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Novel Unsymmetrical Polydiacetylenes as Materials for Second- and Third-Order Nonlinear Optics

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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 2-fold. 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 are expected to prevent the randomization of the NLO chromophores in the noncentrosymmetric environment. This paper focuses on the synthesis, structural analysis, and NLO properties of the unsymmetrical diacetylene monomers 9-((butoxycarbonyl)methylurethanyl)-1-(4-urethanyl-4′-nitrobiphenyl)nona-2,4-diyne and 9-((butoxycarbonyl)methylurethanyl)-1-(4-urethanyl-4′-nitroazobenzene)nona-2,4-diyne.

Introduction

There is significant current interest in polydiacetylenes (PDAs) as nonlinear optical (NLO) materials due to the extensive π-conjugation along their backbones.[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 in which flexible urethanyl side groups incorporating a number of methylene spacers produces a PDA which is soluble in common organic solvents.[4]

The extensive π-conjugation of the PDA backbone leads to large and ultrafast third-order NLO effects ($\chi^{(3)} \sim 10^{-9}-10^{-10}$ esu).[5] 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 large second- and third-order NLO properties. Further, enhancement in the third-order properties through cascade effects may be possible. The electroactive side groups 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. The chromophores utilize biphenyl and azobenzene π-bridges with urethanyl and nitro functionalities as the donor and acceptor groups, respectively. This paper will focus on the synthesis and polymerization of the diacetylene monomers and the NLO properties of the corresponding polymers.

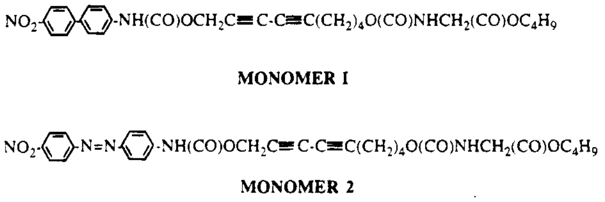

Figure 1. Chemical structure of the diacetylene monomers.

Experimental Methodology I. The synthesis of 9-((butoxycarbonyl)methylurethanyl)-1-(4-urethanyl-4′-nitrobiphenyl)nona-2,4-diyne was carried out via Scheme 1.

Monomer I Preparation. *Chemicals.* Butyl isocyanatoacetate was obtained from Eastman Kodak Co., 4,4′-dinitrobiphenyl was obtained from TCI America Organic Chemicals, and trichloromethyl chloroformate was obtained from Lancaster Synthesis. All of the above-mentioned 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 (0.1 M) was added dropwise to a NaOH/H_2O solution (0.02 M/100 mL) under stirring at 0–5 °C. A pale yellowish solution of NaOBr was observed to form immediately.

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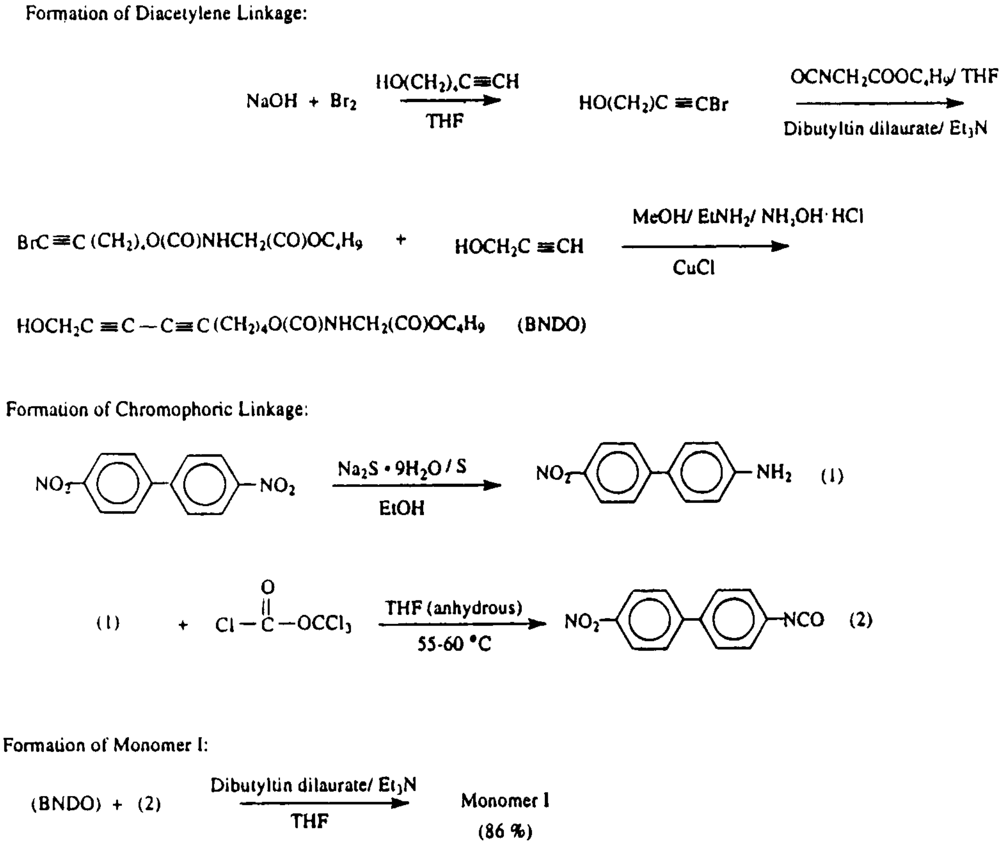
Scheme 1



5-Hexyn-1-ol (0.01 M) was added to 25 mL of 1,4-dioxane to increase the solubility of the compound. The NaOBr solution was added dropwise to the above mixture over 30 min at 5–10 °C under nitrogen and vigorously stirred for 30 min. This mixture was extracted with ethyl ether and dried with $MgSO_4$, and a pale yellow liquid was obtained by removing the solvent; yield 55%. IR (KBr) 3338 (OH), 2217 cm^{-1} (C≡C).

Synthesis of 6-((Butoxycarbonyl)methylurethanyl)-1-bromo-1-hexyne. To a solution of butyl isocyanatoacetate (0.055 M) and 6-bromo-5-hexyn-1-ol (0.05 M) 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 3 h at room temperature. A brown liquid is obtained after removal of the solvent; yield 90%. IR (KBr) 3305 (NH), 1690 cm^{-1} (C=O).

Synthesis of 9-((Butoxycarbonyl)methylurethanyl)-nona-2,4-diyn-1-ol (BNDO). BNDO was prepared via the Cadiot–Chodkiewicz coupling of 6-((butoxycarbonyl)methylurethanyl)-1-bromo-1-hexyne and propargyl alcohol.[6] A catalytic solution of CuCl, 70% aqueous ethylamine (20 mL), $NH_2OH{\cdot}HCl$ in H_2O (2 g/20 mL), and 100 mL of methanol was prepared in a three-necked round-bottomed flask. The reaction was carried out in a nitrogen atmosphere. The propargyl alcohol (0.075 M) was added to the catalytic solution in one portion with the formation of a yellow solution. 6-((Butoxycarbonyl)methylurethanyl)-1-bromo-1-hexyne (0.05 M) in 20 mL of methanol was added dropwise over 2 h at 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) 3321, 3285, (OH and NH), 2256 (C≡C), 1693, 1657 cm^{-1} (C=O).

Synthesis of 4-Amino-4′-nitrobiphenyl. The synthesis was based on the method of Sherwood et al. with some modifications: 4,4′-Dinitrobiphenyl (5.0 g/0.020 mol) was dissolved in a minimum amount of boiling ethanol.[7] Powdered sulfur (0.9 g/0.028 mol) was dissolved in a warm aqueous sodium sulfide nonahydrate solution (1.25 M, 7.2 g of $Na_2S{\cdot}9H_2O$ in 24 mL of distilled water). The polysulfide solution was added dropwise to the alcoholic solution of 4,4′-Dinitrobiphenyl over 20 min. After the reaction mixture was refluxed for 20 min, 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 concentrated hydrochloric acid in 100 mL of water). To remove any remaining product, the residue was extracted with boiling, concentrated hydrochloric acid. The filtrate was allowed to cool and gravity filtered, and the extracts were 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

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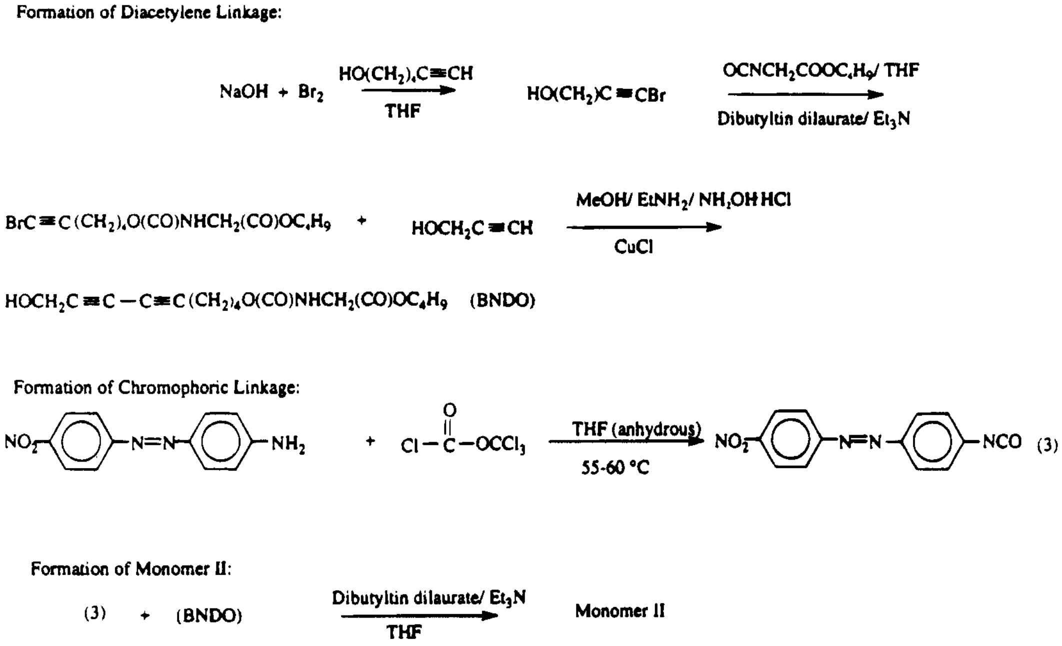
Scheme 2



orange crystals. The yield of 4-amino-4′-nitrobiphenyl was 2.0 g; yield 48%; mp 203–204 °C. IR (KBr) 3490, 3385 (N–H stretch), 1629 (N–H bend), 1496 (ν_{asym}(N=O)$_2$), 1332 (ν_{sym}(N=O)$_2$), 826 cm^{-1} (C–N stretch); ^{1}H NMR (DMSO-d_6) δ = 5.64 (s, 2H), 6.72 (d, 2H), 7.56 (d, 2H), 7.80 (d, 2H), 8.24 (d, 2H); UV–vis(methanol) 247, 371 (λ_{max}), 500 nm (λ_{cutoff}).

Synthesis of 4-Isocyanato-4′-nitrobiphenyl. To a 50 mL three-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 (0.50 g/0.0023 mol), and trichloromethyl chloroformate (0.56 mL/0.0046 mol). The mixture was stirred and heated at 55–60 °C. The yellow solid formed upon addition of the trichloromethyl chloroformate dissolves after approximately 30 min. The reaction is monitored by TLC, and the heating discontinued after 10 h. The yield of yellowish orange 4-isocyanato-4′-nitrobiphenyl was 0.40 g; yield 80%; mp 99–100 °C. IR (KBr) 2267 (N=C=O), 1759 (C=O), 1595 (Ar ring), 1510 (ν_{asym}(N=O)$_2$), 1343 cm^{-1} (ν_{sym}(N=O)$_2$).

Synthesis of Diacetylene Monomer I. To a solution of 4-isocyanato-4′-nitrobiphenyl (0.34 g/0.0014 mol) and BNDO (0.60 g/0.0019 mol) 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 h 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 0.66 g; yield 86%. IR (KBr) 3319 (NH), 2269 (w, C≡C), 1693 (C=O of ester), 1657 (C=O of urethane), 1540 (ν_{asym}(N=O)$_2$), 1344 cm^{-1} (ν_{asym}(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). UV–vis (acetone) 339 nm (λ_{max}), 455 nm (λ_{cutoff}).

Experimental Methodology II. The synthesis of 9-((butoxycarbonyl)methylurethanyl)-1-(4-urethanyl-4′-nitroazobenzene)nona-2,4-diyne was carried out via Scheme 2.

Monomer II Preparation. The synthesis of BNDO follows the same procedure as reported for monomer **I**. The synthesis of the chromophoric isocyanate and attachment of the isocyanate to BNDO follows.

Synthesis of 4-Isocyanato-4′-nitroazobenzene. The reaction conditions are the same as those above using 4-amino-4′-nitroazobenzene (disperse orange 3, 1.0 g/0.0041 mol) and trichloromethylchloroformate (1.0 mL/0.0082 mol). The yield of the red product was 0.84 g; yield 76%; mp 109–110 °C. IR (KBr) 2259 (N=C=O), 1763 (C=O), 1602 (Ar ring), 1520 (ν_{asym}(N=O)$_2$), 1343 cm^{-1} (ν_{sym}(N=O)$_2$).

Synthesis of Diacetylene Monomer II. The reaction conditions are the same as above using 4-isocyanato-4′-nitroazobenzene (0.80 g/0.0030 mol) and BNDO (1.0 g/0.0032 mol). The crude product was recrystallized from acetonitrile to give red crystals. The yield of monomer **II** was 1.4 g; yield 82%. IR (KBr) 3291 (NH), 2257 (w, C≡C), 1708 (C=O of ester), 1656 (C=O of urethane), 1521 (ν_{asym}(N=O)$_2$), 1343 cm^{-1} (ν_{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). UV–vis (acetone) 377 (λ_{max}), 560 nm (λ_{cutoff}).

NLO Measurements. The initial investigation of the second-order NLO properties of monomer I, monomer II, and their corresponding polymers was performed in the powdered state versus urea. In addition, second harmonic generation (SHG) was carried out using monolayers and bilayers of monomer I and its corresponding polymer. Attempts to prepare monolayers of monomer II were unsuccessful. The films were prepared using the Langmuir–Blodgett (LB) technique. The second harmonic coefficient (d_{33}) was measured at 1.064 μm laser radiation relative to Y-cut single-crystal quartz. Both methods utilized an experimental setup discussed previously.[8]

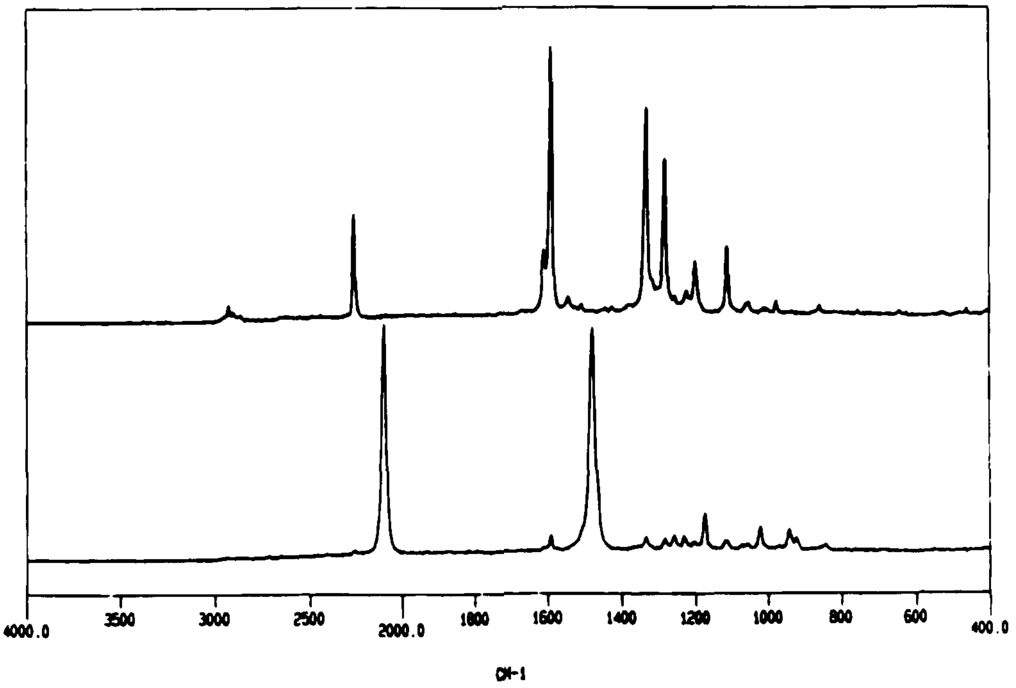


Figure 2. FT-Raman spectra of monomer I (top) and monomer-free polymer (bottom).

Polymer Preparation. Both polymers were prepared by annealing the monomer samples in an oil bath at 100 °C (±1 °C) for 24 h.

FT-Raman Measurements. The Raman spectra were recorded by a Perkin-Elmer 1760X FTIR spectrophotometer equipped with a FT-Raman accessory in a 180° optical collection geometry. The excitation was achieved at 1.064 μm wavelength and 100 mW of laser power with a continuous–wave 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 4 cm^{-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 24 h. 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 Soxhlet extraction of the unreacted monomer from the partially polymerized samples with methylene chloride. The initial 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 1). The second harmonic coefficients (d_{33}) of an LB bilayer of monomer I and an LB monolayer of PDA I were found to be 12 and 23 pm/V, respectively (Table 1).

Table 1. d_{eff} **and** d_{33} **of the Diacetylene Monomers I and II and Their Corresponding Polymers**

	monomer I	partial polymer I	monomer II	partial polymer II
d_{eff}[a]	36	7.0	16	20
d_{33}, pm/V	12	23		

[a] $d_{eff} = (I^{2w}_{urea}/I^{2w}_{sample})^{0.5}$.

Table 2. Raman Shifts of Monomer I

Raman shifts (cm^{-1})	molecular vibration
2261	C≡C stretching of monomer
1592	C=C stretching of monomer
1335	sym $(N{=}O)_2$ stretch
1284	C–C stretch of biphenyl bridge

Table 3. Raman Shifts of Monomer II

Raman shifts (cm^{-1})	molecular vibration
2261	C≡C stretching of monomer
1588	C=C stretching of monomer
1446	N=N stretching of trans azo group
1340	sym $(N{=}O)_2$ stretch

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 2261 cm^{-1} ($\nu_{C\equiv C}$) and 1592 cm^{-1} ($\nu_{C=C}$). The monomer-free polymer showed two peaks at 2102 and 1481 cm^{-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 2261 cm^{-1} ($\nu_{C\equiv C}$) and 1588 cm^{-1} ($\nu_{C=C}$). The monomer free polymer showed two peaks at 2099 cm^{-1} from C≡C stretching and 1481 cm^{-1} from C=C stretching. The complete Raman shift assignments for monomers I and II are shown in Tables 2 and 3, respectively.

Conclusion

Two novel PDAs containing second-order NLO-active chromophoric side groups and exhibiting second-order

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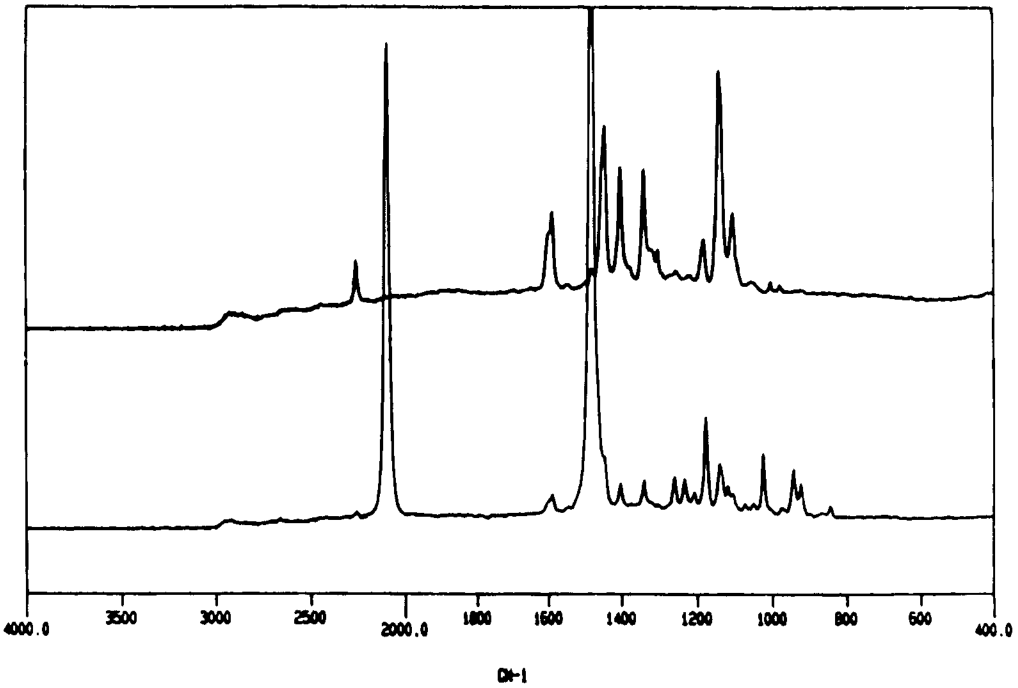

Figure 3. FT-Raman spectra of monomer II (top) and monomer-free polymer (bottom).

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. In addition, noncentrosymmetric LB bilayers of monomer I and monolayers of PDA I which exhibit d_{33} coefficients of 12 and 23 pm/V, respectively, have been prepared.

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