

## Optical limiting action in poly(para-methoxy phenylacetylene)

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**Optical limiting action is demonstrated at 532 nm with unfocused nanosecond laser pulses in poly(para-methoxy phenylacetylene) in the solution state with a threshold limiting fluence of 65 mJ/cm<sup>2</sup>.**

POLY(para-methoxy phenylacetylene) is a conjugated polymer with carbon atoms on the backbone, and hydrogen and para-methoxy groups as the sidegroups. Conjugated polymers are known<sup>1</sup> to have high values for the susceptibility tensor  $\chi^{(3)}$  due to the presence of the delocalized  $\pi$ -electrons. In this communication, the method of preparation of this polymer sample is given followed by a discussion of the linear and nonlinear optical studies and the results.

The method of preparation is as follows: A 50 ml single-necked round-bottomed flask with magnetic stirring bar, capped with a rubber septum, is flame-dried and under nitrogen atmosphere, Mo(Co)<sub>6</sub> (0.145 g, 0.54 mole) is taken in the flask and about 6 ml of toluene is added. The resulting solution is refluxed for 6 h in an oil bath and cooled. Para-methoxy phenylacetylene (1.45 g, 10.9 mole) is added and refluxed with stirring for 24 h. The reaction mixture is cooled and the polymer is precipitated by pouring into excess ethanol. It is filtered, washed with hot methanol and dried under vacuum. The yield is 0.68 g (47%) of dark brown polymer in amorphous powder form.

The polymer dissolves well in organic solvents. The as-prepared solution is yellowish brown when the solvent is 1,2-dibromoethane and yellow when dissolved in toluene. Accordingly, the absorption edge has a longer tail in the visible region for the former sample. The polymer is stable at room temperature. The IR spectrum of the sample taken in a KBr pellet shows the characteristic absorptions at 3200 cm<sup>-1</sup> (C-H stretch), 1600 cm<sup>-1</sup> (benzene double bonds), 1504 cm<sup>-1</sup> (backbone conjugation), 1456 cm<sup>-1</sup> (trans-rich nature), etc.

When illuminated with the intense Q-switched second harmonic radiation at a wavelength of 532 nm from a frequency-doubled Nd:Yag laser (Quanta-Ray, DCR 2(10)), the solution prepared in 1,2-dibromoethane turns to dark brown under visual observation. The optical absorption of this laser-treated sample shows the for-

mation of a new band in the visible region centred around 550 nm. When the solution is prepared in toluene, there is change neither under visual observation nor in the recorded absorption spectrum after treating with 532 nm laser pulses.

The formation of the band at 550 nm under 532 nm excitation is observed if the polymer is dissolved in other halogenated solvents like CCl<sub>4</sub> and CHCl<sub>3</sub> and polar solvents such as dimethylsulphoxide and tetrahydrofuran. However, the optical absorption of the laser-treated polymer powder dissolved in 1,2-dibromoethane failed to show the new band. This is indicative of solvent effect in the formation of the band at 550 nm. That the change could be due to a charge transfer effect is suggested by the observation of a small band at 550 nm even without the excitation at 532 nm when the polymer is dissolved in the acceptor solvent nitrobenzene. The band however remains when this solution is excited at 532 nm. If the polymer is extracted from the laser-treated solution in 1,2-dibromoethane, where the new band had been observed, and then redissolved in toluene, there is no band at 550 nm before and after 532 nm excitation. This is also indicative of the solvent effect and leads us to conclude that there is no permanent change in the polymer as far as the new band at 550 nm is concerned.

The <sup>13</sup>C and <sup>1</sup>H NMR spectra are taken for both the as-prepared polymer and the polymer extracted from the solution excited at 532 nm in the solvent 1,2-dibromoethane. The as-prepared polymer shows bands corresponding to fused cyclobutane rings in addition to those of backbone carbons and the para-methoxy groups. The band due to the fused cyclobutane rings is not present for the laser-excited sample. The thermal gravimetric analysis and molecular weight measurements of the two samples, however, show no significant differences.

Q-switched laser pulses at 532 nm are incident on the polymer solutions contained in 1-mm thick quartz cuvettes. The value of the optical absorption coefficient measured with very low intensity laser pulses is different from the values obtained from the spectrophotometer which has an incoherent source. The incident and transmitted laser pulse energies are measured and a plot of transmittance (the ratio of the transmitted to incident energies) versus the incident energy indicates a reduction in transmittance with increase in intensity above a threshold value. This is indicative of optical limiting action which is an effect opposite to that of saturable absorption.

The basic requirements of an optical limiter<sup>2</sup> are an excited state absorption cross section that is higher than the ground state absorption cross section, a fast intersystem crossing rate with the presence of a metastable state and the duration of the exciting pulse lower than the excited state lifetime, so that there is a cumulative

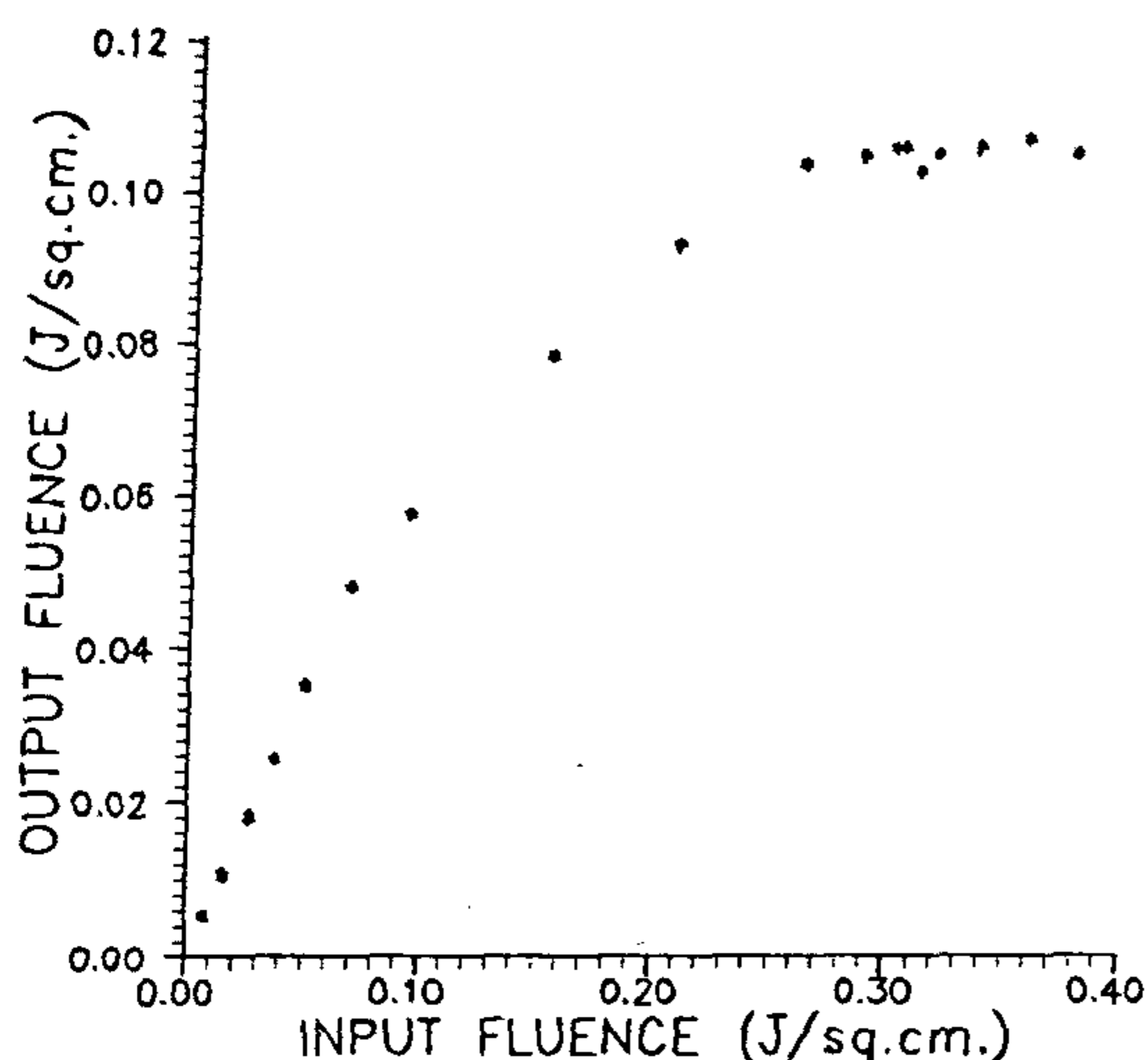


Figure 1. The variation of output fluence with input fluence in solution of poly(para-methoxy phenylacetylene) in the solvent 1,2-dibromoethane for excitation under a Q-switched doubled Nd:Yag laser.

buildup of population in the excited state, leading to increased levels of absorbance for the pumping beam.

Figure 1 shows variation of output fluence with different values of input fluence, in  $\text{J}/\text{cm}^2$ . The relation starts differing from linearity when the input fluence is  $65 \text{ mJ}/\text{cm}^2$ , ultimately clamping the output fluence at a fixed value when the input fluence reaches  $250 \text{ mJ}/\text{cm}^2$ . In comparison,  $C_{60}$  is known<sup>3</sup> to show a change from linearity in transmittance when the input fluence reaches  $100 \text{ mJ}/\text{cm}^2$  for a sample with an initial transmittance of 63%. Our sample had an initial transmittance value of 69%. The variation in transmittance during an increase and a decrease in the incident intensity enables us to see the extent of recovery of the initial transmittance values. The results are indicative of minimum photodegradation of the samples. It is found that the recovery of the initial transmittance is not degraded due to repeated illumination under the laser pulses. There is no change in transmittance when the sample is illuminated with microsecond pulses at 532 nm from the same laser under non-Q-switched conditions which is due to the lower peak power of these pulses.

The third-order susceptibility  $\chi^{(3)}$  as found from the optical phase conjugation experiment in a degenerate four-wave mixing geometry<sup>4</sup> is  $1.2 \times 10^{-18} \text{ m}^2 \text{V}^{-2}$ . It is found that the value of the phase conjugate reflectivity continues to increase with an increase in pump intensity even in the region of optical limiting. This is another indication that the limiting action is not a consequence of sample degradation but is a true optical effect. No change was observed in the spatial and temporal profiles of the transmitted laser pulse in comparison to the input pulse, suggesting that the effect of nonlinear scattering may be minimal unlike in  $C_{60}$  (ref. 5).

In conclusion, it is found that poly(para-methoxy phenylacetylene) acts as an optical limiter at 532 nm under near resonant conditions. The threshold for limiting occurs at a fluence of  $65 \text{ mJ}/\text{cm}^2$  and is easily realizable for practical applications. The changes in transmittance are more due to induced transitions than from thermal effects. Photodegradation of the sample is minimal as inferred by conducting nonlinear transmission studies both on freshly prepared samples and well-illuminated samples. High values of phase conjugate reflectivity obtained beyond the limiting threshold also emphasize this point. Though the solvent effects are present in the linear absorption for excitation with 532 nm laser pulses, the limiting action is not solely governed by the solvent as seen from the identical trends in the variation of high intensity transmittance for the polymer when dissolved in different solvents.

1. Chemla, D. S. and Zyss, J. (eds), *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press, New York, 1987.
2. Hoffman, R. C., Stetyick, K. A., Potember, R. S. and McLean, D. G., *J. Opt. Soc. Am.*, 1989, **B6**, 772-777.
3. Tutt, L. W. and Kost, A., *Nature*, 1992, **356**, 225-226.
4. Vijaya, R., Murti, Y. V. G. S., Sundararajan, G. and Prasada Rao, T. A., *Opt. Commun.*, 1990, **76**, 256-260.
5. Mishra, S. R., Rawat, H. S., Joshi, M. P. and Mehendale, S. C., *J. Phys. At. Mol. Opt. Phys.*, 1994, **B27**, L-157-163.

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