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Linear and nonlinear optical properties of a ladder poly(*p*-phenylene) polymer

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Abstract

Linear and nonlinear optical properties of a ladder polymer based on the poly(*p*-phenylene) backbone (LPPP) have been investigated. Femtosecond degenerate four-wave mixing (DFWM) was used for the determination of the nonlinear refractive index n_2 at 800 nm. Values of $|n_2| = (3\text{–}7) \times 10^{-13}$ cm^2/W were obtained from DFWM measurements on thin films and solutions of the polymer. The two-photon absorption coefficient of LPPP is estimated to be $\beta = 5 \times 10^{-9}$ cm/W at 800 nm.

Keywords: Ladder polymers; Nonlinear refractive index; Two-photon absorption

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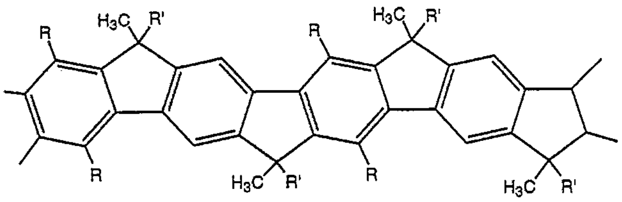
1. Introduction

Third-order nonlinear optical properties of π-conjugated polymers are of interest because of their potential use in photonic devices making use of the high nonlinear refractive index n_2 and fast nonlinear optical response of these materials. We evaluate in this paper the nonlinear optical properties of a polymer with ladder structure:



where $R = C_6H_{13}$ and $R' = C_6H_5C_{10}H_{21}$ [1–3].

The backbone of this polymer is formed by the poly(*p*-phenylene) (PPP) chain; however, unlike in the ordinary PPP polymer, the benzene rings are held rigidly in place by the ladder structure. In PPP the π-electron overlap is limited by the tendency of the benzene rings to rotate out of planarity due to the steric hindrances caused by close encounters of hydrogen atoms. The properties of the ladder polymer investigated here (hereafter referred to as LPPP) should be expected to correspond to a well-conjugated π-electron system. Since the presence of side chains R and R′ renders the polymer well soluble in common organic solvents such as chloroform, it has been possible to perform studies both on solutions of the polymer and on thin films obtained by solution casting (spin coating and doctor blading).

2. Results

The absorption spectrum of a chloroform solution of the LPPP polymer (Fig. 1) shows well-structured bands indicative of a relatively high degree of conjugation and high intrachain order [4]. The maximum absorption for a solution spectrum is at 455 nm (corresponding to the decimal absorption coefficient $\alpha_{max} = 1 \times 10^5$ cm^{-1}). The absorption bands are at essentially unchanged positions for a thin film spectrum of LPPP.

The refractive index values for thin films of LPPP were determined using a Metricon 2010 prism coupler operating

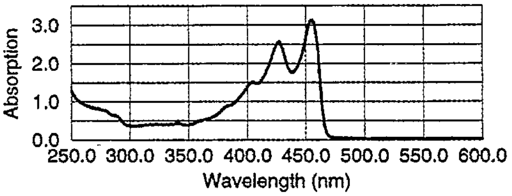


Fig. 1. Absorption spectrum of a 1 mm cell with LPPP solution in chloroform (0.034%).

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Table 1
Indices for TE and TM modes

Wavelength	n_{TE}	n_{TM}
633 nm	1.610	1.589
810 nm	1.588	1.572

at the wavelengths of 633 and 810 nm. The indices for TE and TM modes are given in Table 1.

A slight anisotropy of the refractive indices (about 0.02 for 633 nm) indicates that the polymer chains may be partially oriented parallel to the film surface. The anisotropy is, however, much smaller than that in, e.g., PPV polymers [5] where the anisotropy of n for spin-coated and thermally converted films can be as high as 0.6. We expect therefore that an assumption of random orientation of LPPP chains in the film is not unjustified.

The optical nonlinearity of LPPP was assessed using the degenerate four-wave mixing technique (DFWM) both for thin LPPP films and for LPPP solutions in chloroform. The measurements were performed with a laser system consisting of an Ar-ion laser-pumped femtosecond Ti–sapphire oscillator (Coherent Mira) operating at 800 nm and a Ti–sapphire regenerative amplifier pumped at 30 Hz with a frequency doubled output of a Spectra Physics GCR-130 Nd:YAG. The technique of chirped pulse amplification was used. The amplified 800 nm pulses, after recompression, were about 100 fs long (FWHM), nearly transform limited [6] and with energies in the μJ range. The DFWM setup used the BOXCARS geometry [7].

The temporal behaviour of the DFWM signal from an LPPP film is shown in Fig. 2. The temporal dependence of the DFWM intensity is interpretable in terms of a transient grating involving a fast, essentially instantaneous response accompanied by some contribution of slower processes, possibly due to the excitons formed by two-photon absorption. The lifetime of this slower response is power dependent. The theoretical fits in the picture were obtained assuming a sech^2-shaped laser pulse with FWHM of 109 fs. It has been assumed that the tail is due to transient species generated by two-photon absorption and decaying according to the first-order kinetics. For the two DFWM curves shown in the picture the lifetimes are 50 ps for the low-power curve and 7.8 ps for the higher power curve. The lifetime of about 5 ps could be observed at even higher power.

The observed behaviour can be compared to that reported by Graupner et al. [8] in pump–probe experiments on LPPP with the pump in the one-photon absorption region (390 nm) and the probe in the range of 440 nm to 1.1 μm. The authors of [8] found the lifetime of the decay of the induced absorption (present in the range 530 to 1150 nm) to be about 2 ps. However, between 440 and 530 nm a photoinduced gain was observed, the lifetime of its decay at about 450 nm being 8 ps. These two lifetimes, i.e. 2 and 8 ps, were attributed to the thermalization of hot intrachain charged polarons $P^{\pm}$ and to the decay of the population of emitting species (excitons), respectively. Since DFWM probes the decay of the complex susceptibility change, it should contain contributions from all transient species whose presence changes the absorptive or refractive component of the susceptibility of the material. It is therefore surprising that the short lifetime (2 ps) species are not observed here. Differences in the populations of excited species formed by two-photon absorption at 800 nm (as in the present experiments) and by one-photon absorption at 390 nm (as in the experiment of Graupner et al.) may be responsible for this different behaviour.

Fig. 3 shows the power dependence of the DFWM signal in a 4 μm thick film of LPPP. The signal follows roughly the cubic dependence on the input power ($I_{DFWM} \propto I^3$) and starts to saturate at a higher power (in the range which corresponds approximately to about 100 GW/cm^2), possibly due to two-photon absorption or fifth-order processes.

The presence of a cubic dependence makes it justified to use the description of the nonlinearity in terms of the nonlinear refractive index n_2. The value of $|n_2|$ was determined by comparing the intensity of the DFWM signal from LPPP with that from silica for which $n_2 = 3 \times 10^{-16}$ cm^2/W was assumed. The values of $|n_2|$ obtained for several samples within the cubic range of the intensity dependence were in the range $(4–7) \times 10^{-13}$ cm^2/W. These values are therefore

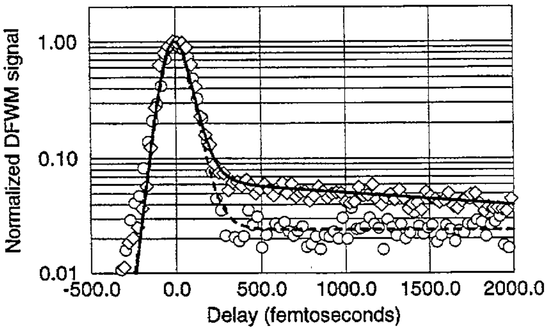

Fig. 2. DFWM signal from a 4 μm thick film of LPPP obtained by spin coating from a chloroform solution: circles (experimental) and dashed line (fit) denote lower power (about 30 GW/cm^2); diamonds (experimental) and full line (fit) denote higher power (about 55 GW/cm^2).

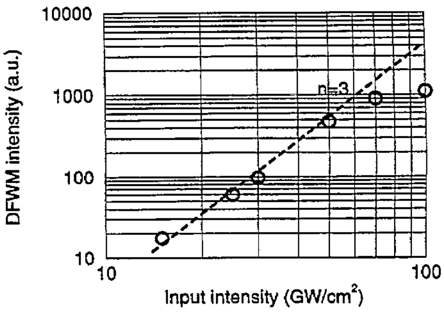

Fig. 3. Input intensity dependence of the DFWM signal from an LPPP film (4 μm thick). Permanent grating formation is observed at light intensities above 100 GW/cm^2.

quite high, although lower than those measured at 800 nm for poly(p-phenylenevinylene) [9].

A series of DFWM measurements was also performed for solutions of LPPP in $CHCl_3$. The results of these measurements cannot, unfortunately, be considered fully conclusive because LPPP solutions were found to be not photochemically stable under the conditions of the experiment performed by us, especially at the highest light intensities used (up to 200 GW/cm^2). The solutions were prepared under ambient atmosphere. Formation of dark blue species was observed in the solution region irradiated with the laser beams. The photoreaction appeared to be reversible and the coloration of the solution disappeared within the time on the order of a minute after blocking the beam. It is, however, not clear whether the DFWM signal could be influenced by the presence of the transient photochemical product. The concentration dependence of the DFWM signal obtained on LPPP solutions in a 1 mm glass cell (Fig. 4) shows saturation-like behaviour which can be attributed to increasing nonlinear absorption at higher concentrations. The behaviour at lower concentrations — a minimum in the signal versus concentration curve — can be taken as an indication of the negative value of the real part of the hyperpolarizability of LPPP at 800 nm. However, in view of the observed formation of the photochemical transient species, other explanations are also possible.

The full line in Fig. 4 shows a numerical fit to the concentration dependence obtained assuming that the signal is limited by two-photon absorption and introducing two-photon absorption correction as described in [10]. By calibrating the signal from solutions of LPPP and from chloroform against the nonlinearity of silica we can determine the best fit value of the hyperpolarizability of the polymer unit. Taking the repeat unit as containing two phenylene groups one obtains the hyperpolarizability $\gamma = 4 \times 10^{-32}$ e.s.u. for such a unit. The value of n_2 of LPPP obtained from this hyperpolarizability using Lorentz-type local field factors and the experimental refractive index value is 7×10^{-13} cm^2/W, in reasonable agreement with the values obtained from measurements on LPPP films.

We note here that, while the transient species were not visually observed during the measurements performed on the film samples, some permanent (or long-lived) grating formation at higher powers was seen.

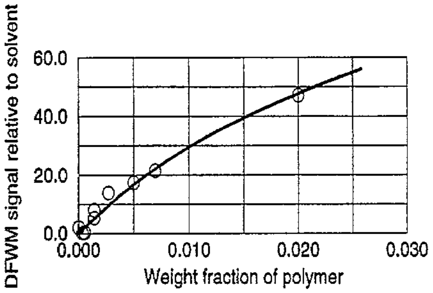

Fig. 4. Concentration dependence of the DFWM signal from solutions of LPPP in chloroform at 800 nm.

Relatively strong two-photon absorption in LPPP at 800 nm is manifested as blue–green fluorescence of the polymer and its solutions under the excitation with 800 nm fs pulses. Investigation of the importance of this process as well as that of the photochemical stability of LPPP under different conditions is necessary in order to assess further its potential suitability as a candidate material for nonlinear optical device applications (it is especially important to determine the so-called T factor [11]). Measurements of Z-scan [12] were attempted on thin-film samples of LPPP (4 μm thick) obtained by spin coating. Unfortunately, at the power levels high enough to obtain well detectable signals (on the order of 100 GW/cm^2 and above), the films of LPPP are not photochemically stable and some permanent refractive index changes are induced in the films. As a result, closed-aperture Z-scans, which would normally be used to determine the real part of n_2, were generally unreliable. On the other hand, we were able to record open-aperture Z-scans which give information on the imaginary part of n_2, related to the two-photon absorption coefficient. An estimate of the two-photon absorption coefficient obtained from these measurements (taken at 100–300 GW/cm^2) is $\beta = 5 \times 10^{-9}$ cm/W. One notes that this value, together with the $n_2 = 5 \times 10^{-13}$ cm^2/W would give the T merit factor taken here as $T = \beta\lambda / n_2 = 0.8$, a value just below unity. However, since the values of n_2 and β were not obtained within the same range of intensities, the value of T can only be considered approximate.

3. Conclusions

We have determined the nonlinear optical parameters of LPPP at 800 nm obtaining a reasonably high value of the nonlinear refractive index. The measured $|n_2|$ is much lower than that determined, e.g., in unsubstituted PPV (up to 1×10^{-11} cm^2/W) [9]. However, comparing LPPP to PPV two factors have to be taken into account. The presence of bulky side groups in LPPP dilutes the density of the active components (the π-conjugated chains). The relatively weak ordering of chains of LPPP in the plane of thin films can be contrasted to the behaviour of PPV where the polymer chains lie parallel to the surface. Assuming that a single component of a fourth-rank tensor dominates the hyperpolarizability of a rigid-rod polymer chain, one finds an orientation averaging factor of 1/5 in the case of random orientation of the molecules in three dimensions and a factor of 3/8 in the case of molecules lying in a plane. Therefore, enhancement of the nonlinearity by approximately a factor of two (15/8) will be present in PPV, which is absent in LPPP films.

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