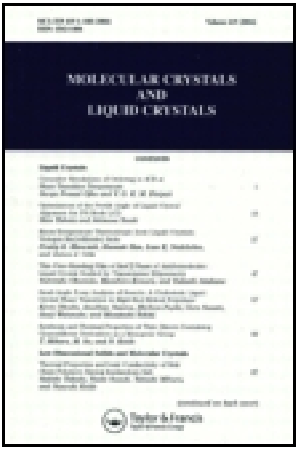

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Cubic Nonlinear Optical Properties of π-Conjugated Polymers from Reflection-Mode Measurements

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We describe experimental studies of cubic nonlinear optical properties performed in reflection mode on thin films of polyaniline. It is shown that pump-probe and degenerate four-wave mixing reflection techniques are sensitive enough to obtain readily detectable nonlinear optical signals from polyaniline with femtosecond pulses at light intensities on the order of $100\,GW/cm^2$. *The results are compared with previous studies indicating that nonlinear coefficients of polyaniline are in the range of* $|n_2| = 10^{-12}$–$10^{-11}\,cm^2/W$ *and that the relaxation of the nonlinear effects involves picosecond range processes.*

Keywords: degenerate four-wave mixing; nonlinear refractive index; polyaniline; pump-probe

INTRODUCTION

Among numerous effects due to the presence of the cubic nonlinear susceptibility $\chi^{(3)}$, two simple manifestations of the optical nonlinearity are the nonlinear refractive index n_2 and the nonlinear absorption coefficient β. In most cases, these two nonlinear coefficients

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are studied and utilized in geometries in which a light beam is allowed to propagate through a certain length of a nonlinear material, L. The relevant quantity in respect to the refractive nonlinearity expressed by n_2 is the nonlinear phase shift $\Delta\Phi = 2\pi n_2 IL/\lambda$. For the absorptive nonlinearity one can consider either the imaginary part of the nonlinear phase shift treated as a complex quantity or the nonlinear absorption strength expressed as $A = \beta IL$. Consideration of the phase shift which is possible to obtain on the distance of a one photon absorption length α^{-1} or two-photon absorption length $(\beta I)^{-1}$ leads to well-known nonlinear merit factors T and W [1].

Less often has the application of cubic nonlinearity been considered in geometries where the main effects come from reflections rather than from propagation of light beams. However, such geometries are quite important, an example of that may be the semiconductor saturable mirror (SESAM). In the case of reflection nonlinear optical properties the effects can be considered to come not from the propagating component of the electromagnetic field but from the evanescent field component at the interface.

Recently, much interest has been focussed on optical properties of periodic structures (e.g. photonic crystals) in which light propagation involves more complicated interactions, both the propagating and evanescent fields being of importance. Thus, nonlinear optical effects occurring on reflection can be considered relevant also for such structures.

We have started a study of cubic nonlinear optical properties of some π-conjugated polymers in reflection geometries. These geometries may be considered particularly suitable for those conjugated polymers that exhibit strong one-photon absorption which may be due to doping: under such conditions the use of these materials in transmission mode is virtually impossible because the absorption leads to very short propagation lengths. Experiments can be performed using reflection-mode analogues of classical nonlinear techniques such as Z-scan [2–6] or, in time-resolved mode using degenerate four-wave mixing [7] and pump-probe measurements. However, we find that the Z-scan technique suffers from the usual disadvantage of being vulnerable to artefacts due to photochemical changes in the materials occurring at high light intensities. Therefore, we concentrated here on the use of reflection geometry for time-resolved experiments such as DFWM [7] and pump-probe. The results shown in this paper have been obtained on samples of polyaniline which is a good example of a strongly absorbing π-conjugated polymer with high nonlinearity.

SAMPLES

Measurements were performed on polyaniline films fabricated at the University of Potsdam. Aniline was distilled prior to use and then was mixed with a 1 M HCl solution in water. The oxidant (ammonium persulfate in water) was slowly added under magnetical stirring. The mixture was allowed to react for three hours and then the polymer was filtrated, washed with water and acetone and dried under vacuum for 24 h. The polymer was added into a solution of NH_4OH, and after two hours the polymer was again filtrated, washed with water and acetone and dried under vacuum. A certain amount of polyaniline was dissolved in N-methylpyrrolidone, the solution was then filtered, cast onto the substrates and dried on a hot plate at 65 degrees.

LINEAR OPTICAL PROPERTIES

The complex refractive index of polyaniline films was determined from reflection spectra taken with a Shimadzu 3101 UV-VIS-NIR spectrophotometer. The reflection spectrum taken in a near-normal incidence geometry was converted to spectra of the real and imaginary parts of the complex refractive index $\tilde{n} = n + ik = n(1 + i\kappa)$ using a Kramers-Kronig analysis algorithm [8]. The reflectivity R was used to calculate the spectrum of the reflection phase shift θ from the relation:

$$\theta(E_0) = \frac{E_0}{\pi}\int_0^{\infty} \frac{\ln(R(E))}{E^2 - E_0^2}\,dE \tag{1}$$

The phase shift was then used to compute n and k using:

$$n = \frac{1 - R}{1 + R - 2\sqrt{R}\cos(\theta)}, \qquad k = \frac{2\sqrt{R}\sin(\theta)}{1 + R - 2\sqrt{R}\cos(\theta)} \tag{2}$$

The results are shown in Figure 1. It might be noted that the complex index at the wavelength of NLO measurements, 650 nm, is $0.75 + 0.63i$.

NLO EXPERIMENTS IN REFLECTION MODE

The NLO experiments were performed using a laser system consisting of a Clark-MXR CPA-2001 Ti-sapphire regenerative amplifier and a Light Conversion TOPAS travelling wave optical parametric amplifier. The repetition rate of the CPA-2001 was set to 250 Hz. The 775 nm pulses from the regenerative amplifier were converted into the signal and the idler in the TOPAS and the signal at 1300 nm

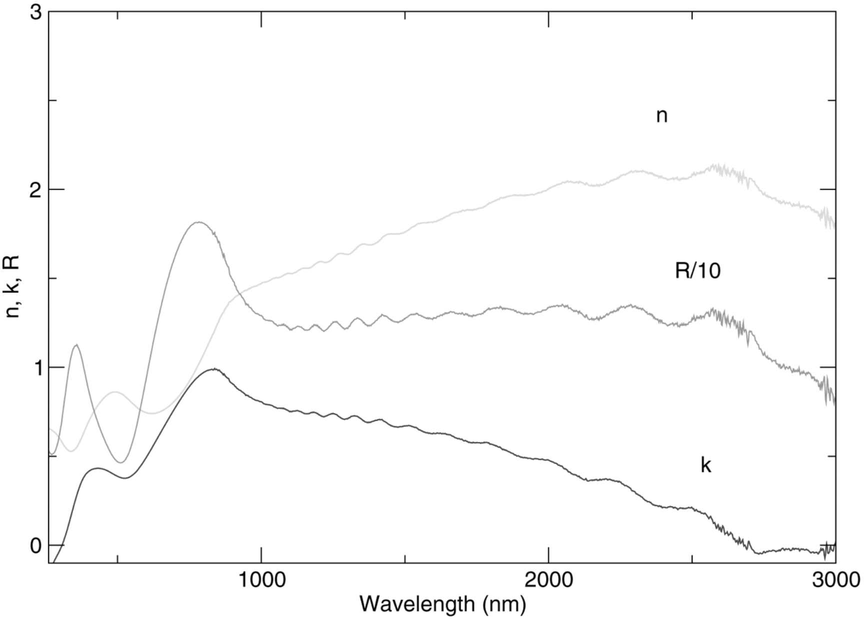

FIGURE 1 Linear optical properties of the polyaniline film used in the investigations. The three lines are: the refractive index, n, reflection coefficient R (in per cent), and the imaginary part of the complex index, k.

was frequency doubled to obtain a beam at 650 nm with nominal 150 fs pulse duration.

The 650 nm beam was then split into two parts of different intensities to form the pump and the probe beams. The probe beam was directed through a computer controlled delay line to provide for the time-resolved capability of the measurement. Both beams were focussed to an overlapping spot on the sample and the different types of experiments were performed by monitoring intensities of various beams as a function of the relative delay between the pump and the probe. Both beams were p polarized. Figure 2 shows the scheme of the experimental geometry.

As shown in the Figure, the simultaneous action of the pump and the probe beams on the sample (thin film of a conjugated polymer deposited on a glass slide) leads to the formation of two degenerate four-wave mixing signals which are the result of self diffraction of the both beams on the transient grating formed by them. At the same time, changes introduced to the dielectric properties of the polymer by

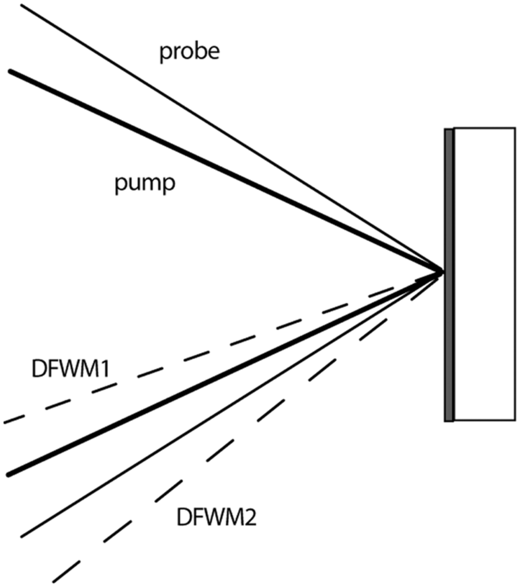

FIGURE 2 Scheme of time-resolved NLO measurements in reflection. The pump and the probe are derived from the same femtosecond laser beam.

the pump beam can also be monitored by measuring the intensity of the reflected probe beam as a function of its delay vs. the pump beam.

Figure 3 shows an example of the signals which could be obtained by monitoring the intensity of the self-diffracted DFWM signals marked DFWM1 and DFWM2 in Figure 2. As can be expected from the consideration of self diffraction on a transient grating, the signals are curves having a halfwidth (FWHM) of about 200 femtoseconds, close to the width expected for a third-order correlation of pulses appr 100–150 fs in width. The more detailed interpretation of the features of these curves would require assumptions on the exact shape of the laser pulses (e.g., whether they are close to the sech^2 shape or to Gaussian shape) and on the relaxation and dephasing mechanisms of the transient grating [7].

The presence of the DFWM signal is an indication of the formation of a surface grating of sufficient strength to give measurable reflectivities in the first order of diffraction. It should be noted that this is despite the intensities of the two interfering beams being quite different (approximately, probe:pump = 1:6). It is relatively more difficult to precisely assess the magnitude of the effective third-order nonlinearity giving rise to the DFWM signal in reflection compared

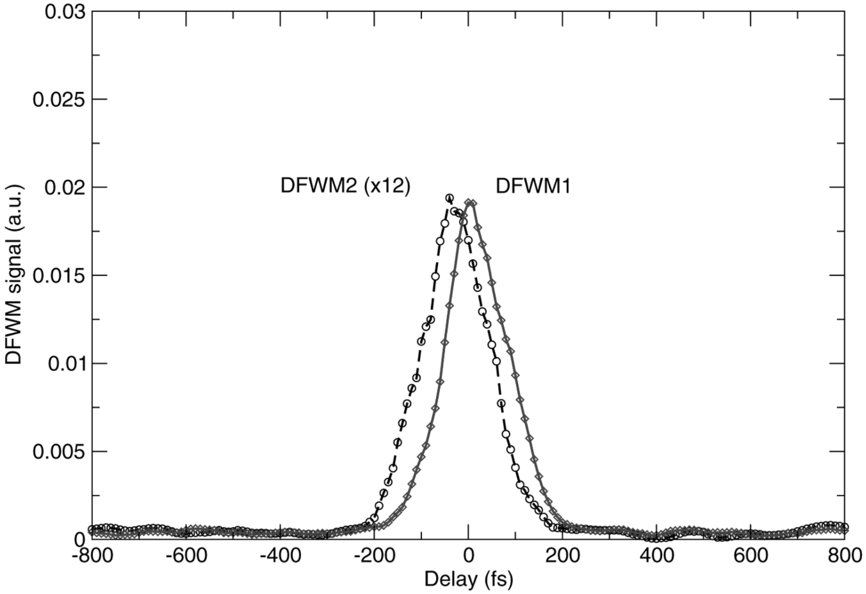

FIGURE 3 Self-diffraction degenerate four-wave mixing signal in reflection from polyaniline film. Light intensity appr. 80 GW/cm^2.

to the case of transmittive DFWM. A rough estimate can be made on the basis of a relative measurement against films of poly(phenylene-vinylene) (PPV) and poly(dimethoxyphenylenevinylene) (DMPPV) with nonlinearities roughly $|n_2| = 2 \times 10^{-12}\,\mathrm{cm}^2/\mathrm{W}$ [9]. The signals from polyaniline were similar in magnitude to those from the PPVs, thus, not taking into account any other factors influencing the DFWM reflectivities (that is the different linear optical properties of the polymers) one may conclude that the results are consistent with effective $|n_2|$ for polyaniline being on the order of a few times $10^{-12}\,\mathrm{cm}^2/\mathrm{W}$. This is in agreement with previous studies of polyanilines [10–21] and other results shown below.

The nonlinear effect can also be measured by monitoring the intensity of the probe beam itself as a function of its delay vs the pump. Figure 4 shows an example of the measurement performed in this way. It is clearly seen that the temporal superposition of the pump and the probe leads to the decrease of the intensity of the reflected probe. This decrease, however, is not limited to the range of temporal overlap of the two beams but extends also into the range of positive delays of the probe suggesting the presence of excitations with relaxation times on the order of a picosecond.

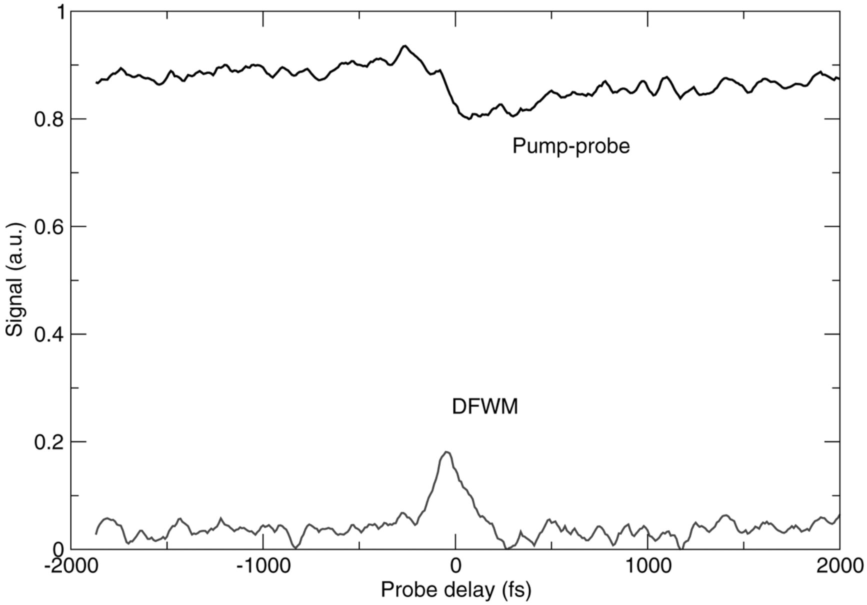

FIGURE 4 A reflection mode pump-probe experiment on a film of polyaniline at 650 nm. Also shown is the simultaneously recorded DFWM signal. Pump intensity appr. 80 GW/cm^2.

The relative change of reflectivity in Figure 3 is about 7%. This value is of importance for the discussion of the nonlinearity of PANI. The reflectivity of a thick film at normal incidence (taken for simplicity, since expressions for non-normal incidence are more complicated) can be expressed as [22]:

$$R = \left|\frac{\widehat{n}-1}{\widehat{n}+1}\right|^2 = \frac{n^2(1+\kappa^2)+1-2n}{n^2(1+\kappa^2)+1+2n} \tag{3}$$

where the complex refractive index is equal to $\widehat{n} = n(1+i\kappa)$ and κ is the attenuation index as defined in [22]. Differentiating the above vs. intensity one obtains:

$$\frac{1}{R}\frac{dR}{dI} = -\left|\frac{2d\widehat{n}}{(\widehat{n}+1)(\widehat{n}-1)}\right| \tag{4}$$

which indicates that changes in the complex refractive index will lead to changes in the reflectivity of roughly the same order of magnitude. Knowing that the complex refractive index is 0.75 + 0.63i, one expects that, given $\Delta R/R = 0.07$ (at $I = 80\,GW/cm^2$), changes of $|\Delta n|$ on the order of 0.1 are present. This is in agreement with $|\Delta n| = |n_2|I$, the intensities used being on the order of $10^{11}\,W/cm^2$ and the nonlinearity $|n_2|$ on the order of $10^{-12}\,cm^2/W$.

COMPARISON WITH NLO MEASUREMENTS IN TRANSMISSION MODE

A feature of polyanilines is the broad range of properties that can be achieved in these materials by modifying the degree of doping and applying different processing to the material. In principle, polyaniline may be present in several canonic forms: those of emeraldine, pernigroaniline and leucoemeraldine which differ in the degree of oxidation but which can also have a different degree of protonation and may be additionally different because of presence of various counterions modifying the properties of the polyaniline chains. Thus, comparisons between various NLO measurements performed also at different wavelengths and with different laser pulse durations and fluences are difficult. For example, the degree of protonation influences the nonlinear optical properties of polyaniline considerably, as shown by us previously [20,21]. Table 1 shows results obtained using Z-scan at 800 nm.

It should be noted that, for comparative purposes, the results in the above table have been extrapolated from low concentration solution studies to 100% content of the PANI base. Therefore, such high values of the nonlinearities are not really available for practical use. In addition to the work on solutions, we have produced some composites containing both PANI base and PANI salt and investigated their properties in the form of thin solid films. Good optical quality composites have been obtained by using polyvinylalcohol and glutaric aldehyde as the host material [21].

Figure 5 shows typical time-resolved degenerate four-wave mixing signals obtained in transmittive mode at 800 nm for films of PANI

TABLE 1 Comparison of Extrapolated Values of the NLO Parameters for Base and Salt Forms of Polyaniline from Z-scan at 800 nm [21]

Substance	Real part of n_2 (extrapolated) (cm^2/W)	Imaginary part of n_2 (extrapolated) (cm^2/W)
PANI base	-4.4×10^{-12}	~ 0
PANI salt (H_2SO_4)	-6×10^{-12}	-4.4×10^{-11}

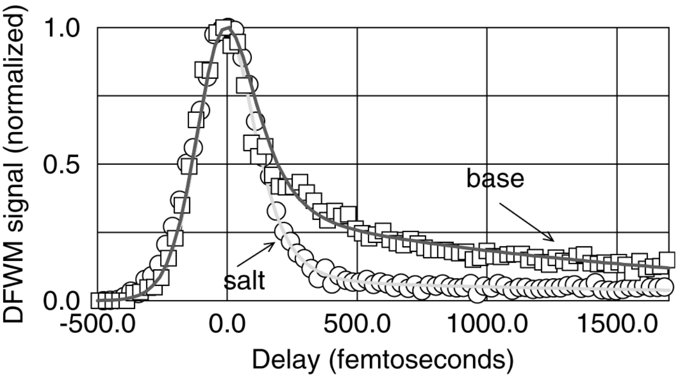

FIGURE 5 Comparison of time-resolved DFWM signals obtained on thin films of polyaniline salt and base composites with PVA-GLUT. 100 fs pulses at 800 nm were used. Lines denote numerical fits performed assuming that the DFWM is due to superposition of an instantaneous response and a delayed component decaying according to a first order decay law.

composites with PVA-GLUT. The numerical fits shown in the figures have been produced assuming that the nonlinear response contains two parts: an instantaneous response and a delayed response which may be due to changes in the population of the excited state molecules (population grating). It was found that the decay time of the excited state population grating was about 5 ps in both cases: that of the base form and that of the salt form. The difference between the curves recorded for the two forms is only in the relative contributions of the two mechanisms to the DFWM signal: in the case of the salt form the contribution of the instantaneous response was dominant.

The effective nonlinearity $|n_2|$ could be calculated by comparing DFWM signals from PANI samples with those of fused silica and assuming that the intensity of the DFWM signal fulfils the relation:

$$I_{DFWM} \propto C^2(n_2L)^2 \tag{5}$$

where L is the sample thickness and C is the correction for absorption of the pump beams and the signal beam assumed to be

$$C = \frac{\exp(-\alpha L/2)[1-\exp(-\alpha L)]}{\alpha L} \tag{6}$$

The samples showed relatively strong single-photon absorption at 800 nm (optical densities varying between 0.05 and 3) and hence the

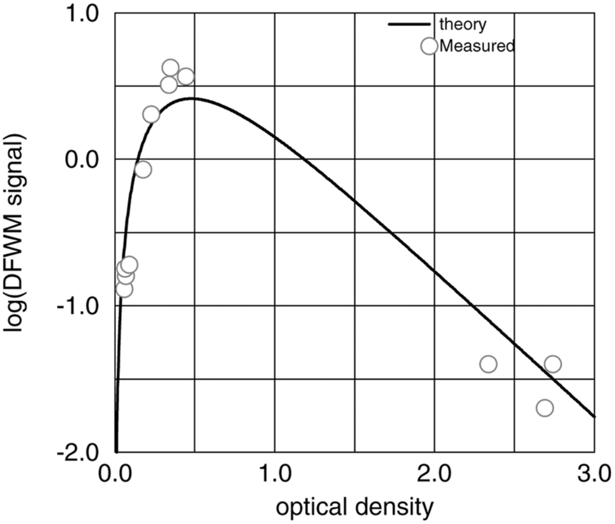

FIGURE 6 Degenerate four wave mixing signal amplitudes (at 800 nm) for a series of polyaniline salt composite samples with different thicknesses (and therefore different optical densities) compared with a theoretical curve calculated as described in the text.

absorption correction, C, was quite important. It is interesting to compare the DFWM signal for different thicknesses and optical densities of the samples. Figure 6 shows such a comparison, indicating that the transmission mode NLO effects are strongly influenced by absorption. However, as seen from Table 2, the nonlinear parameters obtained in these measurements are in a similar range of values to those obtained by other techniques, including the reflection technique on neat PANI.

TABLE 2 Extrapolated Values of $|n_2|$ Determined by DFWM at 800 nm in PANI-H_2SO_4 Composites with PVA-GLUT [21]

Acid:base mole ratio	Absorption coefficient at 800 nm (cm^{-1})	$|n_2|$ at 800 nm	$|n_2|/\alpha$
0:1	3.9×10^4	4.2×10^{-12}	1.1×10^{-16}
5:1	8.1×10^4	2.4×10^{-11}	3.0×10^{-16}
7:1	7.4×10^4	1.1×10^{-11}	1.5×10^{-16}
18:1	7.4×10^4	9.7×10^{-12}	1.3×10^{-16}

CONCLUSIONS

It has been shown that reflection techniques are sensitive enough to obtain readily detectable nonlinear optical signals from polyaniline (and also from some other conjugated polymers like polyphenylene-vinylenes) with femtosecond pulses at light intensities on the order of 100 GW/cm^2. This opens interesting possibilities for investigating cubic nonlinear optical effects on micro- and nanoscale, since reflection mode measurements can be easily adapted to confocal microscopy or near field scanning probe microscopy.

The general conclusion from the investigations of NLO effects in polyanilines is that their nonlinear optical properties, while sizeable, may be difficult to exploit in transmission mode. The changes in the complex refractive index may be of interest because of their relatively high magnitude and their fast response which occurs on a timescale shorter than 100 fs with only a relatively small part of the change relaxing with a lifetime of $\approx$5 ps. However, the fluences needed to induce large changes in transmission or reflection may not be practical ($\approx$J/cm^2).

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