PHYSICAL REVIEW B VOLUME 53, NUMBER 8 15 FEBRUARY 1996-II

Third-harmonic-generation spectroscopy of poly(p-phenylenevinylene): A comparison with oligomers and scaling laws for conjugated polymers

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(Received 23 May 1995)

The third-order nonlinear optical susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of thin films of poly(p-phenylenevinylene) (PPV) and several corresponding oligomers (OPV-n) has been investigated by third-harmonic generation using variable laser wavelengths from 900 to 1520 nm. The oligomers show a single three-photon resonance of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ which is closely related to the linear absorption spectrum. We can identify, however, two maxima in the $\chi^{(3)}$ spectrum of PPV. They are assigned to three-photon resonances with the maximum of the exciton absorption and with the threshold of the continuum of states, which can be located at 3.2±0.1 eV. This corresponds to an exciton binding energy of 0.7±0.1 eV. We observe a general scaling behavior for PPV, OPV-n, and other one-dimensional conjugated π-electron systems in their neutral form. Their $\chi^{(3)}$ values, evaluated at comparable resonant or low-resonant conditions, follow an empirical scaling relationship $\chi^{(3)}/\alpha_{\max}\sim\lambda_{\max}^{x}$, where $\alpha_{\max}$ and $\lambda_{\max}$ denote the absorption coefficient and wavelength of the low-energy absorption maximum. We obtain an exponent $x=10\pm1$ which is much larger than expected from an earlier theory. Possible reasons for the difference between theory and experimental results are discussed.

I. INTRODUCTION

The electronic and nonlinear optical properties of organic materials with extended conjugated π-electron systems have generated much interest recently.[1–7] There is a continuing controversy as to the physical nature of the excitation states of conjugated polymers, which possess a conjugated π-electron system delocalized along the polymer backbone.[8] Poly(p-phenylenevinylene) (PPV) belongs to this class of polymers. It has been studied by many groups because of its promising third-order nonlinearities[9–13] and electroluminescence.[14] Two contrary views exist on the assignment of the optical absorption of PPV.

The first view is based on the observation that the low-energy onset of photoconductivity in PPV occurs very close to the onset of the optical-absorption edge at the energy E_0 or wavelength λ_0. This onset is defined as the intercept between the baseline and the tangent to the absorption edge, and yields E_0 around 2.4 eV. It was concluded that PPV behaves like a semiconductor, and that the optical absorption is caused by a direct photogeneration of free charge carriers via a transition between the valence and conduction bands.[15–17] The band gap E_g, sometimes also called the conduction-band threshold energy, should then be identical to E_0.

In an alternative view, the optical-absorption band is assigned to an exciton transition, where bound electron-hole pairs are formed initially. The singlet excitons can dissociate rapidly via polaron pairs to single-charge carriers (polarons) in thermally activated processes.[18] Therefore, the exciton model of the primary photoexcitation in PPV is compatible with an onset of the photoconductivity at E_0.[19] Major support for the exciton concept of PPV comes from fluorescence investigations.[20–23] According to the exciton concept, the energy gap E_g should be observed at significantly higher energies than E_0. The energy difference between E_g and the zero-vibrational level of the exciton is the exciton binding energy ΔE_b. Recent theoretical and experimental studies yield very different values of ΔE_b for PPV such as 0.4 eV,[24] 0.9 eV,[25] or 1.1 eV.[26] Hence the existence of the exciton state in PPV is far less clear than in the case of polydiacetylenes (PDA's), where $\Delta E_b\simeq 0.5$ eV was found consistently in various experiments.[27–29]

According to recent theories of Abe *et al.*[30] and Guo *et al.*,[31] the energy levels of the exciton absorption and the conduction-band threshold should be visible as two separate three-photon resonance maxima in third-harmonic-generation (THG) experiments. THG can be used as a spectroscopic technique, if the fundamental laser frequency ω is varied. This allows the detection of multiphoton resonances with electronic states, which are not visible in the linear absorption spectrum. Therefore, we have applied THG spectroscopy to the study of electronic states of thin films of PPV, and to compare them with those of its oligomers OPV-n of different but well-defined lengths. The chemical structures are shown in Fig. 1. It will be seen that the THG spectra of PPV and its oligomers differ considerably, and it will be shown how this relates to the existence of exciton and band states in PPV.

The second part of this work is concerned with the magnitude of $\chi^{(3)}(-3\omega;\omega.\omega.\omega)$, its dependence on the length L of the oligomer and the linear optical properties of OPV-n and PPV. The third-order nonlinearities of conjugated systems are strongly influenced by the π-electron delocalization length L_d, which is also called the conjugation length. For short conjugated chains, where L_d is limited only by the chain length L, early investigations showed $\chi^{(3)}\sim L^{5}$.[32,33] For polymers with a one-dimensional (1D) conjugated π-electron system, Flytzanis and co-workers used Hückel theory to derive a universal scaling behavior between $\chi^{(3)}$ and L_d.[34–37] As they found that L_d is also related to the linear optical properties of 1D systems, this scaling law can be written in the simplified form

$$\chi^{(3)}\sim\lambda_{\max}^{6}, \tag{1}$$

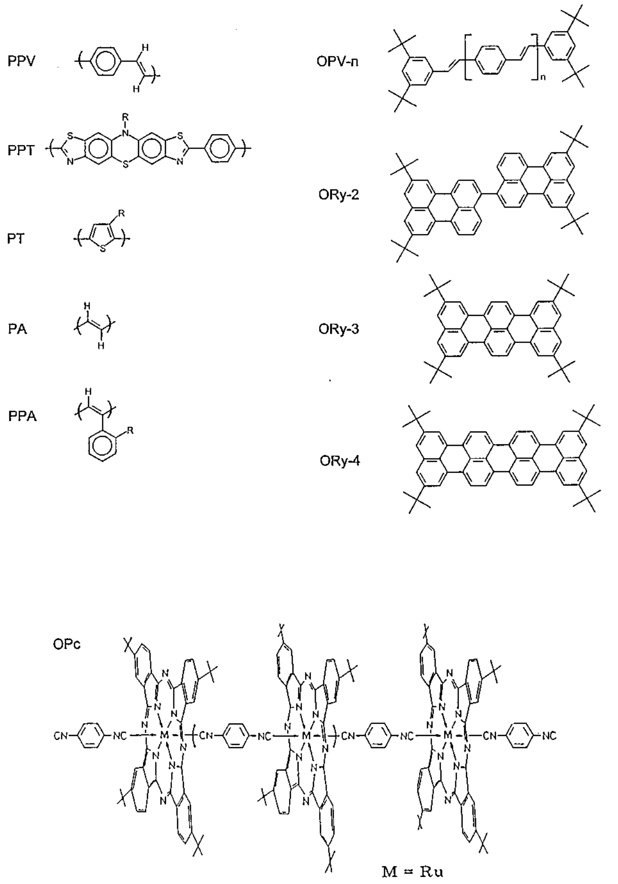

FIG. 1. Chemical structures and abbreviations of some conjugated polymers and oligomers. The substituents R represent alkyl chains of various lengths.

where $\lambda_{\max}$ is the wavelength of the low-energy absorption maximum of the 1D conjugated polymers. Although this scaling law became very popular and was frequently used to interpret the third-order nonlinearities of conjugated systems,[38] a final experimental proof of its validity has not been presented.

The systematic behavior of the $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ data of various 1D conjugated polymers was observed in our earlier THG experiments with a single laser wavelength $\lambda_L=1064$ nm,[39–41] and was discussed in context with the scaling law (1). However, we always noted in these earlier reports that THG studies at variable λ_L would be required for a final quantitative proof of the scaling law. Now we are able to perform these experiments with variable λ_L obtained using an optical parametric generator/amplifier configuration.

In a search for general structure-property relations, the 1D systems PPV and OPV-n will be compared with other conjugated systems. Their chemical structures and abbreviations are also shown in Fig. 1. The focus of the second part of this paper is on correlations between chemical structures and linear and nonlinear optical properties of conjugated π-electron systems. We present a masterplot which shows that a general relation between the linear and nonlinear optical properties of 1D conjugated systems really exists. However, we find significant deviations from the scaling law (1). In particular the exponent is much larger than 6. Possible reasons for this discrepancy will be discussed.

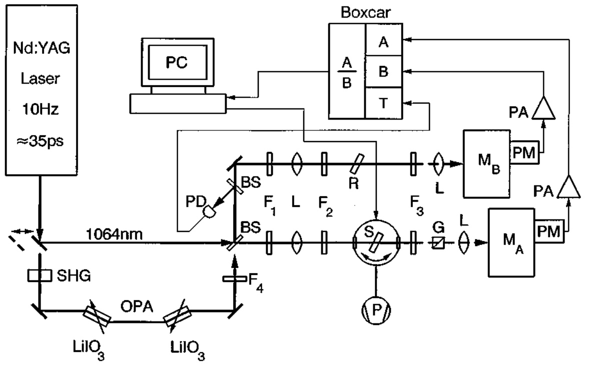

FIG. 2. Experimental setup used for the THG measurements, OPA: optical parametric generator/amplifier configuration. F_i: filters. BS: beamsplitter. G: Glan-polarization prism. PM: photomultiplier. $M_{A,B}$: monochromator. PD: photodiode. PA: preamplifier. S: sample. R: reference. P: pump. SHG: crystal for second-harmonic generation.

II. EXPERIMENT

Thin films of PPV were obtained by spin coating of the tetramethylene sulfonium chloride precursor polymer on fused silica substrates, followed by thermal annealing at 285 °C for 6 h in vacuum. This precursor polymer route to PPV has recently been described in detail.[42,43] The synthesis and spectroscopic characterization of the oligomers OPV-n has been reported elsewhere.[44,45] Thin films of OPV-$n$on fused silica were prepared by vacuum sublimation below 10^{-5} Torr. The film thicknesses were measured with a Tencor Instruments α-step profiler. The typical film thicknesses for the THG experiments were 50–100 nm.

Transmission and reflection spectra were measured with a Perkin Elmer model Lambda 9 spectrophotometer. The reflection spectrum at nearly perpendicular incidence was used to calculate the spectrum of the refractive index in the TE polarization for PPV and OPV-5 by solving the Fresnel equations by an iteration procedure without any fit parameter.[46–48] The results of this technique agree very well with a Kramers-Kronig analysis, which requires a fit of the background index of refraction. For thin films of OPV-3 and OPV-4, only the latter technique was used.

Measurements of THG by using the Maker fringe technique were performed by means of the experimental setup which is shown in Fig. 2. An actively/passively mode-locked Nd:YAG (yttrium aluminum garnet) laser was used (Quantel model YG 501). The typical duration of the fundamental laser pulses was on the order of 30 ps. The laser pulses were amplified in a double-pass amplifier, and transformed into the second harmonic with a KDP crystal. The second-harmonic pulses of 2–3-mJ energy were used to pump an optical parametric generator/amplifier configuration (OPA) based on two $LiIO_3$ crystals.[49] The parametric signal and idler waves could be used for THG in the range between 900 and 1520 nm. The laser beam was focused on the sample, which was placed in an evacuated chamber and mounted on a rotation stage. The harmonic signals of the sample and reference were measured simultaneously to compensate for the effect of laser intensity fluctuations, as shown in Fig. 2.

The Maker fringes were evaluated taking into account the measured data of the sample (thickness, refractive index, and absorption coefficients at the fundamental and harmonic wavelengths), the free and bound harmonic waves and their reflections at the interfaces as described earlier.[50,51] The only fitting parameters were the modulus and phase angle Φ of the complex value of $\chi^{(3)}=|\chi^{(3)}|\exp i\Phi$. The $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ values were determined with respect to the same reference value $\chi^{(3)}(-3\omega;\omega,\omega,\omega)=3.11\times10^{-14}$ esu for the fused silica substrate[52] for all laser wavelengths λ_L. Since this reference value is not accurately known, its weak spectral dependence was not taken into account. The data of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ given in this work always refer to the orientation average.

III. RESULTS

A precise knowledge of linear optical properties is crucial for an exact evaluation of the nonlinear optical susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of thin films. Studies of ultrathin films with thicknesses smaller than 100 nm require special care, since the reflection losses at the film/air and film/substrate interfaces become comparable to the internal absorption losses of the films. Therefore the absorption spectrum 1 of the PPV film, which is displayed in Fig. 3(a), shows an apparent tail toward longer wavelengths. The reflection losses are calculated by means of the dispersion of the refractive index presented in Fig. 3(b). They are subtracted from spectrum 1, and the corrected intrinsic absorption spectrum 2 results.

The intrinsic absorption spectrum of a thin film of the oligomer OPV-5 is shown in Fig. 4(a). It is obtained after correction of the reflection losses, as described above. The modulus and phase angle Φ of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ measured at various laser wavelengths λ_L are also shown in Fig. 4. The scales of the wavelength of the absorption spectrum λ and of λ_L are appropriately chosen to visualize a three-photon resonance of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$.

The THG spectrum of OPV-5 shows only *one* pronounced three-photon resonance at $\lambda_L=1222$ nm, which corresponds closely to the linear absorption maximum. The dispersion of the phase angle Φ displayed in Fig. 4(b) is representative of a single three-photon resonance, which leads to the characteristic value $\Phi=90°$ at the peak of the three-photon resonance. The oligomers OPV-4 and OPV-3 show similar resonances of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ to those seen in OPV-5. They are only shifted to shorter wavelengths.

A representative selection of the linear and nonlinear optical data of thin films of the oligomers OPV-5, OPV-4, and OPV-3 is shown in Table I. In the case of OPV-2 and OPV-1 it was not possible to prepare thin films with sufficient optical quality and stability by the sublimation technique. The absorption coefficient and wavelength of the absorption maximum are denoted $\alpha_{\max}$ and $\lambda_{\max}$. The onset of the optical absorption at the wavelength λ_0 corresponds to the energy E_0 as defined in Sec. I. The absorption maxima of diluted solutions of OPV-*n* are also shown in Table I for comparison with the thin-film data. The absorption spectra of OPV-*n* systematically show a blueshift in going from dilute solution to solid, condensed films.

The modulus and phase angle Φ of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of the thin film of PPV are shown in Fig. 5 for various laser wavelengths λ_L. The spectra of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ and α are also displayed together to visualize three-photon resonance enhancements. A major maximum of $\chi^{(3)}$ is observed at $\lambda_L=1336\pm25$ nm. This main resonance occurs at λ_L close to $3\lambda_{\max}$, and corresponds to a phase angle $\Phi=115°\pm15°$. This phase angle is only slightly larger than $\Phi=90°$, which would be the typical value at a three-photon resonance. In contrast to the case of the oligomers, a second maximum in the THG spectrum of PPV is visible at $\lambda_L<3\lambda_{\max}$. This additional resonance at $\lambda_L=1155\pm25$ nm has no corresponding feature in the linear absorption spectrum. But its existence is confirmed by Φ near 270°. Representative $\chi^{(3)}$ data of PPV are given in Table I at the characteristic laser wavelengths $\lambda_L=1064$ nm, $\lambda_L\simeq3\lambda_{\max}$, and $\lambda_L\simeq3\lambda_0$ for comparison with the data of the oligomers and of other conjugated π-electron systems.

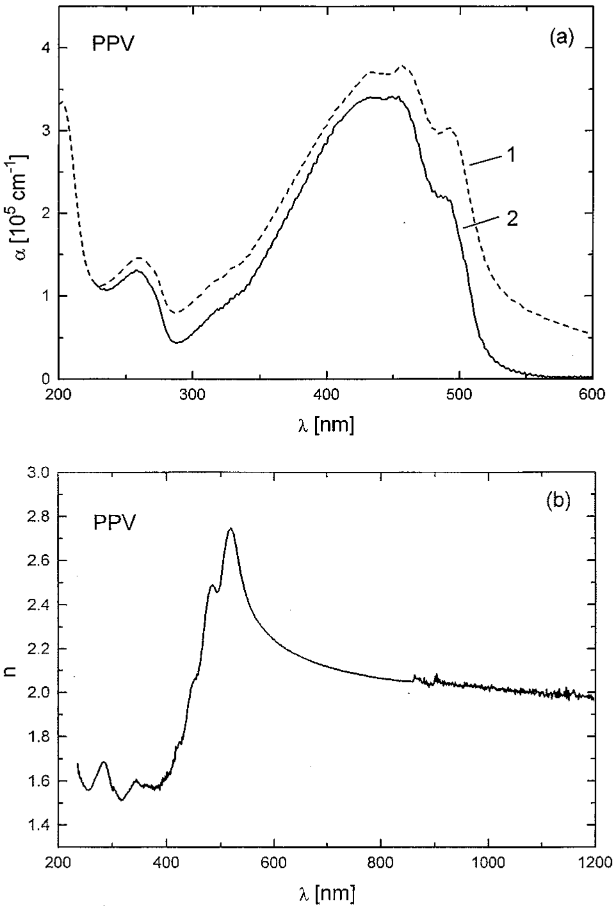

FIG. 3. Spectra of the absorption coefficient α and the refractive index n of ultrathin films of PPV. (a) Spectrum 1 (dashed line) contains reflection losses, which are corrected in spectrum 2 (full line), which shows the intrinsic absorption of a 62-nm-thick film of PPV. (b) Dispersion of the refractive index n obtained from reflection spectroscopy of a 33-nm-thick film on fused silica.

We emphasize that the THG spectra of the oligomers OPV-*n* show *only one* resonance maximum, in contrast to the polymer PPV, which show *two* resonances at $\lambda_L\simeq3\lambda_{\max}$ and $\lambda_L<3\lambda_{\max}$. We further note a very strong and systematic increase of the representative $\chi^{(3)}$ values with increasing $\lambda_{\max}$ of OPV-*n* and PPV. These characteristic features will be discussed and compared with other conjugated π-electron systems in the following sections.

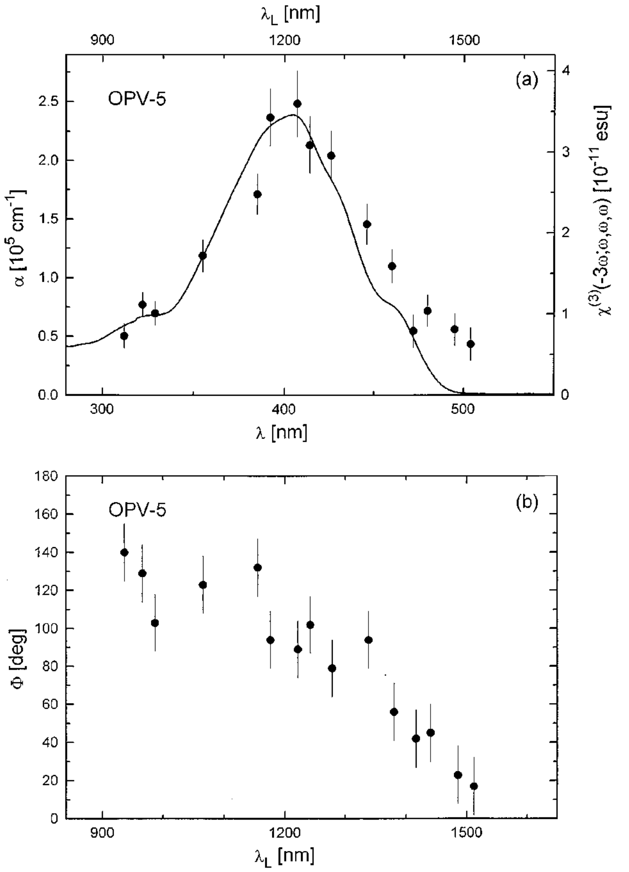

FIG. 4. Modulus and phase angle Φ of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ measured by THG with variable laser wavelengths λ_L and correlated with the linear absorption spectrum $\alpha(\lambda)$ of a thin film of OPV-5.

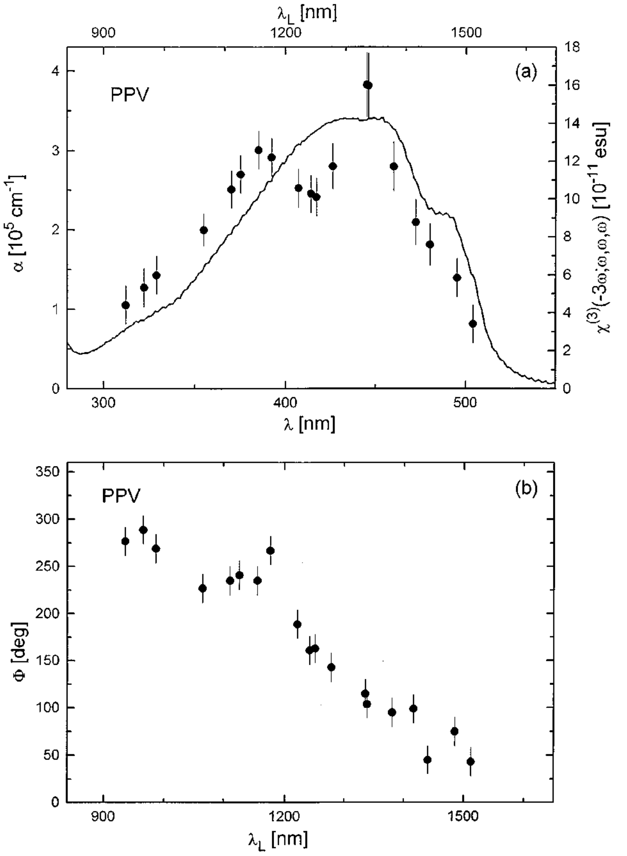

FIG. 5. Comparison of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ with the absorption spectrum of a thin film of PPV displayed similarly as in Fig. 4.

IV. DISCUSSION

A. THG spectra of PPV and its oligomers

The appearance of a second resonance maximum in the THG spectrum of PPV leads to the question of which additional electronic state exists in the polymer, that is not present in the oligomers OPV-*n* with $n \leqslant 5$. The more general question is: What is the appropriate description of conjugated polymers—molecular states or band states?

Clearly, the electronic properties of short conjugated chains like OPV-*n* can be well described by molecular states.[45] The THG spectrum of OPV-5 can be understood on the basis of a three-photon resonance, with the one-photon-allowed optical transition including the vibrational levels of the resonant electronic state. This situation is rather similar to the behavior of all-trans β-carotene (β-C). Recent THG investigations of β-C by Aramaki *et al.*[53] and van Beek and co-workers[54,55] also revealed a single three-photon resonance. The dispersion of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ in the range of the three-photon resonance could be modeled well, if inhomogeneous broadening and various Frank-Condon-allowed vibronic levels were taken into account.

Our observation of two resonance maxima in the THG spectrum of PPV appears very similar to observations of other conjugated polymers. They have been reported, for example, in studies of all-trans polyacetylene (*t*-PA),[56,57] polydiacetylenes (PDA),[58–60] and polythiophene (PT).[61] Therefore we have to consider the physical nature of the ground and excitation states of PPV in connection with the other one-dimensional (1D) conjugated polymers.

Many arguments derived from studies of polydiacetylenes (see, for example, Refs. 62 and 63) strongly support a 1D semiconductor model as sketched in Fig. 6. It consists of a valence-band (VB), a conduction-band (CB), and an exciton state (EX) located below the CB. According to very general principles derived by Haug and Koch,[64] the one dimensionality leads to a shift of oscillator strength from the VB-CB transition to the VB-EX transition. In contrast to three-dimensional semiconductors, the threshold of the conduction band of 1D semiconductors is usually not visible in the linear absorption spectrum, which is dominated by the exciton absorption. For example, in PDA the CB edge is located approximately 0.5 eV above the exciton which can be concluded from photoconductivity and electroreflection experiments.[27–29] The exciton picture of the absorption spectra of conjugated polymers is widely accepted, at least for polydiacetylenes. There is strong experimental evidence from fluorescence investigations [20–23] that it can also be applied to PPV.

Therefore, we assign the strong maximum of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ in the THG spectrum of PPV at $\lambda_L=1336$ nm to a three-photon resonance with vibronic states of the exciton (process 1 in Fig. 6), which corresponds to a maximum of the exciton absorption at $\lambda_{\max}=458$ nm ($E_{\max}=2.7$ eV).

The additional resonance at higher energies can have two possible origins, as indicated by processes 2 and 3. Process 2

TABLE I. Linear and nonlinear optical data of thin films of PPV and OPV-*n*, which are explained in the text. The $\lambda_{\max}$ data in brackets are from OPV-*n* dissolved in $CHCl_3$ (20 °C).

	$\alpha_{\max}$ (10^5 cm^{-1}) (±0.1)	$\lambda_{\max}$ (nm)	λ_0 (nm)	λ_L (nm)	$n(\lambda_L)$ (±0.02)	$n(\lambda_L/3)$ (±0.002)	$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ (10^{-11} esu)	Φ (°)
PPV	3.4	458	521	1064	2.01	1.572	8.36± 0.7	227±15
				1336	1.98	2.047	16± 1.7	115±15
				1512	1.97	2.625	3.21± 0.7	43±15
OPV-5	2.4	406	492	1064	1.609	1.130	1.72± 0.2	123±15
		(418)		1222	1.608	1.591	3.60± 0.4	89±15
				1485	1.605	1.833	0.81± 0.2	23±15
OPV-4	2.1	394	475	1064	1.574	1.174	1.70± 0.2	101±15
		(412)		1155	1.573	1.393	1.91± 0.2	95±15
				1485	1.570	1.720	0.4 ± 0.1	10±15
OPV-3	2.0	383	460	1064	1.559	1.208	1.61± 0.2	102±15
		(403)		1155	1.558	1.506	1.52± 0.2	93±15
				1440	1.555	1.670	0.32± 0.1	23±15
OPV-2		(387)						
OPV-1		(360)						

is a three-photon resonance with the threshold of the continuum of states,[30,31] which may be identified with the CB threshold. Process 3 is a two-photon resonance with a two-photon state which consequently should be located energetically *below* the exciton level. Because processes 2 and 3 could lead to a resonance enhancement of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ at the same fundamental laser wavelength λ_L, it is not possible to distinguish between them only by means of THG experiments.

Two-photon absorption spectroscopy or other nonlinear optical techniques can help to elucidate the origin of the additional THG resonance of PPV. Recently the two-photon fluorescence excitation spectrum of PPV was reported by Baker, Gelson, and Bradley.[65] The strong peak of this excitation spectrum locates the energy of the lowest even-parity-excited singlet state at 2.95 eV. This agrees with the results of Lemmer *et al.*[66] that the two-photon resonance lies energetically well above the lowest dipole-allowed optical transition. This was also found in theoretical investigations by Soos *et al.*[67] A two-photon level of PPV at 2.95 eV would correspond to process 4 in Fig. 6. It should be visible as a two-photon resonance in THG at λ_L around 840 nm, which is not accessible with our present experimental setup.

These investigations exclude process 3, and strongly support a three-photon resonance with the CB threshold (process 2) as an explanation for the additional resonance in the THG spectrum of PPV. Our observation of the two THG resonance maxima of PPV is in good accordance with the theoretical models of Abe *et al.*[30] and Guo *et al.*[31] Because the additional resonance occurs at $\lambda_L=1155\pm25$ nm, we can locate the CB threshold at 3.2 ± 0.1 eV above the valence-band edge of PPV. This is in good agreement with the experimental value 3.1 ± 0.1 eV for the CB threshold of Chandross *et al.*[25] derived from photoconductivity, although their sample had an absorption maximum $E_{\max}\simeq2.5$ eV. Our experimental results and the arguments presented above agree very well with the exciton concept for PPV, and give further support for this model. However, they contradict other previous assignments of the CB threshold to gap energies such as $E_g=3.5$ eV (Ref. 26) or $E_g\simeq2.4$ eV.[15,16,68] If we identify the relative maximum of the inhomogenously broadened absorption spectrum of PPV at 492 nm (2.5 eV) with the zero-vibrational state of the exciton, we obtain an exciton binding energy $\Delta E_b=0.7\pm0.1$ eV. This value of PPV is only slightly larger than that of $\Delta E_b\simeq0.5$ eV for polydiacetylenes.[27–29]

Now we have interpreted the THG spectra of OPV-*n* in terms of molecular states, and the THG spectrum of PPV by means of band states, this raises the question: What is required for the existence of band or continuum states? A periodic structure is surely needed. But which number of repeat units is necessary for band states in 1D systems and what is the influence of the crystal size or the morphology of the sample?

Obviously, we do not observe band states in thin films of OPV-5. This could be for two reasons: (1) The number of repeat units of OPV-5 is not large enough. As longer oligo-

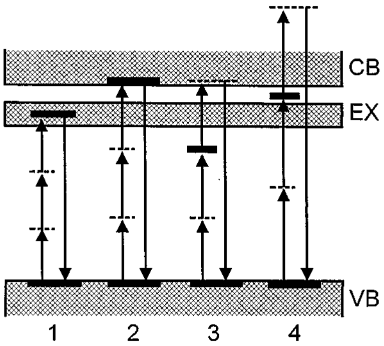

FIG. 6. Energy-level scheme of a one-dimensional semiconductor model of conjugated polymers, VB: valence band. CB: conduction band. EX: exciton. In third-harmonic generation, processes 1 and 2 correspond to three-photon resonances with the exciton and the CB threshold. Processes 3 and 4 describe two-photon resonances with levels located either below the exciton or between the exciton and the CB threshold, respectively.

mers are not available, we have no answer yet to the interesting question of which chain lengths or number of repeat units the transition from molecular electronic states to band states can occur. (2) Owing to the different preparation techniques for thin films of PPV and OPV-*n*, their morphologies differ significantly. The size of crystalline areas in OPV-*n* films is not known yet, and may be much smaller than in PPV films, where this size was found to be in the range of 27 nm.[69] The morphology of the sample, indeed, has a profound influence on its electronic properties which can be concluded from recent electroreflectance studies of PDA single crystals.[29,70] It was observed that the size of the signal located 0.5 eV above the main exciton absorption can vary widely in different samples. It was assigned to the Franz-Keldysh effect for free-electron states. These observations indicate that the morphology of the sample can indeed have a strong influence on the visibility of such continuum states, and that it is very difficult to verify them experimentally.

B. Masterplot of third-order nonlinearities for one-dimensional conjugated systems

Since OPV-*n* and PPV show the systematic increase of $\chi^{(3)}$ with $\lambda_{\max}$, this can be used to test the general scaling law (1). Therefore the modulus of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ is displayed in a double-logarithmic scale versus $\lambda_{\max}$ in Fig. 7(a). To visualize the extent of the resonance enhancement, the range of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ obtained at various laser wavelengths is symbolized by vertical bars between triangles facing up and down. They represent the maximum of $\chi^{(3)}$ at the three-photon resonance ($\lambda_L \simeq 3\lambda_{\max}$, up-triangle) and the low-resonant $\chi^{(3)}$ value (down-triangle) obtained at $\lambda_L \simeq 3\lambda_0$, respectively. As many $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ values have been measured at 1064 nm, these data are given in Fig. 7 by the individual symbols for various oligomers and polymers.

To reveal characteristic structure-property relations, several additional data of conjugated π-electron systems are included in this masterplot. The data of polyphenylacetylenes (PPA's),[50,51] polythiophenes (PT's),[71] polyphenothiazinobisthiazole (PPT),[72] oligorylenes (ORy-*n*),[73,74] and an oligomeric-bridged phthalocyaninato ruthenium complex (OPc) (Ref. 75) are from our own work. The chemical structures of these compounds are shown in Fig. 1. The optical data of substituted PPA's and PT's can vary significantly, because different synthetic routes were used.

Additionally some results of other groups are included for comparison, such as data of all-trans polyacetylene (*t*-PA),[56,57,76] cis polyacetylene (*c*-PA),[76] and all-trans β-carotene (β-C), which was diluted in polystyrene.[53–55] Because β-C can be viewed as an oligomer of *t*-PA, the comparison of these materials is related to our study of OPV-*n* and PPV. The $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ value at $\lambda_L = 3\lambda_0$ was not available for *t*-PA. Therefore the data point represents in this case the smallest $\chi^{(3)}$ value, which was found at $\lambda_L = 1064$ nm.[57]

The low-resonant ($\lambda_L \simeq 3\lambda_0$) and resonant ($\lambda_L \simeq 3\lambda_{\max}$) data of OPV-*n* and PPV are connected by dotted lines in Fig. 7(a). The slope of these lines is 11. The line which connects the resonant data fits quite well to *c*-PA and *t*-PA. This seems to disprove the general scaling law (1), which should lead to the slope of 6 as indicated by the full line. Deviations from the power law (1) were also observed by others.[76,77] Furthermore, we see that the $\chi^{(3)}$ data of several conjugated π-electron systems which have $\lambda_{\max}$ in the range between 450 and 500 nm can scatter over more than two orders of magnitude. This can lead to doubts as to whether a general scaling between linear and nonlinear optical properties exists at all.

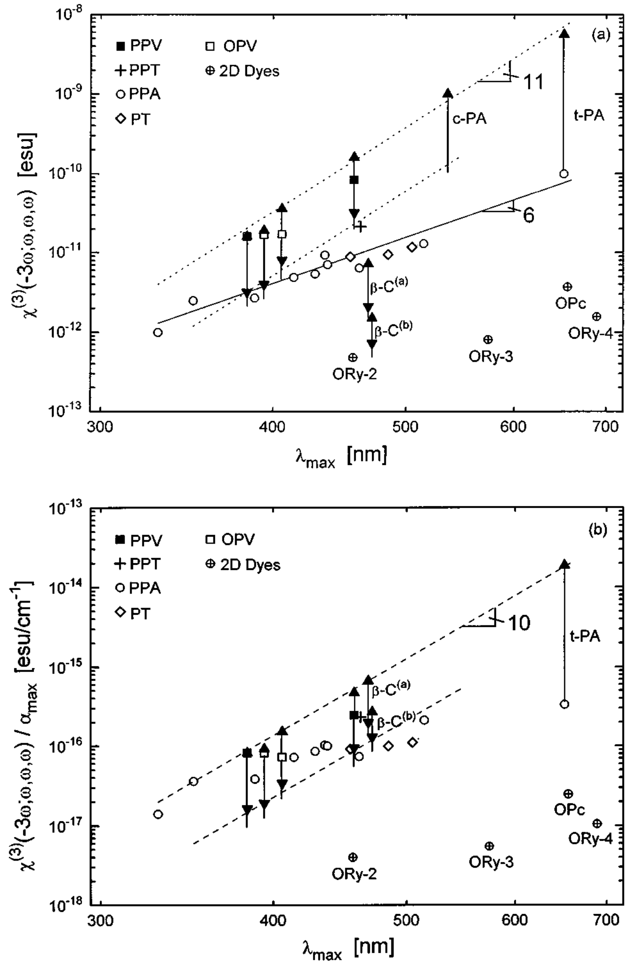

FIG. 7. Masterplots of 1D conjugated polymers and oligomers in a double-logarithmic scale to visualize different scaling laws with exponents given by the slopes of the full, dotted, and dashed lines, respectively. The individual data points represent the orientation averages of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ for various compounds with 1D and 2D electron delocalization (for assignments, see insets and text). They are plotted vs $\lambda_{\max}$, which are the wavelengths of their absorption maxima. Their $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ data are measured at the laser wavelength $\lambda_L = 1064$ nm. The up- and down-triangles show their resonant ($\lambda_L \cong 3\lambda_{\max}$) and low-resonant ($\lambda_L \cong 3\lambda_0$) $\chi^{(3)}$ data, respectively. The vertical bars between them indicate the ranges of $\chi^{(3)}$ values, which are obtained at variable λ_L. Plot *a* shows that the $\chi^{(3)}$ data can scatter significantly due to different concentrations of chromophores. In plot *b* this dilution effect is compensated for by the ratio $\chi^{(3)}/\alpha_{\max}$ where $\alpha_{\max}$ denotes the absorption coefficient of the thin films at $\lambda_{\max}$ and the unique scaling behavior of the 1D conjugated systems can be seen.

However, closer inspection and comparison with the chemical structures of the different materials does indeed reveal a systematic behavior. First, it must be taken into account that the chromophores of the materials can be very diluted. This happens in the case of β-C dissolved in polystyrene and in the case of the polymers PT, PPT, and PPA, which have long alkyl substituents. The different number of π electrons per unit volume also influences the absorption coefficient $\alpha_{\max}$ of the thin films. The easiest way to compensate for this dilution effect is to plot the ratio $\chi^{(3)}(-3\omega;\omega,\omega,\omega)/\alpha_{\max}$ versus $\lambda_{\max}$ as shown in Fig. 7(b). In this normalized masterplot, we recognize that the nonlinearities of PPV, PPT, and β-C are indeed very similar, which is not clear in Fig. 7(a).

The $\chi^{(3)}$ data measured at $\lambda_L = 1064$ nm also fit to the masterplot in a systematic manner. For materials which have $\lambda_{\max}$ close to one-third of $\lambda_L = 1064$ nm, the three-photon resonant $\chi^{(3)}$ values are obtained; see, for example, OPV-3 and OPV-4. For materials with $\lambda_{\max}$ in the range between 450 nm and approximately 500 nm, the $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ values which are measured at 1064 nm and $3\lambda_0$ have a similar magnitude. If $\lambda_{\max}$ is larger than 500 nm, the $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ value measured at 1064 nm can be much smaller than at $\lambda_L = 3\lambda_0$, because the harmonic wavelength falls into the spectral window of low absorbance which is usually observed between the strong bands in the visible and UV spectral ranges. This is the case for *t*-PA.

Now we are able to derive the scaling behavior of 1D conjugated systems from the normalized masterplot shown in Fig. 7(b). The dashed lines show that it can be written in the form

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega)/\alpha_{\max} \sim \lambda_{\max}^{x}, \tag{2}$$

with an exponent $x = 10 \pm 1$. As multiphoton resonances lead to large variations of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$, relationship (2) is valid only for those experimental data which are measured at comparable resonant, low-resonant or nonresonant conditions. The 1D conjugated systems indeed follow a general scaling of their third-order nonlinearities with respect to their linear optical properties, as expected in the early work of Flytzanis and co-workers.[34–37] However, our exponent x differs significantly from the exponent 6 given in the scaling law (1). A possible reason for this difference is discussed in Sec. IV C.

We emphasize that our relationship (2) is valid only for those conjugated π-electron systems which have 1D electron delocalization. To substantiate this important point we have included our recent results of ORy-*n* and OPc in the masterplot. These dyes have a π-electron system which is delocalized in two directions of space. It is obvious from Fig. 7 that the nonlinearities of these 2D dyes deviate strongly from the 1D systems. This difference can be explained with the model of an electron in 1D and 2D potential wells.[78,79] Owing to additional degeneracies, the energy levels in a 2D well are more closely arranged than in the 1D well. With this argument, it can be qualitatively understood that a 2D well of the same maximum lateral length L as the 1D well should have a larger $\lambda_{\max}$ value. Thus the 2D dyes appear at a very different position in the masterplot as the 1D conjugated systems.

The crucial quantity which determines the third-order nonlinearities is the electron delocalization length L_d and not $\lambda_{\max}$. In the case of short oligomers L_d is limited not least by their size L. Taking standard bond lengths and angles, we estimate the maximal sizes of the dyes and oligomers: $L(\text{ORy-2}) \simeq 0.7$ nm, $L(\text{ORy-3}) \simeq 1.1$ nm, $L(\text{ORy-4}) \simeq 1.6$ nm, $L(\text{OPV-3}) \simeq 2.9$ nm, $L(\text{OPV-4}) \simeq 3.5$ nm, and $L(\text{OPV-5}) \simeq 4.2$ nm, with an uncertainty of ± 0.1 nm. With this argument it can be qualitatively understood that ORy-4 has a much smaller $\chi^{(3)}$ value as OPV-3.

C. Discussion of scaling theories

For a discussion of the disagreement of the exponents in relations (1) and (2), we have to consider the major steps in the theory of Flytzanis and co-workers.[34–37] The general scaling law was derived for systems with extended 1D π-electron delocalization within the tight-binding approximation by linear combination of atomic orbitals (Hückel approximation). For extended chains of length L, which are much larger than the delocalization length L_d of the π electrons, it was found that the third-order optical susceptibility $\chi^{(3)}$ should follow the power law

$$\chi^{(3)} \sim L_d^6. \tag{3}$$

The crucial quantity here is the delocalization length L_d. In the model of Flytzanis and co-workers the relation

$$L_d \sim E_F/E_g \tag{4}$$

was derived, where E_F is the Fermi energy and E_g is the band gap, which in this context was called the "optical gap where the main absorption peak is located." Therefore, we have to identify E_g with $E_{\max} \sim 1/\lambda_{\max}$, and obtain

$$L_d \sim \lambda_{\max}. \tag{5}$$

The general scaling law in the form of relationship (1) results from the combination of relationships (3) and (5).

The major disagreement exists in the assignment of the optical absorption maximum of 1D semiconductors. In the model of Flytzanis and co-workers the optical-absorption maximum results from a singularity of the density of states at the semiconductor band gap. In the exciton concept for 1D semiconductors of Haug and Koch,[64] the singular 1D density of states is not visible in the optical-absorption spectrum, which is dominated by the exciton absorption. Two possible reasons for the discrepancy between the exponents remain to be discussed: (i) The exponent in relation (3) is either much larger than 6, or (ii) relations (4) and (5) do not correctly describe the linear optical properties of conjugated oligomers and polymers.

The electron delocalization length L_d is not easily available for extended 1D systems. Therefore, short oligomer chains are considered. If their length L is shorter than L_d of the corresponding polymer, quantum confinement occurs, and limits the electron delocalization. In this case several theories lead to a scaling law of the form

$$\chi^{(3)} \sim L^{\mu}. \tag{6}$$

In the early work of Ducuing *et al.* and Flytzanis and co-workers, $\mu = 5$ was derived.[33,35] Later, other theories led to smaller exponents, e.g., $\mu = 4.6$,[80] $\mu = 4.25$,[81] $\mu = 4.0$,[82,83] and $\mu = 3.5$.[84] These theories are in fair agreement with experimental studies of oligomers.[85,86] Therefore, a larger exponent than 6 in relationships (3) and (6) is improbable, and can be ruled out.

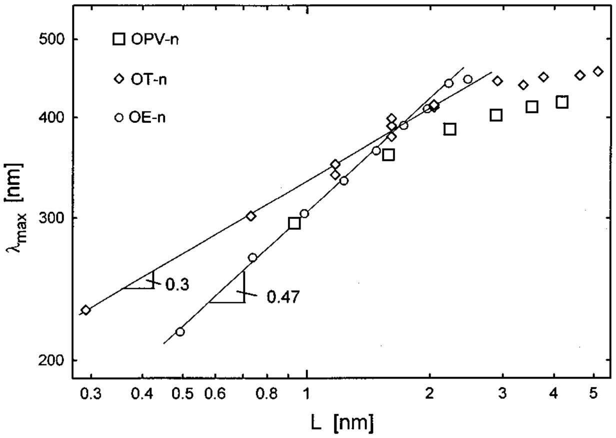

FIG. 8. Length dependence of λ_{max} for 1D conjugated oligomers. The experimental data are from diluted solutions (for references, see text).

Now we consider the length dependence of λ_{max} for 1D conjugated oligomers. Figure 8 shows experimental data of diluted solutions of OPV-*n* and Stilbene,[87] which is structurally related to OPV-*n*. For comparison some literature data of oligoenes (OE-*n*) (Ref. 88) and oligothiophenes (OT-*n*) (Refs. 85, 89, and 90) are also shown. At the limit of very short chains with $L<2$ nm, the experimental data of λ_{max} follow a power law

$$\lambda_{max} \sim L^{\nu}, \tag{7}$$

with $\nu=0.47$ for OE-*n* and $\nu=0.3$ for OT-*n*. The exponent ν for OE-*n* is quite similar to the value 0.5 which was already found in the early studies of oligoenes.[91,92] For chains longer than ~ 2 nm, λ_{max} deviates from (7) and approaches the saturation values of extended polymer chains at $L>5$ nm. The lengths of OPV-*n* with $n=3$–5 are located in the transition regime 2 nm$<L<$5 nm.

In the case of quantum confinement we would expect that relationship (5) leads to a linear increase of λ_{max} with the oligomer length L. Figure 8 shows that this is not the case. Therefore, we conclude that relation (5) is not appropriate to describe the experimental results obtained from 1D conjugated oligomers and polymers. The invalidity of relationship (5) is seen as the primary reason for the disagreement of the exponents in the scaling laws (1) and (2).

More refined theories than Hückel calculations are necessary for a relevant description of these conjugated systems.[93] They should take into account electron correlation effects and excitons in 1D conjugated chains. This would lead to a more appropriate functional dependence of λ_{max} on L_d for 1D conjugated systems as expressed by (5). However, this extended theoretical treatment is beyond the scope of this paper.

Our experimental value $x=10\pm1$ in relationship (2) can be interpreted in a speculative manner for short chains: If we take into account that the extinction coefficient of short oligoenes increases nearly linearly with L,[87] we have to set $\alpha_{max} \sim L^{\kappa}$. For OPV-*n*, the value of κ is found in the range $0<\kappa<1$. Using (7) we obtain $x=(\mu-\kappa)/\nu$. With $\mu=5$ and a typical value $0.3<\nu<0.5$, a rough agreement with the experimental value of x is obtained.

D. Implications of the masterplot

A large variety of 1D conjugated polymers and oligomers with very different chemical compositions and morphologies of thin films can be described by the masterplot shown in Fig. 7(b). This underlines that the search for a unifying concept, which can describe the third-order nonlinearities of 1D conjugated systems by an electron delocalization length L_d, is justified. The theoretical difficulties of this concept have been reviewed recently by Silbey.[93] We also consider L_d as the crucial quantity which determines the linear and nonlinear optical properties of 1D systems. Although a quantitative functional relationship between L_d and λ_{max} is not yet known, λ_{max} of 1D systems is correlated with L_d. Therefore, our scaling relationship (2) describes only the cases where similar relationships between λ_{max} and L_d exist. Consequently, relationship (2) is not valid in other cases, for example 2D systems or when substitution effects (e.g., the incorporation of electron donor or acceptor groups) occur.

The observation that the oligomers OPV-*n* and *β-C* fit closely to the nonlinear optical properties of the 1D conjugated polymers demonstrates that relatively short chain segments of the polymers are responsible for their optical properties and not their entire chain length. As such, conjugated polymers can be considered as arrays of chromophores originating from subunits of the polymer chain.[21,93] High degrees of polymerization, therefore, are not necessary to achieve large $\chi^{(3)}$ values. Conjugated oligomers with a chain length in the order of several tens of nm should have similarly large $\chi^{(3)}$ values. An important question, still to be addressed, is which process limits the delocalization length of the π electrons in conjugated systems. The relative importance of chemical and topological defects versus torsional motions of the polymer backbone,[94] and other physical processes[83] needs to be clarified. This is a prerequisite for the development of improved materials for nonlinear optics.

For applications of the third-order nonlinearities, e.g., in waveguide devices, a large nonresonant $\chi^{(3)}$ value and a negligible absorption of the material at the laser wavelength are required. Figure 7(b) shows that systems with 1D electron delocalization are much better suited for this application than systems with 2D electron delocalization.

V. CONCLUSIONS

We have applied the measurement of third-harmonic generation (THG) as a spectroscopic technique to the characterization of thin films of poly(*p*-phenylenevinylene) (PPV) and several corresponding oligomers (OPV-*n*) of well-defined lengths. We observe a single three-photon resonance in the THG spectrum of the oligomers OPV-*n* and two such resonances in the case of PPV. To interpret our experimental results we consider the question of how the electronic states of OPV-*n* and PPV can be described most appropriately by molecular states, excitons, or a semiconductor model which involves valence and conduction bands. Oligomers OPV-*n* with $n\leqslant5$ have molecular electronic states. PPV has two resonances in the THG spectrum showing an additional electronic state which does not exist in short oligomers. In agreement with recent theories on excitons,[30,31] we assign these three-photon resonances to the peak of the exciton absorption at 2.7 eV, and to the threshold of the continuum of states at 3.2±0.1 eV. The latter can be identified with the edge of a conduction band, because a steep rise in the photoconductivity of PPV occurs approximately at this energy.[25]

We have shown that the third-order nonlinearities of PPV, OPV-n, and a large variety of other 1D conjugated polymers and oligomers can be described by a scaling relationship $\chi^{(3)}/\alpha_{\max}\sim\lambda_{\max}^{x}$. Such a general scaling law was predicted by the theory of Flytzanis and co-workers.[35–37] However, our exponent $x=10\pm1$ is much larger than the theoretical value of 6. Presumably, this Hückel approach does not appropriately describe the relationship between $\lambda_{\max}$ and the electron delocalization length L_d of these 1D conjugated systems. Refined theories should take into account electron correlation effects and excitons.

ACKNOWLEDGMENTS

This work has been supported by the Bundesministerium für Forschung und Technologie and the Volkswagen-Stiftung. We thank Professor G. Wegner for helpful discussions, and H. Menges and W. Scholdei for technical assistance.

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