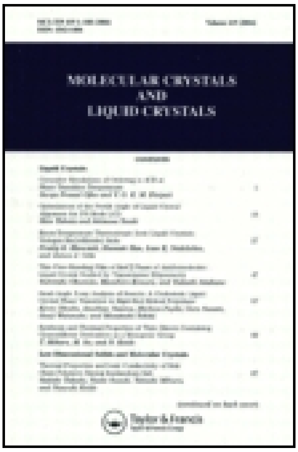

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

RE$\chi^{(3)}$, RE$\chi^{(5)}$, and RE$\chi^{(7)}$ Measured in Poly(Phenylene Ethynyl Silane)S by the Z Scan Technique

R. K. Meyer [a], R. E. Benner [a], Z. V. Vardeny [b], Y. Ding [c] & T. Barton [c]

[a] Department of Electrical Engineering, University of Utah, Salt Lake City, Utah, 84112

[b] Department of Physics, University of Utah, Salt Lake City, Utah, 84112

[c] Department of Chemistry, University of Iowa, Ames, Iowa, 50011

Version of record first published: 04 Oct 2006.

To cite this article: R. K. Meyer, R. E. Benner, Z. V. Vardeny, Y. Ding & T. Barton (1994): RE$\chi^{(3)}$, RE$\chi^{(5)}$, and RE$\chi^{(7)}$ Measured in Poly(Phenylene Ethynyl Silane)S by the Z Scan Technique, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 597-604

To link to this article: http://dx.doi.org/10.1080/10587259408039297

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 597–604
Reprints available directly from the publisher
Photocopying permitted by license only

RE$\chi^{(3)}$, RE$\chi^{(5)}$, AND RE$\chi^{(7)}$ MEASURED IN POLY(PHENYLENE ETHYNYL SILANE)S BY THE Z SCAN TECHNIQUE

R. K. MEYER AND R. E. BENNER
Department of Electrical Engineering,
Z. V. VARDENY
Department of Physics, University of Utah,
Salt Lake City, Utah 84112

Y. DING AND T. BARTON
Department of Chemistry, University of Iowa,
Ames, Iowa 50011

Abstract Optical nonlinear susceptibilities were measured in Poly(phenylene ethynyl silane) (PPES1) and Poly(phenylene ethynyl disilane) (PPES2) at 590nm and 1064nm. Both the real and imaginary parts of $\chi^{(3)}$ were evaluated with the Z scan technique using closed and open apertures, respectively. Closed aperture scans of PPES1 exhibited the classic negative Re$\chi^{(3)}$ peak valley signature, whereas, closed aperture scans of PPES2 displayed interesting additional features. These features are present at both 590nm and 1064nm, and indicate the presence of alternating sign higher order nonlinearities with negative $\chi^{(3)}$, positive $\chi^{(5)}$, and negative $\chi^{(7)}$.

INTRODUCTION

Poly(phenylene ethynylene silane) (PPES) are novel polymers in which Si atoms with σ-bonding are incorporated in the back bone structure with mostly π-bonding. As shown in Fig. 1 (inset), the PPES polymers consist of units of phenylene and methyl-silane, alternatively connected via carbon-carbon triple bonds, and thus they can be regarded as conducting polymers of the copolymer type. Average molecular weights ranged from 7000 to 17000 (~100-200 monomers/chain)[1]. The polymers are soluble in various organic solvents, easily cast into films and apparently quite stable in air [1]. Since PPES exhibit blue photoluminescence (PL), they have potential applications in the new field of polymer-based light emitting diodes in the blue spectral range.

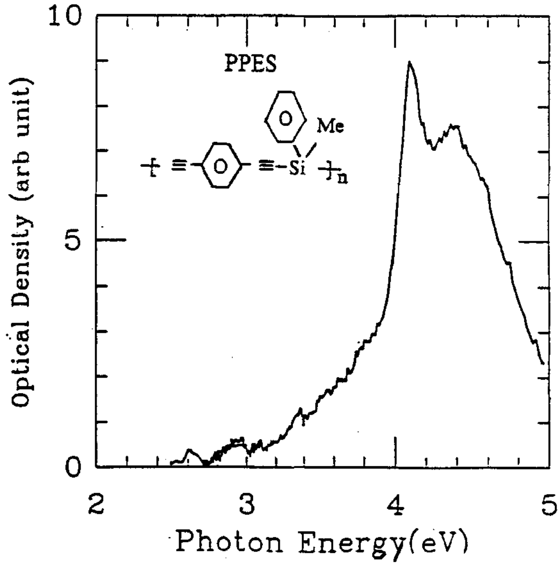

FIGURE 1 Linear absorption spectrum for PPES. Inset: PPES backbone structure.

We have conducted measurements of the nonlinear susceptibilities of two types of PPES, Poly(Phenylene ethynyl silane) (PPES1) and Poly(Phenylene ethynyl disilane) (PPES2), using the Z scan technique. Investigations were performed at 590 nm on both PPES1 and PPES2. PPES2 was also examined at 1064nm. Measurements were conducted on the polymers in chloroform solution placed in 1 mm thick glass cuvettes. Scans were also performed on CS_2 at similar power levels to validate our technique. Both the real and imaginary parts of $\chi^{(N)}$ were evaluated using closed and open aperture Z scans, respectively.

APPARATUS AND VALIDATION

Nonlinear studies necessitate the use of short pulses at slow repetition rates. Short pulses provide high peak powers and probe the more desirable fast nonlinear mechanisms. Slow repetition rates are required to ensure that the observed effects are not due to accumulated long-time effects which may occur when there is insufficient relaxation time between pulses. To satisfy these requirements we used a frequency doubled Nd:YAG Regenerative Amplifier with a 1 kHz repetition rate to pump a Dye Amplifier containing kiton red. This combination provided us 590nm, 10 psec light pulses at a 1 kHz repetition rate and with intensities up to 60 GW/cm^2. We obtained 1064 nm pulses by simply removing the regenerative amplifiers second harmonic crystal and by-passing the dye amplifier.

To validate our apparatus we conducted a closed aperture Z Scan on CS_2 at 590nm. This scan was conducted at a peak on axis intensity of 20 GW/cm^2, a relatively large value, to demonstrate the classic $\chi^{(3)}$ Z Scan signature[2,3] even at large transmission excursions. The CS_2 validation Z Scan, Fig. 2, clearly depicts the usual positive $\chi^{(3)}$ signature, giving values within 10% of those reported using the same technique[2,3]. In addition, CS_2 scans were used to ascertain the focusing distances, z_o, and, thereby, calculate the beam waist radius.

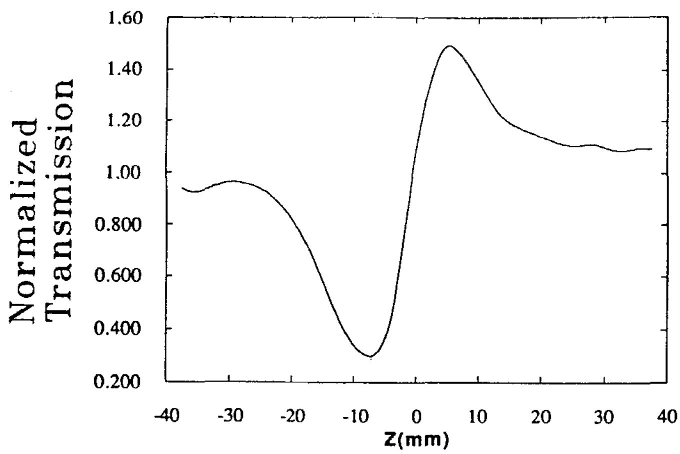

FIGURE 2 Measured Z scan of a 1mm thick CS_2 cell at λ=590nm. The focusing distance, z_o, is 7mm.

Low intensity scans were also conducted following each high intensity scan. This was done to insure that the observations were not due to surface inhomogeneities caused by film deposition at the glass solution interface.

LINEAR ABSORPTION

Fig. 1 shows the linear absorption data for PPES. At 590nm(2.1eV) and 1064nm(1.17eV) we are well below the strong 4.0 eV exciton and the weaker excitons in the long absorption tail. Thus, any resonant enhancements will be the result of multi-photon absorption. The low linear absorption in this wavelength range bodes well for future application in all-optical switches that will operate at wavelengths currently used in fiber optic communications.

CLOSED APERTURE SCANS

Closed aperture Z Scans were conducted on both PPES1 and PPES2 at 590nm. PPES1 displayed the negative $\chi^{(3)}$ structure as can be seen from Fig. 3 below.

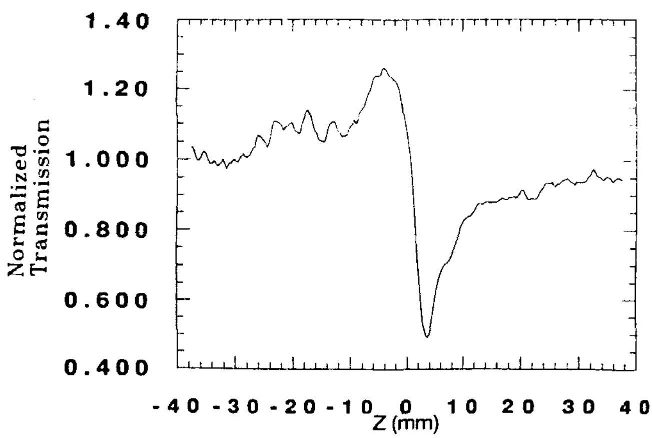

FIGURE 3 Measured Z scan of a 1mm thick cell of PPES in chloroform solution at 590nm. $\Delta T_{P\text{-}V} \cong 0.75$.

Scans on PPES2, however, illustrated some very unique and interesting features. In order to determine the nature of these features scans were conducted at varying on-axis excitation intensities. These scans are illustrated progressively in Figures 4a, b, and c. The figures demonstrate the gradual extinction of the double hump structure as intensity decreases. Scans on PPES conducted at 1064 nm also exhibited the double hump feature.

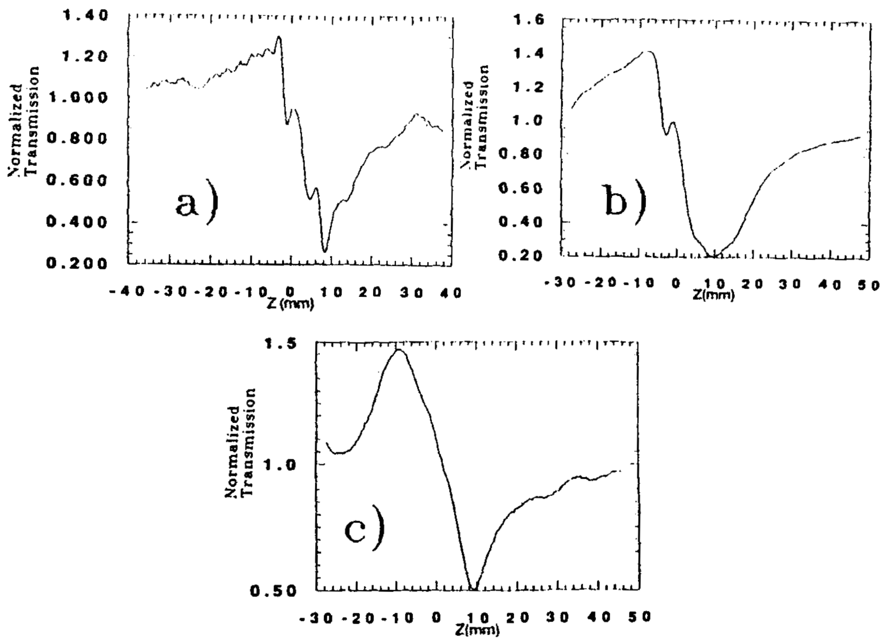

FIGURE 4 Measured Z scans of a 1mm thick cell of PPES2 in chloroform solution at 590nm. a) I_0=60 GW/cm^2, z_0=4.5mm; b) I_0=42 GW/cm^2, z_0=7mm; c) I_0=14 GW/cm^2, z_0=7mm.

OPEN APERTURE SCANS

Open aperture scans for PPES1 and PPES2 at 590nm did not indicate the presence of strong two-photon absorption. The nonlinear absorption was so small as to preclude meaningful quantification. Attempts to see the effect at higher intensities resulted in boiling. The structure of the open aperture scans (sharp "V" at the z=0 position) did, however, indicate the presence of higher order absorption mechanisms. Open aperture scans of PPES2 at 1064nm were, essentially, flat with no perceivable high order absorption.

ANALYSIS

The normalized transmission at the aperture for a sample exhibiting a third order nonlinearity in the index of refraction is given by[2,3]

$$T(z)=1+\frac{4\cdot\Delta\phi\cdot\frac{z}{z_o}}{\left[1+\left(\frac{z}{z_o}\right)^2\right]\cdot\left[9+\left(\frac{z}{z_o}\right)^2\right]} \qquad (1)$$

where,

$\Delta\phi$ is the on axis phase change due to $\chi^{(3)}$,
z is the position of the sample relative to the lens focal point,
and z_o is the focusing distance related to the minimum beam radius.

From this it can be shown that the on-axis phase change and, therefore, n_2 and $\chi^{(3)}$ are determined from the total change in transmission between the Z scan peak and valley using the relation, $\Delta\phi \cong \Delta T_{P-V}/0.406$.[2,3] Using this procedure a $Re(\chi^{(3)})$ for PPES1 is calculated to be -9.3 x 10^{-13} esu. It is not, however, possible to achieve a good curve fit with Eq. (1) since the actual Z scan is not completely antisymmetric. Therefore, it is likely that higher order effects are present.

Calculating the $\chi^{(N)}$ for PPES2 is considerably more difficult. It is clear that Eq. (1) cannot describe the features in the PPES2 Z scans. A new equation was derived using the method of Gaussian decomposition and following the approach of Sheik-Bahae, et al.[2] In this approach the field at the sample exit is expressed as a sum of Gaussian beams and then propagated to the aperture. The behavior of this equation is illustrated below in Fig. 4. The curve, labeled T4(z), is a $\chi^{(3)}$ only curve whereas curves T1, T2, and T3, respectively, represent Z scans of decreasing intensity, each possessing $\chi^{(3)}$, $\chi^{(5)}$, and $\chi^{(7)}$ nonlinearities of alternating sign (i.e., $-\chi^{(3)}$, $+\chi^{(5)}$, and $-\chi^{(7)}$). As in the experimental results, the double hump feature gradually disappears with decreasing intensity. Furthermore, the Δz distance between the lowest valley and highest peak appears to be a function of intensity and is greater than the Δz distance for $\chi^{(3)}$ only. This trend is also observed in the experimental results.

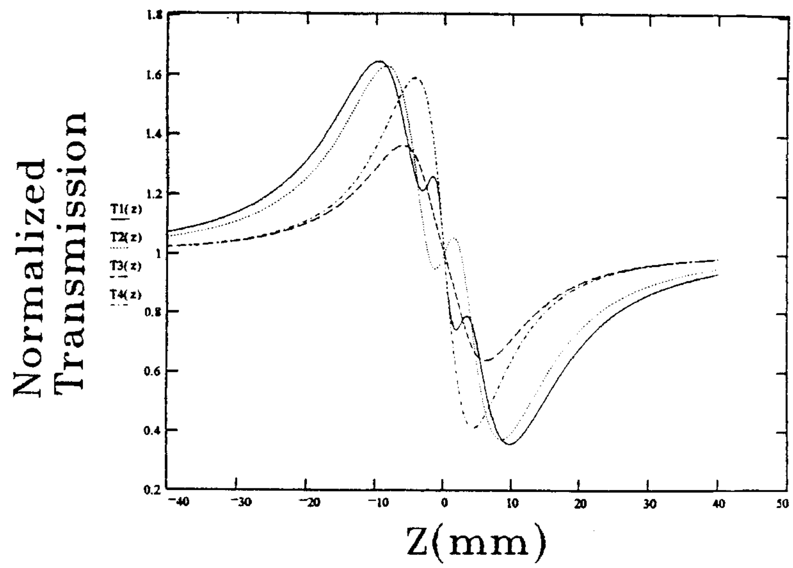

FIGURE 5 Simulated closed aperture Z scan evolution as intensity is decreased. The double hump feature occurs for the highest intensity Z scan curve, T1. This becomes a single hump at a lower intensity scan, T2, and disappears altogether with the lowest intensity scan, T3. The T4 curve depicts a third order effect alone.

It is important to note the antisymmetric nature of the above curves. The departure from an antisymmetric structure indicates the need for a more exact equation to fit the data. Although the $\chi^{(3)}$ values for PPES2 appear to be on the order -10^{-11}esu, a better mathematical model must be developed to accurately quantify $\chi^{(5)}$, and $\chi^{(7)}$.

The speed and apparently large magnitude higher order nonlinearities are likely due to resonant enhancement. At 1064nm, according to the linear absorption data, there are levels available for resonant enhancement of two-photon, three-photon, and four-photon transitions. For 590nm a two-photon resonance can occur with the exciton level at 4.0eV. We would also expect to find levels near 6.3 eV and 8.4 eV in the absorption (not shown in Fig. 1). It should be possible, then, to find wavelengths where the nonlinear susceptibilities change sign. For example, if $\chi^{(5)}$ became negative the Z scan would be indistinguishable from a $\chi^{(3)}$ only effect.

CONCLUSIONS

Open and closed aperture Z scans were conducted on PPES1 and PPES2 in order to measure the real and imaginary nonlinear susceptibilities. These measurements were conducted well below the one-photon resonance and neither material exhibited strong multi-photon absorption in open aperture scans. Closed aperture scans in PPES2 displayed interesting features attributed to simultaneous contributions from $\chi^{(3)}$, $\chi^{(5)}$, and $\chi^{(7)}$ nonlinear susceptibilities.

ACKNOWLEDGEMENTS

This work was supported in part by NSF grant No. DMR-92-22947 and byy ONR grant No. N00014-91-C-0104 at the Utah Laser Institute

REFERENCES

1. Y. Ding, Ph.D. thesis, Iowa State University, 1994(unpublished).
2. M. Sheik-Bahae, A. A. Said, and E. W. Van Stryland, IEEE J. Quantum Electron. **26**, 760 (1990).
3. A. A. Said, Ph. D. thesis, University of North Texas, 1991.
4. D. Weaire, B. S. Wherrett, D. A. B. Miller, and S. D. Smith .Opt. Lett **4**, 331 (1979).