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Nonlinear optical responses and laser damage thresholds of films of a
polarized stilbene side chain liquid crystal polymer and a phthalocyanine

by

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**Nonlinear optical responses and laser damage
thresholds of films of a polarized stilbene side chain
liquid crystal polymer and a phthalocyanine**

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Thin films of a side chain liquid crystal polymer (P-10) with a 4-dimethylaminostilbene-4'-carboxylic ester mesogen were measured to have degenerate four wave mixing efficiencies at 532 nm 18 times that of carbon disulfide and 0.55 times that of a film of 1.5 weight percent 4-dimethylamino-4'-nitrostilbene (DANS) in poly(methyl methacrylate) [PMMA] and second harmonic generation efficiency at 1064 nm 0.17 times that of a film of DANS in PMMA. A film of 2.0 weight percent of octakis(2-ethylhexyloxy)phthalocyanatocopper(II) in polystyrene was measured to have degenerate four wave mixing efficiency at 532 nm 19 times that of carbon disulfide. Single shot and cumulative laser induced damage thresholds were measured for all three materials at both wavelengths.

Introduction

Organic compounds and polymers with donor-acceptor substituted aromatic structures are of continuing interest due to their large second-order nonlinear optical coefficients $\chi^{(2)}$.¹⁻⁶ Their responses are electronic and nonresonant (which means the response is fast with little or no lattice phonon contribution and with low absorptive loss), they have low DC dielectric constants, and they can be fabricated into thin films and other useful forms by the common methods of processing thermoplastics.

Two approaches have been used to incorporate the structure of choice into the nonlinear optical (NLO) material. One approach has the active NLO structure dissolved in a polymer solvent that is then fabricated into films. An example of this approach is 4-dimethylamino-4'-nitrostilbene (DANS), shown in Fig. 1, doped into a glassy polymer such as poly(methyl methacrylate) [PMMA]. Films of this material oriented by DC electric fields in glassy polymers have been measured to have $\chi^{(2)}$ greater than that of inorganic crystals such as lithium niobate.⁷⁻⁹ The initial $\chi^{(2)}$ values of solutions of DANS in PMMA are not temporally stable due to relaxation of the polymer glass and of the solute toward an equilibrium isotropic state.¹⁰

Greater temporal stability has been achieved by a second approach, incorporation of DANS-like structures as side chains of glassy polymers such as polystyrene.¹¹ Further improvement in temporal stability is expected in this second approach when the NLO structure is the mesogen of a polymer liquid crystal (LC). A liquid crystal polymer will retain anisotropic structure indefinitely, whereas a non-liquid-crystalline polymer will relax slowly to an isotropic state after electrical poling. LC copolymers with dyes in the side chains have higher order parameters than dyes dissolved in LC polymers.¹² Numerous side chain polymers have been prepared for second order NLO applications,^{4,5,13} but many of the structures are proprietary, and most of them probably do not have liquid crystal

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phases. Some of the proprietary polymers have been tested extensively as frequency doubling and waveguide devices.¹⁴

Somewhat less is known about the structural requirements of organic materials for $\chi^{(3)}$. Polymers with long conjugated π -electron systems such as polyacetylene, polydiacetylenes, polythiophenes, poly(1,4-phenylenevinylene), polybenzodithiazoles, and heteroaromatic ladder polymers have shown the largest $\chi^{(3)}$ values.¹⁵ Theory predicts that nonresonant $\chi^{(3)}$ will depend on the number of conjugated carbons N of polyacetylene chains as $N^{4.6}$ with a leveling of $\chi^{(3)}$ for chains with end-to-end distance of 6.0 nm or more.¹⁶ Calculations on simple polyenes indicate that donor and acceptor substituents such as those on **DANS** and on our polymers should enhance nonresonant $\chi^{(3)}$. Significant $\chi^{(3)}$ values have been measured on resonance and in the band edges of various phthalocyanines.¹⁷

In the results presented here we describe here preliminary DFWM, SHG, and laser damage threshold experiments on films of a side chain liquid crystal polymer **P-10**¹⁸ and of an octaalkoxyphthalocyanine [**CuPc(OR)**]₈¹⁹ prepared in this laboratory. **P-10** contains a polarized stilbene mesogen and is expected to show a significant $\chi^{(2)}$. The results obtained for **P-10** and for **CuPc(OR)**₈ are compared with values for **DANS** in PMMA that were also measured.

Degenerate Four Wave Mixing (DFWM)

The liquid crystal polymer sample was a 100 μm thick film of **P-10**, which was contained in an area 1 cm x 2.5 cm with a lead spacer designed for a solution infrared spectroscopy cell, sandwiched between two microscope slides, annealed in a vacuum oven under slight pressure at 140 °C, and cooled to room temperature over 2 h to form a non-scattering, slightly birefringent, yellow polymer glass. The **DANS** sample was a 90 μm film on a 1 mm microscope slide prepared by evaporation of a chloroform solution of a

1.25 weight percent dispersion of DANS in PMMA and drying in air for 2 days. The average film thickness was calculated from measurements of the thicknesses of the coated and the uncoated glass slide with a micrometer caliper. Without magnification the DANS sample appeared orange and nonscattering. Examination with a polarizing microscope revealed small birefringent crystals of DANS dispersed in the PMMA and a low concentration of DANS dissolved in the PMMA, giving the clear regions of the film a pale yellow color in normal transmitted light. The CuPc(OR)₈ sample was a 97 μm film on a 0.2 mm glass cover slip prepared by evaporation of a chlorobenzene solution of 2.0 weight percent CuPc(OR)₈ in polystyrene.

$\chi^{(3)}$ was measured by DFWM using a frequency-doubled, mode-locked Nd:YAG laser (Quantel Model YG571C) producing single 20 ps pulses at 532 nm. The pulses were split into two pump beams and a probe beam. The pump beams were focused and crossed at an angle of 60° in the samples with incident intensities in the range 1.0-10.0 GW/cm². The probe beam exactly counterpropagated to one of the pump beams with incident intensities in the range 0.02-0.13 GW/cm². With this geometry phase matching is automatically satisfied, and the signal beam emerges from the sample exactly counterpropagating to the second pump beam. A portion of the signal beam was deflected by a beamsplitter and detected with a Si photodiode. The signal was recorded with either a PAR Model 4202 signal averager or a PAR Model 162 boxcar averager and analyzed with a microcomputer. The two pump beams were σ -polarized, and the probe beam was p-polarized. This combination of orthogonal polarizations of the pump and probe beams enabled the stray light background to be reduced by polarization sensitive detection. The temporal overlap of the three input pulses was adjusted using optical delay lines. In the same manner the temporal response of the DFWM signal was examined by varying the arrival time of the probe pulse relative to the pump pulses. The quantitative measurements were made at $t = 0$ when all three pulses were coincident in the material.

The absolute magnitude of $\chi^{(3)}$ for the polymer films was determined by using a 1 cm reference cell containing CS₂ under the same experimental conditions.²⁰ The small angle between the two pump beams results in a large overlap region allowing the cell thickness to be used for the interaction length. The value of $\chi^{(3)}$ is calculated using

$$\chi_{\text{polymer}}^{(3)} = \chi_{\text{CS}_2}^{(3)} \left(\frac{n}{n'} \right)^2 \left(\frac{L}{L'} \right) \sqrt{\frac{\eta}{\eta'}} \left(\frac{F'}{F} \right) \quad (1)$$

where n is the refractive index at 532 nm ($n = n'$ is assumed for our calculations), L is the interaction length, η is the measured scattering efficiency, and F is the incident laser intensity.²¹ The primed quantities represent measurements taken with the CS₂ reference cell. In our experimental arrangement the absolute scattering efficiency is

$$\eta = I_{\text{sig}}/I_{\text{probe}} \quad (2)$$

The DFWM data adjusted for the concentrations of the active components are given in Table 1. All films examined here show a $\chi^{(3)}$ greater than that of the CS₂ sample, increasing by factors of 18, 33, and 19 for P-10, 1.25% DANS in PMMA, and 2.0% CuPc(OR)₂ in polystyrene, respectively. The molar extinction coefficients, also given in Table 1, show that the films have considerable absorption at the wavelength of the experiment, and the measured values of $\chi^{(3)}$ may be enhanced by band-edge effects. Experiments at 1064 nm would be required to yield a true nonresonant value of $\chi^{(3)}$.

The strength of the signal from P-10 was measured as a function of the total input laser energy, and the results are shown in Fig. 2, which shows the measured absolute scattering efficiency versus the incident fluence in mJ/cm². The intensity of the signal is related to the three input beams by

$$I_{\text{sig}} = \beta[\chi^{(3)}]^2 L^2 I_1 I_2 I_{\text{probe}} \quad (3)$$

where I_1 , I_2 , and I_{probe} are the beam intensities defined earlier, L is the interaction length, and β is a proportionality constant.²² In terms of the absolute scattering efficiency

$$\eta = I_{\text{sig}}/I_{\text{probe}} = \beta[\chi^{(3)}]^2 L^2 I_1 I_2 \quad (4)$$

and a quadratic dependence of η on the input laser intensity is expected. A straight line fit to the log plot in Fig. 2 yields a slope of 2.5, slightly greater than that predicted. A possible mechanism that would yield a greater than quadratic intensity dependence is two photon absorption.

The intensity of the signal from **P-10** was measured as the arrival time of the probe pulse was varied, as shown in Fig. 3. There are two components of the signal: one centered at $t = 0$ when all three optical pulses are coincident in the sample, and a second component taking at least several hundred picoseconds to build up. The origins of the signal at $t = 0$ are the fast physical processes contributing to the third order susceptibility associated with the FWM of the two pump beams, probe beam, and signal beam. The real time width of this peak is about 50 psec and is the expected autocorrelation width of the three optical pulses. Contributions to the susceptibility would have relaxation times comparable with or less than the optical pulse width and may include $\chi^{(3)}$ contributions from electronic Kerr nonlinearities associated with electrons delocalized along the polarized aromatic side chain of **P-10**. Experiments on the conjugated polymer, poly-*p*-phenylenebenzobisthiazole (PBT) showed the response time of the optical nonlinearity to be subpicosecond, but still not resolvable outside the laser pulse width.²³ Measurements with femtosecond optical pulses will be required to determine the absolute speed of these effects.

The second feature in Fig. 3 is a diffracted signal that takes at least several hundred picoseconds to build up. The full extent of the rise time of this component could not be observed due to limitations on the length of the optical delay available. This component is probably associated with a $\chi^{(3)}$ contribution due to orientational Kerr nonlinearities. However, thermal effects cannot be ruled out until future measurements accurately determine the maximum signal intensity and its rise time.

Second Harmonic Generation

The P-10 sample was prepared by filtering a 10% weight/volume solution of the polymer in 1,4-dioxane through a 0.5 μm filter and spin coating the filtrate onto a 2.5 cm x 2.0 cm sheet of indium tin oxide (ITO) coated glass. The glass was cleaned by washing with sulfuric acid, *n*-amyl alcohol, and isopropyl alcohol with water rinses after each washing step. The film was dried under vacuum before poling. Its thickness of 1.5 μm was calculated from its weight, area, and density (1.155 g/cm³, measured by pycnometry). The film was covered with a second sheet of ITO-coated glass, and wires were cemented to each of the conductive surfaces with electrically conductive epoxy resin (Zymet SL 100-ZX). On a microscope hot stage the film was heated above its isotropization temperature ($T_i = 125^\circ\text{C}$) for 10 min, and an electrical field of 800 kV/cm was applied. The sample was cooled at 0.2 $^\circ\text{C}/\text{min}$ to a temperature 5 $^\circ\text{C}$ below T_i , maintained there for 24 h, and then cooled quickly to room temperature before the field was turned off. The SHG experiments were performed after the sample had been kept at room temperature for 3 days.

The DANS in PMMA sample for SHG measurements was prepared similarly by spin coating a 1,4-dioxane solution of 1.0 weight percent DANS in PMMA onto ITO-coated glass, drying under vacuum, and sandwiching the film with another sheet of ITO-coated glass. The thickness of the orange, transparent film was calculated to be 7 μm from its weight, area, and density. The sample was heated on a microscope hot stage to 120 $^\circ\text{C}$ at 10 deg/min, annealed at 120 $^\circ\text{C}$ (T_g of PMMA = 105 $^\circ\text{C}$) for 2 h, and then poled with

voltage slowly increased to 400 V (570 kV/cm) and held at 400 V for 2 h. The sample cooled slowly to room temperature with the field on. No microscopic changes in the sample were observed throughout this procedure. Unlike the sample used for DFWM, there was no sign of DANS crystals in the film at 400x magnification. Apparently a solution of DANS in PMMA was maintained during rapid evaporation of dioxane in the spin coating process, and DANS crystallized out of PMMA during slow evaporation of chloroform in the preparation of the DFWM sample. After the SHG experiments microscopic examination revealed no sign of laser damage to the sample.

SHG experiments on P-10 and on DANS in PMMA were performed with a modelocked Nd:YAG laser producing 20 ps single pulses at 1064 nm. After passing through a bandpass filter the pulses were incident on the polymer film that was free to rotate about an axis perpendicular to the plane of the experiment. The transmitted fundamental and the 532 nm second harmonic produced were focused on the entrance slit of a 0.25 m monochromator. In some cases the transmitted fundamental was rejected before the monochromator by a suitable infrared absorbing filter. The absolute conversion efficiency was determined by measuring the ratio of the 532 and the 1064 nm signal intensities and applying corrections for the relative responses of the monochromator and photomultiplier tube to the two wavelengths.

The second harmonic conversion efficiency is

$$\frac{I^{2\omega}}{I^{\omega}} = \frac{2 \omega^2 d_{\text{eff}}^2 L^2}{c^3 \epsilon_0 (n^{\omega})^2 (n^{2\omega})} I^{\omega} \frac{\sin^2 \left(\frac{\Delta k L}{2} \right)}{\left(\frac{\Delta k L}{2} \right)^2} \quad (5)$$

where

$$d_{\text{eff}} = (d_{33} \sin^2 \theta^{\omega} + d_{31} \cos^2 \theta^{\omega}) \sin \theta^{2\omega} + 2 d_{31} \cos \theta^{\omega} \sin \theta^{\omega} \cos \theta^{2\omega} \quad (6)$$

is the effective nonlinear optical coefficient.²¹ The transmitted second harmonic intensity depends upon the angle (θ) between the incident fundamental beam and the film normal. These angular variations, known as Maker fringes, can be analyzed using the theory of Jerphagnon and Kurtz.²⁴ The conversion efficiency as a function of θ is shown in Fig. 4 for the **P-10** sample.

The conversion efficiency of the **P-10** sample was measured as a function of input intensity at an angle of $\theta = 50^\circ$, and the results obtained are shown in Fig. 5. The data fit a straight line of slope 1.1, close to the value of 1.0 predicted by equation (5). Absolute efficiencies approach 10^{-7} , which are typical values for organic polymer films. Fewer SHG experiments were performed on the **DANS** sample, but preliminary experiments at an incident fluence of 6 mJ/cm^2 indicate the conversion efficiency is a factor of 2.1 less than that of the **P-10** sample. (Corrected for path length and concentration differences the molecular contribution to $\chi^{(2)}$ of the polarized stilbene of **P-10** is a factor of 5.6 less than that of **DANS**.)

Laser Damage Thresholds

Laser induced damage of the samples took on many forms, and experiments were conducted to measure the intensity thresholds for these effects. Light pulses of 20 ps FWHM at both 532 nm and 1064 nm from the Nd:YAG laser were focused to diameters of 1.08 mm and 1.28 mm respectively in the films, and decreases in the ratio of transmitted to incident intensity were monitored. In some experiments the transmission of a weak c.w. HeNe laser was monitored as a probe of the laser induced damage.

The single shot damage thresholds were measured for **P-10**, **DANS**, and **CuPc(OR)₈** at both wavelengths, and the results are in Table 2. The thresholds were calculated from the intensity of a single pulse that produced visible damage and measurable

changes in the transmittance. The appearance of the damage was different for each sample. **P-10** suffered bulk cracking of a 100 μm film and blackening of a 2 μm film. The DFWM sample of **DANS** in PMMA developed dark spots, which disappeared upon standing over several days, and also developed bleached spots, which were permanent. The green color of **CuPc(OR)₈** disappeared, leaving colorless spots on the film.

Damage was caused also by the accumulation of many less intense pulses. Figure 6 shows the transmission of the **CuPc(OR)₈** sample plotted as a function of the total incident energy for the two beam intensities indicated. Each data point represents the transmission averaged over 100 laser pulses at 1064 nm. When incident intensity of 10 mJ/cm^2 was used, no change in the sample transmission was observed after several thousand pulses. This is in contrast to the case where each laser pulse has an intensity of 48 mJ/cm^2 . The transmission decreases sharply after only a few hundred pulses have impinged on the sample. The results obtained for **P-10** are shown in Fig. 7 where the incident intensity was 71 mJ/cm^2 . The closed and open squares correspond to data points taken at two different regions of the sample, and the results show that the effects of cumulative damage are reproducible. The results of the cumulative damage experiments are summarized in Table 2. Neither **P-10** nor **DANS** has measurable absorbance at 1064 nm, whereas both absorb at 532 nm (Table 1). **CuPc(OR)₈** has a local absorption minimum at 532 nm and significant absorbance at 1064 nm from the tail of the strongest visible band. Two-photon absorption processes leading to photochemical decomposition may be occurring in the absorbing samples.

Conclusions

Optically clear thin films of a new liquid crystal polymer (**P-10**) containing a polarized stilbene side chain, **DANS** in PMMA, and a phthalocyanine [**CuPc(OR)₈**] in polystyrene have been shown to exhibit strong picosecond DFWM responses at 532 nm.

P-10 and **DANS** in PMMA also have strong picosecond SHG responses at 1064 nm. The DFWM response of **P-10** is about three orders of magnitude less, and the DFWM responses of **DANS** and of **CuPc(OR)₈** are about two orders of magnitude less, than those of the best long conjugated polymers, which are difficult to obtain in optically clear form. All of the samples suffer damage from the cumulative laser pulses at both wavelengths.

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Table 1. DFWM $\chi^{(3)}$ values and molar extinction coefficients.

sample	----- $\chi^{(3)}$, esu ^b -----		----- ϵ , M ⁻¹ cm ⁻¹ -----	
	of film	of active component	532 nm ^c	1064 nm ^c
CS ₂ ^a	6.8 x 10 ⁻¹³	6.8 x 10 ⁻¹³		
DANS	2.2 ± 0.9 x 10 ⁻¹¹	1.76 x 10 ⁻⁹	1.3 ± 0.1 x 10 ⁴	0 ± 300
P-10	1.2 ± 0.5 x 10 ⁻¹¹	1.2 x 10 ⁻¹¹	33 ± 10	0 ± 1
CuPc(OR) ₈	1.3 ± 0.4 x 10 ⁻¹¹	6.5 x 10 ⁻¹⁰	2.21 ± 0.02 x 10 ³	300 ± 100

^aN. P. Xuan, J.-L. Ferrier, J. Gazengel, and G. Rivoire, Opt. Commun., **51**, 433 (1984).

^bEstimated errors due to uncertainties of the interaction length in CS₂ and to random errors in measured scattering efficiencies. ^cEstimated errors due to uncertainties in scattering by the films. Absorbances of films were measured relative to assumed absorbance of zero at the lowest minimum in the range 400-2000 nm. The 532 nm value for CuPc(OR)₈ was obtained with a chloroform solution.

Table 2. Laser induced damage thresholds.

sample	single shot		cumulative	
	mJ/cm		pulses (mJ cm ⁻¹ pulse ⁻¹)	
	532 nm	1064 nm	532 nm	1064 nm
P-10	350	460	>300 (100)	400 (70)
DANS	78	420	100 (30)	100 (82)
CuPc(OR)₈	300	500	10 (100)	400 (48)

Figure Captions

Fig. 1. Structures of materials studied.

Fig. 2. Dependence of DFWM scattering efficiency of **P-10** on incident fluence.

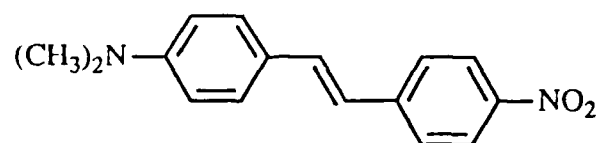
Fig. 3. Dependence of DFWM scattering efficiency of **P-10** on probe pulse delay.

Fig. 4. Dependence of SHG conversion of **P-10** efficiency on the angle between the input fundamental beam and the film normal.

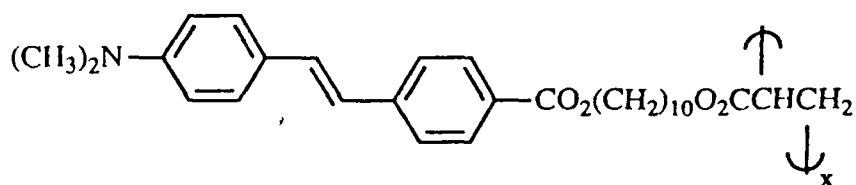
Fig. 5. Dependence of SHG conversion efficiency of **P-10** on incident fundamental beam fluence.

Fig. 6. Transmission of **CuPc(OR)₂** at 1064 nm for incident intensities of 10 mJ/cm²/pulse and 48 mJ/cm²/pulse. Laser induced damage is only apparent at the higher intensity, even though the same total intensity was incident.

Fig. 7. Fraction of 1064 nm light transmitted by **P-10** after repeated 71 mJ/cm² pulses. Filled and open data points are from independent experiments.



DANS



P-10

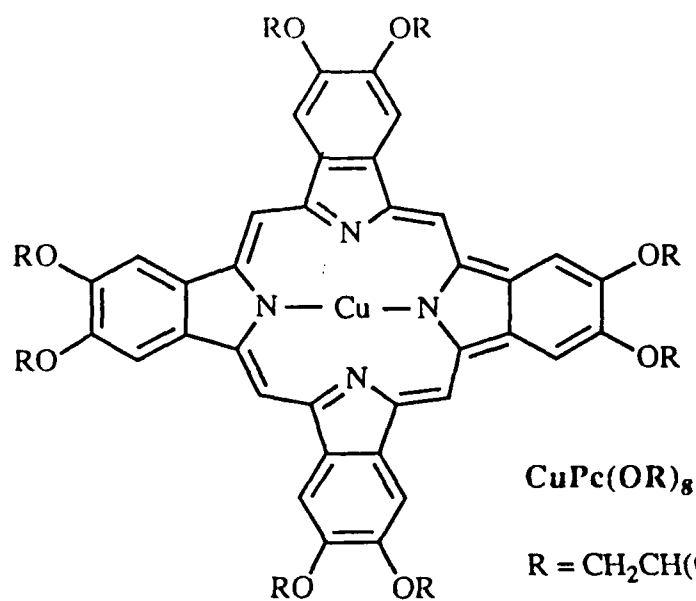


Fig 1

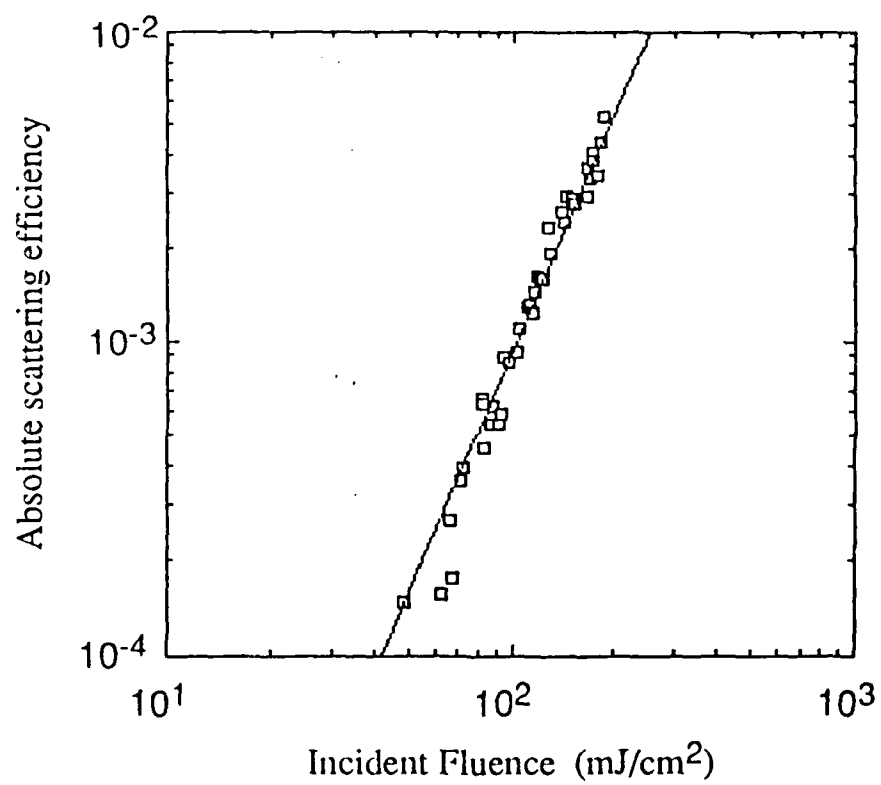


Fig 2

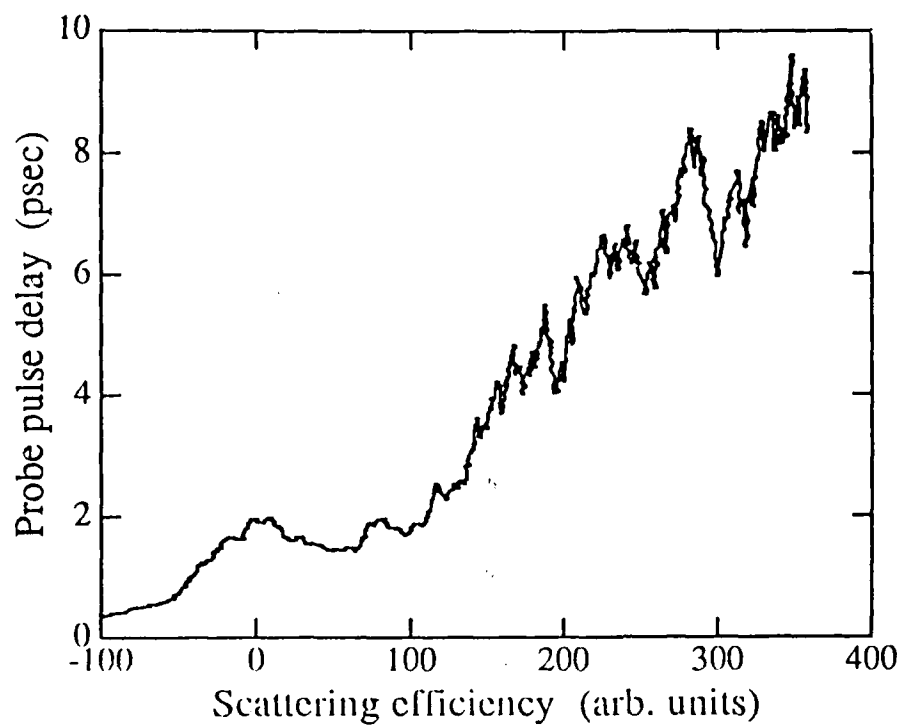


Fig 3

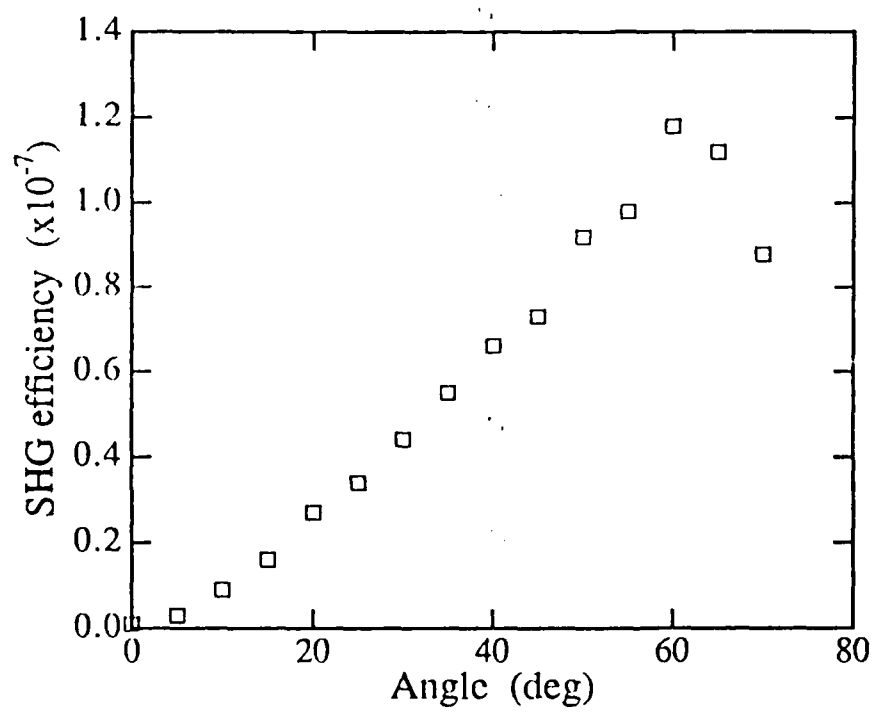


Fig4

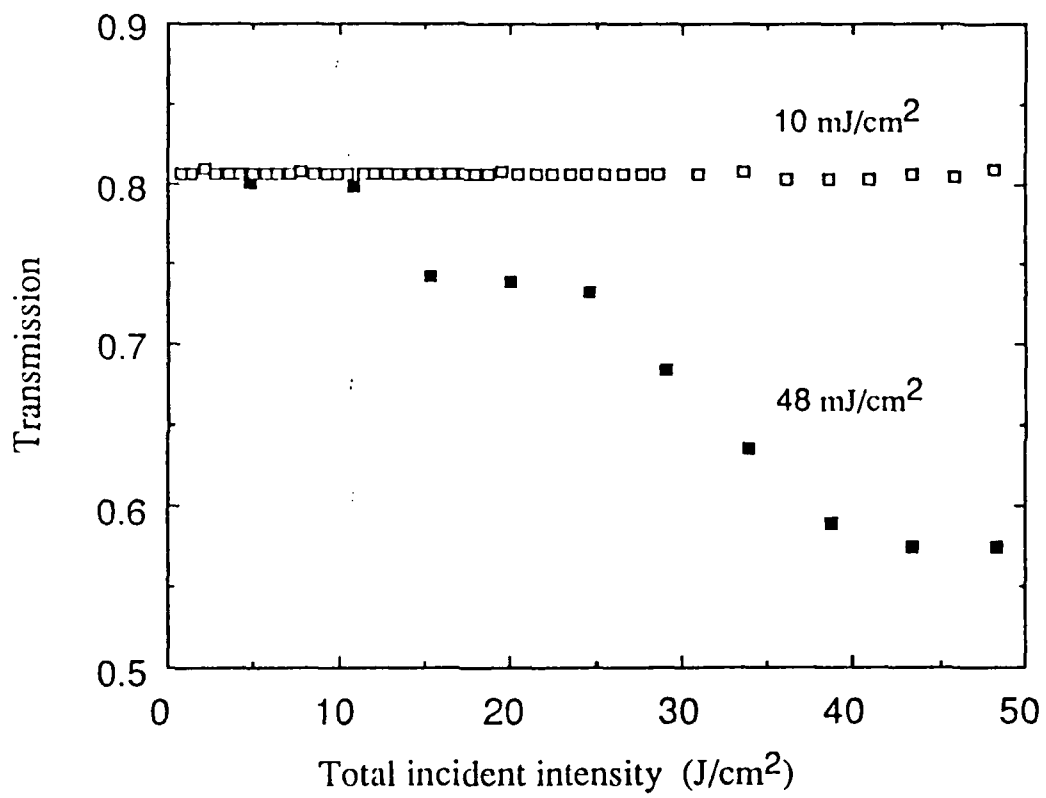


Fig 6

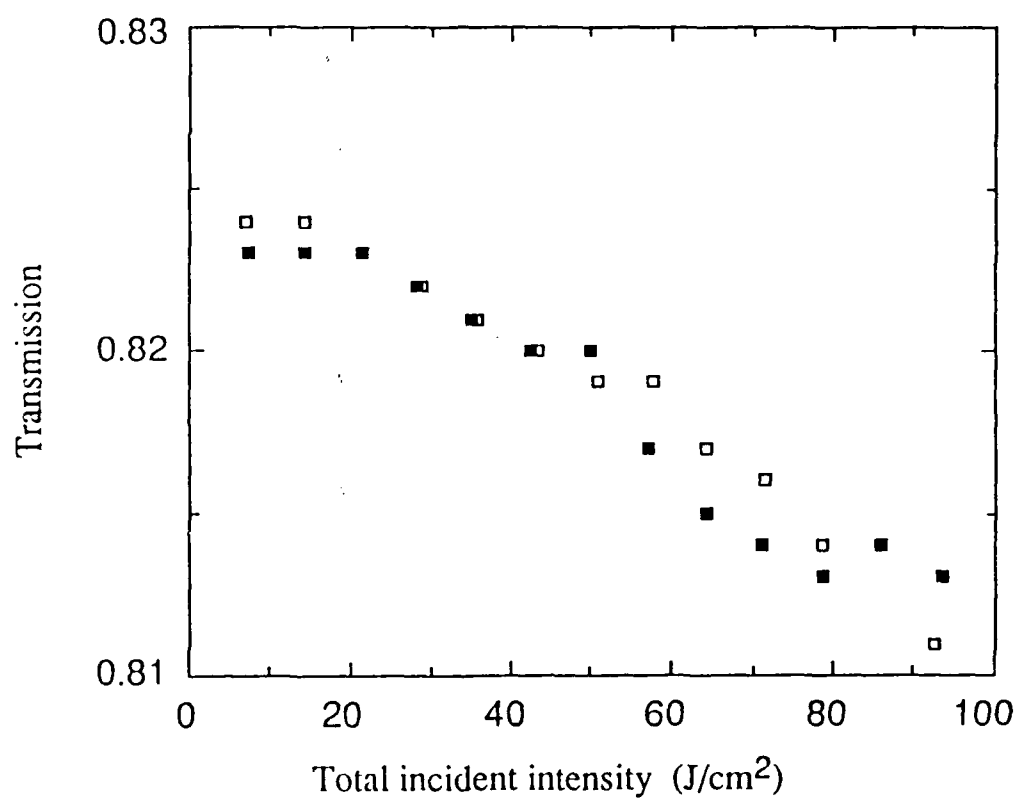


Fig 7