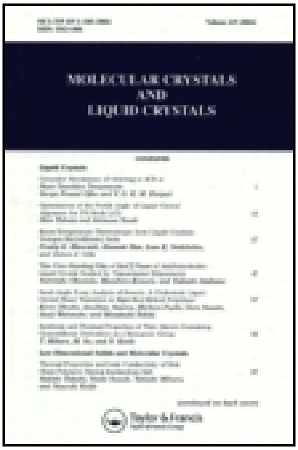

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Third Order Resonance Enhanced Nonlinearities of Polymethylmethacrylate Polymers Containing Nickel Dithiolene Host Molecules

A E Underhill [a] , C A.S Hill [a] , C S Winter [b] , S N Oliver [b] & J D Rush [b]

[a] Department of Chemistry, University of Wales, Bangor, Gwynedd, LL57 2UW, U.K.

[b] BT Laboratories, Martlesham Heath, Ipswich, IP5 7RE, U.K.

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THIRD ORDER RESONANCE ENHANCED NONLINEARITIES OF POLYMETHYLMETHACRYLATE POLYMERS CONTAINING NICKEL DITHIOLENE HOST MOLECULES

A E UNDERHILL, C A S HILL
Department of Chemistry, University of Wales, Bangor,
Gwynedd, LL57 2UW, U.K.

C S WINTER, S N OLIVER AND J D RUSH
BT Laboratories, Martlesham Heath, Ipswich, IP5 7RE, U.K.

Abstract The third order optical nonlinearity, $\chi^{(3)}$, of two polymers consisting of nickel dithiolene guest molecules in a polymethylmethacrylate host have been measured. The optical nonlinearity was measured by degenerate four wave mixing experiments at a wavelength of 1.06 µm using 100 ps laser pulses. $\chi^{(3)}$ coefficients of up to 10^{-17} m^2/V^2 were observed corresponding to nonlinear refractive index, n_2, of up to 10^{-8} cm^2/KW with a damaged threshold > $1GW/cm^2$.

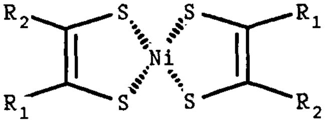
INTRODUCTION

A wide range of polymers have been studied for their usefulness as materials for all-optical signal processing. However it has proved difficult to produce materials which combine materials processability and low linear and nonlinear absorption with the large nonlinear refractive index required for devices. An alternative route is to start with an easily processable polymer such as polymethylmethacrylate (PMMA) and then dope the polymer with guest molecules which have a high nonlinear refractive index. We have recently shown that metal dithiolene complexes in solution possess the switching speed, size of response and low linear and nonlinear absorptions that are required for all-optical signal processing.[1-3]

We have, therefore, selected a nickel dithiolene complex which has a large optical nonlinearity and good device figures of merit and synthesised derivatives expected to be reasonably soluble in polymer hosts. These materials have been fabricated into guest-host polymers films. The nonlinear characterisation of these guest-host polymers is reported below.

RESULTS AND DISCUSSION

The metal dithiolene complexes were synthesised by the method of Mueller-Westerhoff *et al*[4]. Figure 1 shows the schematic chemical structure of the compounds studied:



Compound 1: $R_1 = C_2H_5$; $R_2 = C_6H_5$
Compound 2: $R_1 = n\text{-}C_4H_9$; $R_2 = C_6H_5$

FIGURE 1

The metal dithiolenes were studied in solution in dichloromethane and as a guest species in PMMA films. The concentration of Compound 1 in the polymer was 2.5 x 10^{20} molecs/cc and that of Compound 2, 4.0 x 10^{19} molecs/cc. Compound 2 was studied as a 70μm thick cast film and Compound 1 as a 3μm thick spun film made by spinning three separate 1μm layers. Linear absorption spectra were measured in a Perkin-Elmer Lambda 9 spectrophotometer. The wavelength of the absorption maxima of either compound does not alter from 795-800 nm on moving from dichloromethane solution to the polymer host but there is a slight broadening (about 10 nm at FWHM) and a distinct tail on the long wavelength side of the absorption band. The films were distinctly more absorbing than the solutions at 1.06 µm but as will be seen below, this has no effect on the observed molecular hyperpolarisability but does degrade the figure of merit for these polymers.

Nonlinear optical studies were carried out using a mode-locked, Q-switched, amplified Nd:YAG in which a single 100ps pulse was selected from the pulse train. A retro-reflection degenerate four wave mixing set-up was used to measure $\chi^{(3)}$ as described in reference 1. The beam was telescoped down to give a final beam diameter of 0.55 mm. The experiment was calibrated using CS_2, for which $\chi^{(3)}$ was taken to be 2.5×10^{20} m^2/V^2.[5,6] By inserting a half wave plate into the pump beam it was possible to measure $\chi^{(3)}$ with the pump and probe beams either cross or parallel polarised and thus distinguish between certain possible mechanisms giving rise to the nonlinearity. By inserting a block into either the pump or probe beam it was possible to confirm the phase conjugate nature of the signal. The relationship between $\chi^{(3)}$ and the reflectivity, R, (phase conjugate signal/probe signal) for samples with low absorption is[7]

$$\chi^{(3)} = 4c^2\epsilon_0 n^2 R^{1/2}/3\omega IL \qquad (1)$$

where I is the pump beam intensity, ω the laser frequency and L the sample length. The observed real part of $\chi^{(3)}$ can be converted into a nonlinear refractive index by means of the identity relationship:

$$n_2(m^2/W) = \frac{1}{c\epsilon_0 n^2_0} \chi^{(3)}(m^2/V^2) \qquad (2)$$

From which a figure of merit can be calculated relating the linear loss to the nonlinear refractive index:[8]

$$W = \Delta n_{sat/}/\alpha\lambda \qquad (3)$$

where Δn_{sat} is the maximum change in index, which is the product of n_2 and the damage intensity for most organic materials, α is the linear loss and λ the operational wavelength. In order for a waveguide device such as a directional coupler or Mach Zender Interferometer to show some switching at reasonable power levels then W>1 is required. Full switching of a directional coupler requires W=10 and a Mach-Zender W=5[8].

Table I summarises the calculated values of n_2 and the absorption coefficient of the nickel dithiolenes in both the solution and polymer matrix. The damage thresholds observed lay in the range 0.8-1.4 GW/cm^2 and a value of 1.0 was used to calculate W. The ratio of the molecular nonlinearities (γ) in solution and polymer for each compound differ by 20-30% which is within experimental error. This suggests that the origin of the nonlinearity is the same in both the film and in solution. The ratio of $\chi^{(3)}$xxxx to $\chi^{(3)}$xyyx for both materials was 3.0-3.5 which is consistent with a non-absorptive origin for $\chi^{(3)}$. This and the agreement of the solution and polymer film results show that the observed nonlinearity does not have a thermal origin.

TABLE I - Results for Compounds 1 and 2 corrected to 10^{18}molecs/cc.

		Concentration (molecs/cc)	n_2 (cm^2/KW)	γsol/ γpol	α (cm^{-1})	W
1	Solution	7.4×10^{17}	3.5×10^{-11}	1.3	0.09	3.7
1	Polymer	2.5×10^{20}	9.2×10^{-9}		87.0	1.0
2	Solution	5.0×10^{17}	2.4×10^{-11}	0.9	0.06	3.8
2	Polymer	4.0×10^{19}	2.1×10^{-9}		57.0	1.2

Using this experimental data and equation 2 above a value for n_2 of nearly 10^{-8}cm^2/KW can be calculated for polymer containing Compound 1 and 2.10^{-9}cm^2/KW for polymer containing Compound 2. However the value of W has been reduced from about 4 for a solution to 1-1.5 in the case of the polymer films due to the long wavelength tail of the absorption band as described above.

Z-scan studies were undertaken on Compound 2 to try and clarify the origin of the large nonlinear refractive index and to measure the contribution from two photon absorption. The samples studied were a solution of Compound 2 in a 1mm cuvette and a PMMA host doped with 8.10^{19} molecules/cc of Compound 2. The polymer was spin-coated onto a silica cover-slip to give a 11μm thick film of uniform appearance. The results are summarised in Table II. The solution and solid state results were again in good agreement and reasonably close to the DFWM results, given the differences in beam profile, characterisation technique, etc. However, a much higher damage threshold, >3 GW/cm^2, was measured. This is either due to the single mode characteristics of the laser eliminating any 'hot spots' or due to the better quality of the spun films. The ratio of the real to imaginary parts of the nonlinearity was about 1.5π less than the value of 2π chosen for the figure of merit given in reference 10.

TABLE II - Z-Scan measurements on Compound 2

	N molecs/cc	L μm	n_2 cm^2/KW	Re$\chi^{(3)}$/ Im$\chi^{(3)}$	γ m^{5}V^{-2}
Solution	2.1×10^{18}	1000	-2.1×10^{-11}	4.5	-1.5×10^{-45}
Polymer	8.0×10^{19}	11	-1.4×10^{-11}	3.9	-2.6×10^{-45}

The negative n_2 could arise from saturable absorption or the optical Stark effect and is consistent with a two-level system. It is not of thermal origin because of the agreement of the solution and polymer values.

It should be possible to produce polymer films doped with 2.10^{20} molecules/cc. This corresponds to a nonlinear refractive index at least ten times greater than those observed in the best polydiacetylenes such as 4-BCMU[11,12]. W could also be improved by detuning further from the absorption maxima but derivatives with absorption bands below 750-770 μm are not available. This could be overcome by measuring at 1.3 μm. Theoretical studies[13] suggest that extended conjugated sulphur systems may be preferable to conjugated carbon systems for static $\chi^{(3)}$, and we are currently exploring whether such extended systems lead to further increases in n_2 or W.

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