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NONLINEAR OPTICAL PROCESSES IN ORGANIC MEDIA: LARGE

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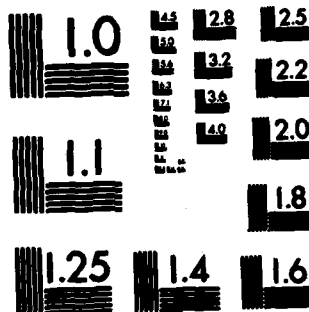
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Nonlinear optical processes in organic media: large non-resonant
third order electronic responses in high performance liquid crystal polymer structures

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Abstract

Organic and polymer structures exhibit unusually large, ultrafast second and third order nonlinear optical properties in a large number of structures, phases, and states. Rapid advances in the field can be achieved through further development of stable, high performance polymer structures having outstanding secondary properties as demonstrated, for example, by high performance liquid crystal polymers. For two such polymer systems, PBI and PBT, third harmonic generation measurements show that they possess large non-resonant third order optical susceptibilities whose origin resides in ultrafast, lossless excitations of highly charge correlated π -electron states.

Introduction

Physical studies have demonstrated that organic and polymer structures possess unusually large, ultrafast second and third order nonlinear optical properties in a large number of material structures, phases, and states that include organic crystals, monomolecular films, polymer structures, liquid crystals and liquid crystal polymers¹⁻³. Theoretical calculations have shown that the basic origin of these properties resides in highly charge correlated excited states of the π -electron distribution comprising these structures^{4,5}. These striking properties, together with demonstrations of phase conjugate wave generation⁶, optical bistability⁷, and associative memory networks⁸ have stimulated considerable growth in research and development activities in centers throughout the world. A wide variety of potential applications in advanced optical technologies are being actively pursued that include optical signal processing and computing, image reconstruction, data storage and telecommunications.

The intrinsic response time for electron excitations is ultrafast (10^{-14} - 10^{-15} sec). In general, a nonlinear optical polarization in a medium involves either resonant absorptive, or non-resonant reactive, nonlinear responses. A reactive nonlinear response is due to lossless virtual optical excitations in the nonlinear medium with no net population changes or any material transformations which do occur in an absorptive response. Examples include non-resonant harmonic generation, frequency mixing, and optical Kerr effects. By far the fastest response times occur in reactive nonlinear media since reactive responses do not involve relatively slow material changes of the nonlinear medium. Moreover, among the possible virtual excitations of reactive responses, electron excitations of order 10^{-15} seconds (1 fs) are intrinsically faster than phonon excitations which involve much slower nuclear displacements and vibrations of order 10^{-12} seconds (1 ps).

For large classes of conjugated molecules and polymer structures, the remarkable property is that the nonlinear optical responses are dominated by lossless virtual excitations of the π -electron states, especially those possessing large charge correlations. This property was first demonstrated in second order responses. For example, in crystalline solids only electronic excitations contribute to second harmonic generation, whereas both electron and phonon excitations contribute to the linear electrooptic effect. For MNA (2-methyl-4-nitroaniline) crystals, for example, the large second harmonic susceptibility $\chi_{111}^{(2)}(-2\omega, \omega, \omega)$ of 500×10^{-12} m/v was shown to be the same as the linear electrooptic susceptibility $\chi_{111}^{(2)}(-\omega, \omega, 0) = 540 \times 10^{-12}$ m/v within experimental error demonstrating that the second order response is primarily purely electronic with little or no lattice contribution, and thus intrinsically fast. Examples at the molecular level include the magnitude, sign, and frequency dependence of the microscopic second order response of organic molecular structures such as MNA and the parent PNA. In third order processes for the case of a liquid crystal polymer, values of the non-resonant, electronic

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third order optical susceptibility for divinylidiacetylene (DVDA) liquid crystal monomers and polymers were found to be two orders of magnitude greater than that of reference glass and quartz^{3,10,11}.

High performance nonlinear optical polymer structures

As discussed earlier^{1,3,12}, rapid advances in the field will be achieved only through further development of stable, high performance polymer structures because optical media must ultimately possess important secondary properties that include mechanical, thermal, chemical, and oxidative stabilities in addition to optical quality fabrication and high through-put processing into desired shapes and conformations. Furthermore, polymer structures can be designed for their linear and nonlinear optical properties at the microscopic scale by suitable selection of pendant side groups and monomer repeat units. Macroscopic symmetry can be controlled, for example, by incorporating chiral centers for noncentrosymmetry¹³, or by applying external mechanical stress, electric, or magnetic fields, especially in liquid crystal phases.

Classes of lyotropic liquid crystal polymers have been shown under Air Force sponsored research to possess exceptional secondary properties as high performance polymers. Two such examples are PBI (polybenzimidazole)¹⁴ and PBT (polybenzobisthiazole)¹⁵ (Figure 1) whose repeat units containing a delocalized π -electron system link to form centrosymmetric rigid rod polymers. Thin films (< 50 nm) appear light yellow in color and exhibit optical transparency from the near infrared spectral region (3 μ m) to the visible blue region where there is a large, sharp on-set of π -electron excitations near 0.5 μ m. However, optical scattering loss in the transparency range is observed from domain boundaries. In polarized microscopy, both film samples show a domain morphology with the PBT film having a ribbon-like appearance.

The rigid rod polymer chain structure generally possesses an inherent tendency of self-alignment in regions of high uniaxial molecular order oftentimes in the form of microdomains. Uniform orientation of these domains, as in a mechanical stress field, leads to unusually high mechanical properties as illustrated in Figure 2 by the tensile strength and modulus values for PBT when compared to different structural materials.

Third harmonic generation experiments and results

The experimental set-up, which is similar to that described earlier⁵, consists of a pulsed Nd:YAG Q-switched laser as a pump source for a compressed hydrogen Raman cell yielding an output laser beam at 1.907 μ m from the first Stokes line. The output beam was then divided into two optical paths: the reference path to eliminate signal instabilities due to input beam power fluctuations, and the sample path to provide the fundamental beam for third harmonic generation. The sample was located on a computer controlled rotational stage for obtaining the Maker fringes of the third harmonic signal. The measurement was relative to glass which has a third order optical susceptibility $\chi_G^{(3)}(-3\omega; \omega, \omega, \omega) = 4.67 \times 10^{-14}$ esu¹⁶. By comparing the third harmonic signal from the sample $I_S^{3\omega}$ with that from glass $I_G^{3\omega}$, the third order optical susceptibility $\chi_S^{(3)}(-3\omega; \omega, \omega, \omega)$ of the sample can be evaluated according to:

$$\frac{I_S^{3\omega}}{I_G^{3\omega}} = \left(\frac{\chi_S^{(3)} I_C^S}{\chi_G^{(3)} I_C^G} \right)^2 \left(\frac{I_S^\omega}{I_G^\omega} \right)^3$$

where I_C^S and I_C^G are the coherence lengths of the sample and glass, respectively:

$$I_C = \frac{\lambda}{6(n^{3\omega} - n^\omega)}$$

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I_S and I_G are the input beam intensities for the sample and glass third harmonic generation, respectively.

The PBI thin film (~ 50 μm) was prepared by dissolving 15% of the PBI polymer into dimethyl acetamide with 2% of LiCl and casting the solution onto a substrate. A thin film formed and separated from the substrate after the solvent dried out. The PBT film was prepared from a PBT polymer/polyphosphoric acid dope by blowing to impart biaxial orientation. Absorption spectra showed both samples to be transparent at the fundamental optical wavelength (1.907 μm) and the third harmonic wavelength (0.636 μm).

For the 50 μm thick PBI film, the coherence length l_S^3 of the thin film was estimated to be about 1/6 of the coherence length l_G^3 of glass ($l_G^3 = 16.72 \mu\text{m}$). The third order optical susceptibility $\chi_S^{(3)}$ of the PBI film was determined as $0.8 \pm .5 \times 10^{-12}$ esu. For the poorer quality PBT film, the coherence length could only be approximated as 0.3-0.6 μm . The $\chi_S^{(3)}$ of the PBT film obtained is 50-100 $\times 10^{-12}$ esu, which is two orders of magnitude larger than that of the PBI film.

Discussion

In our third harmonic measurements, both the fundamental and third harmonic frequencies lie well above vibrational and rotational modes and below electronic resonances. Only the electronic contribution to the nonresonant macroscopic third order susceptibility $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ is measured in third harmonic generation. As we reported earlier¹⁷⁻¹⁹, the measured $\chi^{(3)}$ value of 50-100 $\times 10^{-12}$ esu for PBT is among the highest nonresonant $\chi^{(3)}$ values observed for nonlinear optical media. The origin of this large value resides in the excited states of the π -electron system comprising the individual polymer chain structure. Currently, these π -electron excitations are viewed as occurring on individual polymer chains interacting off-site through weak local fields and providing macroscopic sources of nonlinear optical response through the on-site microscopic nonlinear third order electronic susceptibility $\gamma_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3)$. In the rigid lattice gas approximation, the macroscopic third order response $\chi_{ijkl}^{(3)}$ is expressed in terms of the corresponding microscopic response γ_{ijkl} .

$$\chi_{ijkl}^{(3)}(-\omega_4; \omega_1, \omega_2, \omega_3) = N f_1^{\omega_1} f_2^{\omega_2} f_3^{\omega_3} f_4^{\omega_4} \langle \gamma_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3) \rangle$$

where N is the number of polymer chains per unit volume and $f_i^{\omega_i}$ represents local field factors, and γ_{ijkl} is evaluated over the orientational distribution function for the polymer chains.

The π -electron states and their microscopic third order susceptibility contributions can be theoretically calculated in the finite chain molecular limit by an all-valence electron, self-consistent field procedure including multiple configuration interactions (SCF-MCI) to account for electron-electron correlations^{3,4}. Since each rigid rod polymer chain is essentially a densely packed, linear array of linked monomer units, a repeat unit can be viewed as the finite chain limit to the corresponding infinite polymer chain.

Initial results of SCF/MCI calculations of γ_{ijkl} for the PBT monomer repeat units show the π -electron states important to the large third order response are highly charge correlated and consist of alternating single and double bonds in analogy to the earlier reported case of centrosymmetric divinylidiacetylene (DVDA) linear chain polyenes^{3,10,11,20,21}. In such structures, accompanying the singlet 1A_g bond alternating ground state, the principle singlet excited states are a dominant 1 photon 1B_u state and a nearly degenerate 2 photon 1A_g state, and, at higher energy, a 1 photon 1A_g state. In DVDA's, the 2 photon 1A_g state lies well above the 1B_u state. For the non-resonant third harmonic susceptibility, a major contribution comes from virtual excitations to the 1 photon 1B_u state and illustrates the importance of charge correlations. As described earlier, they are mainly responsible for the large optical first moments that directly determine the microscopic third order response. For example, in bis diphenylsubstituted DVDA polyenes, the low energy excitation $^1B_u \rightarrow ^1A_g$ possesses a large optical transition moment μ_{ng} greater than 10 Debye.

As regards the measured $\chi^{(3)}$ value for PBI, we note that in addition to the replacement of nitrogen for sulfur, the molecular structure, and thereby, the π -electron states of the repeat unit in PBI are markedly different from those of PBT. Whereas the π -

electron structure of the 5-membered thiazole rings of PBT are directly coupled through a central conjugated ring, in PBI each 5-membered imidazole ring in PBI is widely separated and relatively weakly coupled by meta-bridged benzene rings. Correspondingly, in contrast to PBT, the PBI chain structure tends to be helical¹⁵, and the measured $\chi^{(3)}$ value is drastically reduced by two orders of magnitude compared to PBT.

For the π -electron delocalization length in a rigid rod polymer to extend beyond a single repeat unit requires phase coherence between the molecular state functions on adjacent sites. In the rigid lattice approximation, the intrinsic nature of the electron states, such as their symmetry and electron correlations, will remain essentially the same. For extended polymer states, Dalton²² has further proposed that electron-phonon interactions can markedly alter the electron states of PBT by causing the formation of domain wall, defect-like states of opposite bond alternation sequence that are lowest in energy. Further studies, of course, are required to evaluate the importance of electron-phonon coupling in PBT and the role of defect-like states on nonlinear optical properties.

Conclusion

In summary, we have reported that high performance liquid crystal polymers such as PBI and especially PBT possess large non-resonant third order nonlinear optical responses whose origin resides in ultrafast, lossless excitations of highly charge correlated π -electron states delocalized on the repeat units comprising the polymer structures. These large third order properties of rigid rod liquid crystal polymers together with their well-known outstanding mechanical, thermal, chemical, and oxidation properties should provide further advances in nonlinear optical device development and implementation. Device optical processes include examples such as frequency synthesis, parametric oscillation, optical beam modulation, phase conjugation, and optical bistability. Both bulk thick film devices and thin film guided wave structures can be fabricated. These device developments together with related fundamental polymer and nonlinear optical physics issues presented above are being actively pursued and will be reported separately.

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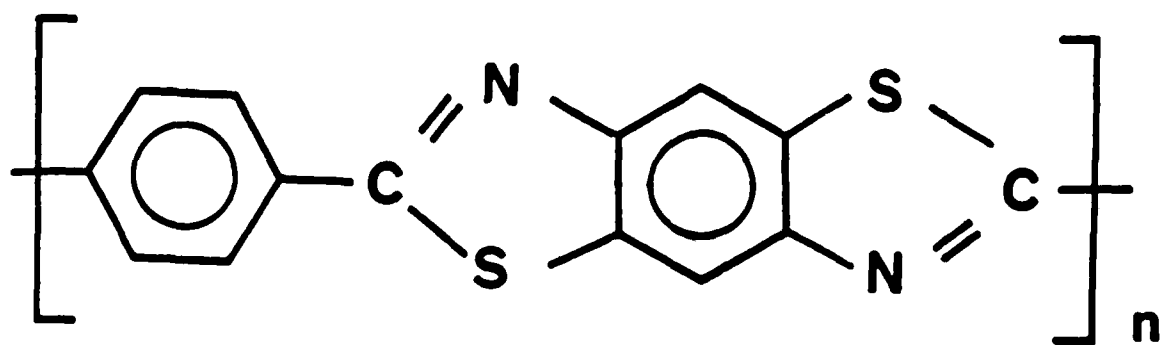
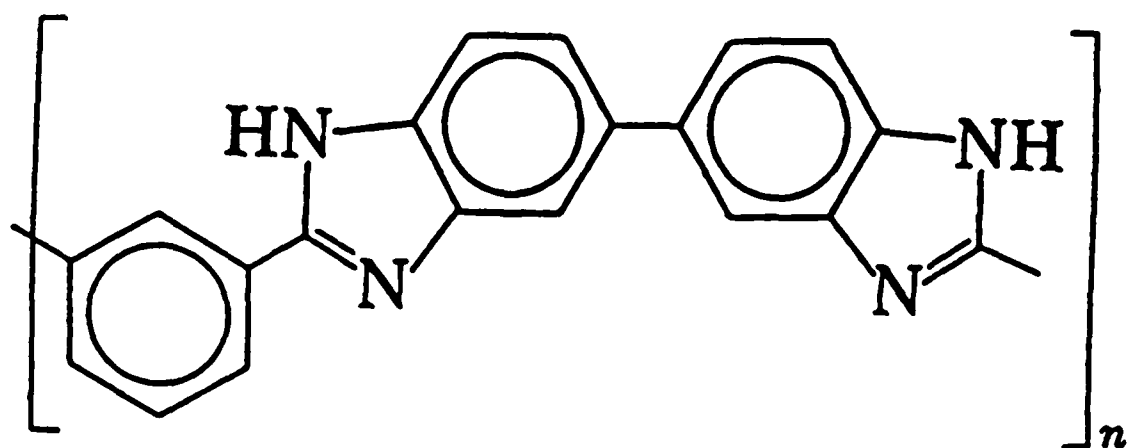
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Figure 1: Molecular structure of PBI (top) and PBT (bottom).

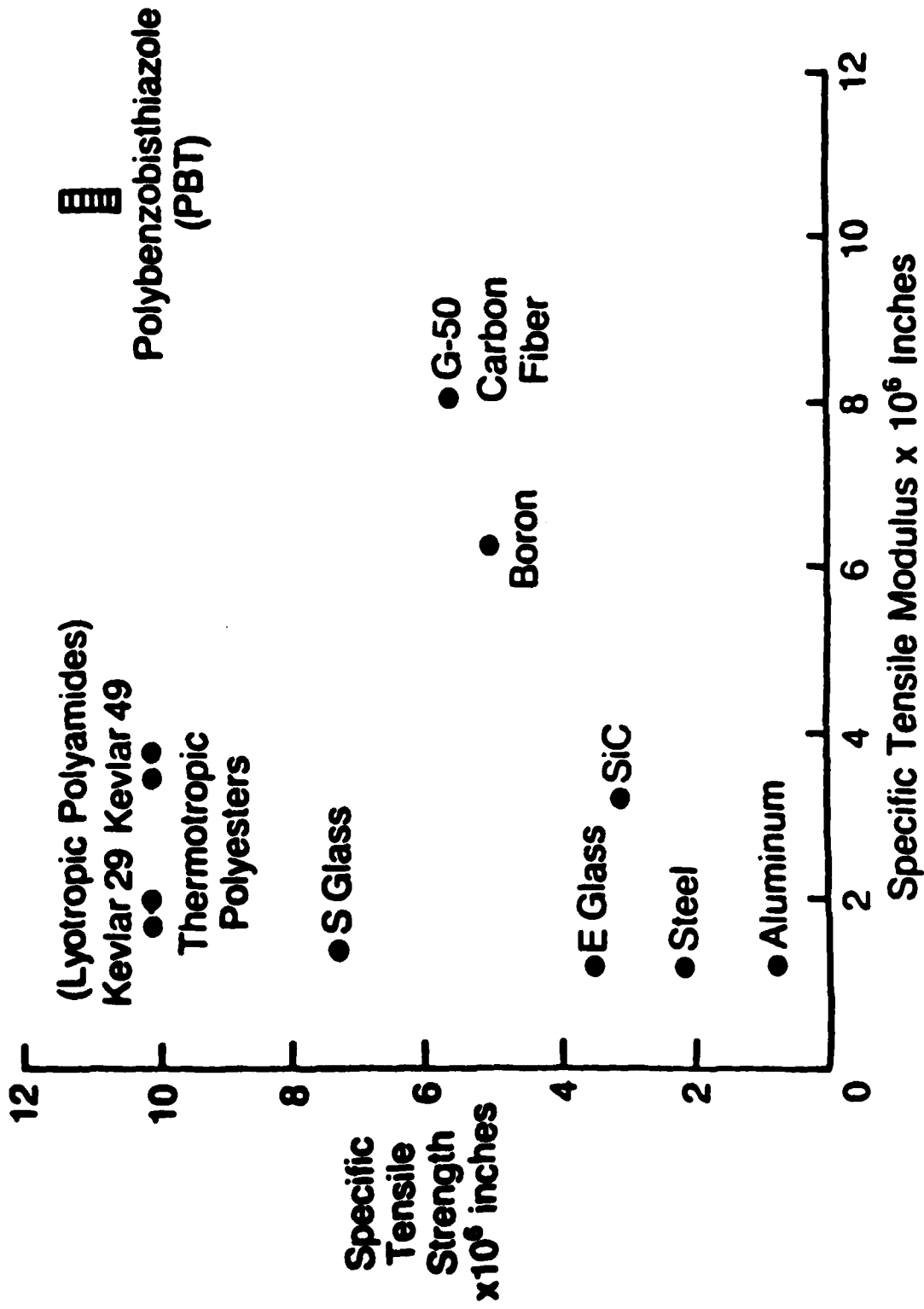
Figure 2: Comparative structural figures of merit for different materials.



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