

Saturable absorption in poly(indenofluorene): a picket-fence polymer

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Poly(indenofluorene) shows a strong degenerate four-wave mixing (DFWM) response when it is excited with 100-fs pulses at 800 nm. The DFWM signal scales with the 1.5 power of the input intensity, which we interpret as being due to absorption saturation phenomena. The saturation was studied by open-aperture Z scan in dilute solutions of poly(indenofluorene) in chloroform. The changes in the absorption coefficient α are described by the formula $\alpha = \alpha_0/[1 + (I/I_{\text{sat}})^{1/2}]$, where I_{sat} is the saturation intensity, which is found to be of the order of 100 MW/cm². © 1998 Optical Society of America

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Nonlinear optical (NLO) properties of oligomeric and polymeric structures containing π -electron conjugated chains have been of continuing interest. In particular, polymers such as polyacetylene, poly(*p*-phenylene vinylene), and polydiacetylenes have been found to possess high third-order optical nonlinearities (see, e.g., Refs. 1–3). Because the π -conjugated chain of such polymers is much less susceptible to deformation than chains of typical σ -bonded polymers (such as polyacrylates and polyethylene), the term “rigid rod” polymers is sometimes used to describe some of these structures. The term “ladder polymers” refers to structures in which the π conjugation has a multistrand character. We describe here the results of NLO studies of a recently synthesized conjugated polymer, poly(indenofluorene) (PIF),⁴ which has the chemical structure shown in Fig. 1. We suggest the name “picket fence” for this structure, which apparently results in a high conjugation of π electrons: PIF shows a relatively long wavelength absorption with a maximum of the range 600–800 nm (Fig. 1). Such a small bandgap of a conjugated polymer is likely to lead to enhanced NLO properties. We have started an investigation of the NLO properties of PIF; here we describe the results obtained at 800 nm. Because this is the wavelength of strong one-photon absorption, one may expect absorption saturation to be a major source of NLO effects.

PIF was synthesized as described in Ref. 4. The polymer is soluble in several organic solvents, such as chloroform and toluene. Chloroform solutions with known concentrations of PIF (in the range 0–0.1%) were used for some measurements. Other measurements were performed on thin films of PIF that were obtained by casting from chloroform solution upon microscope glass substrates.

All NLO measurements were performed with an amplified Ti:sapphire laser system operating at 800 nm with 100-fs pulses and a 30-Hz repetition rate. As a first step of these investigations we performed degener-

ate four-wave mixing (DFWM) measurements. A boxcars geometry was used (cf. Ref. 3). Figure 2 shows semilog plots of a series of DFWM curves obtained with various beam energies. It can be seen that the DFWM response is dominated by a process described by a first-order decay law with a lifetime of the decay (~ 1.3 ps) that does not seem to depend on the input power. Assuming that the DFWM signal is proportional to the square of the susceptibility change induced by the irradiation, the lifetime of the induced species that contributes to this susceptibility change should be taken as twice the DFWM decay lifetime, i.e., 2.6 ps. We note that Graupner *et al.*⁵ attributed a lifetime of 2 ps observed in transient absorption studies on a ladder poly(*p*-phenylene) to the thermalization of hot intrachain charged polarons P^\pm . It is possible that a similar process dominates the decay in PIF.

As can be seen from the increase of the signal magnitudes with the input power in Fig. 2, the dependence of the magnitude of the DFWM signal on the light intensity I is quite different from the usual cubic dependence that is characteristic of nonresonant third-order nonlinearity. The observed power dependence corresponds roughly to I_{DFWM} proportional

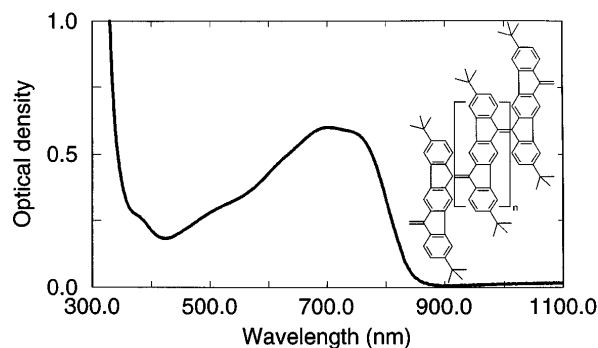


Fig. 1. Absorption spectrum of a thin PIF film ($\sim 0.1 \mu\text{m}$ thick). The chemical structure of PIF is shown in the inset.

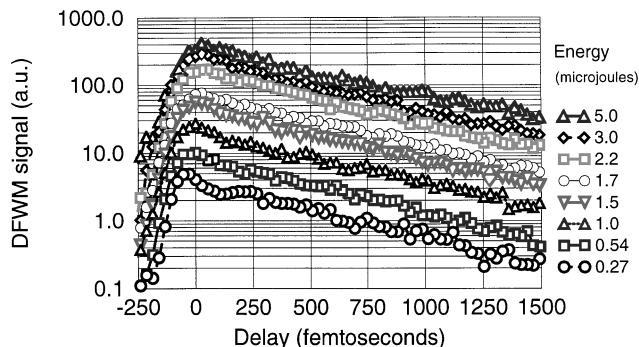


Fig. 2. Semilog plots of DFWM curves obtained at 800 nm with 100-fs pulses in a thin PIF film ($\sim 0.1 \mu\text{m}$). The energies of the beams are marked.

to $I^{1.5}$. The presence of such a dependence makes it unreasonable to use the description of the nonlinearity in terms of the nonlinear refractive index n_2 [or of the third-order susceptibility $\chi^{(3)}$] because the effective value of n_2 would be intensity dependent.

The observed power dependence suggests that the induced change of the complex susceptibility in PIF exhibits a saturationlike behavior in the light-intensity range used in our DFWM measurements. To investigate the saturation phenomenon in more detail we performed pump-probe measurements on PIF films and Z-scan measurements of solutions of PIF. The results of the pump-probe measurements will be described elsewhere; below we analyze the results obtained from open-aperture Z scans of PIF solutions.

Figure 3 shows examples of the open-aperture Z scans that we obtained for a series of chloroform solutions of PIF by using 100-fs pulses at 800 nm. The beam-waist radius w_0 was $34 \mu\text{m}$, and the on-axis intensity was $40 \text{ GW}/\text{cm}^2$, as determined from closed-aperture Z-scans on silica plates (for SiO_2 the value $n_2 = 3 \times 10^{-16} \text{ cm}^2/\text{W}$ was assumed). Strong transmission changes (absorption bleaching) observed here indicate that PIF behaves as a saturable absorber.

We attempted to fit the shapes of the obtained Z scans, assuming simple models for the change of absorption of the investigated medium with light intensity. It was shown previously^{6,7} that open- and closed-aperture Z-scan curves obtained on some conjugated polymers that showed absorption saturation behavior can be interpreted with the assumption that the complex nonlinear refractive index of the material is given by $n_2 = \text{Re}(n_2) + i \text{Im}(n_2)$, that is, in the same way as for the case of two-photon absorption, the difference being in the assumed sign of the imaginary part of n_2 . The modification of the absorption coefficient can then be described by a linear dependence on the intensity:

$$\alpha(I) = \alpha_0 + \beta I, \quad (1)$$

where α_0 is the low-intensity absorption coefficient and β is the nonlinear absorption coefficient (which is negative in the case of absorption bleaching)—an analog of a two-photon absorption coefficient. Attempts to use Eq. (1) for the interpretation of Z scans obtained on PIF solutions were unsuccessful. Therefore it seemed reasonable to investigate the possibility of using other absorption saturation models.

A simple kinetic model is often used when the saturation is considered in terms of depletion of the ground-state concentration; thus, under the steady state,

$$\frac{dN}{dt} = \frac{\sigma I}{h\nu} (N_g - N) - \frac{N}{\tau} = 0, \quad (2)$$

where N is the concentration of excited-state molecules, N_g is the undepleted ground-state concentration, σ is the absorption cross section, $h\nu$ is the photon energy, and τ is the lifetime of the excited-state population. Assuming that the absorption coefficient α is proportional to the ground-state population, $\alpha = \sigma(N_g - N)$, we get the following equation describing the saturation:

$$\alpha = \alpha_0 \frac{1}{1 + \tau\sigma I/h\nu} = \alpha_0 \frac{1}{1 + I/I_{\text{sat}}}, \quad (3)$$

where $I_{\text{sat}} = h\nu/(\sigma\tau)$ is the saturation intensity and $\alpha_0 = \sigma N_g$. The case described by Eq. (3) is often referred to as homogeneous saturation (cf. Ref. 8). The presence of a bimolecular recombination of excited species will modify Eq. (3) but is rather inconsistent with the intensity-independent single exponential decays of DFWM curves.

In the case of a two-level system with inhomogeneously broadened states and hole burning, it has been found^{9,10} that the saturation can be described by

$$\alpha = \alpha_0 \frac{1}{(1 + I/I_{\text{sat}})^{0.5}}. \quad (4)$$

To our knowledge, Eqs. (3) and (4) were not previously used for the interpretation of experimental Z

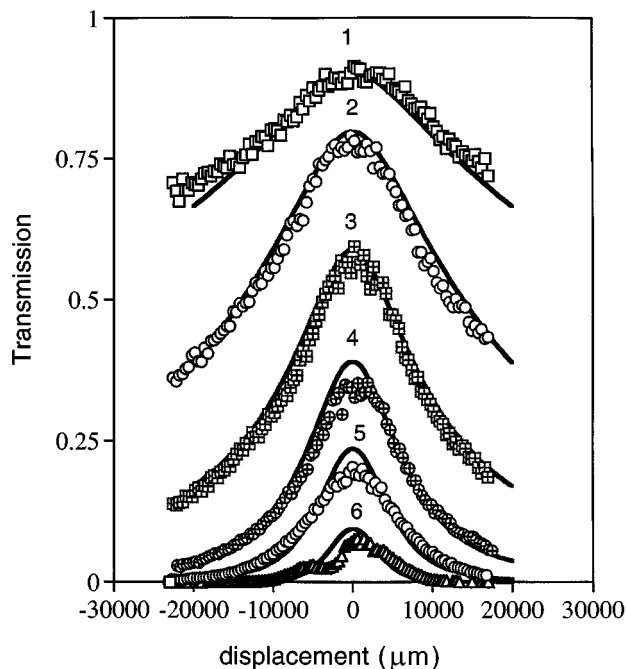


Fig. 3. Experimental and theoretical open-aperture Z scans of 1-mm cells containing chloroform solutions of PIF with the following concentrations: 0.0057% (curve 1), 0.0113% (curve 2), 0.0189% (curve 3), 0.0292% (curve 4), 0.0396% (curve 5), and 0.0576% (curve 6).

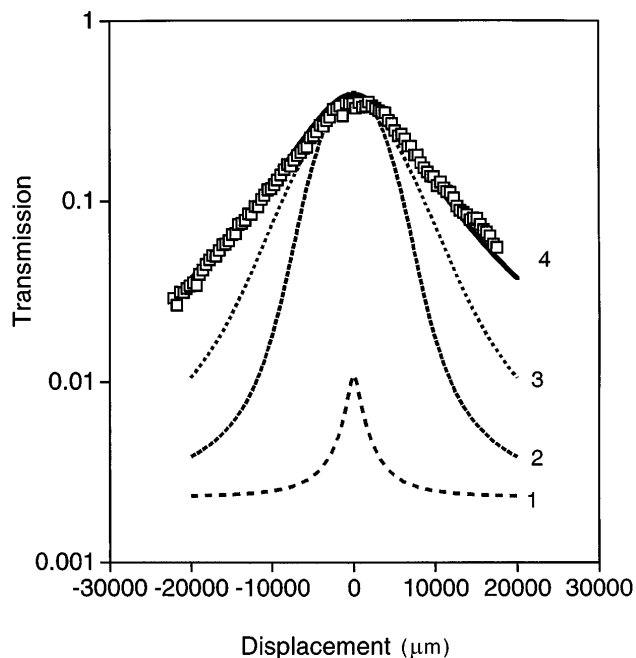


Fig. 4. Comparison of theoretical Z-scan shapes [curves 1, 2, 3, and 4 calculated with Eqs. (1), (3), (4), and (5), respectively] with that of the experimental curve (squares).

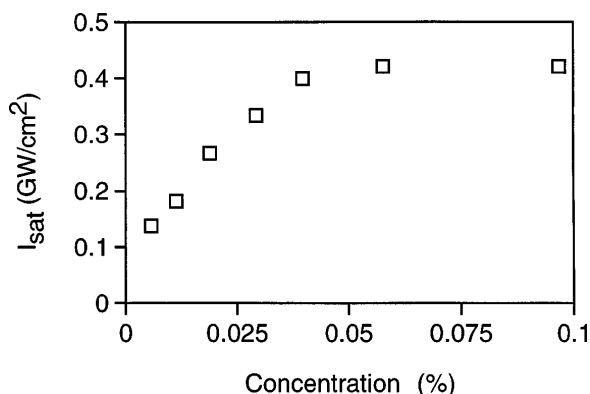


Fig. 5. Best-fit saturation intensity I_{sat} versus the concentration of PIF in chloroform for the data presented in Fig. 3.

scans. We tried to use Eqs. (1), (3), (4) to analyze our experimental Z scans. We obtained the theoretical transmission curves by assuming a thin sample approximation and performing numerical integration over the thickness of the sample and over the area of the beam. The absorption coefficient α_0 was taken to be $2.08 \times 10^5 / c_{\text{PIF}}$ [cm^{-1}], where c_{PIF} is the weight fraction of PIF in the solution. We found that the experimental curves are not well reproduced by any of Eqs. (1), (3), and (4). However, a good fit was obtained with an *ad hoc* formula:

$$\alpha = \alpha_0 \frac{1}{1 + (I/I_{\text{sat}})^{0.5}}, \quad (5)$$

which was used for the curves presented in Fig. 3. Figure 4 shows a comparison of attempts to fit the shape of an open-aperture Z scan for 0.0292% of PIF in chloroform by use of one or another of Eqs. (1), (3), (4), or (5). Note that Eq. (1) is unable to reproduce the absolute value of the transmission at the peak of the curve (within the constraint that the absorption coefficient cannot become negative, i.e., $\alpha > 0$) and Eqs. (3), and (4) give Z-scan shapes that are not fully compatible with those from the experiment.

The shapes of the experimental curves can be relatively well reproduced by use of the saturation model of Eq. (5); however, the curves were calculated with one adjustable parameter, the saturation intensity, which was allowed to be different for different concentrations of the polymer. Figure 5 shows how the saturation intensity changes with concentration for the set of measurements of chloroform solutions of PIF presented in Fig. 3. Saturation intensity I_{sat} ranges from ~ 100 to 400 MW/cm^2 . Note that the saturation intensity defined in Eq. (3) is concentration independent. In derivation of that equation it is assumed, however, that the absorption–excited-state decay processes are in steady state, which is not the case for short-pulse excitation.

We conclude that open-aperture Z-scan studies are a useful tool for studying absorption saturation. The interpretation of the origin of the observed saturation dependence in poly(indenofluorene) needs, however, additional studies.

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