Development of materials with enhanced optical non-linearity by control of ultrastructure

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Copolymers incorporating rigid electroactive moieties and flexible segments have been synthesized in an effort to develop non-linear optical materials which can be processed into optical quality films. A variety of coupling linkages have been employed including ether, ester, amide, imine and azo linkages. Among the most attractive materials examined in this survey are heteroaromatic ladder and tetraazaannulene copolymers which yield optical non-linearities (ratioed to optical loss), $\chi^{(3)}/\alpha$, of 10^{-12}–10^{-13} esu cm^{-1} and have desirable auxiliary properties of high laser damage threshold and fast optical switching (5 ps for three-ring copolymer). Electron donating and withdrawing groups are conveniently incorporated and these have been observed to influence optical non-linearity. The copolymer approach yields linear optical spectra characterized by sharp band edges thus optimizing the window of transparency. Finally, it is noted that this approach yields excellent control of solubility and solution viscosity necessary for spin casting in the fabrication of thin films of uniform thickness.

(Keywords: copolymers; electroactive moieties; coupling linkages; non-linear optical materials)

INTRODUCTION

A number of factors have been observed to influence optical non-linearity for π-electron polymers including π-electron correlation length and electron density distribution[1–5]. The former is controlled by the length of the electroactive unit when end group effects dominate, by the conformation of the electroactive segment, or by intrinsic intramolecular interactions such as electron phonon and electron coulomb interactions. Electron density distribution, including the asymmetry of the distribution, can be dramatically influenced by the presence and positioning of electron donating and/or withdrawing substituents. Optical non-linearity has also been observed to be dependent upon the redox state of π-electron polymers capable of supporting bond phase alternation (polaron, bipolaron) defects[1,6]. The preceding structure–function relationships, which are now verified at least in a general sense by both experiment and theory, provide a useful guide for the synthetic chemist in the development of new materials.

However, large optical non-linearity is a necessary but not sufficient criterion for a practically useful non-linear optical material. For device application, the materials must also typically exhibit good optical transparency, fast optical switching, high resistance to photochemical degradation, low dielectric loss, and be capable of being processed into optical quality films exhibiting excellent long term stability. This final criterion is not easily met as optical quality often requires uniform film thickness and very low levels of contamination (for example, by dust particles). For polymer film fabrication, the requirement of uniform thickness often necessitates the use of spin casting (or coating) techniques which in turn places severe requirements upon polymer solubility and solution viscosity properties. Processing requirements have provided a strong motivation for the development of copolymers containing electroactive units and flexible segments which impart control of solubility and solution viscosity. Another advantage of the copolymer synthesis approach to electroactive materials, is that the solubility of these materials permits a high resolution characterization of structure by techniques such as high resolution n.m.r. spectroscopy. Moreover, this approach permits a rapid survey of a variety of electroactive structures under comparable lattice (local field) conditions.

Our original work in this area involved synthesis of copolymers containing alternating alkoxy ($OC_5H_{10}O$) and triphenodioxazine ladder units[7]. As part of this work, copolymers of substituted aniline oligomers with alkoxy units were investigated as precursors and alternative structures to the fully fused ring ladder structure. As expected, the fully fused ring material exhibited a greater third-order susceptibility than its open chain precursor due to the improved π-orbital overlap in the

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planar material. A significant third-order susceptibility (4.5×10^{-9} esu at 585 nm) was observed which is impressive when the diluting effect of the alkoxy unit is taken into account. A more interesting number for those contemplating device development is the ratio of third-order susceptibility to optical loss. For the copolymers containing planar electroactive structures $\chi^{(3)}/\alpha$ values of 5×10^{-13} esu cm^{-1} or greater were observed in the visible and near i.r. regions. These materials were also characterized by reasonably high laser damage thresholds (e.g. >5 GW cm^{-2} for 20 ps pulses).

A variety of other electroactive units have been incorporated with alkoxy units into processible polymers. The incorporation of carbocyanine dyes[8] permitted the preparation of thin films which yielded an optical non-linearity of $\chi^{(3)} = 10^{-9}$–10^{-10} esu at 532 nm. While an attractive $\chi^{(3)}/\alpha = 9 \times 10^{-13}$ esu cm^{-1} is initially measured, these polymers exhibit rapid photodegradation as is evident from the appearance of a permanent grating. An analogous reaction has been used to incorporate squarylium units into copolymer materials involving an ether linkage coupling of the electroactive and flexible chain segments. Other electroactive materials such as derivatized acridine and stilbene moieties have been incorporated with alkoxy segments via an imine linkage. Unfortunately, these copolymers have failed to exhibit adequate optical non-linearity and/or photochemical stability[8,9].

In this paper, we discuss the extension of early work on polyethers to the development of copolymers based on polyamides and poly(*p*-hydroxystyrene). Focus will be upon incorporation of ladder and heteroaromatic rings into processible polymer materials. The planar conformation of these materials is optimum for π-orbital overlap and the only conformational effects that can result in reduction of optical non-linearity are distortions which maximize bond length alternation. A companion paper focuses upon the incorporation of phenylpolyene and thienylpolyene electroactive units into a variety of copolymer materials[10].

The present discussion is also limited to third-order materials. Similar studies on second-order materials are presented elsewhere[11,12].

EXPERIMENTAL

General methods

Fourier transform infra-red (*FT*i.r.) spectra were taken as pressed KBr pellets, free standing polymer films or polymer films on a sodium chloride disc using a Perkin-Elmer model 1760 *FT*i.r. spectrometer. U.v.–vis. spectra were obtained on a Perkin-Elmer model lambda 4C u.v.–vis. spectrophotometer. N.m.r. spectra were recorded on either a Jeol FX-90 Q *FT*n.m.r. or on a Bruker AC-250 MHz *FT*n.m.r. spectrometer. Thermal analyses were performed using Perkin-Elmer DSC-7 and TGA-7 systems.

Third-order non-linear optical susceptibilities were measured by degenerate four wave mixing (DFWM) as described previously[13]. All pulses are derived from a Quantel model YG471-C Nd:YAG laser and are either frequency doubled (to 532 nm) to yield 20–25 ps pulses having energy of ~2 mJ or used to pump dye lasers permitting measurements at selected frequencies in the range 578–700 nm. As discussed elsewhere, our modification of the DFWM experiment permits discrimination of electronic, thermal and acoustic contributions to optical non-linearity[1]. In the work discussed in this paper, we focus upon the electronic component which will in general exhibit some resonance enhancement.

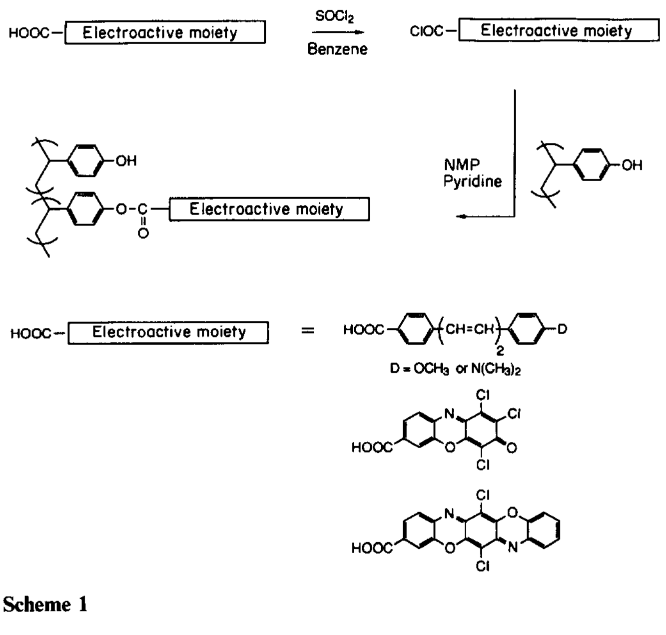
Syntheses

Pendant moieties on poly(p-hydroxystyrene). Scheme 1 illustrates the general procedure for the incorporation of phenylpolyene, three-ring and five-ring electroactive molecules as pendants to a modified polystyrene backbone. The reaction of the functionalized electroactive moiety with poly(*p*-hydroxystyrene) is facilitated in *N*-methylpyrrolidinone (NMP) in the presence of pyridine.

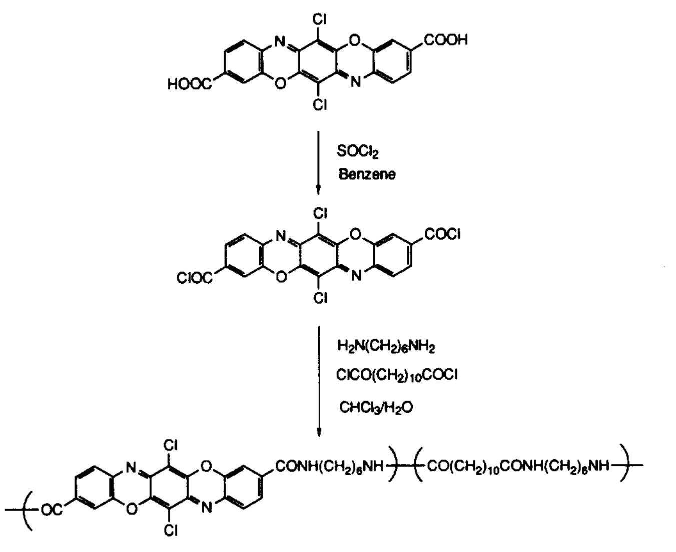
For example a 25% incorporation of the five-ring compound on poly(*p*-hydroxystyrene) was achieved by dissolving the five-ring monoacid chloride compound (0.60 g, 1.4×10^{-4} mol) in NMP (15 ml) and after filtration to remove any solid impurities this solution was added to a solution of poly(*p*-hydroxystyrene) (0.0673 g, 5.6×10^{-4} mol) dissolved in NMP (2 ml) containing pyridine (~0.1 ml). After stirring overnight the solution was poured into methanol in a separating funnel and the finely divided polymer allowed to settle. After filtration the polymer was stirred overnight in water to effectively remove all NMP, filtered again and dried. The yield for this process is essentially quantitative.

Ladder copolyamides. The copolyamides in *Scheme 2* were synthesized by the interfacial polymerization technique by reacting a combination of the five-ring ladder diacid chloride and an aliphatic diacid chloride in chloroform with hexamethylene diamine in an aqueous phase.

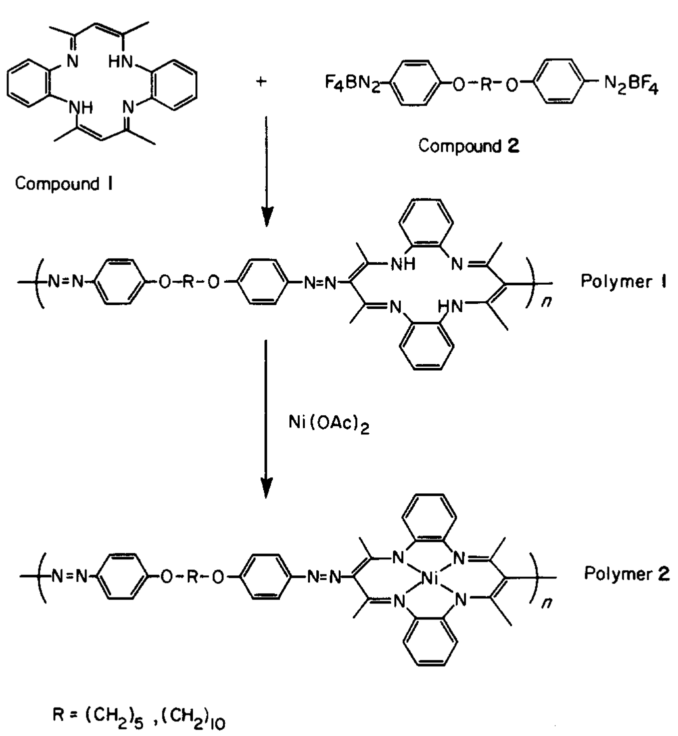
For example, the 10% incorporated five-ring ladder copolymer was prepared by first dissolving the five-ring diacid chloride (0.048 g, 1.00×10^{-4} mol) in chloroform (50 ml) followed by the addition of dodecandioyl dichloride (0.24 g, 9.00×10^{-4} mol). To this vigorously stirred solution was added a solution of hexamethylene diamine (0.08 g, 1.00×10^{-3} mol) in water (50 ml) containing ~0.20 g of sodium hydroxide. The polymer



Scheme 1



Scheme 2



Scheme 3

precipitated at once and the polymer suspension was stirred for an additional 12 h. The aqueous layer was carefully decanted and the polymer collected on a fine fritted glass funnel, washed with ~100 ml of water and finally with acetone. The dried polymer weighed 0.29 g (71%).

Tetraazaannulene copolymers. *Schemes 3* and *4* show the successful incorporation of the tetraazaannulene moiety into copolymers.

In *Scheme 3*, polymers **1** and **2** were synthesized according to the following procedures. Compound **2** (0.97 g, 2.0 mmol) dissolved in acetonitrile (15 ml) was added to a stirring warm solution (50°C) of compound **1** (0.69 g, 2.0 mmol) in acetonitrile (150 ml) and then triethylamine (4 ml) was slowly added to the reaction mixture. The mixture was stirred at 50°C for 2 h, the resulting polymer precipitate was collected by filtration and washed with acetonitrile. The polymer was further purified by extraction in a Soxhlet extractor with acetonitrile and then with acetone and dried under vacuum overnight to yield polymer **1** (0.82 g, 63%).

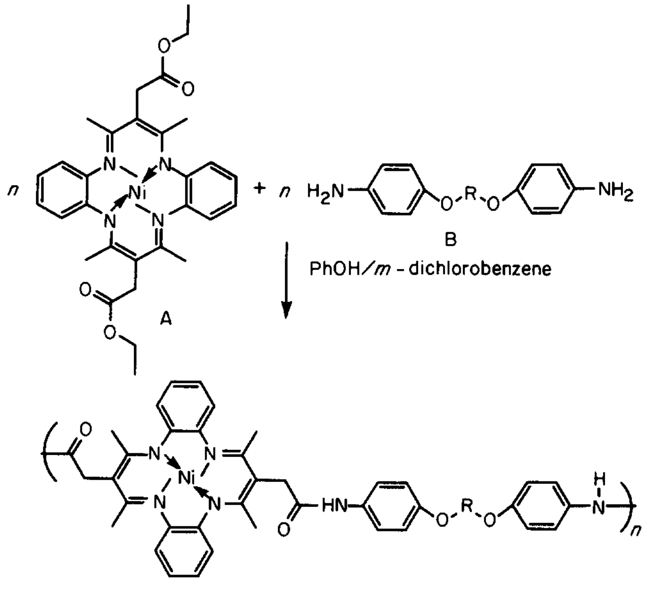
To 1,1,2,2-tetrachloroethane solution (10 ml) containing nickel(II) acetate tetrahydrate (0.10 g) was added polymer **1** (0.20 g). After refluxing for 2 h, the mixture was poured into methanol (20 ml). A dark green polymer precipitate was collected by filtration and washed with methanol. The excess of unreacted nickel(II) salt was removed by extracting the polymer in a Soxhlet extractor with methanol. Polymer **2** was then vacuum dried; the yield was almost quantitative.

In *Scheme 4*, compounds A (1.000 g, 1.20 mmol) and B (0.425 g, 1.20 mmol) were mixed with phenol (5 ml) and *m*-dichlorobenzene (5 ml). The resulting mixture was heated to 140°C for 2 h and then 270°C for 30 min to distill out the solvent. The product obtained was digested with acetone and extracted with ethanol in a Soxhlet extractor.

RESULTS AND DISCUSSION

Structural characterizations

The preliminary characterizations of the copolymeric materials in *Schemes 1* and *2* are presented in the i.r. and u.v.-vis. spectra shown in *Figures 1-3*. As is evident from *Figures 1* and *3*, the optical spectra of the poly(*p*-hydroxystyrene) with pendant electroactive moieties and the five-ring copolyamides are essentially identical to the dilute solution spectra of the dye molecule, i.e. no significant broadening of the $\pi-\pi^*$ band edge is observed. I.r. spectroscopy was used to monitor the formation of the amide linkage in the five-ring copolyamides by observing the shift of the carbonyl band (*Figure 2*). The formation of the ester linkage of the pendant electroactive moieties on poly(*p*-hydroxystyrene) was also monitored (e.g. for the five-ring monoacid chloride $\nu_{C=O} = 1756\ \mathrm{cm}^{-1}$ and for the corresponding pendant polymer $\nu_{C=O} = 1728\ \mathrm{cm}^{-1}$). A more complete characterization of these materials is presented elsewhere[14,15].



Scheme 4

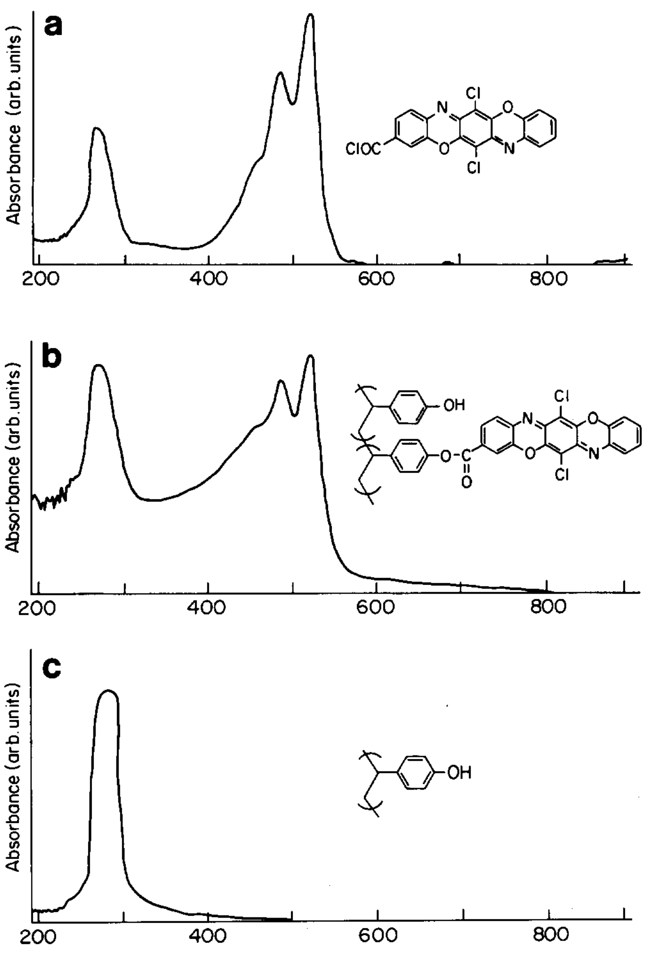


Figure 1 This figure illustrates that optical spectra can be used to follow the incorporation of the five-ring triphenodioxazine molecule as a pendant to the modified polystyrene backbone. (a) Solution spectrum of the monomer, (b) optical spectrum of the incorporated pendant polymer and (c) spectrum of poly(*p*-hydroxystyrene). Note that the copolymer may show evidence of an exciton interaction which is not unexpected for this ultrastructure

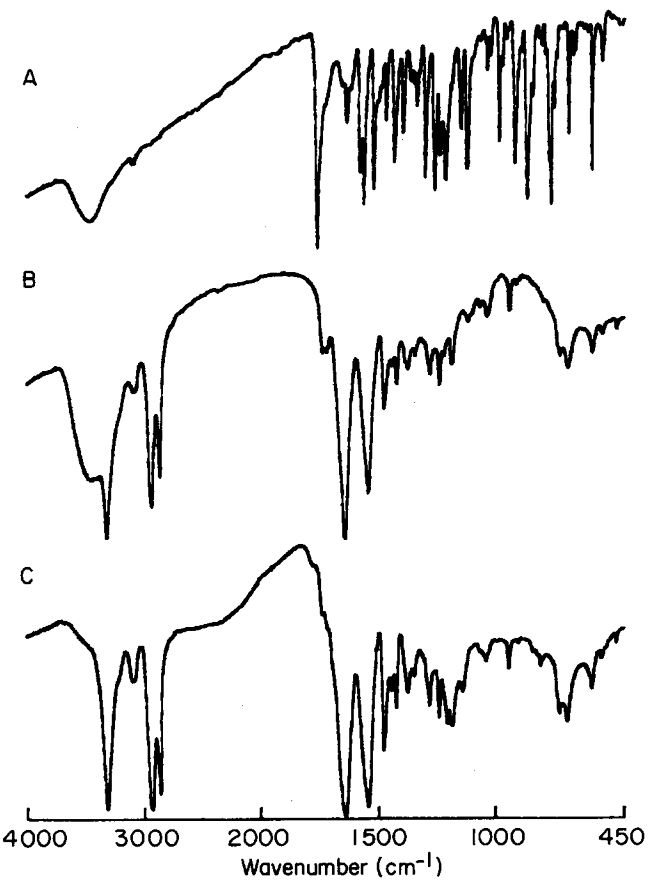


Figure 2 *FT*i.r. spectra of (A) the five-ring diacid chloride, (B) the five-ring copolyamide (20% incorporation) and (C) nylon 6-12 (0% incorporation). The formation of the amide linkage of the copolymer is monitored by the shift of the carbonyl stretch of the five-ring moiety (from 1759 to 1640 cm^{-1})

^{1}H n.m.r. assignments for the tetraazaannulene copolymer of *Scheme 3* are as follows (referenced to $CDCl_3$): polymer **1**, ^{1}H n.m.r. δ ppm: 1.60–1.86 (m, $-CH_2-$), 2.12 (s, $-CH_3$), 2.19 (d, $-CH_3$), 4.00 (broad, $-OCH_2-$), 6.85–7.60 (m, aromatic), 10.91 (s, NH in imine), 14.26 (s, NH in hydrazone); polymer **2**, ^{1}H n.m.r. δ ppm: 1.55–1.86 (m, CH_2), 2.09 (s, CH_3), 4.04 (broad, $-OCH_2$), 6.73–7.55 (m, aromatic).

^{1}H n.m.r. assignments for the tetraazaannulene copolymer of *Scheme 4* are as follows (referenced to $CDCl_3$): 1.3 (s, $-(CH_2)_3-$); 17 (s, $-O-CH-CH_2-$); 2.0 (s, $-CH_3$); 3.7 (s, $-O-CH_2-$), 6.5–6.8 ppm (multiple, aromatic).

Figure 4 compares the optical spectra of the monomers and copolymers synthesized according to *Schemes 3* and *4*.

Non-linear optical characterization

Very large phase conjugate signals are observed for both the three- and five-ring ladder materials at 532 nm; however, optical loss makes investigation and application of the five-member ring ladder unfavourable at this frequency. In the near i.r., a third-order susceptibility of ~5 × 10^{-11} esu is realized for the five-ring ladder

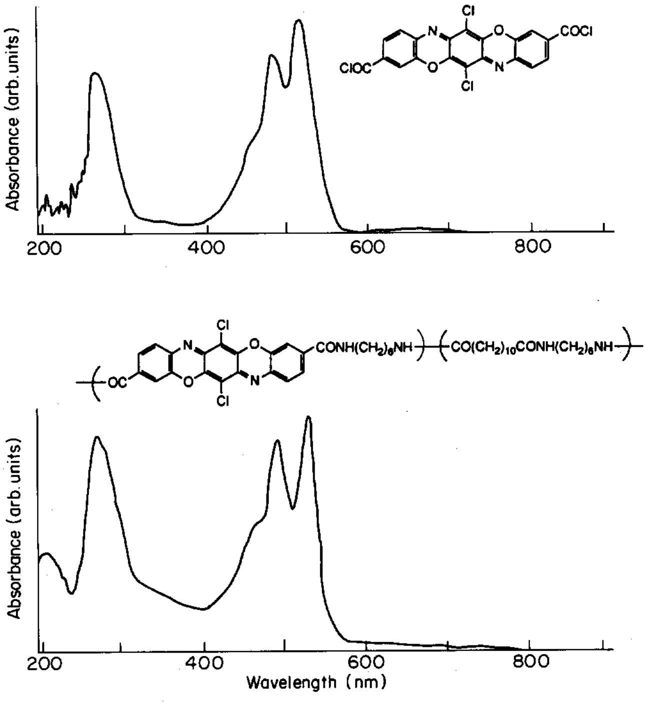


Figure 3 Optical spectrum of the copolymer involving incorporation of the triphenodioxazine moiety into the copolymer backbone via an amide linkage (*Scheme 2*). The sharpness of the band edges is noted

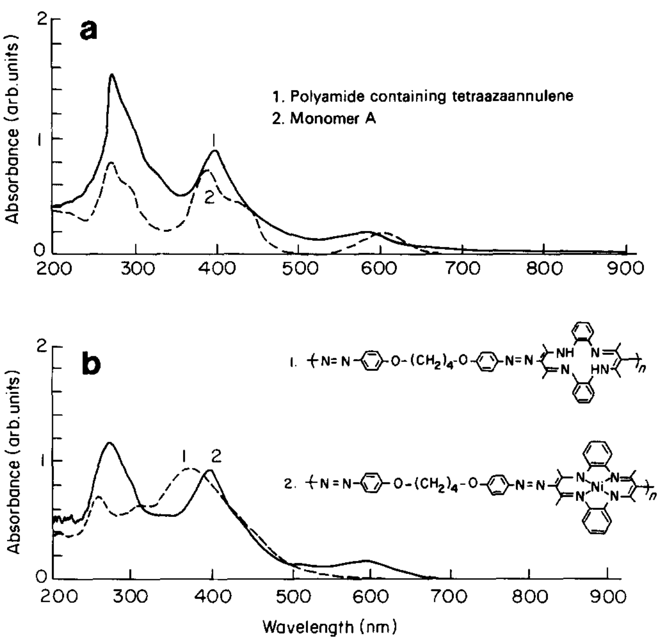


Figure 4 (a) Optical spectrum comparing the nickel free tetraazaannulene copolymer and nickel incorporated copolymer of *Scheme 3*. (b) Optical spectrum comparing the copolymer synthesized in *Scheme 4* with the spectrum of a tetrazaannulene monomer

copolymer involving amide termination of the electroactive moiety. This value likely represents the non-resonant electronic optical non-linearity (based upon the frequency dependence of the optical non-linearity and upon comparison with data obtained for similar structures). This material is not expected to exhibit as great an optical non-linearity as structures containing significant concentrations of polarons/bipolarons. For example, non-resonant third-order susceptibilities on the order of 5×10^{-9} esu have been reported for derivatized ladder materials which have been oxidized or reduced[6]. It is very likely that optical non-linearity can be systematically enhanced by appropriate derivatization of the electroactive unit. It should also be kept in mind, that the measured value was obtained for a copolymer containing ~10% electroactive material. Thus, the third-order susceptibility of the fundamental five-ring ladder unit is likely on the order of 5×10^{-10} esu and greater non-linearity of fabricated films may be realized by incorporation of a greater fraction of electroactive unit into the copolymer. This may in turn become feasible by improving solubility through further derivatization of the electroactive moiety.

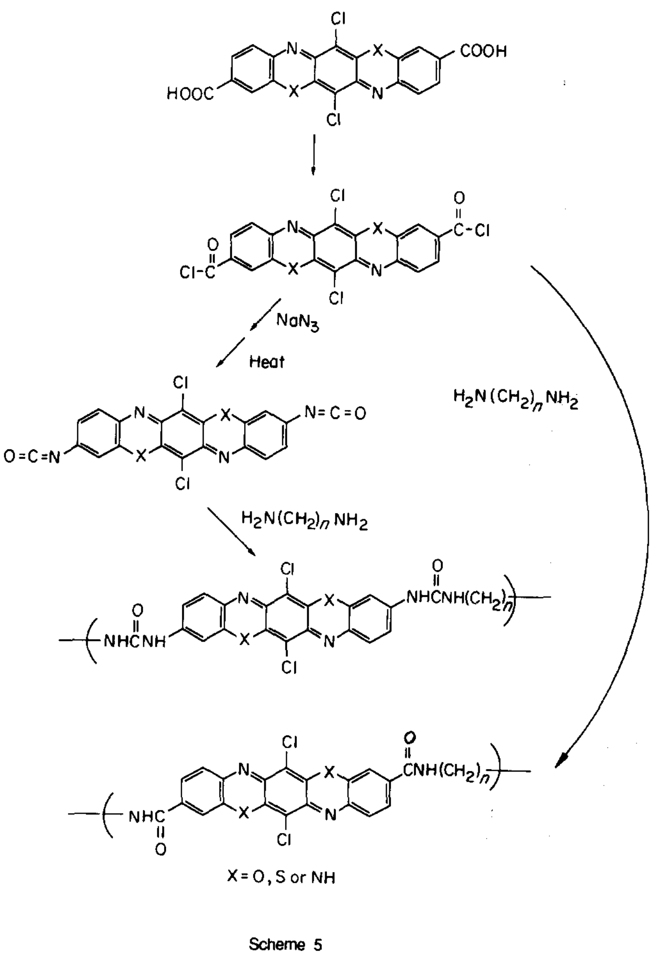
Similar magnitudes of optical non-linearity are observed for the tetraazaannulene copolymer systems. However, it should be noted that these materials have an absorption above 532 nm, namely, centred at ~590 nm. Thus, measurements are conveniently made at 532 nm. For tetraazaannulene nickel complexes derivatized with substituents on the phenyl rings, it was noted that optical non-linearity ($\chi^{(3)}/\alpha$) increases from 1.2×10^{-13} to 2.6×10^{-13} to 4.0×10^{-13} esu cm^{-1} for CH_3, H and Cl substituents, respectively. These measurements were carried out on composite polymer (with polycarbonate) containing ~10% electroactive material. Thus, the intrinsic optical non-linearity of the electroactive unit is approximately an order of magnitude larger than the above values.

While the observed optical non-linearities are sufficiently large to be interesting, the important point is that the copolymer approach has permitted the realization of sufficient polymer solubility and appropriate solution viscosity to permit the fabrication of optical quality films. The ease with which copolymer synthesis and derivatization is accomplished for the tetraazaannulenes is particularly noteworthy as these materials yield optical non-linearities comparable to that obtained for larger ring systems such as the phthalocyanines which are considerably more difficult to synthesize and process.

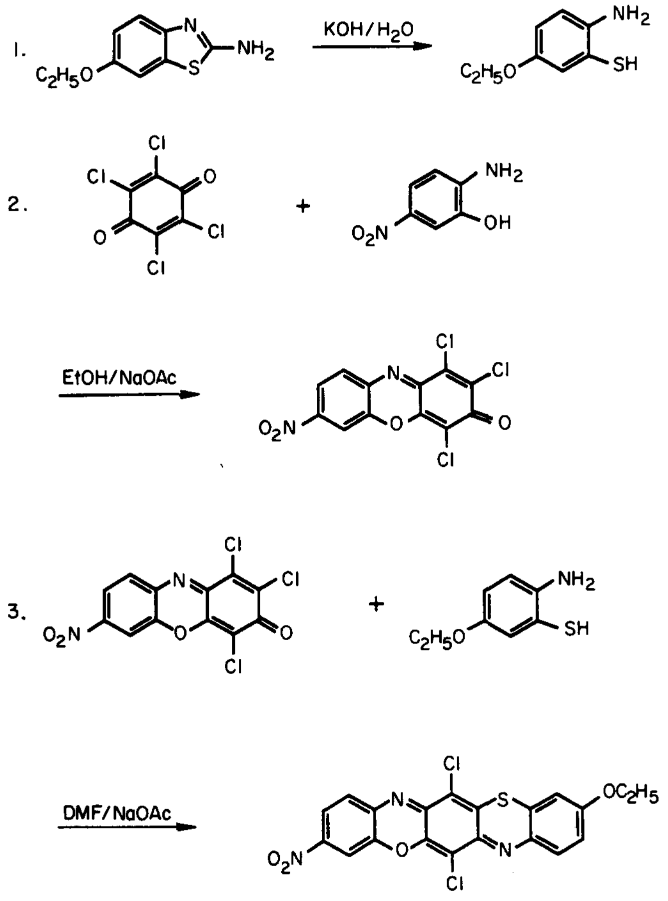
CONCLUSIONS

The advantages of the copolymer synthesis approach can be summarized as follows:

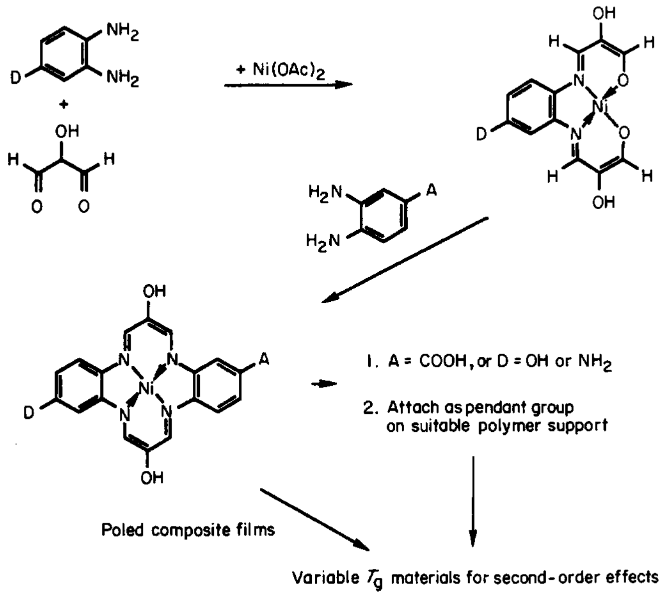
1. Excellent control of processibility is realized and techniques such as spin casting can be employed to prepare optical quality films of controlled thickness.
2. Electron donating and withdrawing substituents are incorporated in a natural way and precisely defined structures are realized.
3. This approach is amenable to a rapid survey of different classes of electroactive units under comparable conditions. Dilution studies can be effected without the complication of molecular motion encountered with liquids.
4. Sharp band edges are realized due to precisely controlled electron confinement. This enhances the region of transparency.



Scheme 5



Scheme 6



Scheme 7

5. Due to self-localization phenomena operative for longer electroactive unit lengths, little or no optical non-linearity is lost by this approach other than due to the normal dilution effect.
6. A better correspondence to traditional polymer chemistry is realized and advantage can be taken of the wealth of data accumulated for traditional polymers.

When correlated with data obtained for other electroactive units incorporated into copolymer materials, the data for multiple ring ladders and tetraazaannulenes demonstrate these to be among the most promising non-linear optical materials exhibiting reasonably large non-linearities, high laser damage thresholds, reasonable transparency and fast optical switching times (5 ps for three-ring pendant polymer)[16].

Further studies include completion of the investigation of the effect of substituents and of the dependence of optical non-linearity upon the length of ladder structures. As shown in *Scheme 5*, depending upon which path is followed, the electroactive unit is terminated either with electron withdrawing or donating groups. Moreover, by appropriate modification of this scheme, an electron donating group is placed at one end of the electroactive unit and a withdrawing unit is placed at the other end. Of particular importance are asymmetric derivatization which will likely yield second-order non-linear optical materials, e.g. see *Schemes 6* and *7*.

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