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## Synthesis and Nonlinear Optical Properties of Poly(4-nitrophenylallylamine) Derivatives

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A series of new NLO-active poly(4-nitrophenylallylamine) derivatives was synthesized by the nucleophilic substitution reaction of several substituted 4-nitrohalobenzenes and poly(allylamine hydrochloride). All polymers obtained were amorphous and their glass transition temperatures ( $T_g$ ) were observed around 148-160 °C. For each of these polymers, their specific  $T_g$  values were dependent on characteristic electronic structures. UV-visible absorption spectra showed maximum absorption intensity at 355-393 nm for  $\pi$ - $\pi^*$  transition of alkylaminonitrophenyl groups. The  $\chi^{(2)}$  value of poly(4-nitrophenylallylamine), as determined by the second harmonic generation at 1064 nm, for a thin polymer film poled at an elevated temperature, was  $1.4 \times 10^{-8}$  esu. The third-order NLO properties of poly(4-nitrophenylallylamine) derivatives were evaluated through measurement of degenerate four-wave mixing technique and  $\chi^{(3)}$  coefficient in the range of  $2.7 \sim 3.2 \times 10^{-12}$  esu at 602 nm was found with 400 fs laser pulses.

### Introduction

Polymeric systems having nonlinear optical (NLO) active groups have attracted much scientific and technological interest because of their potential application in the field of optical communications, optical processing, and optical computing.<sup>1</sup> The NLO polymers could offer many advantages over the traditional inorganic substances and low molar mass organic compounds in chemical, optical, mechanical, environmental properties and cost effectiveness.<sup>2-6</sup> In the early research stage of polymeric NLO materials, guest-host system involving organic NLO chromophores, doped in a glassy polymer or in a liquid crystalline polymer matrix, was intensively studied.<sup>7-13</sup> Guest-host systems were found relatively simple to formulate. However, phase separation due to the limited solubility of chromophore in the host polymer matrix and gradual decay of orientation by thermal relaxation of poled sample have been the major obstacle for fabricating optic devices. During past several years, much efforts have been made to overcome the problem of segregation and relaxation of chromophores by making various side chain, main chain or crosslinked polymeric systems in which the NLO chromophores were covalently incorporated into a polymer matrix.<sup>14-16</sup> Among them, the side chain polymeric systems have been considered best candidate for nonlinear optics

applications, because of their ability to chromophore density, high poling efficiency and reducing optical losses. To date, literature mainly describes the side chain polymers obtained by the free radical polymerization reactions of vinyl monomers having NLO chromophores.<sup>17-23</sup> The main disadvantage of these type of polymers are their low molecular weights and low yields, due to the polymerization inhibition of chromophores. These problems can be solved by the polymer reaction of high molecular weight polymers having reactive groups with NLO chromophore.

This paper describes the synthesis and nonlinear optical properties of amorphous poly(4-nitrophenylallylamine) derivatives having substituted 4-nitroaniline as NLO-active side groups covalently attached to a polyethylene-type backbone, prepared by polymer reactions. The main reason for selecting polyallylamine as the polymer backbone was the ease of synthesis with high degree of functionalization possible, and high  $T_g$ , due to the direct attachment of chromophore, which is expected to increase the rigidity of the matrix and at the same time to prevent the randomization process of the oriented NLO chromophore dipoles. Third-order NLO effect of the polymeric system was also evaluate to gain understanding of NLO activity on the short range of the conjugated system.

## Experimental

**Materials.** The reagents such as 1-chloro-4-nitrobenzene, 2-fluoro-5-nitrotoluene, 5-chloro-2-nitrobenzotrifluoride, 2-chloro-5-nitropyridine, 1-chloro-2,4-dinitrobenzene and poly(allylamine hydrochloride) (number average molecular weight: 50,000-65,000) were obtained from Aldrich Chemical Co. and used without purification. All solvents used in polymer synthesis were purified by vacuum distillation before use.

**Syntheses of Polymers.** NLO active poly(4-nitrophenylallylamine) derivatives, PA-I, PA-II, PA-III, PA-IV and PA-V, were synthesized by the nucleophilic substitution reaction of poly(allylamine hydrochloride) with a slight excess of 4-halonitrobenzene derivatives in the presence of an excess of base, such as anhydrous potassium carbonate. Typical reaction procedure for PA-I-144 was described as follows: 1 g (0.0125 mol) of poly(allylamine hydrochloride), 2.76 g (0.02 mol) of anhydrous potassium carbonate, and 3.5 g (0.025 mol) of 1-fluoro-4-nitrobenzene were placed into a 100 mL three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and a septum, and dissolved in 30 mL of dimethylsulfoxide (DMSO). The mixture was reacted at 80-90 °C for 144 h under nitrogen atmosphere and cooled to room temperature. The reaction mixture was then poured into an ice water and the precipitated polymer was filtered, washed with methyl alcohol and water, then dried in vacua to yield the yellowish polymer, PA-I-144. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) 7.9 (broad, 2H, 2ArH), 7.1 (broad, 1H, NH), 6.4 (broad, 2H, 2ArH), 3.4 (broad, 2H, CH<sub>2</sub>N), 1.8 (broad, 1H, -CH-), 1.4 (broad, 2H, -CH<sub>2</sub>-); IR (KBr, cm<sup>-1</sup>) 3360 (-NH stretching), 1600 (C=C stretching), 1500 and 1320 (NO<sub>2</sub> stretching), 1100 (C-N stretching); Anal. Calc. for (C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>)<sub>n</sub>: C 60.68, H 5.62, N 15.73. Found: C 60.20, H 5.62, N, 15.76.

**Measurements.** <sup>1</sup>H NMR spectra were recorded with a FT-80A 300 MHz spectrophotometer and IR spectra were obtained on a Shimadzu IR-435 spectrophotometer. Elemental analyses were performed using the Perkin-Elmer EA-240 instrument. UV-vis. spectra were recorded on a Shimadzu UV-240 spectrophotometer. Differential scanning calorimetry (DSC) measurements were performed on a DuPont 910 under nitrogen at a heating rate of 10 °C/min. Thermogravimetric analyzer (TGA) measurements were carried out on a DuPont 951 under nitrogen at a heating rates of 10 °C/min. Wide angle X-ray diffractograms were obtained using nickel-filtered CuKα (λ=1.541 Å) radiation on a Rigaku Geiger X-ray diffractometer. Inherent viscosities were measured with a polymer concentration of 0.4 g/dL in N,N-dimethylformamide (DMF) at 25 °C, using Cannon-Fenske viscometer. Thicknesses of the polymer films were measured using an Scheffield RLU type profilometer. Refractive indices were measured by the Brewster angle technique.

**Preparation of Films.** Films were prepared by spin coating from 20 wt.% polymer solutions in DMF. The solutions were filtered through a 0.45 μm teflon membrane filter to remove insoluble particles, then spun at 800-2000 rpm for 5-15 second depending on the desired thickness onto an ITO glass plate and finally dried in a vacuum oven at 150 °C for 24h.

**Poling and SHG Efficient Measurement.** Poling experiments were performed using positive polarity of a 25 μm thick tungsten corona wire. Electric fields were produced

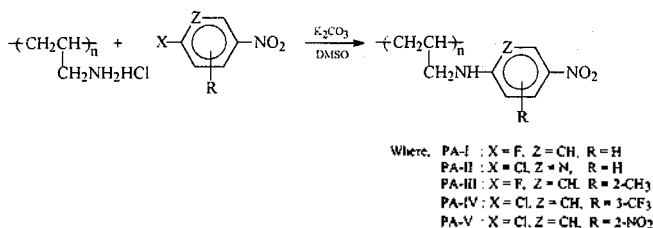
when the distance between the corona wire and the sample surface was around 0.60-0.62 cm and +4.4 kV wire potential. The SHG experiments were performed with the p-polarized beam at the fundamental frequency of a mode locked Q-switched Nd:YAG laser operating at 500 Hz with forty 135 ps sub-pulses in each pulse train. The macroscopic second harmonic susceptibility χ<sup>(2)</sup> of films has been measured using the angular dependence method with the Y-cut quartz plate.

**Degenerate Four-Wave Mixing (DFWM).** The experimental setup used for DFWM utilized a laser system in which the IR output of a mode-locked continuous wave (CW) Nd:YAG laser was first compressed in a grating fiber compressor and then frequency-doubled to sync-pump a CW dye laser. The dye pulses were subsequently amplified by frequency-doubled pulses from a 30 Hz Q-switch pulsed Nd:YAG laser to generate around 400 fs, nearly transform-limited pulses with an energy of 0.4 mJ at 602 nm. A peak power density of around 400 MW/cm<sup>2</sup> was used. The beams in the forward wave geometry for DFWM were focused onto the films. The four-wave mixing signal was detected by a photodiode and processed by a boxcar averager.

## Results and Discussion

**Synthesis and Characterization.** Several poly(4-nitrophenylallylamine) derivatives having NLO-active groups were prepared by the aromatic nucleophilic substitution reaction from poly(allylamine hydrochloride) with p-nitrohalobenzene derivatives, as shown in Scheme 1.

The resulting polymers were characterized by common spectroscopic techniques such as <sup>1</sup>H NMR, FT-IR, UV/vis., and elemental analysis. The experimental results are in good agreement with the structure obtained on the synthetic route. The <sup>1</sup>H NMR spectrum of the PA-I-144 polymer, as a representative of PA series in Figure 1 shows the chemical shift of -NH- proton linked with a primary amine at 7.1 ppm, which resulted in polymer reaction. Two peaks at 7.9 and 6.4 ppm are evident due to chemical shifts of the aromatic protons. The chemical shifts due to aliphatic protons in poly-



Scheme 1.

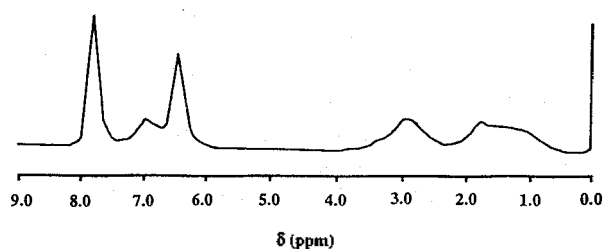


Figure 1. <sup>1</sup>H NMR spectrum of PA-I-144 (TMS, δ=0 ppm).

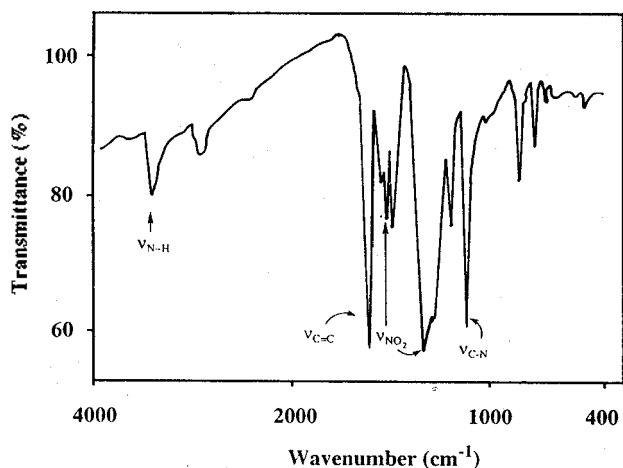


Figure 2. IR spectrum of PA-I-144 (KBr pellet).

mer backbone appeared at 1.4–3.4 ppm. According to IR spectrum of PA-I-144 (Figure 2), the characteristic -NH stretching band due to polymer reaction appeared at  $3360\text{ cm}^{-1}$ . In addition, two strong absorption bands owing to nitro groups were observed at  $1320\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ .

Figure 3 shows the UV-visible absorption spectra of all polymers. The absorption maxima,  $\lambda_{max}$ , due to a  $\pi\text{-}\pi^*$  transition of poly(allylamine) derivatives were centered at 392, 371, 393, 389, and 355 nm, respectively. In the case of PA-II-168 polymer containing pyridine ring instead of phenyl ring, and PA-V-72 polymer substituted by electron-withdrawing nitro group at the ortho position of the phenyl ring, the absorption maxima due to a  $\pi\text{-}\pi^*$  transition showed the blue shift comparative to PA-I-144 polymer. The absorption maxima of PA-III-168 polymer substituted by electron-releasing methyl group at the ortho position of the phenyl ring, and PA-IV-120 polymer substituted by electron-withdrawing trifluoromethyl group at the meta position of the phenyl ring, were similar to PA-I-144 polymer.

The synthetic results and physical properties of the poly(allylamine) derivatives were summarized in Table 1. As the

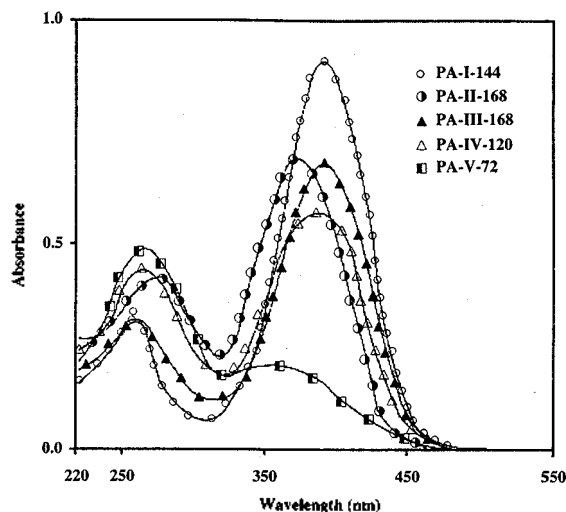


Figure 3. UV/vis. absorption spectra of poly(4-nitrophenylallylamine) derivatives.

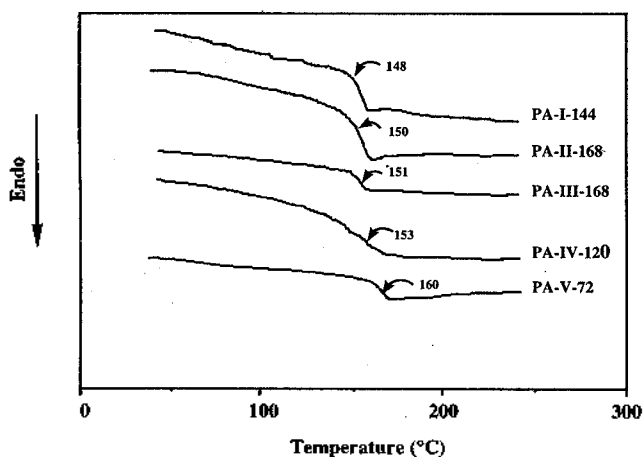
reaction time increased, the polymerization yields, and the inherent viscosities increased. The polymer yields after polymerization were ranged from 40% to 77% and the inherent viscosities measured at a concentration of 0.4 g/dL at  $25\text{ }^{\circ}\text{C}$  in DMF solution were ranged from 0.31 to 0.50 dL/g. The reaction rates were as follows: PA-I > PA-II  $\approx$  PA-III > PA-IV > PA-V. These results imply that the steric hindrance affected the reaction rate stronger than the electron push-pull effect did. In the case of PA-V polymer substituted by electron-withdrawing nitro group at the ortho positions of the phenyl ring, the reaction rate was relatively low due to the steric hindrance of the bulky nitro group. However, in PA-III polymer substituted by electron-releasing methyl at the ortho positions of the phenyl ring, the steric hindrance had little effect. The level of functionalization with NLO chromophore at the side chain of polymeric backbone was over 90%, except PA-II-72.

All polymers obtained could be dissolved in polar aprotic

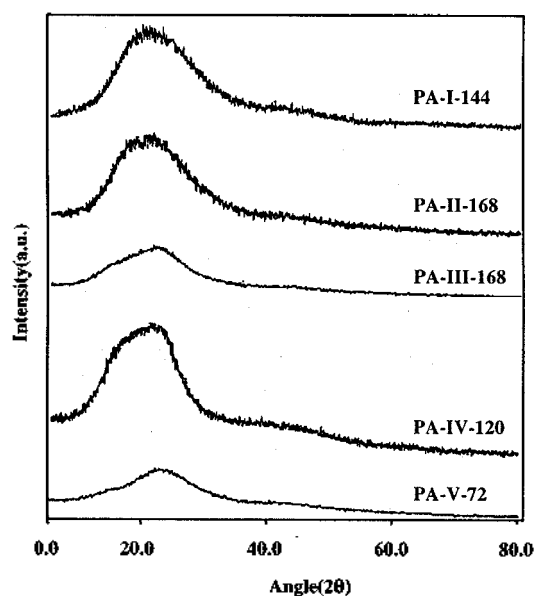
Table 1. Physical Properties of Poly(4-nitrophenylallylamine) Derivatives

Polymers	Yield (%)	Viscosity ( $\eta_{inh}$ ) <sup>c</sup> (dL/g)	Elemental Analysis <sup>b</sup>			Degree of Functionalization <sup>e</sup> (%)	UV/vis ( $\lambda_{max}$ ) (nm)	$T_g$ <sup>d</sup> ( $^{\circ}\text{C}$ )	$T_d$ <sup>f</sup> ( $^{\circ}\text{C}$ )
			C	H (%)	N				
PA-I-24 <sup>h</sup>	45	0.37	59.63 (60.08)	5.63 (5.62)	15.91 (15.73)	94	392	148	250
PA-I-48	63	0.45	59.26 (60.08)	5.75 (5.62)	15.84 (15.73)	96	392	150	250
PA-I-144	77	0.45	60.20 (60.08)	5.62 (5.62)	15.76 (15.73)	99	392	148	250
PA-II-72	50	0.43	51.34 (53.63)	4.77 (5.03)	23.56 (23.46)	77	371	148	220
PA-II-168	68	0.48	53.90 (53.63)	5.16 (5.03)	23.50 (23.46)	90	371	151	225
PA-III-72	44	0.32	62.18 (62.50)	6.35 (6.25)	14.72 (14.58)	96	393	150	260
PA-III-168	69	0.40	62.08 (62.50)	6.34 (6.25)	14.64 (14.58)	98	393	151	260
PA-IV-120	50	0.50	49.05 (48.78)	4.07 (3.66)	11.58 (11.38)	94	389	153	220
PA-V-72	40	0.31	47.88 (48.43)	4.36 (4.04)	18.25 (18.83)	93	355	160	220

<sup>a</sup>Measured at a concentration of 0.4 g/dL in DMF at  $30\text{ }^{\circ}\text{C}$ . <sup>b</sup>The values in parenthesis indicate theoretical value. <sup>c</sup>Indicate the content of NLO-active 4-nitrophenyl group calculated from nitrogen content. <sup>d</sup>Determined by DSC at a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ . under nitrogen atmosphere. <sup>e</sup>Determined by TGA at a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ . under nitrogen atmosphere. <sup>f</sup>The numbers indicate reaction time (h).



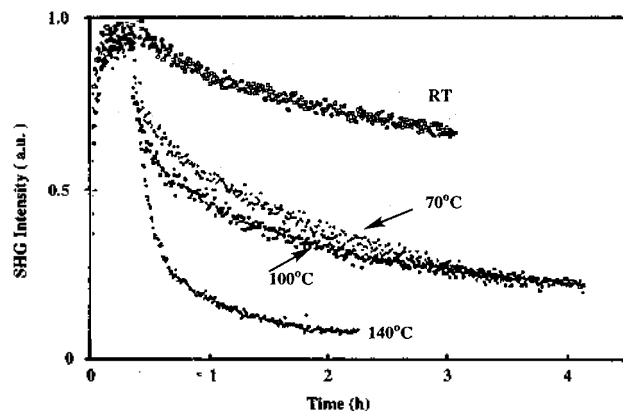
**Figure 4.** DSC thermograms of poly(4-nitrophenylallylamine) derivatives (heating rate: 10 °C/min, N<sub>2</sub> atmosphere).



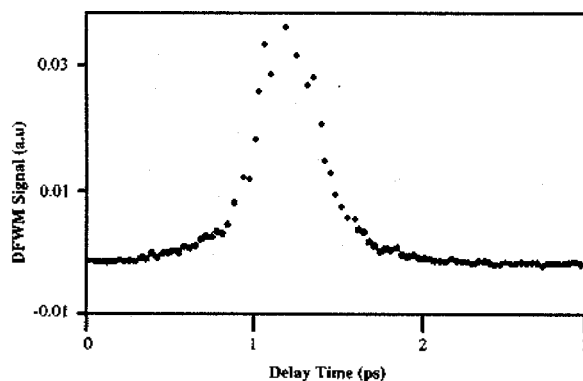
**Figure 5.** Wide angle X-ray diffractograms of poly(4-nitrophenylallylamine) derivatives.

solvents such as N-methylpyrrolidone, DMF, DMSO, and dimethylacetamide etc., at a concentration below 5 wt.% of solution. The C/H/N ratio checked by the elemental analysis was matched with a theoretical value within the limits of experimental error.

**Thermal Properties.** The glass transition temperatures (T<sub>g</sub>) of the polymers have been investigated using DSC at a heating rate of 10 °C/min. under nitrogen atmosphere. Since the chromophores are directly attached to the side chain without any spacer, mobility of the chromophore can be reduced. Due to this structural effect, high T<sub>g</sub> was expected.<sup>24</sup> As shown in Figure 4 and Table 1, T<sub>g</sub> for a series of PA polymers lies in the range of 148–160 °C, depending on the structure of the NLO chromophore and the extent of functionalization. These values are highly compared to general NLO active side chain polymers derived from radical polymerizations.<sup>25</sup> No crystalline melting transitions were detected for all of the polymers, which indicate that the polymers were



**Figure 6.** SHG profile of PA-I-144 as a function of time at different temperature.



**Figure 7.** DFWM profile of PA-I-144 as a function of the forward beam delay (602 nm, 400 fs pulses).

all amorphous.

Initial decomposition temperatures ( $T_{id}$ ) of the polymers were determined using TGA, and tabulated in Table 1. The  $T_{id}$  of the polymers were within 225–260 °C, which is not so high compared with those of conventional polymers. The low initial decomposition temperatures is well known phenomena in NLO active polymers, caused by the activated decomposition due to the push-pull effect of electronic cloud in chromophores. Figure 5 shows the wide angle X-ray diffractograms of the polymers. Only broad amorphous hallow diffractions were observed, which indicates that the polymers are noncrystalline and is consistent with the DSC results.

**Second-Order Nonlinear Optical Properties.** For the SHG experiment, PA-I-144 was chosen because of its better film quality compared with other polymer samples. The polymer film was prepared by spin coating on ITO glasses from 20 wt.% DMF solution and film thickness were 1–4 μm, depending on the spinning rate. The refractive indices of the polymer film were measured by the Brewster Angle Technique. The refractive indices were 1.793, 1.749, and 1.661 at the wavelength 532 nm, 600 nm, and 1064 nm, respectively. Figure 6 shows a typical SHG profile with the temperature change. From the result of the SHG experiment,  $\chi^{(2)}$  value of poled PA-I-144 was  $1.4 \times 10^{-8}$  esu. The SHG signal of a poled polymer was recorded over 3 h period. The decay process in the value of the SHG signal is slow at room temperature and the material still retains almost

**Table 2.** Third-Order Nonlinear Optical Properties ( $\chi^{(3)}$ ) of Poly(4-nitrophenylallylamine) Derivatives

Samples	Film Thickness <sup>a</sup> ( $\mu\text{m}$ )	Refractive Index <sup>b</sup>	Absorbance in 602 nm	DFWM Signal Intensity <sup>c</sup> (mV)	$\chi^{(3)}$ (esu)
PA-I-144	17.4	1.74	0.092	33.5 (48.0)	$2.7 \times 10^{-12}$
PA-III-168	17.0	1.72	0.086	33.0 (34.0)	$3.2 \times 10^{-12}$
PA-IV-120	17.3	1.73	0.069	30.6 (32.0)	$3.2 \times 10^{-12}$

<sup>a</sup>Measured by Profilometer (Scheffield; type RLU, Model 1). <sup>b</sup>Measured by the Brewster Angle Technique using a He-Ne laser. <sup>c</sup>Values in parenthesis indicate intensity of standard THF. <sup>d</sup>The measurements were performed by DFWM at 602 nm with 400 fs laser pulses.

80% of its initial optical nonlinearity. However, when the temperature increased, the SHG signal of the poled polymer rapidly decreased. The SHG signal after being exposed for 2 h at 80 °C retained almost 45% of its initial value. For the poled polymer, after being exposed for 1 h at 140 °C, SHG signal nearly disappeared.

**Third-Order Nonlinear Susceptibility.** The  $\chi^{(3)}(-\omega; \omega, \omega, \omega)$  values of thin films for PA-I-144, PA-III-168, and PA-IV-120 polymers were evaluated by comparing the strength of the conjugated DFWM signal with that of tetrahydrofuran (THF) at the same incident photon flux, according to the following relationship:

$$\chi_s^{(3)} = \chi_t^{(3)} \times \sqrt{\frac{I_s}{I_t}} \times \frac{L_t}{L_s} \times \frac{n_s^2}{n_t^2} \times \frac{\alpha L_s}{\exp\left(-\frac{\alpha L_s}{2}\right) [1 - \exp(-\alpha L_s)]}$$

where  $n$  is the refractive index,  $L$  is the interaction length,  $\alpha$  is the linear absorption coefficient of the polymer sample at 602 nm, and  $I$  is the intensity of the DFWM signal. The subscripts t and s stands for THF and the sample, respectively. Figure 7 shows a typical DFWM temporal profile obtained for the PA-I-144 polymer. All investigated samples showed a similar symmetrical shapes. The values of  $\chi^{(3)}$  obtained by comparing of the DFWM intensities measured for the polymers with that of a THF ( $\chi^{(3)} = 3.7 \times 10^{-14}$  esu) as a standard are given in Table 2. The measured  $\chi^{(3)}(-\omega; \omega, \omega, \omega)$  values of PA-I-144, PA-III-168 and PA-IV-120 were  $2.7 \times 10^{-12}$ ,  $3.2 \times 10^{-12}$  and  $3.2 \times 10^{-12}$  esu, respectively. These values are lower than those reported for conjugated polymers like poly(p-phenylenevinylene), poly(phenylacetylene), and poly(diacetylenes) etc.<sup>2,26-29</sup> The reason for small values of optical nonlinearity in these polymers may be understood by considering the short  $\pi$ -electron conjugation. In the case of PA-III-168 and PA-IV-120, which has electron-releasing substituents at the 2 or 3 positions of phenyl ring,  $\chi^{(3)}$  values were larger due to enhancement of  $\pi$ -electron density in the aromatic ring of the unsubstituted polymers.

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## Synthesis of the New 1,2-Dithiolene Metal Complexes $[M(BDDT)_2]^-$ ( $M=Ni, Cu$ ) and Their Electronic Structures

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The new 1,2-dithiolene, 1,4-butanediylidithioethylene-1,2-dithiolate ( $BDDT^{2-}$ ), has been isolated. In addition, new monoanionic bis-complexes with nickel and copper have been prepared and characterized. In order to investigate the detailed electronic structure of the metal complexes of the new ligand,  $BDDT^{2-}$ , in terms of the oxidation state of the central metal ions, we have carried out molecular orbital (MO) calculations of  $Ni(BDDT)_2^-$  and  $Cu(BDDT)_2^-$  utilizing an Extended Hückel method. Cyclic voltammetry data for both complexes were obtained with a potentiostat. We have also compared these results to the previously synthesized  $Ni(PDDT)_2^-$ ,  $Ni(DDDT)_2^-$ ,  $Cu(PDDT)_2^-$ , and  $Cu(DDDT)_2^-$ .

### Introduction

Over the past 30 years, there has been a great deal of interest in the coordination chemistry of 1,2-dichalcogenolenes. Unsaturated sulfur donors have been particularly well characterized. These ligands first came into prominence in the mid 1930's when they were utilized as analytical reagents.<sup>1,2</sup> However, it was not until 1957 that any really serious efforts were made to characterize some of the metal complexes of these unsaturated 1,2-dithiols.<sup>3</sup>

There have been several important reviews of metal sulfur chemistry. Discussions by Harris and Livingstone,<sup>4</sup> Livingstone,<sup>5</sup> and Jorgenson<sup>6</sup> deal with sulfur ligands in general. Holm and O'Conner<sup>7</sup> discuss the stereochemistry of  $[M(II)-S_4]$  complexes along with other bischelate metal(II) complexes in their review. Many authors<sup>8-13</sup> have reviewed the chemistry of 1,2-dithiolene complexes. Electronic spectral studies of bidentate sulfur containing ligands have been reviewed in detail by Coucouvanis.<sup>14</sup> Systematic examinations of the crystal and molecular structures of 1,2-dithiolene complexes have been carried out by Eisenberg<sup>15</sup> and Mahadevan.<sup>16</sup> Exchange interactions in some low dimensional metal dithiolene complexes have been the subject of a review by Monoharan and co-workers.<sup>17</sup>

Bis(dithiolene) complexes of metals are possible candidates for counteranions in conducting molecular solids.<sup>18-20</sup> Recently (TTF) $[Ni(dmit)_2]_2$  has been shown to be superconducting

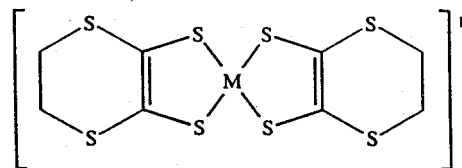


Figure 1. Lewis Structure of  $[M(DDDT)_2]_n$ .

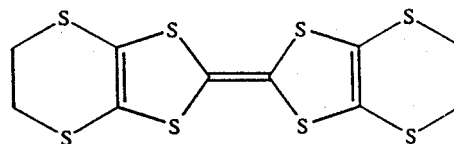


Figure 2. Lewis Structure of BEDT-TTF or ET.

at 1.62 K under a hydrostatic pressure of 7 Kbar.<sup>18b</sup> A good deal of interest has been shown recently in 5,6-dihydro-1,4-dithiin-2,3-dithiolate (DDDT) since its metal complexes  $[M(DDDT)_2]_n$  (Figure 1) are similar in structure to bis(ethylene-dithio)tetrathia-fulvalene (BEDT-TTF or ET, Figure 2) which have led to the ambient-pressure superconductors  $\beta$ -(ET) $X$  ( $X^- = I_3^-, AuI_2^-, IBr_2^-$ ).<sup>21</sup>

Schultz *et al.*<sup>22</sup> recently reported that the  $[Au(DDDT)_2]^0$  molecule and the  $[Ni(DDDT)_2]^-$  ion are isoelectronic in terms of their valence electrons. The metal coordination geometry is square planar in both molecules. They are described