of Polymers. According to the literature,[26] we employed an acetylene coupling reaction catalyzed by a Pd salt to prepare monomer 1 and an azo coupling reaction to synthesize monomer 3 (see Scheme I). The reaction can be carried out easily, but the monomer separation was difficult by following the literature procedure; after many attempts, we always obtained a mixture. However, by using hexane/chloroform (80/20 v/v) as eluent in an alumina column, we were able to obtain pure monomers evidenced by ^{1}H and ^{13}C NMR and elemental analysis results. Polymerization was quite easily carried out in aprotic solvents such as dichloroethane, dioxane, etc. (see Scheme II).

The polymer obtained is a orange-red powder, soluble in common organic solvents, such as chloroform, THF, acetone, dioxane, DMF, etc. Viscosity measurements in N-methylpyrrolidone indicated an intrinsic viscosity of 0.19 dL/g; GPC measurement showed a weight-averaged molecular weight of 2000–10 000 against a polystyrene standard sample. The ^{1}H NMR spectrum of the polymer shows peak broadening, but the spectral feature is consistent with the polymer structure, and the proton integrations account for the number of protons in the

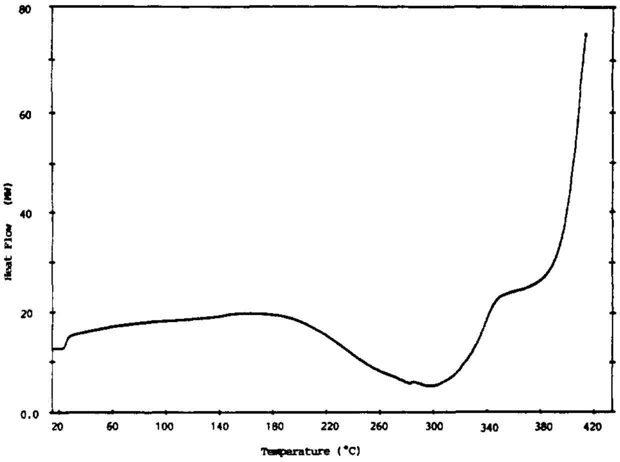


Figure 1. DSC diagram of the polymer.

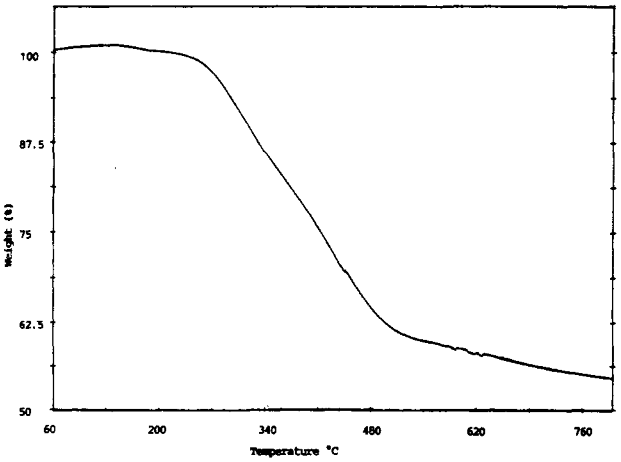


Figure 2. TGA diagram of the polymer.

polymer structure. The FTIR spectrum of the polymer shows the >C=O absorption around 1675 cm^{-1}, which is shifted to low frequency, compared to the >C=O band (1705 cm^{-1}) in the monomer, due to formation of amide bonds. Absorption due to C≡C appears at 2235 cm^{-1} and strong absorptions due to nitro groups appear at 1523 and 1341 cm^{-1}. These results support the structure of polymer 1 proposed in Scheme II. To ascertain that the chromophore survived during transfer of the functional group from the acetic acid moiety to acetyl chloride, we carried out the polymerization of compound 2 with compound 1 using 1,3-dicyclohexylcarbodiimide as catalyst. The polymer obtained has identical spectroscopic features with the polymer 1 reported here, which indicates that the chromophore in polymer 1 has not been destroyed during the transfer process of functional groups. Detailed results of this work will be reported separately.

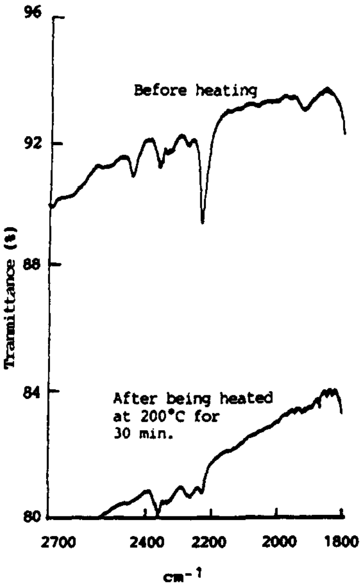


Figure 3. FTIR spectra of the polymer before and after thermal curing.

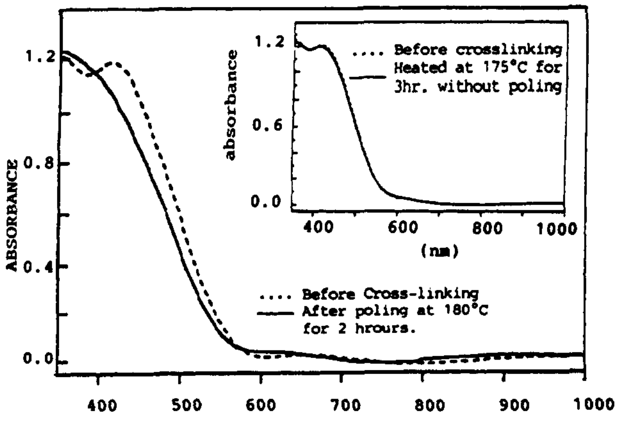


Figure 4. UV/vis spectra of the polymer; the conditions are indicated in the figure.

The interesting point is that the ethynyl groups in the polymer backbone can undergo a thermal intramolecular reaction with amide groups to form a heterocyclic structure or an intermolecular reaction with amide groups on the other polymer chains to form cross-linkages.[28,29] The DSC trace of the polymer shows no obvious glass transition; only a broad exothermic peak was observed (Figure 1). This broad peak actually involves two separated processes, i.e., thermal intra- or intermolecular reaction and decomposition. The thermal reaction starts at 180 °C and the decomposition starts at ca. 270 °C, which is supported by TGA studies (Figure 2). FTIR spectroscopic studies confirmed the expected reaction and cross-linking. After the polymer was thermally treated under vacuum for 40 min at 230 °C, the absorption of C≡C at ca. 2250 cm^{-1} decreased dramatically (see Figure 3). The thermally cured polymer films were insoluble in organic solvents.

Linear and Nonlinear Optical Properties. Since polymer 1 is soluble in common organic solvents, optic quality films can be easily prepared. The electrical poling and thermal curing can be effected simultaneously without the problems encountered with oligomers (like epoxy oligomer systems). This offers benefits for device fabrication.

The cured polymer film was uniform, rigid, and chemically resistant. The UV/vis/NIR spectra of both the cured and uncured polymers are shown in Figure 4; the maximum absorption due to the azo chromophore appears at about 420 nm. Thermal curing has little effect on the absorption structure (see the inset of Figure 4); however, the electrical poling does cause a shift of the absorption peak (about 50 nm). Obviously, this change is caused by the dipole alignment; effects such as dichromism and electrochromism contribute to this change.[13]

Second harmonic generation measurements were performed by using a Nd:YAG laser. Figure 5 shows the intensity pattern of a p-polarized second harmonic wave with a p-polarized incident wave. There is no Maker fringe structures, only a big hump because the film is too thin (0.5–2 μm), resulting in $\Delta\beta Ls/2 \sim 0$ ($\Delta\beta$ is the phase mismatching between the fundamental (ω) and the second harmonic wave (2ω), Ls is the sample thickness).[13] A

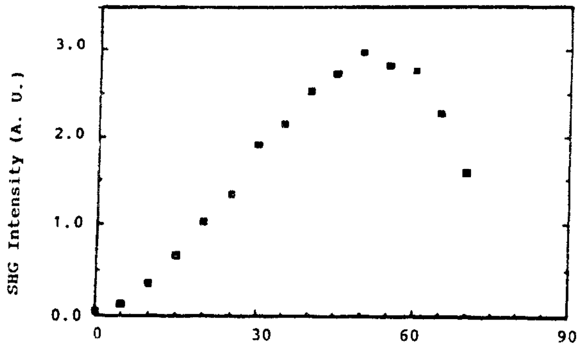


Figure 5. Maker fringe pattern of the p-polarized second harmonic wave with p-polarized incident wave; only one side is shown.

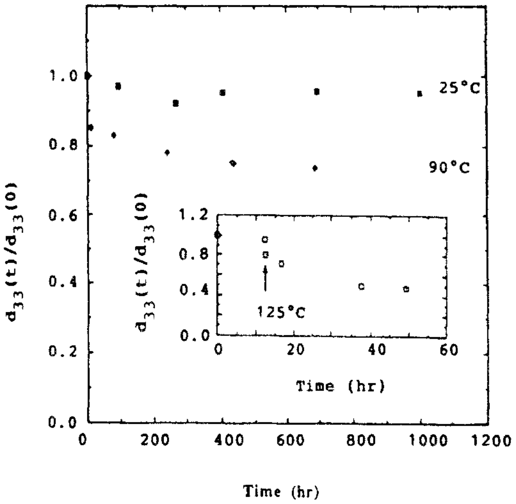


Figure 6. Temporal behaviors of the second harmonic coefficients at room temperature, 90 °C, and 125 °C (see insert).

resonance-enhanced d_{33} coefficient of about 20 pm/V at a fundamental wavelength of 1.064 μm was obtained by comparison with a standard quartz sample. The experimental error is about 20%, which mainly comes from the uncertainty of the reference quartz sample (ca. 10%) and the laser beam instability.

As we expected, the cured polymers indeed exhibit large and stable optical nonlinearity. No obvious decay in the d_{33} value was detected at room temperature after electrical poling for at least 1000 h (see Figure 6, the initial decay of 4% could be due to the effect of long alkyl chain in monomer A). A long-term stability was observed even at 90 °C after 30% initial decay after electrical poling (see Figure 6). When the stability was studied at 125 °C, 45% of the signal intensity remained after 50 h. Clearly the cross-linking indeed plays an important role in stabilizing the dipole orientation. These results show that our polymer is very promising for device fabrication involving semiconductor/polymer hybrid structures. However, decays of the second harmonic coefficient still exist at elevated temperature. Two factors are responsible for these decays: the first is related to the long alkyl chains on the ethynyl groups, which have large flexibility and facilitate relaxation of the dipole alignments; the second factor comes from inadequate cross-linking density due to bulky alkyl groups and chromophores. We should point out that this is just a demonstration of this versatile reaction scheme; more synthetic works to attach different NLO chromophore to polymer backbone and to use different cross-linkable monomers are in progress and will be reported later.

Conclusion

A second order nonlinear optical polymer containing ethynyl groups has been synthesized. This polymer was soluble in a common organic solvent and can be the thermally cured. The cross-linked and electrically poled polymer generated a very stable second harmonic signal at room temperature; a long-term stability of NLO activity was observed even at 90 °C.

References and Notes

(1) Skothelm, T. A., Eds. *Electroresponsive Molecular and Polymeric Systems*; Marcel Dekker: New York, Basel, 1988 and 1990; Vols. 1 and 2.
(2) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987; Vols. 1 and 2.
(3) William, D. J., Ed. *Nonlinear Optical Properties of Organic and Polymeric Materials*, ACS Symposium Series 233; American Chemical Society: Washington, DC, 1983.
(4) Heeger, A. J.; Orenstein, J.; Ulrich, D. R. Nonlinear Optical Properties of Polymers. *Mater. Res. Soc. Symp. Proc.* **1988**, *109*, 1988.
(5) Khanarian, G., Ed. Molecular and Polymeric Optoelectronic Materials: Fundamentals and Applications. *SPIE Proc.* **1986**, *682*.
(6) Boyd, G. T. *J. Opt. Soc. Am.* **1989**, *B6*, 685.
(7) (a) Ye, C.; Minami, N.; Marks, T. J.; Yang, J.; Wong, G. K. *Macromolecules* **1988**, *21*, 2899. (b) Ye, C.; Marks, T. J. *Macromolecules* **1987**, *20*, 2322.
(8) Yu, L. P.; Chan, W. K.; Dikshit, S.; Shi, Y. Q.; Steier, W. H., submitted to *Appl. Phys. Lett.* **1992**, *60*, 1655.
(9) Hill, J. R.; Panties, P.; Abbasi, F.; Hodge, P. *J. Appl. Phys.* **1988**, *64*, 2749.
(10) Singer, K. D.; Kuzyk, M. G.; Holland, W. R.; Sohn, J. E.; Lalama, S. J.; Comizzoli, R. B.; Katz, H. E.; Schilling, M. L. *Appl. Phys. Lett.* **1988**, *53*, 1800.
(11) Meredith, G. R.; VanDusen, J. G.; Williams, D. J. *Macromolecules* **1982**, *15*, 1385.
(12) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1988**, *21*, 526.
(13) Mortazavi, M. A.; Knoesen, A.; Kowel, S. T.; Higgins, B. G.; Dienes, A. *J. Opt. Soc. Am.* **1989**, *B6*, 733.
(14) Singer, K. D.; Sohn, J. E.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, C. D. *J. Opt. Soc. Am.* **1989**, *B6*, 1339.
(15) Thackara, J. I.; Lipscomb, G. F.; Stiller, M. A.; Ticknor, A. J.; Lytel, R. *Appl. Phys. Lett.* **1988**, *52*, 1031.
(16) Girton, D. G.; Kwiatkowski, S. L.; Lipscomb, G. F.; Lytel, R. S. *Appl. Phys. Lett.* **1991**, *58*, 1730.
(17) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.
(18) Rikken, G. L. J. A.; Seppen, C. J. E.; Nijhuis, S.; Meijer, E. W. *Appl. Phys. Lett.* **1990**, *58*, 435.
(19) Eich, M.; Reck, B.; Yoon, D. Y.; Willson, C. G.; Bjorklund, G. C. *J. Appl. Phys.* **1989**, *66*, 3241.
(20) Singer, K. D.; Kuzyk, M. G.; Sohn, J. E. *J. Opt. Soc. Am.* **1987**, *B4*, 968.
(21) Marues, M. B.; Assanto, G.; Stegeman, G. I.; Mohlmann, G. R.; Erdhuisen, E. W. P.; Horsthuis, W. H. G. *Appl. Phys. Lett.* **1991**, *58*, 2613.
(22) Chen, M.; Yu, L. P., Dalton, L. R.; Shi, Y. Q.; Steier, W. H. *SPIE Proc.* 1991, 1409–26.
(23) Chen, M.; Yu, L. P.; Dalton, L. R.; Shi, Y. Q.; Steier, W. H. *Macromolecules* **1991**, *24*, 5421.
(24) Shi, Y. Q.; Steier, W. H.; Yu, L. P.; Chen, M.; Dalton, L. R. *Appl. Phys. Lett.* **1991**, *58*, 1131.
(25) Mandal, B. K.; Chen, Y. M.; Lee, J. Y.; Kumar, J.; Tripathy, S. *Appl. Phys. Lett.* **1991**, *58*, 2459.
(26) Wu, J. W.; Valley, J. F.; Ermer, S.; Binkley, E. S.; Kenney, J. T.; Lipscomb, G. F.; Lytel, R. *Appl. Phys. Lett.* **1991**, *58*, 225.
(27) Muller, W. T.; Ringsdorf, H. *Macromolecules* **1990**, *23*, 2825.
(28) Evers, R. C.; Moore, G. J. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 3213.
(29) Jerphagnon, J.; Kurtz, S. K. *J. Appl. Phys.* **1970**, *41*, 1667.

Registry No. (1)(3) (copolymer), 143172-44-5; (1)(3) (SRU), 143369-91-9; **2**, 143172-43-4; **3**, 143172-42-3; 2,5-dibromo-4-nitroaniline, 25462-68-4; 2,5-dibromo-1,4-diaminobenzene, 29213-03-4; *p*-nitroaniline, 100-01-6; anilinediacetic acid, 1137-73-1.