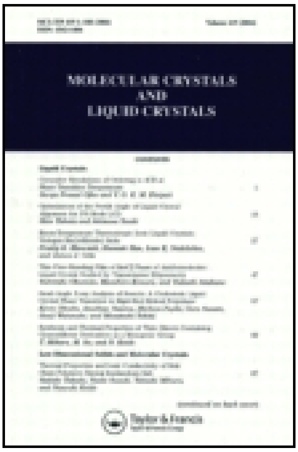

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Novel Polydiacetylenes with Chromophoric Substituents: Materials for Second and Third Order Nonlinear Optics

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NOVEL POLYDIACETYLENES WITH CHROMOPHORIC SUBSTITUENTS : MATERIALS FOR SECOND AND THIRD ORDER NONLINEAR OPTICS.

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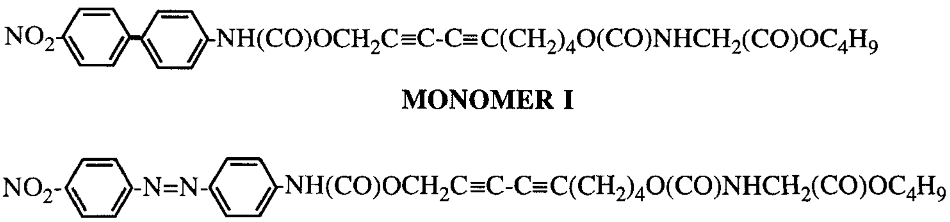
Abstract The objective of this investigation was to develop stable nonlinear optical (NLO) materials which possess both second and third order NLO properties. These materials were envisioned as having a polydiacetylene (PDA) backbone with a second order active NLO chromophoric substituent. The choice of a PDA backbone in this investigation was twofold. In terms of third order NLO properties, the extensive π-conjugation of the PDA backbone leads to large ultrafast third order effects. In terms of second order NLO properties, the high thermal stability and rigidity of the PDA matrix in a perfect polymeric single crystal is expected to prevent the randomization of the NLO chromophores in the noncentrosymmetric environment. This paper focuses on the synthesis, FT-Raman structural analysis, and NLO properties of the unsymmetrical diacetylene monomers, ((9-Butoxy carbonyl) methyl urethanyl)-1-(4-urethanyl-4'-nitrobiphenyl)-nona-2,4-diyne, and ((9-Butoxy carbonyl) methyl urethanyl)-1-(4-urethanyl-4'-nitroazobenzene)-nona-2,4-diyne.

INTRODUCTION

There is significant current interest in polydiacetylenes (PDAs) especially as NLO materials.[1,2] PDAs are formed through a topochemical 1,4-addition of the corresponding diacetylene monomers.[3] A careful choice of high entropy side groups in the diacetylene monomer can enhance the solubility of the PDAs, which are normally insoluble in common organic solvents. An example is the poly (n-BCMU) series of diacetylenes.[4]

The extensive π-conjugation of the PDA backbone leads to large and ultrafast third order NLO effects[5] ($\chi^{(3)} \sim 10^{-9}$-10^{-10} esu). The substitution of a second order NLO moiety consisting of a donor group, a π-conjugated bridge, and an acceptor group as the side group on the PDA backbone could lead to a polymeric material with significant second and third order NLO properties. Further, enhancement of the third order properties through cascade effects may be possible. The electroactive sidegroups may be used to modify and modulate the backbone electronic structure as well.

This investigation is centered around two unsymmetrical diacetylene monomers in which each contained a highly flexible urethanyl side group ($R_1' = R_2' = (CH_2)_4O(CO)NHCH_2(CO)OC_4H_9$) and a chromophoric substituent. The chromophoric substituents chosen were: $R_1 = -CH_2O(CO)NH(C_6H_4)_2NO_2$ (**I**) and $R_2 = -CH_2O(CO)NH(C_6H_4)N{=}N(C_6H_4)NO_2$ (**II**) (Figure 1). The high entropy flexible urethanyl side group was chosen to satisfy the monomer packing requirements for polymerization and enhance the solubility of the PDAs. This paper will focus on the synthesis and polymerization of the diacetylene monomers and some NLO properties of the corresponding polymers.



MONOMER I

MONOMER II

FIGURE 1 Chemical Structures of the diacetylene monomers.

EXPERIMENTAL

Chemicals

The trichloromethylchloroformate was obtained from Lancaster Synthesis and was used as received. All other chemicals were obtained from Aldrich Chemical and used as received.

Synthesis

The details of the three step synthesis of the ((9-Butoxy Carbonyl) methyl urethanyl) nona-2,4-diyn-1-ol (BNDO) and the synthesis of the 4-Amino-4'-Nitrobiphenyl dye have been reported elsewhere.[6]

Synthesis of 4-isocyanato-4'-nitrobiphenyl

To a 50mL 3-necked round bottomed flask equipped with a reflux condenser fitted with a calcium chloride drying tube, a thermometer, and a magnetic stirring bar was added 25 mL of anhydrous dioxane, 4-Amino-4'-nitrobiphenyl (.50g/.0023m), and trichloromethylchloroformate (.56mL/.0046m). The mixture is stirred and heated at 55-60°C. The yellow solid formed upon addition of the trichloromethylchloroformate dissolves after approximately 30 minutes. The reaction is monitored by TLC and the heating discontinued after 10 hours. The yield of yellowish orange 4-isocyanato-4'-nitrobiphenyl was .40g. Yield: 80% mp 99-100°C

IR(KBr): 2267cm^{-1} (N=C=O); 1759cm^{-1} (C=O); 1595cm^{-1} (Ar. Ring); 1510cm^{-1} (υ_{assym} $(N=O)_2$); 1343 cm^{-1}(υ_{sym} $(N=O)_2$)

Synthesis of 4-isocyanato-4'-nitroazobenzene

The reaction conditions are the same as those above using 4-Amino-4'-nitroazobenzene (Disperse Orange 3, 1.0g/.0041m) and trichloromethylchloroformate (1.0mL/.0082m). The yield of red product was .84g. Yield: 76% mp 109-110°C

IR(KBr): 2259cm^{-1} (N=C=O); 1763cm^{-1} (C=O); 1602cm^{-1} (Ar. Ring); 1520cm^{-1} (υ_{assym} $(N=O)_2$); 1343cm^{-1} (υ_{sym} $(N=O)_2$)

Synthesis of Diacetylene Monomer I

To a solution of 4-isocyanato-4'-nitrobiphenyl (.34g/.0014m) and BNDO (.60g/.0019m) in 50 mL of dry THF, 3-5 drops of dibutyltin dilaurate and 3-5 drops of triethylamine were added. The mixture was stirred for 24 hours at room temperature and monitored by TLC. The solvent was removed under reduced pressure and the crude diacetylene monomer isolated. The crude product was recrystallized from methylene chloride to give yellowish orange crystals. The yield of monomer I was .66g. Yield: 86%

IR(KBr): 3319cm^{-1} (NH); 2269cm^{-1} (w, C≡C); 1693cm^{-1} (C=O of ester); 1657cm^{-1} (C=O of urethane); 1540cm^{-1} (υ_{assym} $(N=O)_2$); 1344cm^{-1} (υ_{sym} $(N=O)_2$). ^{1}H NMR (DMSO-d_6): δ = 1.18 (m, 9H, C_4H_9); 2.45 (d, 2H, CH_2); 3.05 (m, 8H, $(CH_2)_4$); 4.14 (s, 2H, CH_2); 4.91 (s, 1H, NH); 7.64 (s, 1H, NH); 7.91 (d, 4H, ArH); 8.27 (d, 4H, ArH).

Synthesis of Diacetylene Monomer II

The reaction conditions are the same as above using 4-isocyanato-4'-nitroazobenzene (.80g/.0030m) and BNDO (1.0g/.0032m). The crude product was recrystallized from acetonitrile to give red crystals. The yield of monomer II was 1.4g. Yield: 82%

IR(KBr): 3291cm^{-1} (NH); 2257 (w, C≡C); 1708cm^{-1} (C=O of ester); 1656cm^{-1} (C=O of urethane); 1521cm^{-1} (υ_{assym} (N=O)$_2$); 1343cm^{-1} (υ_{sym} (N=O)$_2$). ^{1}H NMR (DMSO-d$_6$): δ = 1.20 (m, 9H, C_4H_9); 2.50 (d, 2H, CH_2); 3.00 (m, 8H, $(CH_2)_4$); 4.15 (s, 2H, CH_2); 4.90 (s, 1H, NH); 7.75 (s, 1H, NH); 8.00 (d, 4H, ArH); 8.45 (d, 4H, ArH).

NLO MEASUREMENTS

The second order NLO properties of the monomer I and monomer II and their corresponding polymers were measured in the powdered state versus urea using an experimental set up discussed previously.[7]

RAMAN MEASUREMENTS

The Raman spectra were recorded by a Perkin-Elmer 1760X FTIR spectrophotometer equipped with a FT-Raman accessory in a 180 degree optical collection geometry. The excitation was achieved at 1.064 mm wavelength and 100 mW of laser power with a cw Nd:YAG laser. The scattered radiation from the sample is reflected into the FTIR spectrometer and is detected by a liquid nitrogen cooled InGaAs detector. A wavenumber resolution of 4cm^{-1} was set for all the measurements. A scan speed of 0.1 cm/s was used, and a total accumulation of 32 scans was performed for all samples.

RESULTS AND DISCUSSION

Monomer I exhibited conversion from a yellowish orange crystal to a red polymer upon treatment either with UV irradiation at 254 nm or thermal annealing at 100 °C for a period of 24 hours. Monomer II turned from dark orange to a dark red polymer upon polymerization. Monomer free samples of the PDAs formed from monomers I and II were obtained by extraction of the unreacted monomer from the partially polymerized samples with methylene chloride. The NLO measurements were carried out on powder samples as described earlier and resulted in effective d coefficients which are respectively 7 times and 20 times smaller relative to powdered urea at 1.064 μm for PDAs I and II (Table I).

The FT-Raman spectra of polycrystalline samples of Monomer I and the corresponding monomer free polymer are shown in figure 2. Monomer I shows vibrational bands at 2261cm^{-1} ($\nu_{C\equiv C}$) and 1592cm^{-1} ($\nu_{C=C}$). The monomer free polymer showed two peaks at 2102cm^{-1} and 1481cm^{-1} from the C≡C stretching and the C=C stretching of the polymer backbone. The FT-Raman spectra of polycrystalline samples of Monomer II and the corresponding monomer free polymer are shown in figure 3. Monomer II shows vibrational bands at 2261cm^{-1} ($\nu_{C\equiv C}$) and 1588cm^{-1} ($\nu_{C=C}$). The monomer free polymer showed two peaks at 2099cm^{-1} from C≡C stretching and 1481cm^{-1} from C=C stretching.

TABLE I. deff of diacetylene monomers I and II and corresponding partial polymers.

Monomer I	Partial Polymer I	Monomer II	Partial Polymer II
36	7.0	16	20

$$\mathrm{deff} = (I^{2\omega}_{\mathrm{Urea}} \;/\; I^{2\omega}_{\mathrm{Sample}})^{0.5}$$

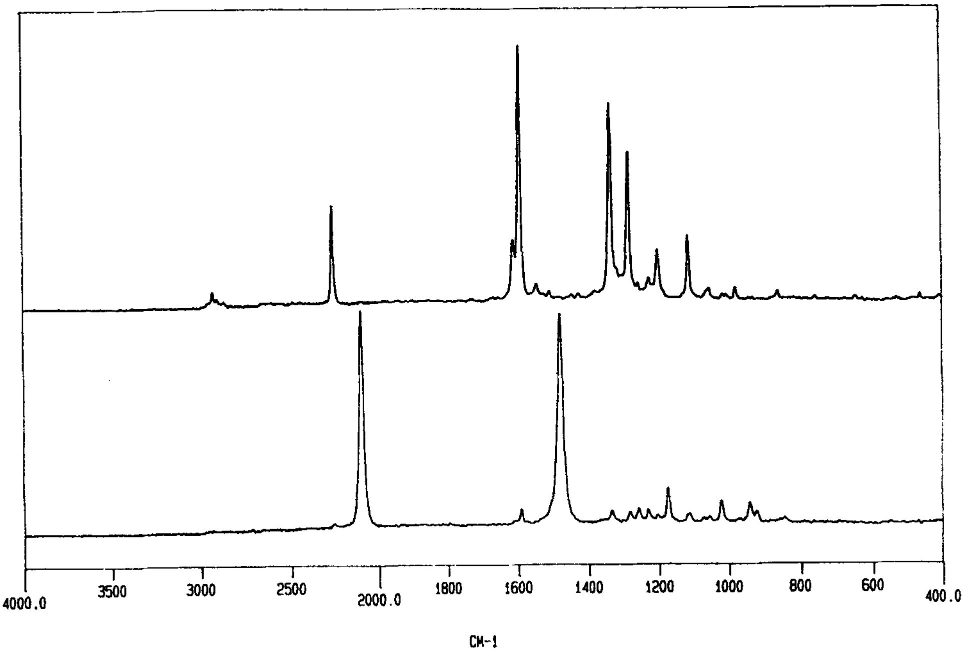


FIGURE 2 FT-Raman Spectra of Monomer I (top) and monomer free polymer (bottom).

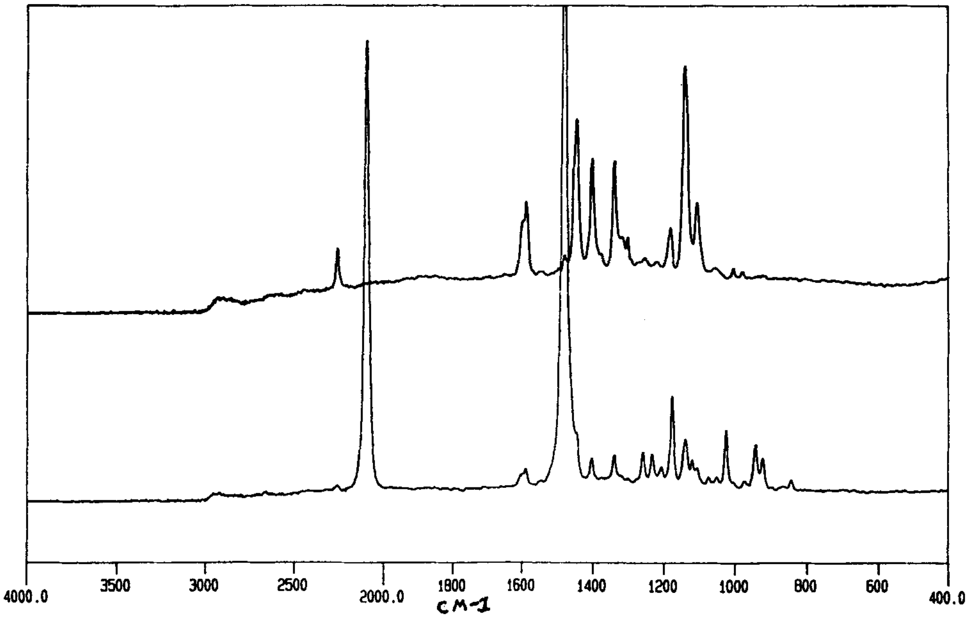


FIGURE 3 FT-Raman spectra of Monomer II (top) and monomer free polymer (bottom)

CONCLUSIONS

Two novel PDAs containing second order NLO active chromophoric side groups and exhibiting second order NLO properties have been synthesized and characterized. Powdered samples of PDAs I and II exhibit effective d coefficients that are 7 and 20 times smaller relative to powdered urea at 1.064 μm.

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