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Nonlinear Optical Susceptibilities Measured in Poly(Paraphenylene Cumulene[3]) by the Z Scan Technique

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NONLINEAR OPTICAL SUSCEPTIBILITIES MEASURED IN POLY(PARAPHENYLENE CUMULENE[3]) BY THE Z SCAN TECHNIQUE

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Abstract Optical nonlinear susceptibilities were measured in Poly(paraphenylene cumulene[3]) (PPC) 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. Open aperture Z scans on PPC at 590nm displayed a negative $Im\chi^{(3)}$, indicating saturation at this energy, as expected due to the close proximity to the absorption band edge. Due to accumulated long time effects, closed aperture scans gave erroneously high $Re\chi^{(3)}$ values and second hyperpolarizabilities of -3.9×10^{-11}esu and -4.67×10^{-28}esu, respectively.[1] The presence of a long time effect was verified by mechanically modulating the 1 kHz pulse train and observing radical changes in $Re\chi^{(3)}$ while peak and average powers remained constant.

INTRODUCTION

Poly(paraphenylene cumulenes[3]) (PPC) are novel polymers in which cumulene structures are incorporated in the back bone structure with mostly π-bonding. As shown in Fig. 1 (inset), the PPC polymers consist of units of phenylene and cumulene, alternatively connected via carbon-carbon double bonds, and thus they can be regarded as conducting polymers of the copolymer type. Cumulene structures apparently can have large nonlinear susceptibilities with reported second optical hyperpolarizabilities as high as 3×10^{-31}esu[1].

We have conducted measurements of the nonlinear susceptibilities of PPC, using the Z scan technique. Investigations were performed on the polymer in solutions of toluene and chloroform at 590 nm and 1064nm. Scans were also performed on CS_2 at similar power levels to validate our technique. Both the real and imaginary parts of $\chi^{(3)}$ were evaluated using closed and open aperture Z scans, respectively.

APPARATUS

Nonlinear studies necessitate the use of short pulses at low 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. By eliminating the second harmonic crystal and dyye amplifier, 200psec pulses at 1064nm could be obtained.

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. Closed and open aperture Z scans were performed on the toluene and chloroform solvents alone to determine their contribution to any measured $\chi^{(3)}$ effect. The contributions were small, on the order of 10^{-14} esu.

LINEAR ABSORPTION

Figure 1 shows the linear absorption data for PPC. At 590nm(2.1eV) we are very near the maximum absorption energy. At 1064nm PPC is transparent. Photo-absorption experiments, however, have verified the existence of long-live photoexcitations.

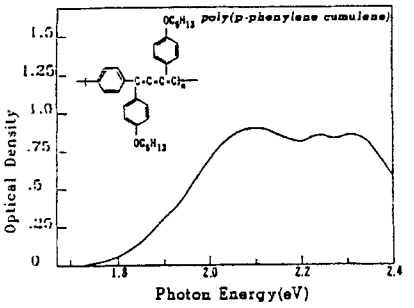

FIGURE 1 Linear absorption and chemical structure(inset) for PPC.

Z SCANS

Open aperture Z Scans of PPC at 590nm exhibited a strong saturation effect as can be seen in Fig. 2b below. This dramatic increase in transmission near z=0 could be seen in the closed aperture scans as well, thereby necessitating division of the closed aperture scan data by the open aperture data to obtain the result depicted in Fig. 2a.[2]

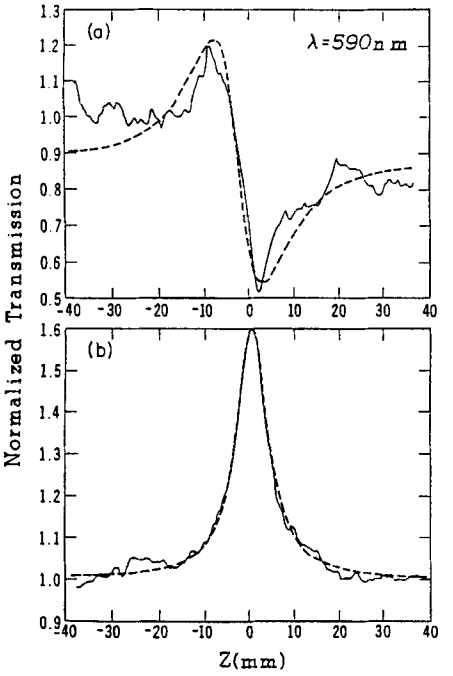

FIGURE 2 Z scan measurements of PPC; a) closed aperture scan, b) open aperture scan.

Open aperture scans at 1064nm exhibited no absorption, while closed aperture scans still displayed a strong nonlinear index of refraction change. Increasing the pulse width to 200nsec and, thereby, decreasing the peak intensity three orders of magnitude did not change the Z scan appreciably.

LONG-TIME EFFECTS

Saturation effects due to one-photon absorption are known to be long-lived and give rise to $Re\chi^{(3)}$ via the Kramers-Kronig relation. This long lifetime can lead to an accumulated effect not attributable to electronic nonlinear responses that are quite fast. A similar difficulty occurs in degenerate four-wave mixing(DFWM) experiments where transient grating are created[1]. Thus, any nonlinear change in the index of refraction observed near a one-photon resonance should be suspect.

A simple method of determining the presence of such an artifact involves mechanically chopping the pulse train at various frequencies and observing the effect on Z scan measurements. Fast electronic mechanisms will be unaffected by such a procedure since the peak powers remain unchanged. This fact has been demonstrated by means of the fast reorientational Kerr effect in CS_2. Accumulated long-time effects, however, should display a definite dependency on the chopping rate with the Z scan peak to valley excursions increasing or decreasing with chopping frequency. This dependency was observed in PPC at 590nm as illustrated in Fig. 3.

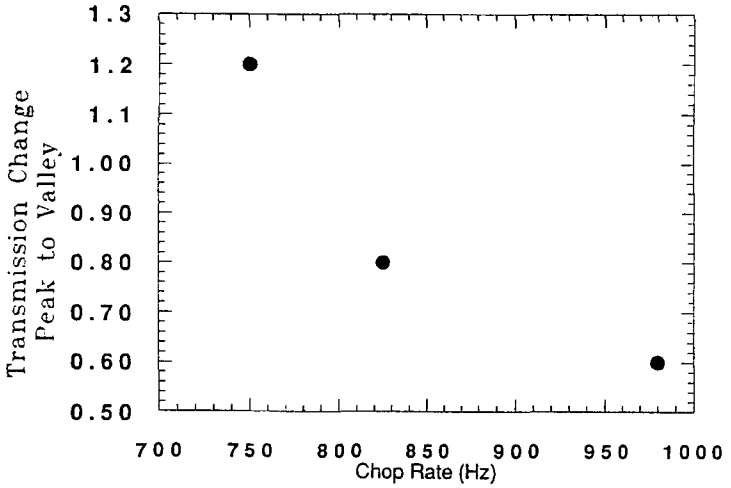

FIGURE 3 Chop rate dependency of ΔT_{P-V} in closed aperture Z scans.

ANALYSIS

The bleaching effect illustrated in Fig. 2b occurs when the linear absorption coefficient, α, becomes dependent on intensity. This effect is exhibited by the following equation.

$$\alpha = \frac{\alpha_o}{\left(1 + \frac{I}{I_s}\right)} \tag{1}$$

where,

α_0 is the low intensity linear absorption coefficient,
I is the incident intensity, and
I_S is the saturation intensity.

By decomposing the field at the sample exit into a sum of Gaussian beams[4], one obtains the normalized transmittance for the open aperture Z scan due to an intensity dependent absorption.

$$T(z) = \sum_{m=0}^{\infty} \frac{(-q_o)^m}{(m+1)^{3/2}} \qquad |q_0|<1 \tag{2}$$

where,

$$q_o(z) = \frac{\alpha_o}{I_s} \cdot I_o \cdot L_{eff} \cdot \frac{1}{\left(1 + \left(\frac{z}{z_o}\right)^2\right)} \tag{3}$$

In Eq. (3)[5], I_0 is the on-axis instantaneous intensity at the focus, z is the distance from the focus, and zo is the focusing distance. L_{eff} is the effective length given by $L_{eff}=[1-\exp(-\alpha_0 l)]/\alpha_0$. The dashed curve in Fig. 2b is obtained by using the first five terms of Eq. (3) with $-(\alpha_0/I_S)= -1.05 \times 10^{-7}$ cm/W. Then with $\alpha_0=24.9$ cm^{-1}, I_S becomes 2.37×10^8 W/cm^2. Using this saturation intensity and the known concentration of PPC, we calculate the excitonic wave function extent to be 15 Å.

The real part of $\chi^{(3)}$ was determined using the relation $|\Delta\phi|=\Delta T_{P-V}/0.406$.[2,3] This result along with an equation for the normalized transmittance seen at the

aperture[2,3] were then employed to give the dashed curve in Fig. 2a. The calculated values of $Re\chi^{(3)}$ and the second hyperpolarizability are -3.9×10^{-11} esu and -4.67×10^{-28} esu, respectively. As previously discussed and demonstrated these nonlinearities are not due to a fast mechanism. Therefore, the high peak intensities obtained from the 10psec pulses cannot be used to calculate n_2 or $Re\chi^{(3)}$. The actual intensity seen by the saturation or long-time effect is considerably lower

It remains unclear as to why closed aperture scans conducted at 1064nm displayed nonlinear effects while one-photon or two-photon absorption were not seen. Since changing the pulse width three orders of magnitude did not change the Z scan similarly the nonlinear effects seen at this wavelength must also be attributed to a long-time effect.

CONCLUSION

Open aperture Z scans of PPC exhibited a strong saturation effect at 590nm due to one-photon absorption. This intensity dependent change in the linear absorption coefficient resulted in a nonlinear change in the index of refraction via the Kramers-Kronig relation. This was observed experimentally in closed aperture Z scans and was found to be a long-time effect by observing the response to mechanical chopping. Scans conducted at 1064nm displayed similar long-time behavior.

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