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13. The objective of this research program has been the development of new materials with enhanced nonlinear optical activity and the exploration of related properties such as electrical conductivity. Initial research efforts focused upon pi-electron materials (polyenes and heteroaromatic polymers) and synthetic routes for overcoming the inherent insolubility of these materials. By steadily improving solubility and processability through utilization of derivatization and precursor routes, we have been able to fabricate optical quality films of ladder-type polymers and achieve high resolution characterization of these materials both in terms of structure and electroactive properties. Electroactive molecules including fused ring (ladder oligomers) dyes, squarylium-heterocyclic moieties, phenylpolyenes, thienylpolyenes, carbocyanine dyes, and tetraazaannulenes have also been synthetically incorporated into a variety of traditional polymers both as pendants and as part of the polymer backbone. Such incorporation has permitted systematic improvement of the intrinsic poor solubility of these materials and has permitted in each case the realization of optical quality films by spin casting techniques. This approach has permitted a comparative survey of a significant number of electroactive moieties and has permitted the systematic investigation of the dependence of second and third order optical nonlinearity upon the presence and nature of electron donating and/or withdrawing substituents, upon the concentration of electroactive units (effects of intermolecular interactions), upon the presence of oxidizing or reducing dopants, etc. Data obtained from copolymer studies were compared, when possible, with data from solution studies and studies of electroactive molecule/polymer composites.

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research program has been the development of new materials with enhanced nonlinear optical activity and the exploration of related properties such as electrical conductivity. Initial research efforts focused upon π -electron materials (polyenes and heteroaromatic polymers) and synthetic routes for overcoming the inherent insolubility of these materials. By steadily improving solubility and processability through utilization of derivatization and precursor routes, we have been able to fabricate optical quality films of ladder-type polymers and achieve high resolution characterization of these materials both in terms of structure and electroactive properties. Electroactive molecules including fused ring (ladder oligomers) dyes, squarylium-heterocyclic moieties, phenylpolyenes, thienylpolyenes, carbocyanine dyes, and tetraazaannulenes have also been synthetically incorporated into a variety of traditional polymers both as pendants and as part of the polymer backbone. Such incorporation has permitted systematic improvement of the intrinsic poor solubility of these materials and has permitted in each case the realization of optical quality films by spin casting techniques. This approach has permitted a comparative survey of a significant number of electroactive moieties and has permitted the systematic investigation of the dependence of second and third order optical nonlinearity upon the presence and nature of electron donating and/or withdrawing substituents, upon the concentration of electroactive units (effects of intermolecular interactions), upon the presence of oxidizing or reducing dopants, etc. Data obtained from copolymer studies were compared, when possible, with data from solution studies and studies of electroactive molecule/polymer composites.

New experimental and theoretical methods for characterization of optical nonlinearity have been developed. Such development was necessary to achieve a meaningful and unambiguous characterization of optical nonlinearity. Contributions to optical nonlinearity have been analyzed in terms of coherent parametric mixing processes, excited state population processes which do not involve significant structural relaxation, and excited state population processes which involve structural relaxation. Moreover, new technologies have been utilized to achieve detailed specification of mechanisms of optical nonlinearity so that optical nonlinearity can be calculated for other experimental configurations. For example, a new phase conjugate interferometric method has been employed to simultaneously measure the real and imaginary parts of the third order susceptibility over the frequency range 532-720 nm. For ladder polymers, the imaginary part of the third order susceptibility from these measurements was shown to correlate well with photobleaching/photo-induced absorption data demonstrating a contribution to optical nonlinearity from photo-induced bipolaron species (a structural relaxation mechanism).

Optical signal processing, particularly when exploiting second order activity, frequently requires the realization of ultrastructure ordering. We have exploited with significant success the utilization of photo-induced chemical (e.g., crosslinking, isomerization, condensation) and physical (phase changes) processes to achieve precise ultrastructure ordering necessary for fabrication of integrated optical circuits and phase-matching in second harmonic generation.

AFOSR Program Manager: Dr. Charles Y-C Lee

Improvement in solubility and processability utilizing the synthesis of copolymers for NLO applications incorporating subunits with defined conjugation lengths

During the past three years it has become more evident that long conjugation sequences in electroactive materials may not be a stringent requirement for high third order nonlinear optical (NLO) activity. Since long conjugation lengths in these materials often make them difficult to process, the resulting insolubility often precludes the formation of optical quality films for device applications. The incorporation of shorter electroactive segments alternating with flexible non-active spacers may allow high NLO activity coupled with good optical film forming capability. We would like to present several approaches to copolymer design which incorporate various electroactive oligomer segments with well-defined conjugation lengths. The control one obtains in this approach allows the design of sharp optical windows, and the ability to tailor absorption characteristics to particular frequencies.

Large third-order nonlinearities have been observed for such electroactive polymers as polyacetylene, polythiophene and poly(p-phenylene vinylene).¹ Several workers in recent years have been interested in the relationship of g and $\chi^{(3)}$ to the extent of conjugation in the nonlinear material. Although Flytzanis and coworkers originally suggested that g might follow a power law dependence on conjugation (delocalization) length as high as the sixth power², more recent calculations indicate a lower power relationship. Beratan, et al.,³ have shown that the third order hyperpolarizability, g increases rapidly for trans-polyenes as conjugation increases up to 10-15 repeat units, then more slowly up to 40 repeat units. They suggested, on this basis, that relatively short oligomeric segments of conjugated sequences could therefore be mixed with non-active sequences to maximize NLO activity, while at the same time maintaining desirable physical properties such as solubility. Garito and coworkers have calculated that the power law dependence of g_{xxxx} with chain length, L , is of the order 4.6 ± 0.2 .⁴ Prasad concurs with the previous workers contention that g/N levels off with increasing N , and ab-initio calculations indicate a power law dependence of g with L of between 3.2 and 3.4.⁵ Thus, it would appear that long conjugation sequences are not necessary for enhanced nonlinear activity and more attention can be focused on designing the optical absorption characteristics of the polymer and to adjusting the structure to maximize solubility, processability and film-forming characteristics.

Over the past several years, well-characterized oligomers of several polymer systems, including polyacetylene, poly(r-phenylene vinylene) (PPV) and poly(2,5-thienylene vinylene) (PTV) have been synthesized (Figure 1).

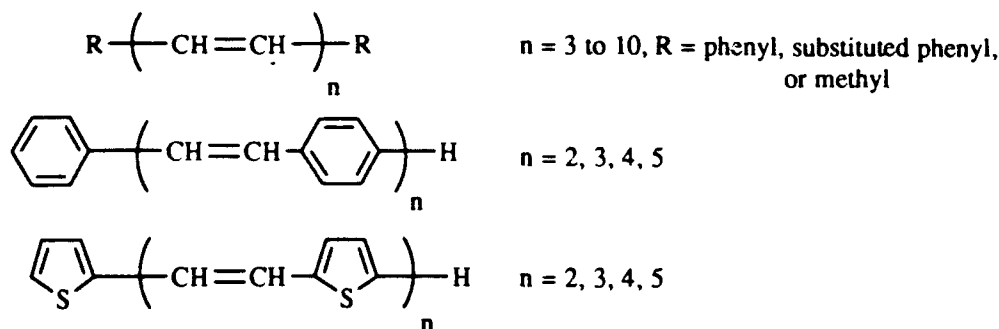


Figure 1. PPV and PTV oligomers

By varying the starting synthetic material, various substituent functionalities can be introduced onto the phenyl or thiophene rings to prepare oligomers functionalized for copolymer formation. This is illustrated for the preparation of bis-carboxylic acids which can be readily converted into polyamides (Figure 2).

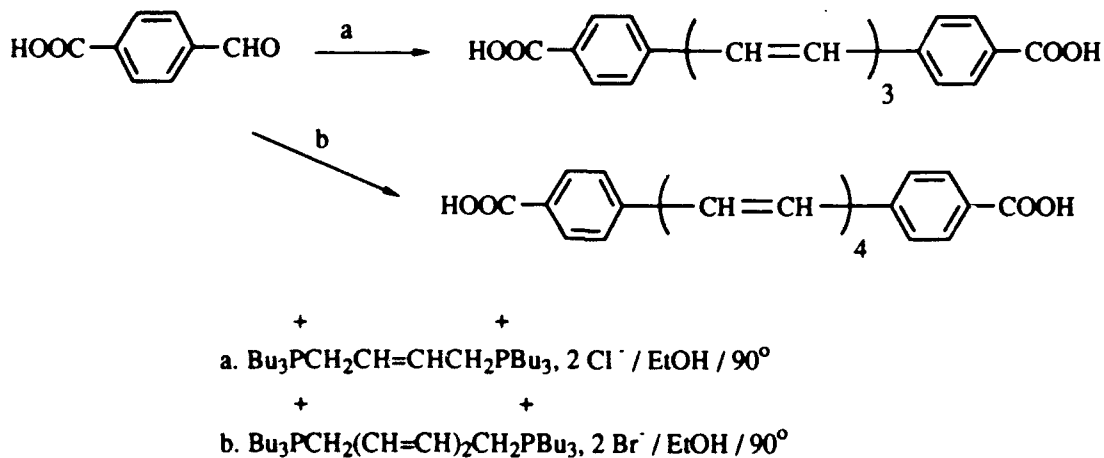
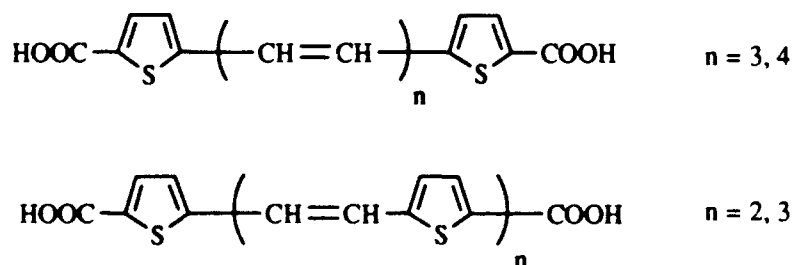


Figure 2. Bis-carboxylic acid monomers

Similar transformations^{6,7} yield the bis-2-thienyl and thienylene vinylene counterparts:



The synthesis of copolyamides of the polyene and polyvinylene monomers was facilitated by interfacial polymerization techniques. Acid chlorides of the bis-

carboxylic acid monomers were prepared by reaction with thionyl chloride (2.5 mole equivalent) in benzene (approximately 4% wt/wt solution). The reactions were heterogeneous in nature but preceded to essentially 100% yield. The bis-acid chlorides so prepared could be crystallized in mixtures of ethyl acetate and hexane, but in most cases were used without further purification in the synthesis of the polymers.

The copolyamides were synthesized by first dissolving the bis-acid chloride monomers in chloroform (approximately 0.2% wt/wt solution) followed by the addition of dodecanedioyl dichloride (30:70 to 90:10 molar ratio to electroactive monomer, as dilution and solubilizing agent). To this vigorously stirred solution was added hexamethylene diamine dissolved in an equal volume of water with an appropriate excess of sodium hydroxide (2 equivalents based on HCl evolution). The copolymers precipitated immediately and the solutions were stirred for an additional 2 hours, after which the chloroform layer was essentially colorless. The chloroform layer was then separated and the polymers filtered off the aqueous layer with repeated water washing, with finally an acetone wash and drying. The range of polymeric materials synthesized as well as the synthetic scheme are shown below (Table I, Figure 3).

The transformation of the bis-carboxylic acids to the corresponding acid chlorides could be easily followed by infrared spectroscopy. The complete loss of the C=O stretching at 1673 cm^{-1} and the appearance of C=O bands at 1768 cm^{-1} (along with the band at 1745 cm^{-1} which is the characteristic Fermi resonance between C=O and overtone band at 875 cm^{-1}), as well as the additional intense C-Cl stretching at 822 cm^{-1} is clearly visible.

Table I. Range of Copolymer Studied

| Polymer | % Incorp. | Decomp. Temp | $\chi^{(3)}/\alpha$ (esu-cm) |
|---|-----------|------------------|------------------------------|
| Nylon 6,12 | 0 | 425 | --- |
| $\text{---}(\text{C}=\text{C})_{n=3}\text{---}$ | 10 | 468 | ---- ^a |
| $\text{---}(\text{C}=\text{C})_{n=3}\text{---}$ | 20 | 486 | ---- ^a |
| $\text{---}(\text{C}=\text{C})_{n=3}\text{---}$ | 40 | 475 | ---- ^a |
| $\text{---}(\text{C}=\text{C})_{n=3}\text{---}$ | 54 | 456 | ---- ^a |
| $\text{---}(\text{C}=\text{C})_{n=3}\text{---}$ | 100 | 517 | ---- ^c |
| $\text{---}(\text{C}=\text{C})_{n=4}\text{---}$ | 20 | 464 | 1.6×10^{-13} |
| $\text{---}(\text{C}=\text{C})_{n=5}\text{---}$ | 20 | 450 | ---- ^b |
| $\text{---}(\text{C}_6\text{H}_4\text{-C}=\text{C})_{n=2}\text{---}$ | 20 | 390 | ---- ^a |
| $\text{---}(\text{C}_4\text{H}_3\text{S-C}=\text{C})_{n=2}\text{---}$ | 20 | 385 | 0.62×10^{-13} |
| $\text{---}(\text{C}_4\text{H}_3\text{S-C}=\text{C})_{n=3}\text{---}$ | 20 | --- ^b | ---- ^b |

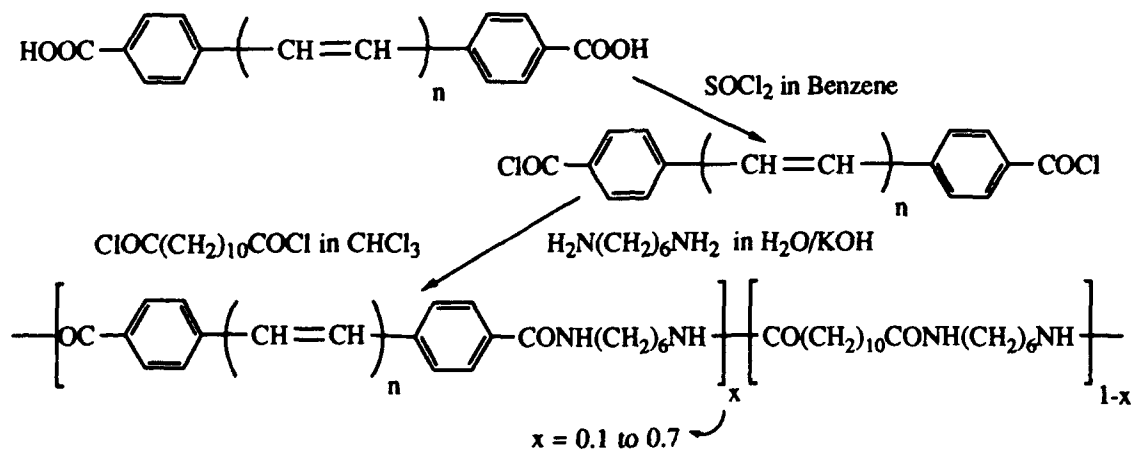
^a No Signal Detected^b Work in Progress^c Unable to Obtain Optical Quality Film

Figure 3. Copolymerization Scheme

The conjugated structure of the monomer is unaltered by the transition from carboxylic acid to acid chloride as indicated by NMR studies. For the phenylpolyenes the splitting is quite complex and there is no appearance of aliphatic protons which could have resulted from side reaction during the transition (such as addition of HCl to the vinyl units, oligomerization, etc.). The thierylvinylenes have a complicated NMR, however it is possible to discern the aromatic (doublet of doublets at 7.70 and 7.35 ppm for the outer rings, and singlet at 7.42 ppm for the internal ring) and vinyl protons (pentet from 7.18 to 7.45 ppm resulting from long range coupling with the thiophene protons). The integration in all spectra supported these assignments.

The copolyamides of the polyenes and polyvinylene monomers were characterized by a number of methods including infrared and UV-Vis spectroscopy, gel permeation chromatography (GPC), thermal gravimetric analysis (TGA), thermal mechanical analysis (TMA), and differential scanning calorimetry (DSC). The transformation of the monomer into the polymer can be followed by the disappearance of the C=O and C-Cl of the acid chloride and the appearance of the characteristic C=O of an amide at 1638 cm^{-1} . The molecular weights of the copolymers were measured to be in the range of 100,000 amu as polystyrene equivalent molecular weights.

The resulting copolymers are yellow to orange in color and exhibit the same type of fluorescence and absorption characteristics as the monomers. The polymers are soluble in acidic solvents such as trifluoroacetic acid (TFA), methane sulfonic acid, hexafluoroisopropanol, etc. Basic solvents such as dimethylformamide, dimethylsulfoxide, dimethylacetamide are less suitable, however, N-methylpyrrolidinone with 1% LiCl is quite efficacious in forming solutions. Optical quality films of the copolymers can be readily formed from carefully filtered TFA solutions onto glass slides at a temperature of 50°C .

The physical properties of the materials were excellent with optical clarity, high thermal stabilities, and low coefficients of thermal expansion. The decomposition temperatures are listed in Table I. We notice almost 0% weight loss up to 520°C (with the exception of a small amount of absorbed water); also, an improvement of approximately 120°C over the parent polymer (nylon 6,12). This prompted us to investigate the liquid crystalline properties of the systems. DSC analysis reveals an initial transition representing the glass transition temperature followed by a flat liquid crystalline region and finally the isotropic melting. This is backed up by an examination of the TMA of the same system which illustrates that the glass transition temperature results in a softening (compression of the polymer),

followed by a reasonably stable liquid crystalline region (no compression), and finally a severe compression (melting).

Nonlinear Optical Characterization

The representative DFWM data in terms of $\chi^{(3)}/\alpha$ are shown in Table I. DFWM measurements yielded initial strong phase conjugate signals, e.g., on the order of $\chi^{(3)}/\alpha = 1 \times 10^{-13}$ esu-cm, however, decay of the signals, presumably due to photochemical reactions, rendered determination of accurate values questionable. The active photochemical reactions likely involve oxygen but studies confirming or disproving this speculation remain to be completed. Also, investigation of the frequency dependence of optical nonlinearity and photodegradation needs to be completed before the dependence of $\chi^{(3)}/\alpha$ upon the length of the electroactive segment can be defined. The present studies do suggest that while attractive optical nonlinearities can be realized for the materials investigated, oxygen will likely have to be excluded for device development.

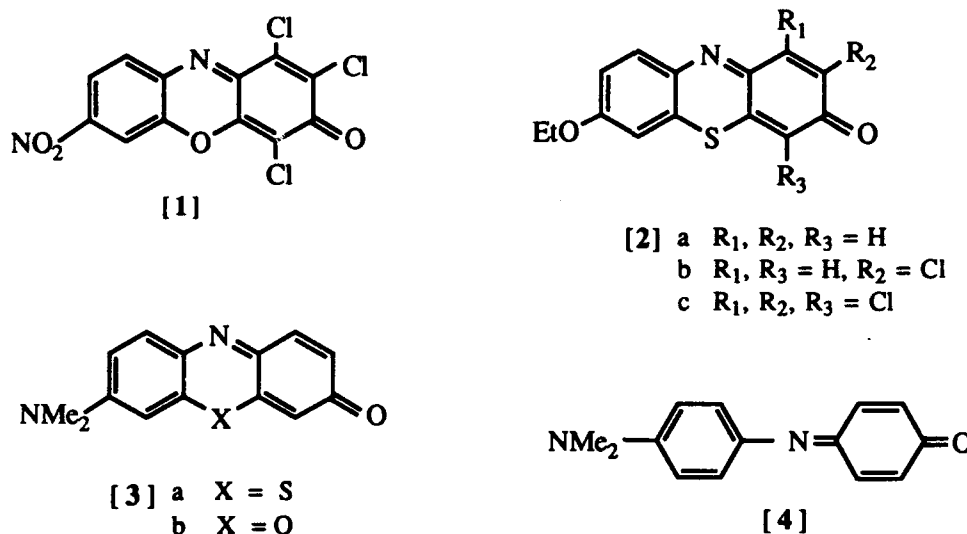
Improved Materials for Second Harmonic Generation

Recent literature activity in the study of the second order nonlinear optical (NLO) behavior of organic molecules has concentrated on either polyene- or azo-type dyes. Very large values of the second order hyperpolarizability, β , have been obtained, with the corresponding expectation of high second order NLO coefficients [$\chi^{(2)}$] for either electro-optic or second harmonic generation (SHG) applications. The successful exploitation of these high β values has, however, encountered several difficulties. In the case of thin-film electro-optic applications using doped polymers, problems such as relaxation of the molecular orientation are well known.⁸ For SHG applications, utilization of bulk organic crystals is the most common approach. Here, however, there are two fundamental problems which must be overcome before a useful crystal can be obtained. The first is to obtain a non-centrosymmetric crystalline structure; a necessary condition for second order NLO properties in crystalline solids.⁹ Unfortunately, approximately 70% of second-order NLO molecules are expected to crystallize in a centrosymmetric structure.¹⁰ The second restraint is that the crystal must be phase-matchable if useful intensities of the second harmonic are to be obtained.¹¹

Our approach to the problem of gaining an order of magnitude in second order effects, which will enable prototype device construction, is two pronged.

Firstly, as part of a continuing effort to develop and evaluate materials with useful NLO properties, we are studying a series of three-ring, dye-like aromatic compounds [cmps. 1-4], see Figure 4.

Figure 4. Schematic of the donor-acceptor compounds, series [1-4].



In addition, we are interested in improving on the traditional and historic azo dyes (i. e., disperse red 1, where the stable azo [N=N] linkage is used to bridge an electron donor/acceptor pair). Improvements can be made through elegantly increasing the charge asymmetry, namely by the substitution of better or more donor/acceptor groups as well as by increasing the conjugation distance between such groups. These points are well illustrated by our recent synthesis of compound [7], as detailed in reaction scheme 1.

The use of double nitro group substitution is expected to increase the β value by a factor of four, as seen in the work by the NLO group at Lockheed Palo Alto research laboratory¹², and the use of two diethylamino groups as the donor moiety is expected to increase β by approximately the same order of magnitude. An increase in length versus disperse red 1 is also expected to be reflected in an enhanced β value. At present, compound [7] is in the process of being fabricated, by spin coating, into a thin film, which will then be aligned by high voltage (10 kV) corona poling (see Figure 5 for experimental setup), enabling an accurate measurement of β , the second order microscopic nonlinear optical susceptibility (a schematic of our method of measurement is illustrated at Figure 6).

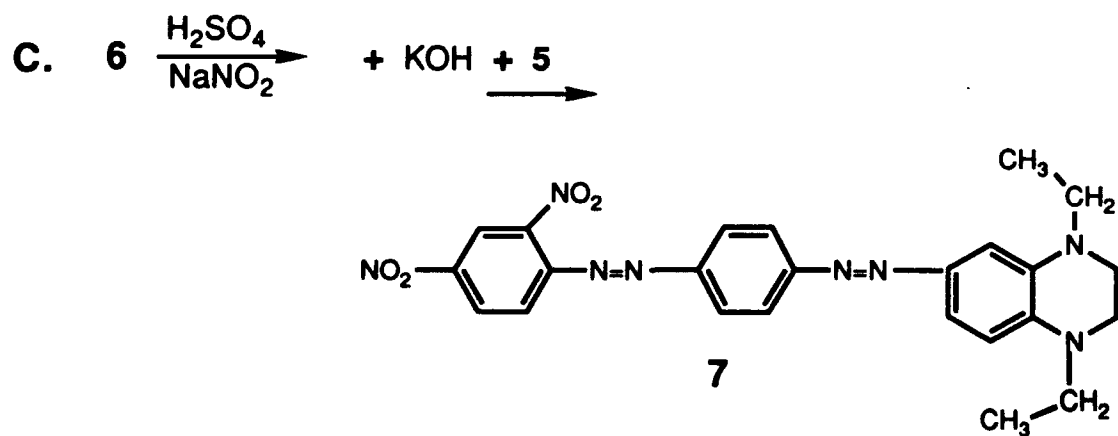
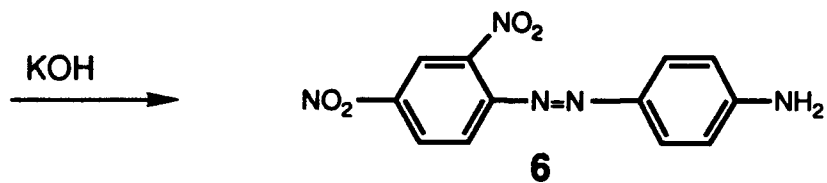
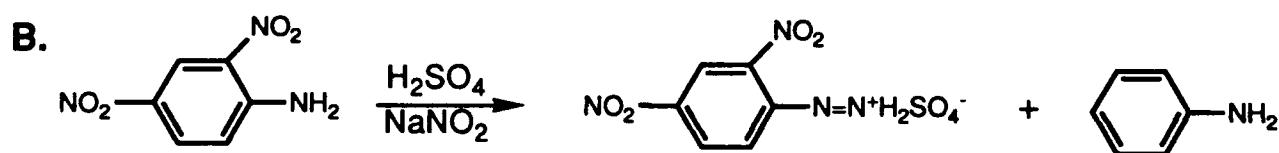
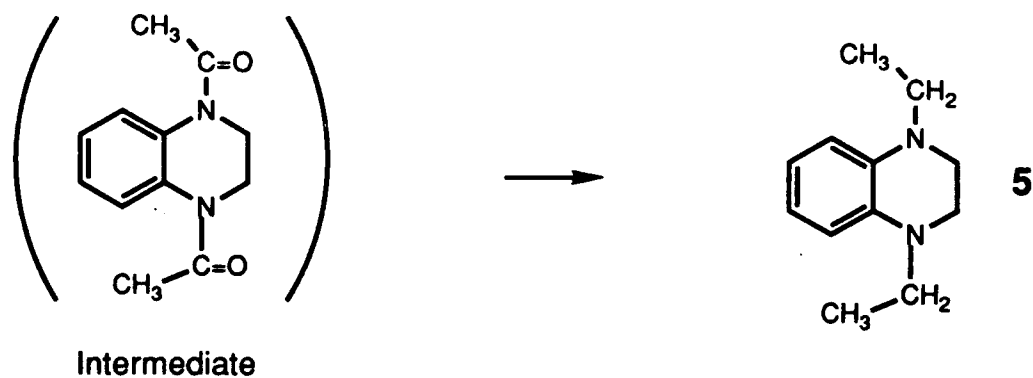
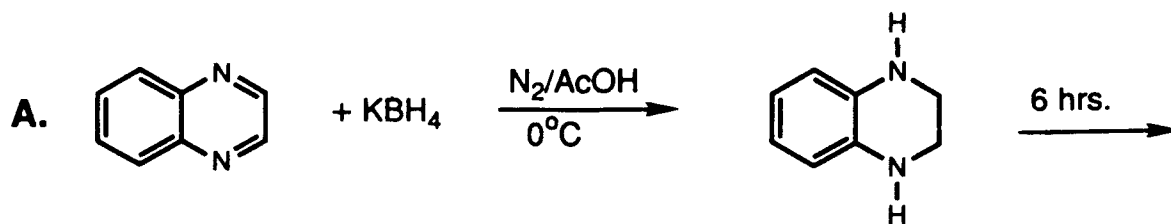
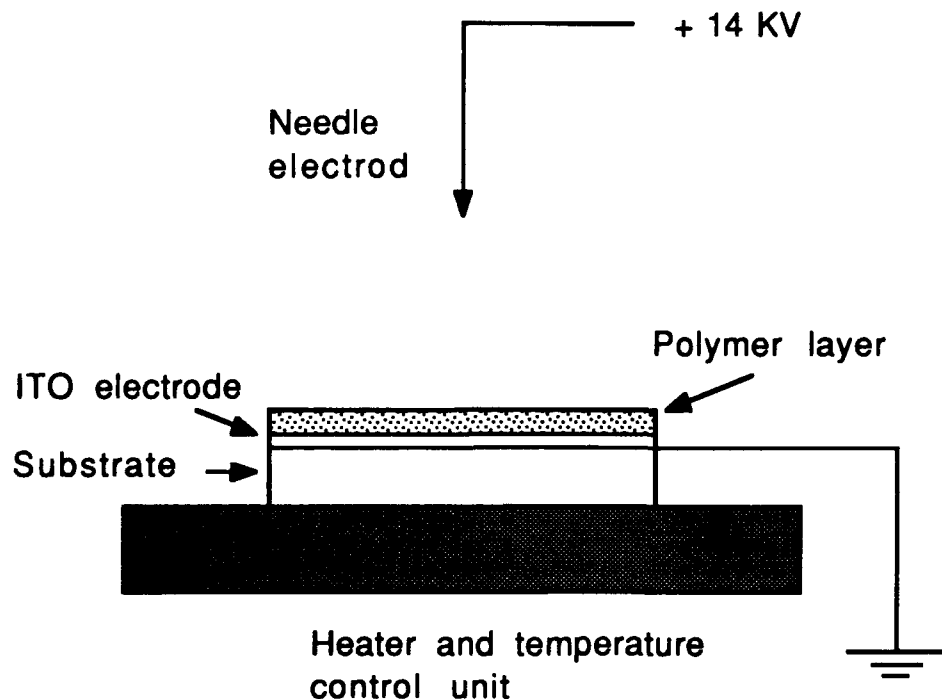


Figure. 5. Corona poling apparatus used in poling polymer thin films.

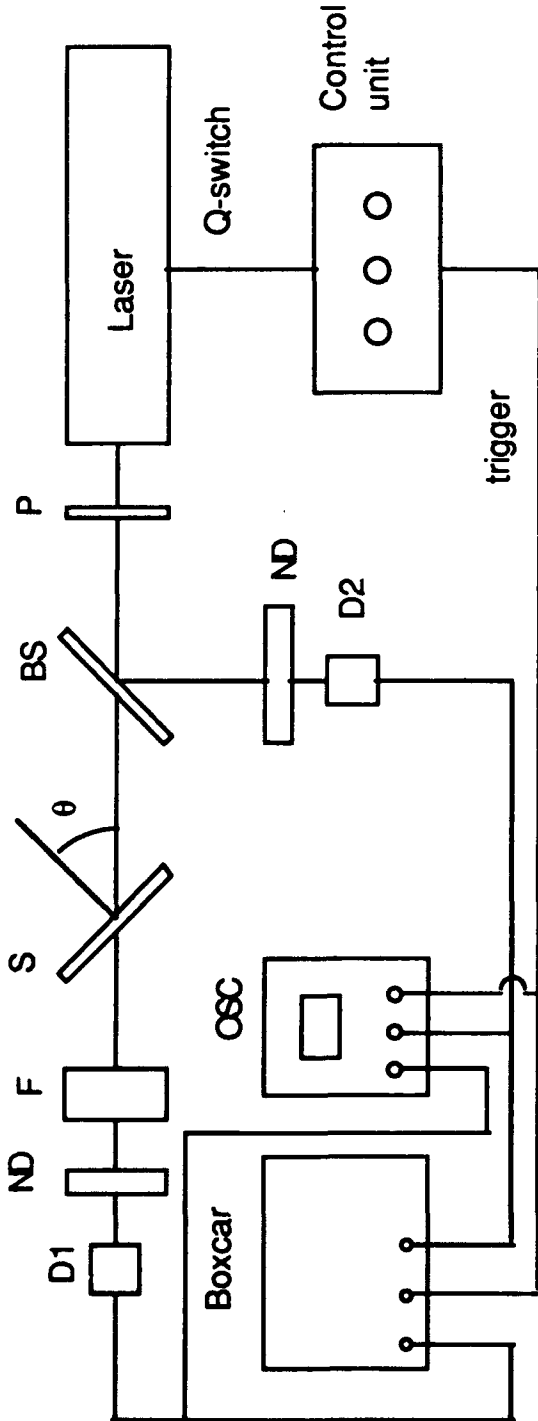


Our second approach to the problem is reflected by our recent publication, "A Photophysical and Structural Study on Dye-type Organic Molecules with Potentially Useful Nonlinear Optical Properties", in the *Journal of Physical Chemistry*, 94, 4386 (1990); this approach utilizes a broad based background knowledge in ladder polymer synthesis from our present and previous work in this field. Ladder polymers are tough, durable, high performance materials, largely due to their double strand or "ladder" backbone. This property can be emulated in three and five ring monomeric materials, which with the correct choice of substituents are potent candidates for thermally and atmospherically stable $\chi^{(2)}$ materials.

The rationale for investigating such systems arose from two considerations. The first concerned the stability of other dyes under investigation as NLO materials, there being some evidence that polyene based chromophores are susceptible to photo-decomposition. Yet another example of instability is the high- β merocyanine chromophore, which decomposes on prolonged exposure to the atmosphere.¹³ Precedent for enhanced durability of the heterocyclic molecules, [1] - [3], came from our own experience with ladder polymers such as polyquinoxaline (PQL), polyphenothiazine (PTL), and the benzimidazobenzophenanthroline ladder polymers BBL and BBB, which exhibit exceptional thermal and photostability.¹⁴

Illustrated below is the experimental setup for second harmonic generation measurements.

Figure 6. Schematic diagrams of SHG experimental setup. P-polarizer, BS-beam splitter, S-sample polymer film, F-fundamental wavelength filter, ND-neutral density filter, D1,D2-detectors, OSC-oscilloscope, Boxcar-boxcar integrator.



The second consideration concerned the attachment of the NLO active chromophores to polymer backbones. In order to obtain a useful material, the resulting functionalized polymer must have a high glass transition temperature, T_g . Experience in our own laboratories has shown that pendant functionalization of polymer backbones often leads to low T_g polymers.¹⁵ However, a dramatic increase in T_g was observed on attaching a two ring heterocycle similar in structure to [1], namely 4-chloro-7-nitrobenzofuran, onto a 25/75% styrene/p-aminostyrene copolymer backbone; the increase in T_g was on the order of 160°C, from 130°C (parent) to 290°C (quantitative substitution on p-aminostyrene).¹⁶ We expect the same order of increase for the series under investigation; this is a current area of research. In addition, the present series contains the same terminal group as merocyanine (carbonyl), which should enhance the β values.

Hence, three-ring monomers [2-5] were examined for their potential as $\chi^{(2)}$ materials. We initiated a photophysical and structural study of organic dye-type compounds containing various donor/acceptor groups and heteroatoms for use in nonlinear optical applications. Trends in the values of the second order hyperpolarizability coefficient, β , have been determined by the solvatochromatic method. Possible applications as organic crystals for second harmonic generation were explored with an X-ray diffraction structure analysis on one member of the series; 1,2,4-Trichloro-8-nitro-phenoxazin-3-one [1] crystallized in the space group $P2_1/n$ (monoclinic), with four molecules in the unit cell.

In addition, an X-ray diffraction crystallographic study of compound [1] is presented as definitive proof of structure and as part of our attempts to generate non-centrosymmetric crystals of the dyes for $\chi^{(2)}$ applications.

Initial measurement of the $\mu\beta_0$ value of [1] appeared promising, with a value comparable to 2-methyl-4-nitroaniline (MNA), but, more importantly, with minimal thermal or photochemical degradation (i. e., [1] has a melting/sublimation point of 249°C and exhibited no photochemical degradation during our measurements). This prompted us to perform an X-ray diffraction crystal structure on [1], to confirm the assigned structure and to investigate whether [1] crystallizes in a non-centrosymmetric form, essential for bulk $\chi^{(2)}$. The orange-red crystal (0.60 x 1.04 x 0.80 mm) used in the X-ray diffraction structural analysis was grown by vapor diffusion from a saturated solution of [1] in benzene utilizing hexane as a co-solvent. Data: space group $P2_1/n$; $a = 9.829(3)$, $b = 8.300(2)$, $c = 15.542(4)$ Å; $V = 1253.7(7)$ Å³; $Z = 4$. Final agreement factors are $R(F) = 0.0939$ and $R(wF) = 0.1091$. The unit cell consisted of four molecules of [1] and contained a crystallographic

center of symmetry. Compound [1] therefore crystallizes in a centrosymmetric space group, in this case $P2_1/n$, and is not expected to exhibit a bulk $\chi^{(2)}$.

Table I shows values of $\mu\beta_0$ obtained for two different series of molecules, [2a-c] and [3a, 3b and 4]. Note that although, strictly speaking, phenol blue [4] is out of place in the present series, we have included it as a reference for the effect of bridging atoms. The values were obtained using solvatochromism, a technique of limited accuracy. The aim here is to show trends in $\mu\beta_0$ for various substituents, rather than obtain accurate absolute values. We have, however, confirmed the usefulness of the solvatochromic method using a series of polyene based molecules for which β values have been measured using the standard electric field induced second harmonic generation (EFISH) technique.¹⁷ The largest uncertainty in the application of the solvatochromic method is in the value of the interaction radius of the solvent cage.¹⁸ Hence, we have compared polyene-based molecules with the same number of carbon-carbon double bonds linking the rings, but with different end groups. In this manner, we have reproduced the trends in β to within $\pm 30\%$. The interaction radii for the set of molecules in the present study should all be similar, and we therefore expect trends in $\mu\beta_0$ to be well reproduced. Inference of real $\mu\beta_0$ values from comparison with the reference set of polyene molecules is, however, more problematic. In the present study we have used the value of $\mu\beta_0$ for DANS as given by Spangler et. al., and estimated the ratio of the interaction radii to be approximately 1.4. Given these uncertainties, we expect the accuracy of the $\mu\beta_0$ values to be no better than $\pm 50\%$. We note, however, that initial studies of second harmonic generation in polymer films doped with these molecules generally confirm the magnitudes obtained from the solvatochromism. A more detailed study of the doped polymer layers was recently completed and submitted to Journal of the Optical Society, Part B.¹⁹

The effect of replacing hydrogen by a more electron withdrawing atom (chlorine) can be observed in Table II. As expected, when all three hydrogens are substituted the resulting $\mu\beta_0$ value is at its lowest within the series. This was of interest because altering substituents can introduce further asymmetry thereby altering the crystalline habit, possibly resulting in a non-centrosymmetric space group. The effect of halogen substituents on the value of β has been examined in a theoretical study by Cheng et. al.,²⁰ who also found that their effect on disubstituted benzenes was to generally lower β . The results obtained for the heterocyclics are not so straightforward, where we can see that the addition of a halogen to the 2-position can actually enhance β . Analysis of the spectroscopic components obtained from the solvatochromism shows this to be due to an increase in the transition dipole

moment. Substitution of three halogens, however, leads to a reduction in the transition dipole moment. Interestingly, compound [2b] gave the highest $\mu\beta_0$ value. The substitution of the stronger electron donating group, dimethylamino, for ethoxy resulted in an increase of $\mu\beta_0$ from 105 to 250×10^{-30} D-esu, illustrating the general trend of increasing values with stronger electron donating groups (Table II).

Table II: $\mu\beta_0$ and λ_{\max} values reflecting the effects of differing bridging and donor atoms.

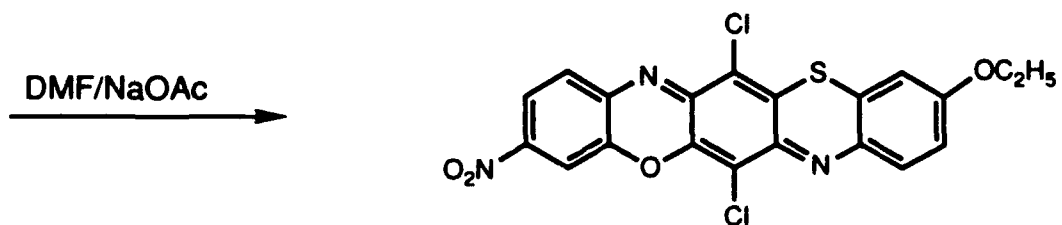
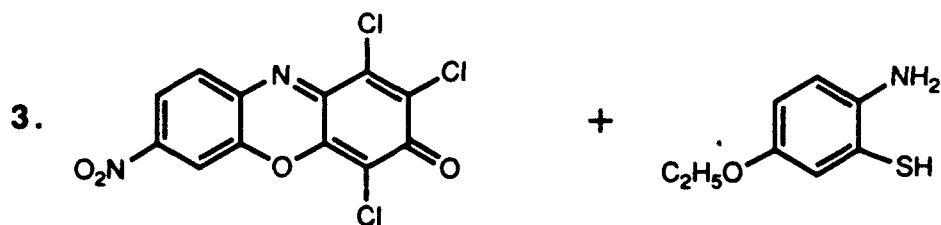
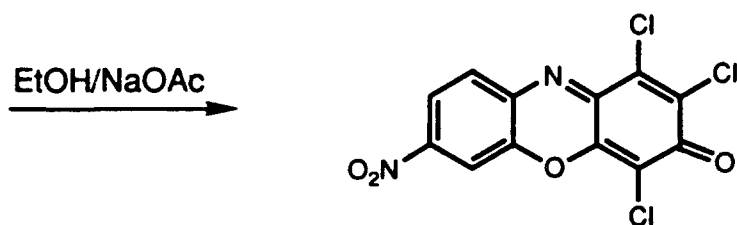
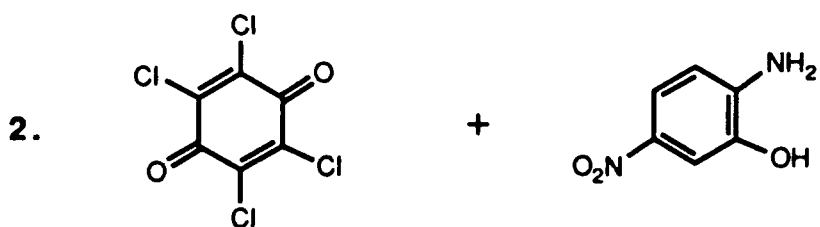
| Cpd. | Donor | X | Cl's | λ_{\max} (nm) | $\mu\beta_0$ ($\times 10^{-30}$ D-esu) |
|------|------------------|------|------|-----------------------|---|
| [2a] | EtO | S | 0 | 483 | 85 |
| [2b] | EtO | S | 1 | 496 | 105 |
| [2c] | EtO | S | 3 | 519 | 50 |
| [3a] | NMe ₂ | S | 0 | 533 | 250 |
| [3b] | NMe ₂ | O | 0 | 508 | 75 |
| [4] | NMe ₂ | none | 0 | 567 | 200 |

The proportional increase is similar to that observed for polyene-type molecules, hence again confirming the utility of the solvatochromatic method. A second trend is noted where the main difference in structure is the heteroatom, either sulfur or oxygen. The respective values for $\mu\beta_0$ are 250×10^{-30} D-esu for the sulfur compound [3a] and 75×10^{-30} D-esu for the oxygen compound [3b], therefore the choice of bridging heteroatom is very important in maximizing the β value, with the larger and more easily polarizable sulfur atom providing the larger number. Interestingly, the analogous open compound [4], i.e., no bridging atom, has a $\mu\beta_0$ value between the oxygen and sulfur bridged compounds.

The three-ring systems examined exhibited high $\mu\beta_0$ values, comparable to or better than MNA, but with improved thermal and photochemical stability. The increase in thermal stability is due in part to the high melting points of the three-ring series [1] - [3] which range from 190°C [3a] to 249°C [1]. Compound [1]

crystallizes in a centrosymmetric space group, and is therefore unsuitable as a crystalline bulk $\chi^{(2)}$ material. However, as a group, the β values were impressive enough to encourage us to press on with the expanding the backbone to a fused five-ring system, entailing the design and synthesis of asymmetrically substituted five-ring systems. The first such system has been recently synthesized according to reaction scheme 2. At present the reaction is being scaled up to provide enough of [8] for full characterization and for fabrication of the thin films necessary for β measurements. An illustration of the expected enhancement over the three-ring compounds is the shifting of the maximum absorbance, λ_{max} , by approximately 100 nm, from 490 nm for the corresponding three-ring nitro compound to 579 nm for the five ring compound [8]. Studies including attachment of similar three-ring compounds as pendant groups on a polymer backbone, and the utilization of stronger electron donor and/or acceptor groups are anticipated.

Reaction Scheme 2: Synthesis of a donor/acceptor couple, asymmetrically substituted five-ring compound



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