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Electroabsorption studies of poly(2,5-pyridinediyl)

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The electroabsorption spectrum of poly(2,5-pyridinediyl) has been measured for thin films with unpolarized and polarized light. The spectrum has been successfully fitted to a linear combination of the linear absorption spectrum and its first and second derivative. The electroabsorption spectrum is dominated by a Stark redshift of the first allowed optical transition, $1A_g \rightarrow 1B_u$ at 3.2 eV, and the emergence of a normally one-photon forbidden $2A_g$ state at 3.7 eV, which becomes weakly allowed in the presence of the electric field. A small contribution of charge-transfer excitons to the electroabsorption spectrum has been found and assigned to be an interchain $n \rightarrow \pi^*$ transition. From the linear coefficients we calculated the average change of the components of the polarizibility tensor $\langle \Delta \vec{\vec{\alpha}} \rangle = 4.2\times 10^{-37}\,\mathrm{C\,m/(V/m)}$ and the average value of the difference between ground- and excited-state dipole moment $\langle \Delta \mathbf{p} \rangle = 5.7\,\mathrm{D}$. The anisotropy ratio $\Delta\alpha(\parallel)/\Delta\alpha(\perp)$, the ratio of the field-induced absorption obtained with light polarized parallel and perpendicular to the applied electric field, has been determined to be 1.6. Furthermore, a Kramers-Kronig analysis has been used to calculate the real and imaginary part of the third-order nonlinear susceptibility $\chi^3(-\omega;0,0,\omega)$. Results are compared and contrasted with those reported for other conjugated polymers. [S0163-1829(99)08135-7]

I. INTRODUCTION

In the study of luminescent conjugated polymers, poly(2,5-pyridinediyl) (PPY) is found to have many unique electrophysical and structural properties. The repeat unit of PPY is an aromatic carbon ring (phenzylring) with one carbon atom being replaced by a nitrogen atom. The nitrogen lone pair electrons reside in an orbital which ''sticks'' out from the ring in the same plane as the polymeric chain and therefore does not contribute to the conjugated π-electron system.[1] Thus the π-electron density along the polymer chain is reduced in comparison to polyparaphenylene making PPY more stable with respect to oxidation. Thus it is nearly impossible to oxidize this polymer, but it can be successfully reduced to become conductive.[2,3]

Another property which emphasizes the uniqueness of PPY among other conjugated polymers is its high photoluminescence quantum yield (PLQY) of 37% in the solid state whereas the PLQY in formic acid solution is determined to be 17%.[1,4] There is also a large energy shift of the emission maximum in the photoluminescence spectrum. While the formic acid solution of PPY emits in the blue (2.7 eV), the emission maximum of the solid PPY (e.g., when spun on a substrate) is in the green (2.2 eV).[2,5]

To understand the electro-optical and physical properties of this interesting polymer, the determination of the energy states of the conjugated π electrons is of great importance. In this respect electroabsorption has proved itself to be a useful tool to probe the electronic energy levels of conjugated polymers.[8–13] In an electroabsorption experiment the relative change of light absorption of a sample which is perturbed by a strong electric field is measured. There are three main effects which contribute to an electroabsorption spectrum of conjugated polymers: the Stark shift of the linear absorption signal, changes of the oscillator strengths of the participating electronic states, and a change of the selection rules for electronic transitions which may cause the appearance of normally forbidden transitions due to the symmetry breaking effects of the applied electric field.

In this paper we present the results and detailed analysis of electroabsorption measurements for PPY for unpolarized and polarized light.

II. EXPERIMENTAL SECTION

The synthesis of poly(p-pyridine-2,5-diyl) can be found elsewhere.[1] PPY was dissolved in formic acid using a concentration of 10 mg/ml. With these solutions thin films were easily spun onto suitable substrates. Typical spinning conditions used were a spin speed of 2000 rpm for 60 sec. This led to a thin PPY film of about 70 nm on top of the substrate, while all the formic acid is removed from the film during spinning.[6] In a vacuum evaporator, gold electrodes were evaporated through a shadow mask on top of the polymer film at a pressure of about 1×10^{-5} mbar. The 100-nm-thick interdigitated electrode layer has an electrode spacing of 160 μm and allows the application of electric fields of up to 65 kV/cm. Samples were then placed into a closed-loop helium cryostat, so that the sample could be held under vacuum and at temperatures as low as 10 K during the measurements.

A 150-W Xe-arc lamp was used to provide light in the visible and ultraviolet (UV) region from 2.5 eV to about 5 eV. The light was monochromated by a grating monochromator consisting of two gratings and appropriate filters to cut off second-order light. An adjustable entrance slit, controlled by computer, always kept the amount of light hitting the sample within the desired region to avoid saturation of the silicon photodetector. After passing the monochromator, the beam was focused by a lens to bring it to the appropriate size on the sample. Behind the sample another lens focused the transmitted light onto the silicon photodetector.

The high voltage electric field was supplied by a Trek

10/10 amplifier which amplified the sinusoidal output signal ($f=173\,\mathrm{Hz}$) of the internal oscillator of a lock-in amplifier. The lock-in amplifier also measured the signal detected by the photodiode with a frequency of $2f$. Thereby the field-induced change in sample transmission, ΔT, is obtained, while the linear transmission of the unperturbed sample T is recorded by a digital voltmeter simultaneously. In this way the energy dispersion of $\Delta T/T$ can be obtained.

III. THEORY

In an electroabsorption experiment the field-induced relative change in sample transmission $\Delta T/T$ is measured, which is related to the field-induced change in absorption $\Delta\alpha$ by the relation

$$\frac{\Delta T}{T}=-d\Delta\alpha, \tag{1}$$

where d is the thickness of the sample. The field-induced change in absorption can be understood to be the difference of the absorption of the sample, which is perturbed by the applied electric field, as compared to the absorption without an electric field applied:

$$\Delta\alpha(E)=\alpha^F(E)-\alpha(E). \tag{2}$$

To achieve an expression for $\alpha^F(E)$ it is assumed that the peak width of the transitions giving rise to the absorption band is not significantly influenced by the electric field. In this case $\alpha^F(E)$ is dominated by three effects: The Stark effect, the redistribution of oscillator strength among two neighboring energy states, and the appearance of transitions to energy states which are normally one photon forbidden. In the latter case the applied electric field breaks the symmetry of the molecular orbitals of the polymer, allowing such transitions.

The Stark effect causes an energy shift of the whole absorption band by an amount ΔE. This means that the transition energy from the ground state G to a given electronic state (whose absorption band is shifted) changes when applying an electric field by ΔE:

$$\Delta E=E(F)-E(0). \tag{3}$$

This difference is determined by the Stark effect:[7]

$$\Delta E=\Delta\mathbf{p}\cdot\mathbf{F}+\tfrac{1}{2}\mathbf{F}\cdot\Delta\vec{\vec{\alpha}}\cdot\mathbf{F}. \tag{4}$$

The first term describes the linear Stark effect where $\Delta\mathbf{p}$ is the difference in electric dipole moment between the ground state and the exited state and usually dominates the right-hand side of Eq. (4) when a polarized charge-transfer transition occurs. In this case $\Delta\mathbf{p}$ represents the dipole moment of a polarized charge-transfer exciton. The second term of Eq. (4) describes the nonlinear Stark effect, where $\Delta\vec{\vec{\alpha}}$ is a second rank tensor of the difference in polarizibility between the ground state and the exited state. In a material with randomly orientated molecules, the transition dipole moments of the excited states are also randomly orientated, hence the spatial average causes $\Delta\mathbf{p}$ to vanish. This is the case for Frenckel excitons, originating from the change of polarizibility in the presence of the electric field.

The redistribution of oscillator strength among energy states lying close to each other results in a change in the intensity of the related absorption bands. Thus, the intensity of an absorption signal may be reduced when applying an electric field if there is another, forbidden transition, close to it in energy terms, that becomes allowed in the presence of the field and to which therefore a certain amount of oscillator strength is shifted. According to this we can now write the field-induced change in absorption in the form

$$\alpha^F(E)=k\alpha(E+\Delta E). \tag{5}$$

Using a Taylor expansion of $\alpha(E+\Delta E)$ up to second order of the Stark shift and substituting in Eq. (2) yields

$$\Delta\alpha(E)=(k-1)\alpha(E)+k\Delta E\frac{d\alpha(E)}{dE}+\frac{k\Delta E^2}{2}\frac{d^2\alpha(E)}{dE^2}. \tag{6}$$

The electroabsorption spectrum is therefore expected to be a linear combination of the absorption describing the shift of oscillator strength to or from neighboring states and its first and second derivative describing the Stark effect, unless a normally forbidden transition becomes allowed and contributes to the spectrum. In other words, if there is a discernible feature in the difference function of the measured field-induced absorption and the fit via Eq. (6), then this feature can be assigned to be the absorption band of a transition to a new electronic state, formally forbidden, becoming allowed because of the symmetry breaking of the electric field.

If the linear coefficients of Eq. (6) are determined by fitting to experiment, the average value of the charge-transfer dipole moment $\langle\Delta\mathbf{p}\rangle$ and the average over the change of components of the polarizibility tensor $\langle\Delta\vec{\vec{\alpha}}\rangle$ can be calculated using Eq. (4).

IV. RESULTS AND DISCUSSION

The absorption spectrum of PPY was measured in the range from 2 to 6.7 eV using a Lambda 19 double-beam absorption spectrometer. The sample was placed in the helium cryostat, which was mounted in the spectrometer to allow the measurement of absorption under the same conditions as the electroabsorption spectrum was taken, i.e., at 10 K and in vacuum. Using the measured absorption coefficient of PPY (Ref. 1) the thickness of the PPY films was deduced to be about 60 nm.

Figure 1 shows the obtained linear absorption spectrum consisting of two main features, one at 3.2 eV and the other at 6.3 eV, which are assigned to the transitions $1A_g\rightarrow 1B_u$ and $1A_g\rightarrow 2B_u$, respectively. Two shoulders can be clearly identified on both sides of the low-energy peak, which become less resolved at room temperature. These have been ascribed to vibronic components.[14] Apart from the sharpening of the vibronics, no considerable changes in the absorption spectrum could be found when cooling down the sample. The high-energy peak is not within the energy range of our electroabsorption spectrometer, and so is not considered further.

The electroabsorption spectrum of PPY was measured in the energy range from 2.7 to 4.3 eV with various values of applied electric field (Fig. 2). All features show a quadratic

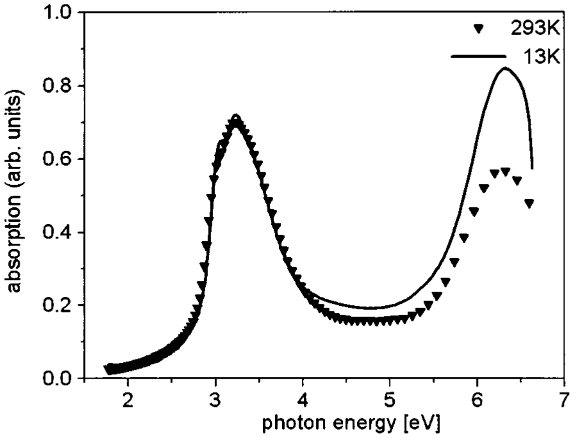

FIG. 1. Absorption spectrum of PPY at 13 K (solid line) and at room temperature (triangles).

voltage dependence which confirms their field-induced origin (see inset).

A least-squares-fitting procedure has been used to fit the spectrum to the linear combination of the absorption spectrum, and its first and second derivative according to Eq. (6) and the following linear coefficients have been determined:

$$\begin{aligned}(k-1)&=-10.7\times10^{-5},\\ k\Delta E&=5.10\times10^{-5}\ \text{eV},\\ \frac{k\Delta E^2}{2}&=2.7\times10^{-7}\ (\text{eV})^2.\end{aligned}\tag{7}$$

The spectrum is dominated by the double feature peaking at 2.94 and 3.07 eV, respectively, resulting from the Stark redshift of the main PPY absorption band. This arises through a change of energy of the transition from the ground state to the first exited state $1B_u$ caused by the applied electric field. Accordingly, the signal follows to a good first approximation the line shape of the first derivative of the linear absorption in this part of the EA spectrum. In the energy range from 3.1 to 3.5 eV, the contribution of the absorption signal becomes significant causing another peak at 3.26 eV. After passing the zero line at 3.62 eV, a third clearly resolvable feature is seen, peaking at 3.82 eV. The fitted curve, with the obtained linear coefficients [Eq. (7)], is shown as a dotted line in Fig. 3(a). An excellent fit to the electroabsorption spectrum up to about 3.2 eV is found. In the part of the spectrum above 3.2 eV the electroabsorption signal clearly deviates from the fit and must therefore be induced by a further contribution. We assign this signal to be the absorption band of a transition to the one-photon forbidden energy state $2A_g$, which becomes allowed in the presence of an electric field. This is more clearly seen in the difference spectrum between the electroabsorption signal and the fit with the absorption and its first and second derivative, which is depicted in Fig. 3(b). The width and shape of the obtained feature are very similar to those of the $1A_g\rightarrow1B_u$ absorption band at 3.23 eV (Fig. 1) and the exact peak position can now be determined to be 3.66 eV with the onset at 3.2 eV. Consistent with the emergence of the new transition, a strong contribution of the linear absorption signal is seen in the fit to the electroabsorption spectrum indicating bleaching of the $1A_g\rightarrow1B_u$ transition and a shift of oscillator strength to the nearby $1A_g\rightarrow2A_g$ transition. This demonstrates the internal consistency of the model leading to the energy-level scheme depicted in Fig. 4.

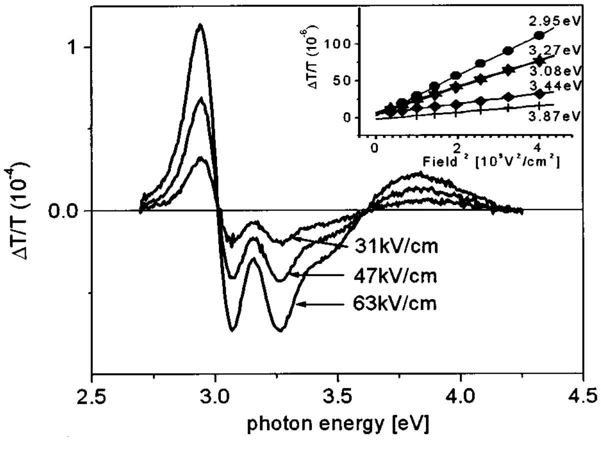

FIG. 2. Electroabsorption spectrum of PPY at various electric fields.

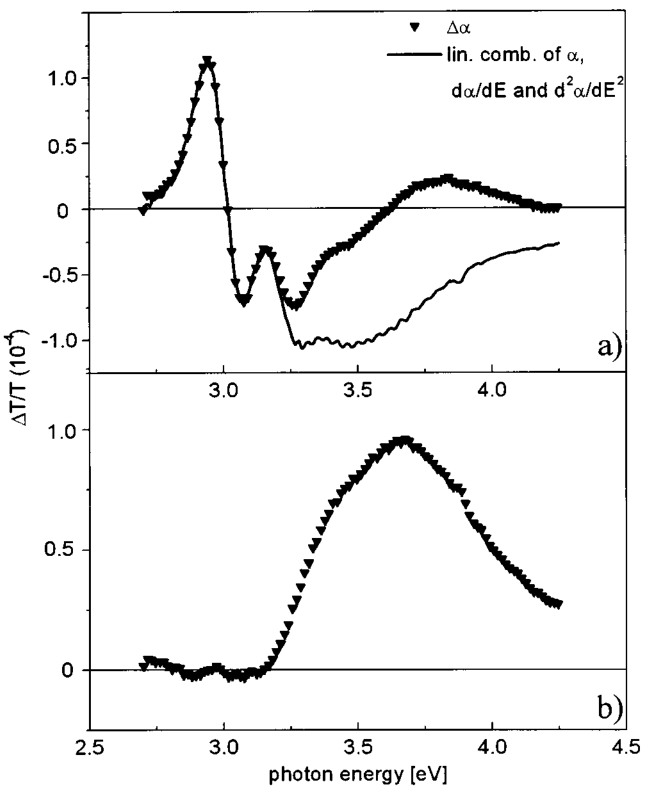

FIG. 3. (a) Electroabsorption signal (solid line) and fit with the absorption spectrum and its first and second derivative (triangles); (b) difference spectrum between the experimental data and the fit.

From the results in Eq. (7) the average value of the difference between the ground-state and excited-state dipole moment $\langle\Delta\mathbf{p}\rangle$ as well as the average change of the compo-

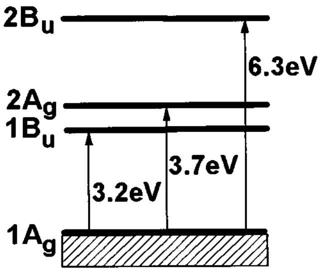

FIG. 4. Energy-level scheme of the conjugated π-electron system in PPY.

nents of the polarizibility tensor $\langle \Delta \overleftrightarrow{\alpha} \rangle$ can be calculated. To do this, Eq. (4) is substituted into the linear coefficients and expanded up to second order in electric field, assuming that the terms which are linear in $\Delta \mathbf{p}$ vanish due to the isotropic orientation of the polymer chains in the plane of the substrate. This yields the following relations for the coefficients of the first and second derivative of the absorption:

$$\begin{aligned} k\Delta E &= \frac{kF^2}{2}\langle \Delta \overleftrightarrow{\alpha} \rangle, \\ \frac{k(\Delta E)^2}{2} &= \frac{kF^2}{2}\langle \Delta \mathbf{p} \rangle^2. \end{aligned} \tag{8}$$

Using our results we find $\langle \Delta \overleftrightarrow{\alpha} \rangle = 4.18\times 10^{-37}\,\mathrm{C\,m/(V/m)}$, which is intermediate between the values obtained for PPV (Ref. 13) and MEH-PPV (Ref. 9) and about one or two orders of magnitude larger than that of other polymers (Table I). This indicates a high degree of delocalization of the excited state in PPY, which is comparable to that of PPV-based polymers.

The average value of the difference between the ground- and excited-state dipole moment is found to be $\langle \Delta \mathbf{p} \rangle = 1.9\times 10^{-29}\,\mathrm{C\,m} = 5.7\,\mathrm{D}$. When compared with the values for polymers whose EA spectrum is dominated by the influence of charge-transfer excitons (second-derivative line shape),[7,10,15] it can be seen that in PPY this effect plays a secondary role (Table II). However, the value obtained allows a rough estimate of the displacement of the excited electron (from its correlated hole) assuming one-electron transfer[7] to be in the region of one to two angstroms.

TABLE I. Average change of the components of the polarizability tensor $\langle \Delta \overleftrightarrow{\alpha} \rangle$ for PPY and other conjugated polymers.

Polymer	$\langle \Delta \overleftrightarrow{\alpha} \rangle / 10^{-38}\,\mathrm{C\,m/V\,m^{-1}}$	Band gap ΔE (eV)	References
PPY	41.8	3.2	This work
PPV	71	2.8	13
MEH-PPV	10.6	2.4	9
PPPV	2.1	3.1	17
PPI	1.7	2.8	13
PPA	1.3	2.6	11
Tetracene	0.19	2.4	7
Pentacene	0.19	1.8	7

TABLE II. Average value of the difference between the ground-state and excited-state dipole moment $\langle \Delta \mathbf{p} \rangle$ and the corresponding electron displacement r.

Polymer	$\langle \Delta \mathbf{p} \rangle$	r/Å	References
PPY	5.7 D	1.2	This work
4-BCMU	48 D	9.9	16
PDES	24 D	4.9	11
EB-polyanilin	19 D	3.9	15
PPV	7.6 D	1.6	13
Pentacene	2.5 D	0.5	7

The electroabsorption spectrum of PPY has also been measured with the incident light being polarized parallel and perpendicular to the applied electric field. The anisotropy ratio (ratio of the field-induced absorption with the polarization of the incident light parallel and perpendicular to the applied electric field) is stated in Table III for the peaks of the EA spectrum. The main feature at 2.94 eV shows an anisotropy ratio of about 3:2, while the ratio is reduced for the features at 3.07 and 3.26 eV due to an increasing contribution of the absorption signal which is polarization independent since the polymer chains are isotropic in the PPY films. The value 3:1 has been reported for a variety of other polymers, for example 4-BCMU (Ref. 16) and PPPV,[17] which was assigned to the alignment of the relevant transition dipole moments parallel to the polymer backbone.[16] However, deviations from this ratio are common in the literature.[21,22] The anisotropy ratio of 3:2 found for PPY indicates a contribution of a transition nonparallel to the dipole moment of the $1A_g \rightarrow 1B_u$ transition. Depending on whether or not the $1A_g \rightarrow 1B_u$ transition dipole moment is aligned along the polymer backbone, this anisotropy ratio may suggest the observed CT transition to be an interchain $n \rightarrow \pi^*$ transition. Further experiments are planned to determine the direction of the dipole moments relative to the polymer backbone.

Finally the third-order nonlinear susceptibility $\chi^3(-\omega;0,0,\omega)$ of PPY was calculated from the electroabsorption spectrum. For this the field-induced change of the real and imaginary part of the refractive index was derived from the field-induced change of absorption via the Kramers-Kronig relation. For the real and imaginary parts of the refractive index the results of spectroscopic ellipsometry measurements have been used.[18] Figure 5(a) shows the real and imaginary parts of $\chi^3(-\omega;0,0,\omega)$ while the absolute value $|\chi^3(-\omega;0,0,\omega)|$ is depicted in Fig. 5(b) with the linear absorption signal for comparison. The obtained maximum

TABLE III. Anisotropy ratios of the electroabsorption signal of PPY.

Feature position (eV)	$\Delta\alpha(\parallel)/\Delta\alpha(\perp)$
2.94	1.6
3.07	1.3
3.26	1.1
3.66	2.0

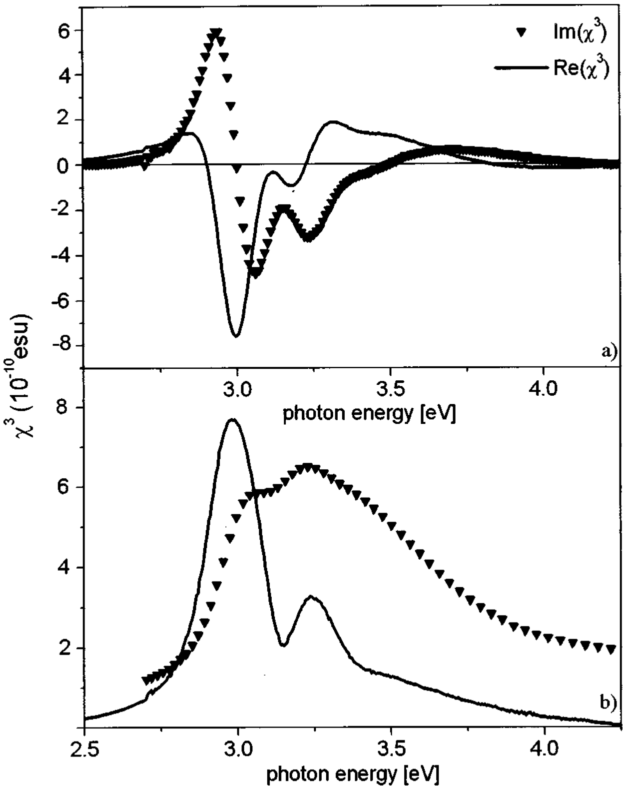

FIG. 5. (a) Real part (solid line) and imaginary part (triangles) of the third-order nonlinear susceptibility $\chi^3(w;0,0,w)$ derived from the electroabsorption spectrum via Kramers-Kronig relation; (b) absolute value of the third-order nonlinear susceptibility $\chi^3(w;0,0,w)$ (solid line) and the linear absorption spectrum (triangles).

value $\chi^3_{\mathrm{max}}(-\omega;0,0,\omega)\approx 6\times 10^{-10}$ esu is comparable to the value measured for poly(3-octylthiophene),[19] one or two orders of magnitude smaller than that for poly(2,5-thienylene vinylene)[20] and *trans*-polyacetylene,[21] respectively, and one order of magnitude larger than $\chi^3_{\mathrm{max}}(-\omega;0,0,\omega)$ measured for polyaniline.[23]

The magnitudes of the optical constants obtained from the electroabsorption spectrum as well as the line shapes and positions of the features of the EA spectrum itself provide detailed information about the electronic transitions occurring within the conjugated π-electron system as described above. The similarity of the results obtained for PPY compared with other conjugated polymers[7–11,13] and the good fit of the EA spectrum to the absorption spectrum and its first and second derivative leads to the conclusion that the one-photon allowed excited states in PPY are excitonic in nature and not principally different from other conjugated polymers. Previously, it had been thought that excimer formation occurred in PPY.[2] This view has been shown to be incorrect,[1,5,6] a conclusion that these EA results further confirm.

V. CONCLUSIONS

The electroabsorption spectrum of PPY has been measured in the energy range from 2.7 to 4.3 eV. A linear combination of the linear absorption spectrum of PPY and its first and second derivative has been used to fit the data. The interpretation of the obtained linear coefficients indicates that the electric field causes a Stark redshift of the $1A_g \rightarrow 1B_u$ transition, the emergence of a transition to a previously forbidden energy state $2A_g$ at 3.66 eV and a transfer of oscillator strengths from the $1A_g \rightarrow 1B_u$ transition to the nearby $1A_g \rightarrow 2A_g$ transition. From the value of $\Delta\alpha$ that we determine here, and comparison with other polymers (see Table I), it is evident that $\Delta\alpha$ and $\chi^3(-\omega;0,0,\omega)$ do not scale linearly with the energy of the $1A_g \rightarrow 1B_u$ transition, i.e., $\Delta\alpha$ is independent of conjugation length. A further second-derivative-like contribution to the electroabsorption spectrum indicates that a small number of charge-transfer excitons is also created during the excitation.

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