

Femtosecond Z-scan and degenerate four-wave mixing measurements of real and imaginary parts of the third-order nonlinearity of soluble conjugated polymers

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We investigated the third-order nonlinear optical properties of several soluble π -conjugated polymers with a goal of reliable determination of the parameters that characterize the nonlinearity, such as the real and imaginary parts of the nonlinear refractive index n_2 and the one-photon loss and two-photon loss merit factors W and T , respectively. The measurements were performed at 800 nm with 100-fs pulses from an amplified Ti:sapphire system. We present results of investigations of several 2,5-substituted poly(*p*-phenylenevinylenes), including poly[2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene] and a soluble ladder poly(*p*-phenylene) polymer. In particular, Z-scan measurements of polymer solutions were found to be useful for the determination of the complex nonlinear refractive index. The results could be verified by time-dependent degenerate four-wave mixing studies performed on thin films of the polymers. We found generally good agreement between the values of n_2 determined from Z scan and those from degenerate four-wave mixing. The results indicate that the nonlinear refractive index of the order of 10^{-12} cm²/W can be readily obtained for various conjugated polymers. However, the two-photon merit factors T larger than unity are commonly encountered within the two-photon absorption ranges of these compounds. © 1998 Optical Society of America [S0740-3224(98)02002-5]

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1. INTRODUCTION

The prospect of using organics as third-order nonlinear optical (NLO) materials for photonic switching applications has been the subject of many investigations during the past decade (see, e.g., Refs. 1–9 for reviews). However, the present status of knowledge of properties of those materials that may be considered of potential practical interest is still far from being satisfactory. Although many contributions to the literature concentrated on the development of organics with high third-order nonlinearities, there have been only a few that investigated in detail all those parameters of interest for photonic switching that uses the refractive nonlinearity, i.e., the refractive-index change induced by the presence of the real part of the third-order nonlinear susceptibility $\text{Re}[\chi^{(3)}(-\omega; \omega, -\omega, \omega)]$. It is now generally agreed (see, e.g., Refs. 10 and 11) that, for a third-order nonlinear ma-

terial to be attractive for photonic switching applications, the nonlinear response has to be strong (a high value of the effective nonlinear refractive index n_2 , which can be defined by assuming the proportionality of the light-induced refractive-index change to the light intensity: $\Delta n = n_2 I$) and fast (that is, the growth and relaxation of the induced refractive-index change have to be sufficiently rapid—possibly in the subpicosecond range), but also the material losses that are due to one-photon and multiphoton absorption and scattering have to be manageable. A convenient way to quantify the importance of the losses is by considering the appropriate merit factors.^{10,11} These merit factors are related to the maximum nonlinear phase shift $\Delta\phi$, given by

$$\Delta\phi = \frac{2\pi}{\lambda} \int_0^L n_2 I(z) dz, \quad (1)$$

obtainable in a given material within a propagation distance L corresponding to an absorption length. $\Delta\phi$ of the order of π is usually required for switching applications. For one-photon absorption as the dominant loss mechanism the absorption depth can be defined as α^{-1} , where α is the absorption coefficient and $\Delta\phi$ is proportional to the merit factor W :

$$W = \frac{n_2 I_{\text{sat}}}{\alpha \lambda}, \quad (2)$$

where λ is the wavelength and I_{sat} is the light intensity at which the nonlinear refractive-index change saturates. More practically, the maximum light intensity desired for technological reasons can be used instead in the above condition. The nonlinear phase shift obtainable on the distance of α^{-1} is equal to $1.26 W \pi$ rad; hence the usually accepted condition is $W \gg 1$.

If the nonlinear losses prevail, as is often the case with materials with strong two-photon absorption, the nonlinear phase shift will be limited, too. The absorption depth can then be defined as $(\beta I_0)^{-1}$, where β is the two-photon absorption coefficient and I_0 stands for the incident light intensity. Inasmuch as the absorption depth is an intensity-dependent quantity, it follows that the maximum obtainable phase shift is now intensity independent. The corresponding merit factor can be presented as

$$\frac{1}{T} = \frac{n_2}{\beta \lambda}, \quad (3)$$

and the phase shift obtainable on an absorption depth distance is in this case equal to $1.39 \pi T^{-1}$; hence $T \ll 1$ is the usually accepted requirement for a nonlinear material. Reliable determinations of the merit factors should be a basis of any discussion of applicability of third-order NLO materials for photonic switching. Unfortunately, the information concerning these parameters in relation to organics is quite fragmentary.

We present in this paper some new results obtained for several π -conjugated polymers that share a property of being relatively well soluble in common organic solvents. This property makes it possible to perform NLO measurements both on thin films of the polymers obtained, e.g., by spin coating, and on solutions of the polymers. One of the goals of these studies has been to perform a comparison of results obtained by two commonly used experimental techniques: degenerate four-wave mixing (DFWM), and Z scan. These two techniques are quite different in the scope of their applicability, but the information obtainable from them should be mutually consistent and complementary.

Z scan¹² is a technique that is particularly useful when the nonlinear refraction is accompanied by nonlinear absorption. One advantage of the technique is that the Z-scan signals are linearly related to the nonlinear phase shift, and therefore Z-scan results do not suffer from the ambiguity of those methods that measure the modulus of $\chi^{(3)}$. However, the use of Z scan for thin films of polymers is quite difficult because of the need to use relatively high light intensities and large refractive-index changes to obtain a measurable signal on a short propagation path, which often leads to the appearance of permanent

refractive-index changes that distort the measurement results. Z scan is, however, a convenient technique for solution measurements. The main deficiency of Z scan is that it provides no information about the time scale of the refractive-index changes that are being detected. Thus one may be misled by phenomena that occur on a longer time scale than the laser pulses but provide cumulative effects from pulse to pulse. One example of such effects is thermal phenomena that have to be avoided carefully, e.g., by use of low average powers in the measurements.

DFWM performed with femtosecond laser pulses is a convenient technique for time-resolved studies of the third-order nonlinear response of thin polymer films (see, e.g., Refs. 13–16 for examples of the use of DFWM for thin organic films). The difficulty of the technique is, however, that the signal is proportional to $|\chi^{(3)}|^2$ and therefore the separation of $\chi^{(3)}$ into the real and imaginary part is not immediately available. Additional experiments are needed to accomplish this task; for example, DFWM measurements of solutions with different concentrations of the highly nonlinear molecules do provide a way of using an inner reference technique (the nonlinearity of the solvent being the reference) to determine both the real and the imaginary parts of the nonlinearity of the solute (e.g., Ref. 17).

Two issues that always need to be addressed in quoting third-order nonlinearity values are the definitions and units of the nonlinear coefficients and the standards used for converting relative nonlinearity values into absolute values. Because of several different conventions that can be used in defining $\chi^{(3)}$ values (see, e.g., Refs. 8, and 18 for discussion), we prefer to avoid any confusion (e.g., due to different definitions of electric-field amplitudes or dealing with degeneracy factors) and quote here the values of the nonlinear refractive index n_2 referenced to the light intensity I rather than the $\chi^{(3)}$ values or the nonlinear refractive index n_2' defined in an alternative way, i.e., as $\Delta n = n_2' |E|^2$, where $|E|^2$ is the square of the field amplitude. This procedure has an advantage of easy comparison with a large number of nonlinear refractive-index values quoted in the literature. We refer both the Z-scan and the DFWM measurements to the standard of n_2 of fused silica. There are several estimates of this parameter in the literature. We assume here that the n_2 of fused silica is 3×10^{-16} cm²/W for 100-fs pulses at 800 nm, which is consistent with the results discussed in Refs. 19 and 20. It should be mentioned, however, that recent Z-scan measurements²¹ indicate a lower value of n_2 for silica $n_2' = 7.8 \times 10^{-14}$ esu at 532 nm and $n_2' = 7.4 \times 10^{-14}$ esu at 1064 nm, which correspond to 2.3×10^{-16} and 2.1×10^{-16} cm²/W, respectively, where $n_2(\text{SI}) = 40\pi/\text{cn}$ n_2' (esu) as defined in Ref. 21.

2. EXPERIMENTAL METHODS

The conjugated polymers used in this study were synthesized as described in the corresponding literature sources. Two of the substituted poly(*p*-phenylenevinylene) (PPV) derivatives, poly[(2,5-di-*n*-nonyloxy-*p*-phenylenevinylene)-*p*-phenylenevinylene] (PPV-9H) and poly[(2,5-di-*n*-octyl-*p*-phenylenevinylene)-*p*-phenylenevinylene] (PPV-

AC8H), were synthesized at the University of Chicago²²; poly[2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene] (MEH-PPV) was synthesized at the Xerox Corporation, Rochester, N.Y.; and a ladder-type poly(*p*-phenylene) polymer (LPPP) (Refs. 23 and 24) was synthesized at the Max-Planck Institute for Polymer Research in Mainz, Germany. We also refer in this paper to results obtained with polyanilines,²⁵ which were synthesized at the Research School of Chemistry of the Australian National University.

Solutions of the polymers were prepared with suitable solvents: tetrahydrofuran (THF), 1,1,2,2-tetrachloroethane (TCE), and chloroform. The range of concentrations studied (approximately 0–0.2% by weight) was limited by the solubility of the polymers and by the viscosity of the solutions, which was exceedingly high in some cases. The solutions were prepared and kept under nitrogen to minimize interaction with atmospheric oxygen. Spectroscopic and NLO measurements were generally performed without special protection against contact with air upon 1-mm-thick glass cuvettes filled with the solutions of the polymers.

The TCE and chloroform solutions were also used to deposit thin polymer films upon glass or silica microscope slides by spin coating or doctor blading. The deposition of the films was carried out and the films were subsequently stored under nitrogen atmosphere; the measurements were, however, performed in air. The thicknesses of the films were obtained by prism coupling or from measurements with a profilometer.

The NLO measurements referred to in this paper were performed at 800-nm with 100-fs pulses from an amplified Ti:sapphire system. The system is based on a Coherent Mira 900-P Ti:sapphire oscillator, which provides a 76-MHz train of ~100-fs pulses. Pulses selected from the train by a Pockels cell are first stretched to ~100 ps by a double-grating compressor and then amplified in a Ti:sapphire regenerative amplifier pumped at 30 Hz with nanosecond pulses from a frequency-doubled Nd:YAG laser (Spectra-Physics GCR-130). After amplification the 800-nm pulses are recompressed in a double-grating compressor. Autocorrelation and frequency-resolved optical gating measurements²⁶ show that near-Fourier-transform-limited 100-fs pulses are obtained from the system.

A. Z Scan

The Z-scan measurements were performed on solutions of polymers in suitable solvents. 100-fs pulses with energies in the range 0.1–0.5 μJ were used. Slightly different focusing arrangements were chosen for different sets of measurements, but in most measurements the focused spot size was in the range $w_0 = 20\text{--}40\ \mu\text{m}$, which resulted in the maximum on-axis light intensities in the range 10–150 GW/cm^2 . For most measurements we also used a simple arrangement shown in Fig. 1 that allowed us to record the open-aperture Z scan and the closed-aperture Z scan simultaneously.

The Z scans obtained were analyzed with expressions derived by Sheikh-Bahae *et al.*¹² to yield the real part of the nonlinear phase shift $\Delta\phi_{\text{real}}$ induced by the third-order nonlinearity and the T factor (defined here as T

$= 4\pi\Delta\phi_{\text{imag}}/\Delta\phi_{\text{real}}$) for a given sample. We performed this analysis by comparing the shapes of closed-aperture and open-aperture scans with those computed theoretically. Roughly speaking, the amplitude of a closed-aperture Z scan (i.e., the peak-to-valley difference in transmission values) is proportional to the real part of the nonlinear phase shift $\Delta\phi_{\text{real}}$, whereas the asymmetry of a closed-aperture scan depends on the T factor (for $T = 0$ the scan is essentially S shaped and symmetric). The imaginary part of the nonlinear phase shift $\Delta\phi_{\text{imag}}$ can be obtained either from the asymmetry of the closed-aperture scan (with $\Delta\phi_{\text{imag}} = T\Delta\phi_{\text{real}}/4\pi$) or from the depth of a dip in the open aperture scan that is directly related to the value of $\Delta\phi_{\text{imag}}$. Alternatively, in some cases we used a procedure consisting of dividing the closed-aperture scan by the open-aperture scan to resolve information on the real part of the phase shift. Such a procedure gives a scan that is essentially free from the influence of the imaginary part of the phase shift (i.e., free from the two-photon absorption effect).¹²

Figure 2 shows examples of closed-aperture scans for a series of solutions of a soluble PPV. It can be seen that the amplitudes of the scans decrease with increasing concentration, indicating that the real part of the nonlinearity of the solute is opposite in sign to that of the solvent. At the same time there is an increasing asymmetry of the scans, indicating the presence of the imaginary part of the nonlinearity. Figure 3 shows open-aperture scans for a series of concentrations of another soluble PPV.

Concentration dependencies of $\Delta\phi_{\text{real}}$ and $\Delta\phi_{\text{imag}}$ can be analyzed to extract information on the NLO properties of the solute. The relation between the nonlinear phase shift and the nonlinear refractive index can be written as

$$\Delta\phi = 2\pi n_2 I L_{\text{eff}}/\lambda, \quad (4)$$

where L_{eff} is an effective sample thickness (e.g., corrected for one-photon absorption). Knowledge of the light intensity can be used for conversion from phase shift values to the nonlinearity values. It is, however, more convenient to perform the measurements in a relative manner. We therefore calibrated the values of the NLO parameters by performing measurements of the nonlinear phase shift for a silica plate for which $n_2 = 3 \times 10^{-16}\ \text{cm}^2/\text{W}$ was assumed. For example, for the measurements presented in Fig. 2 the peak on-axis intensity determined from the magnitude of the phase shift for a 1-mm silica plate sub-

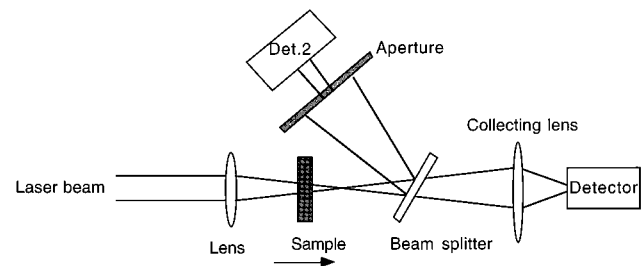


Fig. 1. Schematic of a simultaneous closed-aperture and open-aperture Z-scan measurement. The transmitted beam is split after the sample; the first detector measures the open-aperture transmittance, and the detector marked Det.2 measures the closed-aperture transmittance as a function of the sample position.

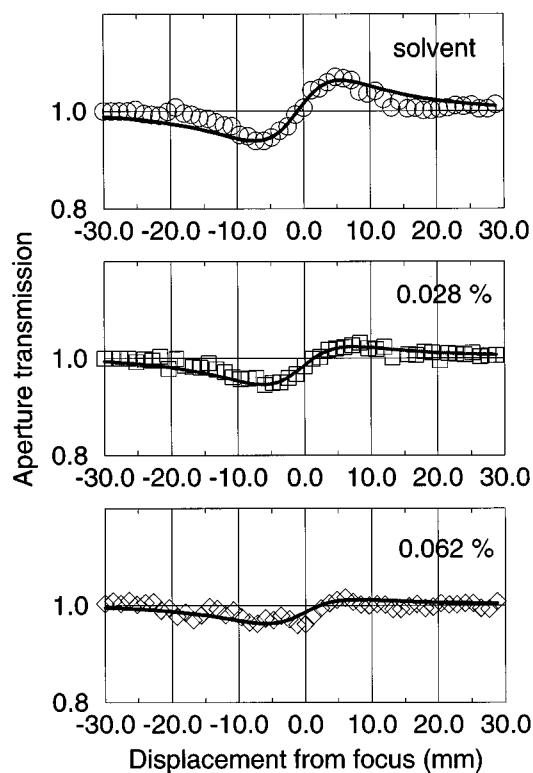


Fig. 2. Normalized closed-aperture transmittances obtained in Z scans on a 1-mm cell filled with the solvent TCE and solutions of the soluble PPV polymer PPV-9H (see Table 1 below for polymer formula).

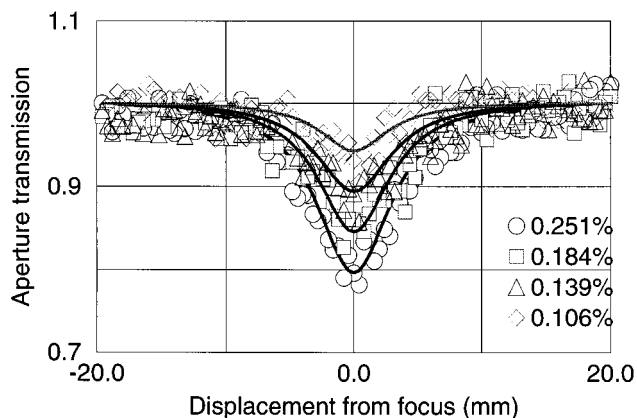


Fig. 3. Concentration dependence of open-aperture Z scans in solutions of PPV-AC8H (see Table 1 below for polymer formula) in tetrachloroethane. The solid curves are theoretical fits.

stituted for a solution cell was 12 GW/cm^2 . For simplicity, we assume that the complex n_2 of a dilute solution can be approximated by the linear expression

$$n_2 = gn_{2,\text{polymer}} + (1 - g)n_{2,\text{solvent}}, \quad (5)$$

where g is the weight fraction of the polymer, $n_{2,\text{polymer}}$ is the polymer's (extrapolated) nonlinear refractive index, and $n_{2,\text{solvent}}$ is the nonlinear refractive index of the solvent. Figure 4 shows an example of a series of measurements performed on TCE solutions of PPV-AC8H that show that the real part of the nonlinearity of the solution actually changes sign from positive to negative when the

concentration increases. The slopes of the linear relations are used to calculate the real and the imaginary parts of $n_{2,\text{polymer}}$.

There are several practical issues concerning the measurements of Z scans on solutions. Although the quality of the beam generated from our regenerative amplifier was usually quite good, the signal-to-noise ratio and the shape of the Z-scan traces did depend to a certain degree on the geometry of the beam (its closeness to the Gaussian shape) used in the Z-scan setup. As an example, the Z scans shown in Fig. 2 exhibit some disagreement with simple numerical fits, especially in the wing regions of the scans. This fact is due partly to the inadequacy of the approximations made in calculating the theoretical curves: the use of thin-medium approximation (i.e., the thickness of the medium assumed to be much less than the Rayleigh length) and the Gaussian beam approximation (whereas the beam used in this particular set of measurements was not properly spatially filtered but only passed through an aperture before the Z-scan setup). An additional complication is that the investigated objects actually consist of three elements, two glass (or silica) walls of a cuvette and the solution inside them. The combination of these factors causes uncertainties in the absolute values of the nonlinearities determined in the Z-scan technique when an oversimplified thin uniform medium approach is used. The $\Delta\phi$ determined from the measurement of, for example, pure chloroform in a 1-mm glass cell with 1-mm-thick walls will contain more or less contribution from the glass, depending on the geometry of the beam. Thus one can expect that the $n_{2,\text{eff, chloroform}}$, determined simply as

$$n_{2,\text{eff, chloroform}} = (\Delta\phi_{\text{chloroform}}/\Delta\phi_{\text{silica}})n_{2,\text{silica}}$$

from a comparison with $\Delta\phi$ measured on a 1-mm-thick plate of silica, will be overestimated. However, the nonlinearities of the solutes dissolved in chloroform and determined from incremental changes of $\Delta\phi$ on the change of concentration should still be determined correctly, as

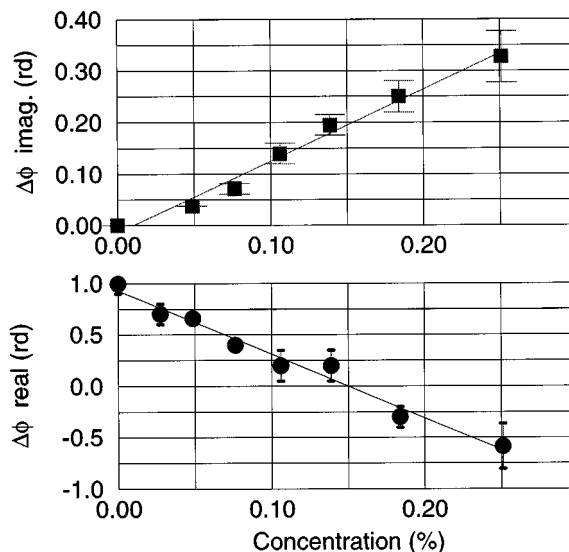


Fig. 4. Concentration dependence of the real and the imaginary parts of the nonlinear phase shift in PPV-AC8H solutions in TCE.

the contribution of the glass walls should stay approximately constant across a range of concentrations of the solute and should not influence the dependence of $\Delta\phi$ on concentration. Therefore no attempt was made to use a more realistic model for computation of theoretical Z scans for purposes of the present study.

It should be noted that the value of $n_{2,\text{polymer}}$ determined from the slope of the n_2 -versus- g_{polymer} dependence may, in principle, be substantially different from the value of n_2 for the pure polymer in the solid phase. Two main factors to consider are the difference in density between the solute and the solvent and the difference in the local-field factors, which we can formally interpret by taking into account that

$$n_2 = C_1 \chi^{(3)}/n^2 \quad (6)$$

[where the constant C_1 depends on the definition of $\chi^{(3)}$ and on the system of units adopted: in the cgs system $C_1 = 12\pi^2/c$ can be used (see Ref. 8, pp. 299 and 302, for tables of formulas); it follows that in the mixed system, i.e., for conversion from $\chi^{(3)}$ in esu units to n_2 in square centimeters per watt, the numerical value of C_1 is ~ 0.039] and

$$\chi^{(3)} = L^4 \Sigma N_i \gamma_i, \quad (7)$$

where L is the local-field factor, often approximated by Lorentz expression $L = (n^2 + 2)/3$, and γ is the hyperpolarizability, which we assume to be concentration independent. N_i are concentrations of molecules of the solution components (which are given by $N_i = N_0 g_i \rho_{\text{solution}}/M_i$, where N_0 is the Avogadro number, g_i is the weight fraction of a solution component, M_i is the component's molecular weight, and ρ_{solution} is the solution density). Comparing Eq. (7) with the expression given by Eq. (5) and assuming that for dilute solutions one can use $n_{\text{solution}} = n_{\text{solvent}}$ and $\rho_{\text{solution}} = \rho_{\text{solvent}}$, we conclude that the relation between the value of the linearly extrapolated n_2 and the value expected for a pure substance should be

$$n_{2\text{extrapol}}/n_2 = (L_{\text{solvent}}/L_{\text{polymer}})^4 (n_{\text{polymer}}/n_{\text{solvent}})^2 \times (\rho_{\text{solvent}}/\rho_{\text{polymer}}) C_{\text{or}}, \quad (8)$$

where C_{or} is the correction for the possible difference in the orientational order of molecules in solution and in the solid. For typical experimental conditions (e.g., solutions in TCE, $n_{\text{solvent}} = 1.493$, $\rho_{\text{solvent}} = 1.586 \text{ g/cm}^3$, $n_{\text{polymer}} = 1.7$, $\rho_{\text{polymer}} = 1 \text{ g/cm}^3$), the ratio of the extrapolated n_2 to that expected for a pure polymer with random orientation of molecules may be not far from unity (~ 1.15 for the quoted parameters for TCE solutions) but has to be taken into account, for example, when one is comparing results obtained for solutions in different solvents (e.g., when THF is used as a solvent, $n_{\text{solvent}} = 1.407$, $\rho_{\text{solvent}} = 0.985 \text{ g/cm}^3$, and the expected $n_{2\text{extrapol}}/n_2 = 0.63$). The influence of the orientational order may be different in different materials; e.g., in films of LPPP the TE-TM anisotropy of the refractive index was found to be rather small²⁴ (at 810 nm $n_{\text{TE}} = 1.588$ and $n_{\text{TM}} = 1.572$), which suggests random orientation of polymer chains, whereas a huge anisotropy is observed in unsubstituted PPV (typically, $n_{\text{TE}} - n_{\text{TM}} = 0.6$), and polymer chains are then ex-

pected to be oriented within the film plane.^{27,28} These differences can lead to quite a substantial variation in the nonlinear properties of materials with different degrees of order. Assuming that a single component of the molecular hyperpolarizability, say, γ_{xxxx} , dominates the γ tensor, one finds that for the random orientation of polymer chains the orientationally averaged hyperpolarizability²⁹ is $\langle \gamma \rangle = 1/5 \gamma_{xxxx}$, whereas for the chains lying randomly in the film plane the averaging in the plane leads to $\langle \gamma \rangle = 3/8 \gamma_{xxxx}$. Thus orientational enhancement of the nonlinearity in the film can be as much as a factor of 15/8 compared with the solution. As our data on the degree of orientational order, the local field factors, and the film densities of various polymers are incomplete, we do not attempt to calculate the thin-film values predicted from solution measurements and quote only the extrapolated n_2 values.

B. Degenerate Four-Wave Mixing

The measurements of DFWM were performed with boxcars (forward) geometry (see, e.g., Refs. 8, 13, 15, and 16). For measurements on thin films we usually monitored two signals, that which is generated as the result of phase-matched interaction of the three incident beams and one of the non-phase-matched signals generated by the polymer film (the geometry is shown in Fig. 5). This technique has an advantage of the possibility of distinguishing between the DFWM signals that are due to the glass or silica substrate and those from the polymer film. We note that the use of non-phase-matched DFWM signals for measurements of the nonlinear properties of thin films deposited upon substrates has recently been extensively discussed.¹⁶ It is worth mentioning that the comparison between the intensities of phase-matched and non-phase-matched signals from a highly nonlinear thin film upon a substrate of low nonlinearity provides an-

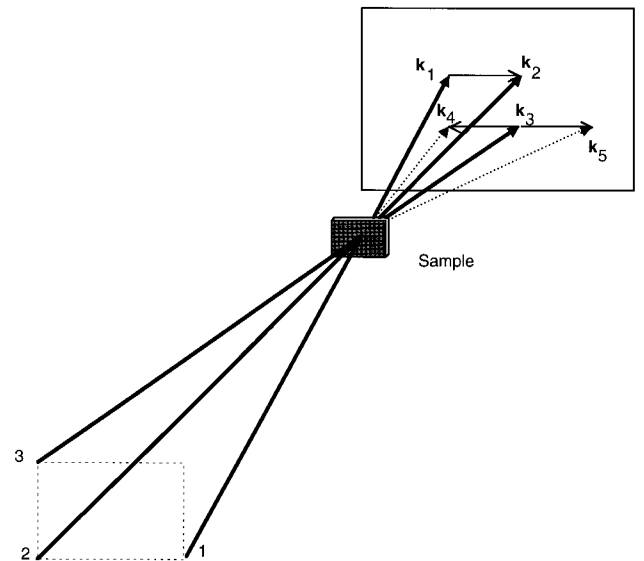


Fig. 5. Geometry of the DFWM experiment. Beams 1–3 are coincident on the sample. Two signals monitored in the experiment are the phase-matched signal that occurs because of the interaction $\mathbf{k}_4 = \mathbf{k}_3 - \mathbf{k}_2 + \mathbf{k}_1$ and a non-phase-matched signal that occurs because of the $\mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1$ interaction.

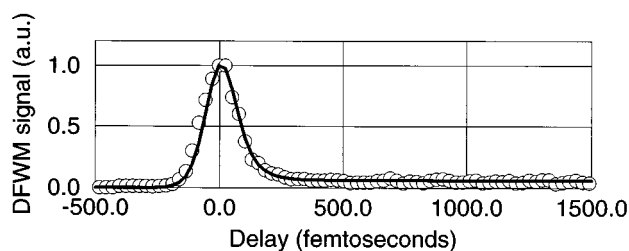


Fig. 6. Example of a time-resolved DFWM scan on a 0.5- μm -thick film of PPV-9H. The solid curve denotes a fit assuming a 100-fs sech^2 laser pulse and a small contribution of a 30-ps lifetime excited species (based on equations presented in Ref. 15). The value of $|n_2|$ determined from the comparison with silica is $1.7 \times 10^{-12} \text{ cm}^2/\text{W}$.

other way of determining the real and the imaginary parts of the third-order nonlinearity.

Figure 6 shows a typical time-resolved DFWM curve obtained for a thin film of one of the soluble PPV polymers. The nonlinear response contains a delayed part, which is probably due to relatively long-lived excitations that decay on a picosecond time scale. The observed decay time does not have a characteristic value for a given polymer. In fact, DFWM studies performed with different experimental conditions (e.g., different light intensities) on the same polymer can lead to various contents of the delayed response and to different decay-time constants.

Figure 7 shows that the shapes of the DFWM curves depend on the input power. We demonstrate this here by using the example of MEH-PPV, but similar behavior is obtained in other PPV's, including the unsubstituted PPV.^{15,27,28} With the increase of the input power the tails of the DFWM signals become more prominent. At the same time, however, the decay-time constants that characterize the decay rate of the delayed part of the DFWM signals are found to decrease with the increasing power. The observed behavior is most likely due to two-photon-generated excited states^{15,27,28} that contribute to the complex susceptibility change and that can decay by monomolecular or bimolecular pathways.³⁰

The power dependence of the amplitude of the DFWM signal in all polymer films was found to follow a pattern similar to that presented in Fig. 8. At relatively low input light intensities the DFWM signal amplitude follows a dependence that is essentially cubic. This indicates that within this power range (usually below $\sim 50 \text{ GW}/\text{cm}^2$) the nonlinearity behaves in an essentially Kerr-like manner; that is, there is no clear indication of the necessity for introducing a fifth-order correction. However, DFWM signal saturation is observed at higher light intensities. There may be several reasons for the saturation behavior. A presence of fifth-order (and higher-order) terms in the expansion of the polarization against the electric-field amplitude can be manifested as deviations from cubic dependence of the DFWM signal on the input intensity (for the *p*-toluenesulfonate polydiacetylene,³¹ saturation behavior is observed at much lower light intensities: of the order of $2 \text{ GW}/\text{cm}^2$). However, a saturationlike behavior of the DFWM signal can be due not only to the saturation of the refractive-index change Δn as a function of the

light intensity but also to other factors such as excessive two-photon absorption losses at higher powers (cf. Ref. 17).

Because of the saturation behavior of the DFWM response we always verified that the DFWM data taken for the calculation of the values of $|n_2|$ were obtained at intensities low enough that we could assume Kerr-like behavior. Equations describing DFWM^{8,13-17} predict that, for negligible depletion of the pump beams, the intensity of the DFWM signal should be given by

$$I_{\text{DFWM}} = \text{const.} \frac{|\chi^{(3)}|^2}{n^4} L^2 I^3 = \text{const.} |n_2|^2 L^2 I^3, \quad (9)$$

where the constants will, again, depend on the definitions used and on the systems of units. We used Eq. (9) for the determination of $|n_2|$ values of the investigated polymer

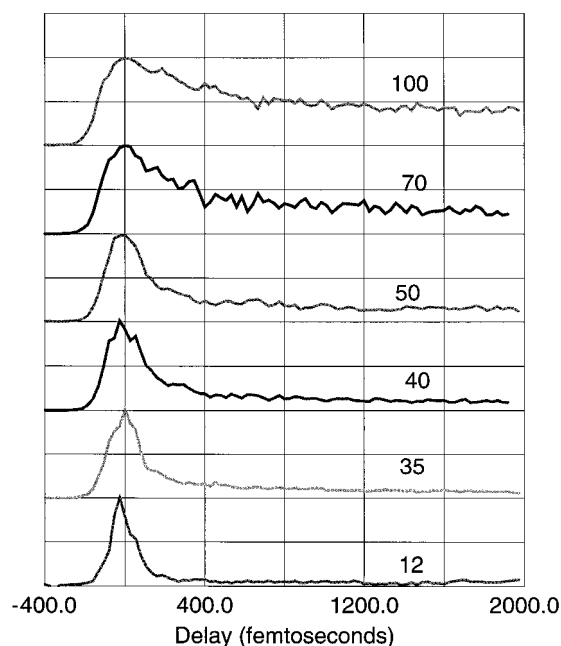


Fig. 7. Dependence of the shape of DFWM time-resolved transients on the input power in a film of MEH-PPV. The numbers correspond to the incident light intensities (in GW/cm^2).

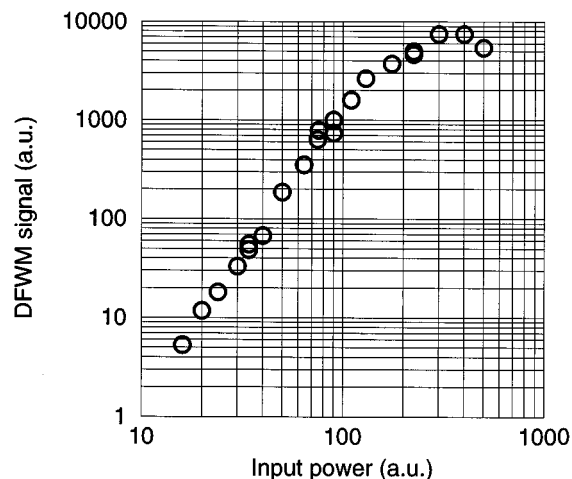


Fig. 8. Power dependence of the magnitude of the DFWM signal from a film of MEH-PPV.

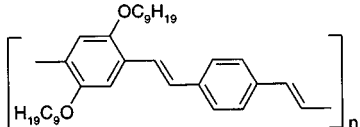
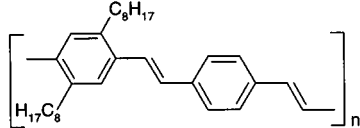
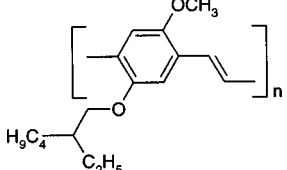
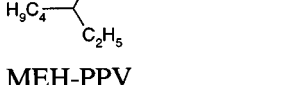
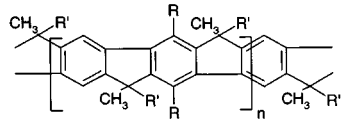
films, performing the measurements in relative manner, i.e., measuring I_{DFWM} for the investigated film of a known thickness L (using non-phase-matched signals when necessary to ascertain that the influence of the DFWM signal from the substrate can be neglected) and comparing it with a DFWM signal obtained at the same input light intensity I from a thin ($L = 300 \mu\text{m}$) silica plate. The results were not corrected for reflection losses.

3. RESULTS

Table 1 shows results of the measurements of the nonlinearities. For Z-scan data we give the extrapolated n_2 values without correcting them for a different density, refractive-index, and local-field factors in the solid state. The DFWM data are those obtained for films of neat polymers (with the exception of polyaniline data).

For all substituted PPV polymers the real (refractive) part of the nonlinearity is found to be negative (self-defocusing). The imaginary part of the nonlinearity is quite high. This leads to T factors of substituted PPV polymers markedly bigger than 1. Because of some photochemical instability of the LPPP polymer observed during the Z-scan measurements in solutions, the T factor for this material could be determined only from a combination of the DFWM data with the result of an open-aperture Z-scan on a LPPP film. Also, in the case of LPPP there is no certainty concerning the sign of the real part of n_2 . To widen the scope of our comparison of Z-scan data with those of time-resolved DFWM, we also include in the table some of our recent measurements of Z scan and DFWM on soluble forms of polyaniline (PANI).²⁵ In that case the Z scans were measured on dimethylsulfoxide (DMSO) solutions, and the DFWM measurements

Table 1. Femtosecond Z-Scan and DFWM-Determined n_2 Values for Several Soluble Conjugated Polymers

Compound	λ_{max} (nm)	Z Scan ($10^{-12} \text{ cm}^2/\text{W}$)		T	DFWM $ n_2 (10^{-12} \text{ cm}^2/\text{W})$
		Re(n_2)	Im(n_2)		
 PPV-9H ($M_n=16000$, $M_w=47000$)	459	-2.2 (TCE)	0.28 (TCE)	1.6	1.7
 PPV-AC8H ($M_n=8800$, $M_w=24000$)	414	-1.1 (TCE)	0.25 (TCE)	2.8	1.1
 MEH-PPV	505	-2.1 (THF) ^a	0.8 (THF) ^a	4.7	1.8
 LPPP	503	-3.4 (CHCl ₃)	1.13 (CHCl ₃)	4.2	
 R= n-hexyl, -C ₆ H ₁₃ R'= p-decylphenyl, -C ₆ H ₄ C ₁₀ H ₂₁ LPPP	454			0.8	0.4-0.7
PANI base form	630	-4.4 (DMSO)	≈0 (DMSO)		4.2 (PVA composite)
PANI salt form	830	-6 (DMSO)	-44 (DMSO)		24 (PVA composite)

^aLater studies showed that n_2 data for MEH-PPV in THF solutions given here might need to be enlarged by a factor of 1.5.

were performed on films of PANI composites with poly(vinyl alcohol) (PVA).

The general conclusion from all the numbers quoted in Table 1 is that there is reasonably good agreement between the Z-scan results and those obtained from the time-resolved DFWM studies. It can be noted that Z-scan experiments carried out in different solvents give somewhat different values of the extrapolated values of n_2 for the solute: qualitatively these differences are as expected from the discussion in this paper. The agreement between Z scan and DFWM is consistent with a conclusion that our Z-scan results are not distorted by the contributions from long-lived refractive-index changes such as those that are due to thermal effects or to long-lifetime-excited species. Simple Z-scan measurements are therefore found useful for the routine studies of nonlinear properties of soluble organics. Nevertheless, it has to be stated that we have seen cases when Z-scan measurements were dominated by long-lived refractive-index changes, for example, when Z-scan measurements were carried out with short pulses with high repetition rates. Time-resolved measurements, or control experiments such as performing Z-scan measurements with various pulse durations and repetition rates are useful in establishing the correctness of the assertion that the true electronic nonlinearity is measured.

Our results indicate that a nonlinear refractive-index of the order of 10^{-12} cm²/W can be readily obtained in various conjugated polymers of the PPV type. However, T factors larger than unity are commonly encountered within the two-photon absorption ranges of these compounds. Fine tuning of the properties of these polymers may lead to some improvement of the T factor (cf. Ref. 28): The question remains open whether a third-order nonlinear material can be useful for a practical application within such a wavelength range. Our present results do not exclude such a possibility.

The evaluation of the W factors is complicated by the fact that the absorption coefficients at 800 nm for most of the investigated polymers are not known with good accuracy. From simple spectrophotometric measurements one can estimate that the absorption coefficients at 800 nm for soluble PPV and poly(*p*-phenylene) compounds are reasonably low (of the order of 10 cm⁻¹ and, possibly, less). Therefore, assuming that $I_{\text{sat}} = 1$ GW/cm², W factors of the order of and greater than unity may be predicted.

Consistent values of the real and the imaginary parts of n_2 are also measured by Z scan and DFWM at 800 nm in base and salt forms of polyaniline (polyemeraldine in the base form and doped with sulfuric acid).²⁵ Strong one-photon absorption of polyaniline leads, however, to unfavorable values of the one-photon merit factor W (cf. Ref. 32) that are 2–3 orders of magnitude worse (of the order of 0.001–0.01) than those for soluble PPV and LPPP at 800 nm. It remains to be established whether π -conjugated polymers with narrower bandgaps and, in particular, doped conjugated polymers can possess figures of merit that would be of interest for photonic switching in other spectral ranges, especially in the telecom windows at 1.3 and 1.55 μm .

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