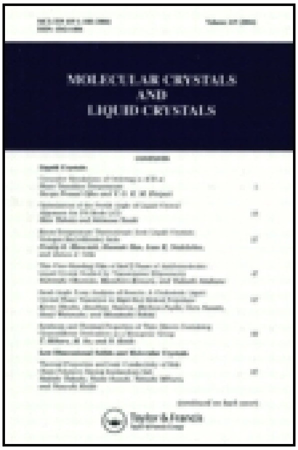

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Development of Materials with Enhanced Optical Nonlinearity: Theory and Practice

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Development of Materials with Enhanced Optical Nonlinearity: Theory and Practice

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Synthetic schemes have been developed for systematically incorporating electroactive π-electron polymer segments together with saturated alkoxy segments into copolymers which exhibit sufficient solubility in common solvents to facilitate characterization and to permit processing of these copolymers into optical quality films. This approach has permitted a rapid survey of the optical nonlinearity of a variety of electroactive structures ranging from phenylpolyenes to ladder-type oligomers. Studies on materials prepared by copolymer synthesis have been correlated with studies of materials with electroactive units incorporated as pendant groups to non-active polymer backbones and with studies of materials where electroactive molecules are incorporated as dopants into non-active polymers to form composite materials. Incorporation of electroactive oligomeric units into polymer systems affords significant advantages in terms of processing and can be adapted to the study of structure/function relationships including the dependence of optical nonlinearity upon the extent of electron delocalization, the effects of electron donating or withdrawing substituents, chemical doping, etc.

I. INTRODUCTION

Considerable interest has been focused upon π-electrons polymers as materials exhibiting potentially useful optical nonlinearity.[1–5] The past two years have witnessed significant progress both in theoretical computation[2–4,6–12] of optical nonlinearity for systems exhibiting π-electron delocalization/quantum confinement and in the experimental investigation of the dependence of optical nonlinearity upon electron delocalization,[10] substituent effects, and resonance/non-resonance contributions[13,14] to optical nonlinearity. Values of third order susceptibility on the order of 10^{-8} esu have been observed near the π-π* bandedge for a number of materials.[4,5,13–15] These values are approximately two to four orders of magnitude greater than the purely non-resonant optical nonlinearities for the materials. Given that the large resonance-enhanced values are characterized by picosecond response or switching times, they are worthy of further consideration for device development. This is particularly the case for materials which exhibit high laser damage thresholds.

On the other hand, reports of measurements in conflict with theory have appeared including suggestions that optical nonlinearity is not correlated with electron delocalization length[15] or that optical nonlinearity does not increase with increasing polaron/bipolaron concentration upon chemical or electrochemical doping.[2–4]

However, care must be exercised in viewing controversial reports at this time due to the extremely limited data sets available. The studies of Barbara and coworkers[15] on polyacene quinones involve molecules with quite different substituents as well a different electron delocalization lengths so it is not clear what are the relative contributions of various effects. In the same sense, comparison of optical nonlinearity of doped and pristine polymer films is suspect unless the frequency dependence of the optical nonlinearity has been carefully studied. For example, we have observed optical nonlinearity to increase with doping for several systems, but these isolated measurement hardly establish trends. These comments do not say that the above measurements are not of value. At this point in time any measurement is important in providing a data resource from which conclusions about structure/function relationships can ultimately be deduced; however, patience must be exercised in forming conclusions about structure/function relationships until adequate data sets are available.

It is also important to address several misconceptions regarding the comparison of organic and inorganic nonlinear optical materials. The first is the assertion that the magnitude of optical nonlinearity in organic materials is always small to moderate and the response time for this nonlinearity is fast. Materials with long-lived states involved in the excitation/relaxation cycle can exhibit large third order susceptibilities characterized by slow response times. For example, Tompkin *et al.*[16] have observed acridine orange and acridine yellow dyes dissolved in lead-tin fluorophosphate glass to exhibit third order susceptibilities on the order of 0.1 esu characterized by response times of approximately 1 msec. As might be expected, this observation is lattice-dependent consistent with the dependence of triplet state lifetimes on lattice. This observation suggests the importance of considering lattice in discussing optical nonlinearity. This is particularly important when the lattice is being significantly modified by a process such as chemical doping. For example, some of our doping studies suggest that counter-ion size may influence hyperpolarizability in chemically and electrochemically doped systems. A second misconception is that organic materials are inherently processible. The π-electron delocalization which gives rise to optical nonlinearity also leads to strong interchain Van der Waals interactions which in turn reduce solubility and processibility. Thus, a substantial amount of research activity has focused upon development of soluble electroactive polymers or precursors to such polymers which can be processed into optical quality films for evaluation of optical nonlinearity. However, even with improved solubility certain problems remain with investigation of homopolymer systems. One of the most serious is the existence of low molecular weight oligomers in the final polymer film. The length of these materials may be sufficiently short as to limit electron delocalization and thus influence the optical gap. These segments can result in a diffuse bandedge and can obscure the relationship between observed hyperpolarizability and electron delocalization length (ideally, this would be the intrinsic electron correlation length in a perfect π-electron polymer of infinite length).

In order to gain more control over definition and variation of polymer lattices, polymer solubility and processibility, control of polymer molecular weight distributions, and control of the length of electroactive segments, as well as to permit a more systematic investigation of the effect of length of the electroactive segment and of substituent effects, we have undertaken the systematic investigation of copolymers of electroactive and non-active polymer systems. Electroactive materials were incorporated both as alternating segments in the polymer backbone and as pendants to a non-active polymer backbone. The relative lengths and placement of active and non-active segments are adjusted to vary polymer solubility as well as to influence electroactivity. Composites of these materials with various host polymers were investigated to further study the effect of lattice upon optical nonlinearity.

II. EXPERIMENTAL

Third order susceptibilities were determined by degenerate four wave mixing (DFWM) experiments as described elsewhere.[17] Measurements were carried out at 532, 1064, and between 580 and 600 nm.

Copolymers containing various electroactive units were prepared by reacting appropriate monomers with 1,5-bis(4-aminophenylene,oxy)-pentane. For example the reaction of this monomer with chloranil is demonstrated in Figure 1. When the

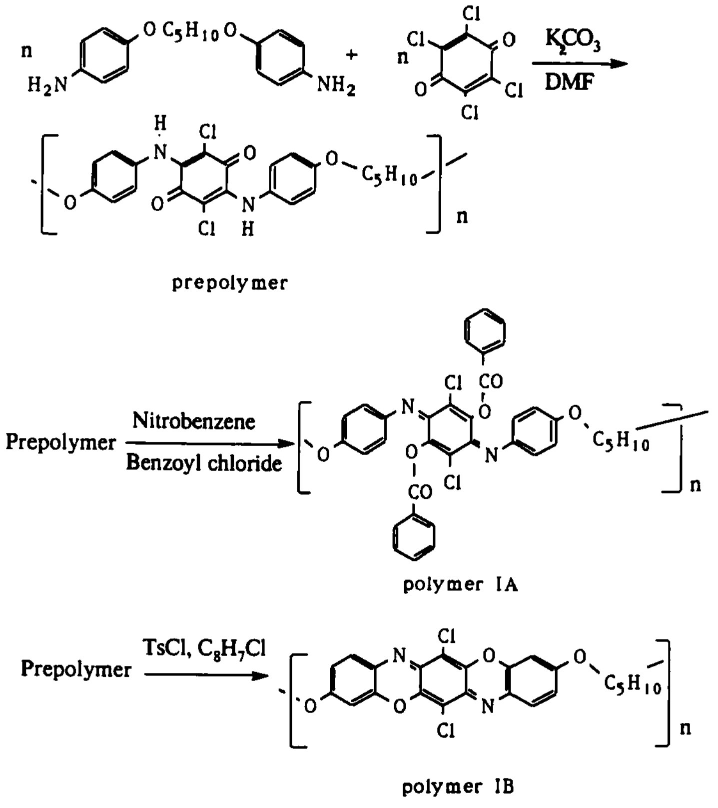


FIGURE 1

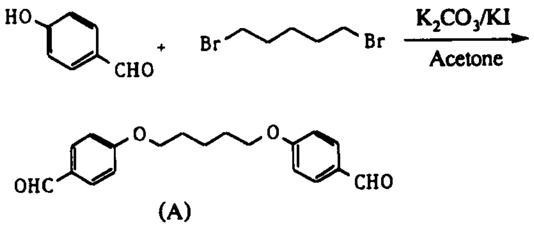


FIGURE 2

reaction is carried out in a DMF solution containing potassium carbonate, an open chain electroactive segment copolymer is obtained which can be converted either to a substituted polyaniline (polymer IA) electroactive segment or a ladder type (polymer IB) electroactive polymer segment. The assignment of structures to various reaction products is supported by IR, NMR, optical, and elemental analysis data as discussed elsewhere.[18]

The synthesis of an oxy-pentane with a reactive aldehyde (denoted A) is shown in Figure 2. This material has been reacted as shown in Figure 3 to produce copolymers containing phenylpolyene segments. In Figure 4, the reaction with a diaminoacridine is demonstrated while in Figure 5, the reaction with diaminostilbene is shown.

Polymerization based upon the condensation reaction involving acetylchloride and amine groups has also been employed to synthesize copolymers containing alternating electroactive and alkoxy segments as shown in Figure 6. The meracyanine electroactive segment has been incorporated into copolymers as shown in Figure 7; also shown in Figure 7 is the reaction to form a copolymer system incorporating a squaric acid moiety. As shown in Figure 8, metallomacrocyclic polymers containing flexible chain segments can be produced.

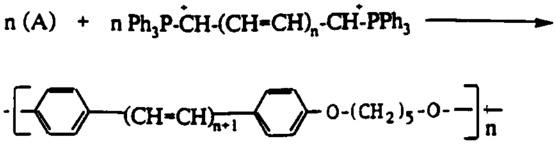


FIGURE 3

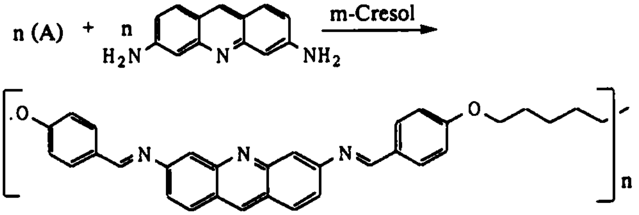


FIGURE 4

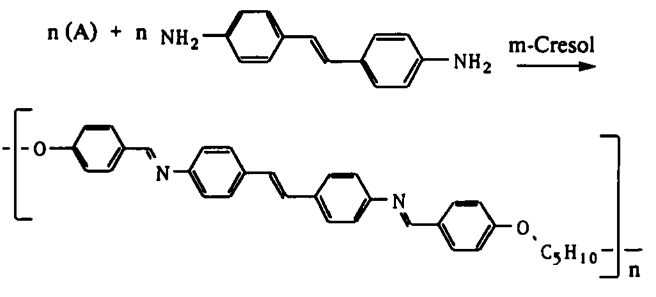


FIGURE 5

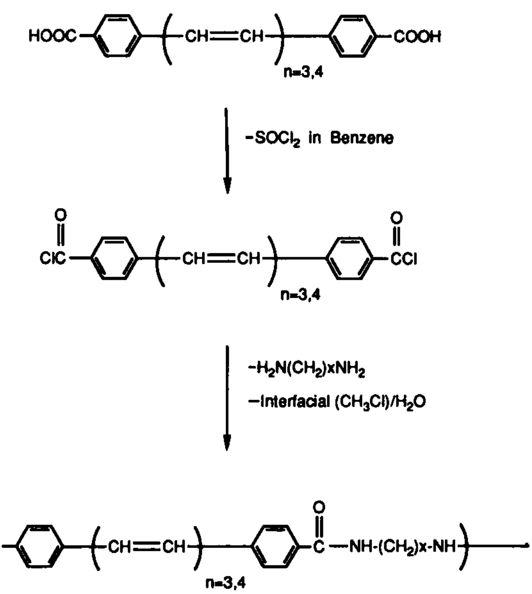


FIGURE 6

As a reference sample, we have prepared a 2 micron thick polycarbonate film doped with 3 × 10^{-4} mol of chromium phthalocyanine (CrPc) per gram of polymer. The optical and nonlinear optical properties of this material has been presented elsewhere.[14]

III. RESULTS AND DISCUSSION

It is instructive to compare optical nonlinearity measured for the above copolymers with that of the CrPc/polycarbonate composite film. For the CrPc film, the ratio of third order susceptibility to linear absorption, $\chi^{(3)}/\alpha$, was found to vary between 2.7 × 10^{-13} esu cm (at 582 nm) and 4.7 × 10^{-13} esu cm (at 590 nm). This DFWM signal decays over several hundred picoseconds. The DFWM signal decays for the

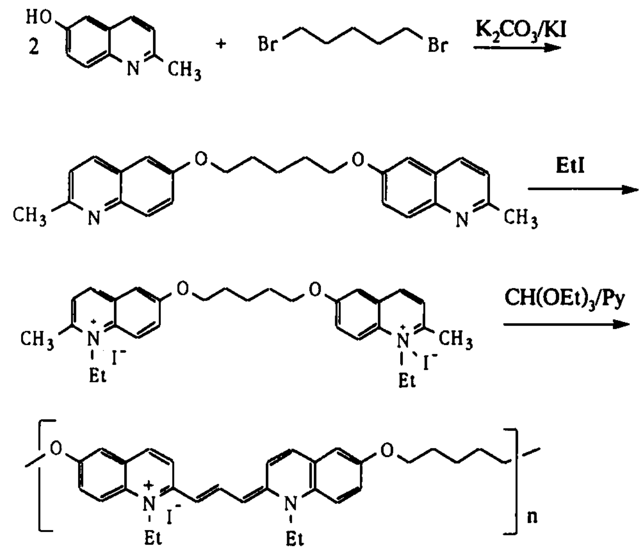
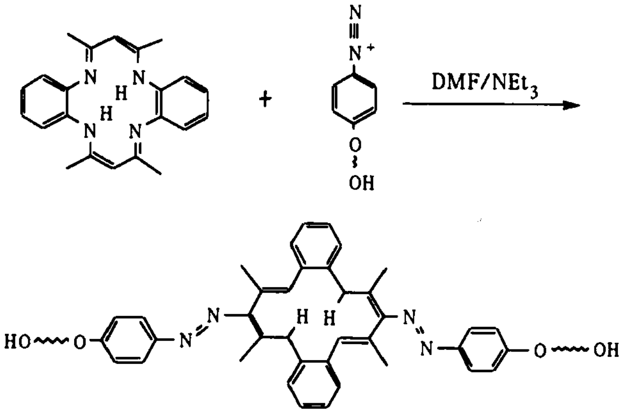


FIGURE 7



(M)

n(M) + n ClOC-R-COCl $\longrightarrow$ Copolymer

Copolymer + $NiAc_2\ 2H_2O$ $\longrightarrow$ Matallocycle Copolymer

Where = aliphatic chain, R = alkyl, aryl group.

FIGURE 8

polymers (I) of Figure 1 are at least a factor of 4 faster. $\chi^{(3)}/\alpha$ for polymers I were found to vary between 4–5 $\times$ 10^{-13} esu cm (at 579.5 nm) and 1.1 $\times$ 10^{-12} esu cm (at 591 nm). At 585 nm, the third order susceptibility was determined to be 4.5 $\times$ 10^{-9} esu. This nonlinearity is significantly greater than that of the prepolymer shown in Figure 1, which is consistent with the dependence of nonlinearity upon electron delocalization. Comparing the data for polymers I with other ladder systems containing different substituents, it is reasonable to speculate that the alkoxy termination of the electroactive units enhances optical nonlinearity as predicted by semi-empirical calculations.[5] Both ladder and CrPc films exhibit high thresholds to laser damage (greater than 3 GW/cm^2) and resistance to thermal decompositions as indicated by TGA studies.

The optical nonlinearity observed for the nickel tetraazaannulene material is very similar to the CrPc system.

The optical nonlinearity of the other systems studied was noticeably less than that of CrPc with the exception of the meracyanin copolymer system.

While preliminary survey studies of various substituted materials and of variable length oligomers yield results in qualitative agreement with semi-empirical calculations,[5] sufficient data does not exist to define mechanisms of optical nonlinearity. A variety of mechanisms have been proposed for other high symmetry electroactive polymers including (1) rapid conformational deformation leading to a shift of oscillator strength to photogenerated polaronic (or solitonic depending on symmetry) species[19] and (2) phase space filling involving unrelaxed excitons.[20–22] As we have observed shifts in oscillatory strengths from interband to intraband transitions for ladder oligomers and ladder polymers exposed to chemical and electrochemical doping[23] or generated by pump-probe optical methods,[24] mechanism (1) must be carefully considered for ladder copolymers. The main argument against this mechanism at this time is the very fast response observed. However, it is not clear at this time exactly how fast the structural relaxation can occur. We have performed some DFWM studies on doped samples but we have not completed analysis of data.

Investigation of optical nonlinearity as a function of concentration of electroactive units in polymer composites suggests the potential for intermolecular contribution in some cases. For example, the effects may involve charge-transfer interactions or exciton interactions. Further studies are needed to unambiguously define the relative contributions from various mechanisms.

The frequency dependence of third order susceptibility suggests that optical nonlinearity is dominated, in these systems, by resonant contributions, at least near the interband absorption edge.

Acknowledgments

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