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Novel Polydiacetylenes as Materials for Second and Third Order Nonlinear Optics.

by

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13. ABSTRACT *(Maximum 200 Words)*

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 consisting of a donor group, a p-conjugated bridge, and an acceptor group. The choice of a PDA backbone in this investigation was twofold. In terms of third order NLO properties, the extensive p-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 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. The high entropy flexible urethanyl side group was chosen to satisfy the monomer packing requirements for polymerization and enhance the solubility of the PDAs.

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NOVEL POLYDIACETYLENES AS 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 consisting of a donor group, a π-conjugated bridge, and an acceptor group. 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 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. The high entropy flexible urethanyl side group was chosen to satisfy the monomer packing requirements for polymerization and enhance the solubility of the PDAs.

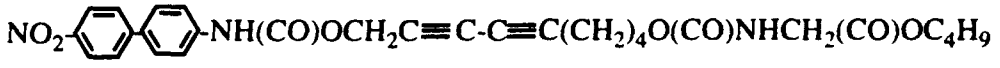
INTRODUCTION

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] ($\chi^{(3)}$~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 both 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**) (Fig. 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 the NLO properties of the corresponding polymers.



MONOMER I

MONOMER 2

Figure 1. Chemical Structure of the Diacetylene Monomers

EXPERIMENTAL

Chemicals

Butyl isocyanatoacetate was obtained from Eastman Kodak Company, 4,4'-dinitrobiphenyl was obtained from TCI America Organic Chemicals, and trichloromethylchlorofromate was obtained from Lancaster Synthesis. All of the aforementioned chemicals were used as received. All other chemicals were obtained from Aldrich Chemical and used as received.

Synthesis of 6-Bromo-5-Hexyn-1-ol

Bromine (0.1M) was added dropwise to a $NaOH/H_20$ solution (0.02M/100ml) under stirring at 0-5 °C. A pale yellowish solution of NaOBr was observed to form immediately. 5-Hexyn-1-ol (0.01M) was added to 25mL of 1,4 Dioxane to increase the solubility of the compound. The NaOBr solution was added dropwise to the above mixture

over 30 minutes at 5-10 °C under nitrogen and vigorously stirred for 30 minutes. This mixture was extracted with ethyl ether, dried with $MgSO_4$, and a pale yellow liquid was obtained by removing the solvent. Yield: 55%

IR(KBr): 3338cm^{-1} (OH), 2217cm^{-1} (C≡C)

Synthesis of ((6-Butoxy carbonyl) methyl urethanyl)-1-bromo-1-hexyne

To a solution of butyl isocyanatoacetate (0.055M) and 6-Bromo-5-Hexyn-1-ol (0.05M) in 50mL of dry THF, 3-5 drops of dibutyltin dilaurate and 3-5 drops of triethylamine were added. The mixture was stirred for 3 hours at room temperature. A brown liquid is obtained after removal of the solvent. Yield: 90 %

IR(KBr): 3305cm^{-1} (NH), 1690cm^{-1} (C=O)

Synthesis of ((9-Butoxy carbonyl) methyl urethanyl) nona-2,4-diyn-1-ol (BNDO)

BNDO was prepared via the Cadiot-Chodkiewicz coupling [6] of ((6-Butoxy carbonyl) methyl urethanyl)-1-bromo-1-hexyne and propargyl alcohol. A catalytic solution of CuCl, 70% aqueous ethylamine (20 mL), NH_2OH•HCl in H_2O (2g/20ml), and 100 mL of methanol was prepared in a 3-necked round bottomed flask. The reaction was carried out in a nitrogen atmosphere. The propargyl alcohol (0.075M) was added to the catalytic solution in one portion with the formation of a yellow solution. ((6-Butoxy carbonyl) methyl urethanyl)-1-bromo-1-hexyne(0.05M) in 20mL of methanol was added dropwise over a period of 2 hours at a temperature of 30-35 °C. The reaction was continued overnight. After the reaction is completed, a large portion of the methanol was removed and the mixture was poured into ice cold water under stirring. The white solid was filtered, dried, and recrystallized from benzene.Yield: 60%

IR(KBr): 3321cm^{-1}, 3285cm^{-1} (OH and NH), 2256cm^{-1} (C≡C), 1693cm^{-1}, 1657cm^{-1} (C=O)

Synthesis of 4-Amino-4'-nitrobiphenyl

The synthesis was based on the method of Sherwood et al [7] with some modifications: 4,4'-Dinitrobiphenyl (5.0g/.020m) was dissolved in a minimum amount of boiling ethanol. Powdered sulfur (0.9g/.028m) was dissolved in a warm aqueous sodium sulfide nonahydrate solution (1.25M, 7.2g Na_2S • $9H_2O$ in 24 mL of distilled water). The polysulfide solution was added dropwise to the alcoholic solution of 4,4'-Dinitrobiphenyl over a 20 minute period. After refluxing the reaction mixture for 20 minutes, the mixture was evaporated to dryness on a steam bath with a nitrogen purge. The resulting residue was boiled in 100 mL of distilled water to dissolve inorganic impurities. The mixture was allowed to cool and the crude product collected by gravity filtration. The filtrate containing the inorganic salts was discarded. The crude product was extracted with boiling water and

subsequently with boiling, aqueous 20% Hydrochloric acid (16 mL of concd Hydrochloric acid in 100 mL of water). To remove any remaining product, the residue was extracted with boiling, concd Hydrochloric acid. The filtrate was allowed to cool, gravity filtered, and the extracts rendered basic with an aqueous ammonia solution. The orange product was collected by suction filtration and washed with hot water. The crude product was recrystallized from a hot, saturated methylene chloride solution to give bright orange crystals. The yield of 4-Amino-4'-nitrobiphenyl was 2.0g Yield: 48%.

IR(KBr): 3490cm^{-1}, 3385cm^{-1} (N-H stretch); 1629cm^{-1} (N-H Bend); 1496cm^{-1} (υ_{assym} (N=O)$_2$); 1332cm^{-1} (υ_{sym} (N=O)$_2$); 826cm^{-1} (C-N stretch); ^{1}H NMR(DMSO-d_6): d 5.64 (s, 2H), 6.72 (d, 2H), 7.56 (d, 2H), 7.80 (d, 2H), 8.24 (d, 2H); UV-Vis(Methanol): 247nm, 371nm (λ_{max}), 500nm (λ_{cutoff}).

Synthesis of 4-isocyanato-4'-nitrobiophenyl

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%

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%

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} $(N=O)_2$)

Synthesis of Diacetylene Monomer II

The reaction conditions are the same as above using 4-isocyanato-4'-nitroazobennzene (.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} $(N=O)_2$)

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 [8].

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 dark red polymer upon polymerization. The NLO measurements were carried out 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.

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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