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Optical spectroscopy of oriented films of poly(2,5-pyridinediyl)

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Absorption and electroabsorption measurements on (stretched) oriented and spun cast nonoriented films of the rigid rod conjugated polymer poly(2,5-pyridinediyl) have been carried using different directions for the polarization of the incident light and the direction of the applied electric field. This has allowed us to separate the parallel and perpendicular components (with respect to the polymer chain axis) of the allowed optical transition $1A_g \rightarrow 1B_u$. The analysis of the spectral dependence and anisotropy ratios of the absorption and electroabsorption signals provides an indication of the existence of a small number of delocalized Wannier-like excitons photogenerated by light polarized perpendicular to the polymer chains. The majority of excited states are, however, generated parallel to the chains forming Frenckel excitons. In addition, we present results of electroabsorption measurements on disordered (spin cast) poly(2,5-pyridinediyl) films in a typical polymer light emitting diode configuration (sandwiched between indium tin oxide and gold electrodes). We observe that the electroabsorption signal is reduced by a factor of 100–1000 when compared to the planar configuration, indicating a high intrinsic order and alignment of the polymer chains parallel to the substrate in exact agreement with elliposometric results on spun cast films. This property is a consequence of the rigid rod nature of the poly(2,5-pyridinediyl) chain.

I. INTRODUCTION

The characterization of the nature and energies of electronic excitations in conjugated polymers plays a key role in the way we understand the physical processes of conjugated polymers. This then leads on to improvements of their performance in technical applications. Conductivity and luminescence, the electrical and optical properties of conjugated polymers that make them so potentially useful for commercial applications, are all directly or indirectly correlated to the quasi-one-dimensional molecular structure of these materials. Therefore direction dependent measurement of the electrical and optical properties in aligned polymer samples is an essential tool for directly addressing the correlation between the one-dimensional molecular structure and the conjugated π-electron system.[1] The combination of absorption and electroabsorption (EA) measurements are techniques that allow us to probe both the electronic energy levels of a material and to explore the nature and spatial extend of the excited states.[2–4] However, measurements are normally carried out on disordered films and the values obtained are thus averages over isotropic chain orientation.

The conjugated polymer poly(2,5-pyridinediyl) (PPY), a promising conjugated polymer[5,6] because of its luminescence properties,[7] its electron transporting behavior,[8] and its stability with respect to oxidation.[9] Previously we have reported in-plane EA measurements made on spun cast films. Analysis of the experimental line shape, taking into account the effective ‘‘bleaching’’ of the singlet ground state as well as contributions relating to $\delta\alpha/\delta E$ and $\delta^2\alpha/\delta E^2$,[2] we show that nearly all the excited states in PPY are Frenckel excitons, with only a minor contribution from charge-transfer excitons. This initial EA work also allowed us to identify a two photon state at ca. 0.5 eV above the first singlet excited state. The electron transporting nature of PPY was also recently confirmed using spectrally resolved photoconductivity (PC) measurements.[8] These measurements were made in a sandwich cell configuration, as used in the fabrication of organic light-emitting diodes (LED’s). The PC results clearly show that negatively charged species have a far higher mobility than positively charged species, in excellent agreement with our work using PPY as an electron transport layer on bilayer polymer LED’s.[5] Here we report on absorption and EA measurements in highly aligned PPY films, fabricated by a stretch orientation technique, and EA measurements on films made in the sandwich electrode configuration. Previously we have shown that thin spun cast films of PPY have a high degree of natural alignment parallel to the substrate which they are spun onto,[10] therefore making measurements in this configuration allows us to measure the EA response of our polymer at very high applied electric fields which are perpendicular to the chain axis of the polymer. The measurements were conducted using different directions for the polarization of the incident light and the applied electric field with respect to the polymer axis. This allows us to separate the on-chain and off-chain components of the ground- and excited-state electronic wave functions.

We are able to expand on these measurements using our previous findings on the ordering of PPY in thin films. Ellipsometry measurements by Pettersson *et al.*[10] show that the absorption coefficient of thin disordered (spin cast) films of PPY, for light polarized parallel and perpendicular to the plane of the film, is highly anisotropic. The spectra obtained for $\kappa(E)$, the imaginary part of the complex refractive index, which is proportional to the absorption coefficient $[\Delta\kappa(\omega) = c/2\omega\Delta\alpha(\omega)]$, are depicted in Fig. 1. An anisotropy coefficient of 15 can be determined indicating the very good alignment of the polymer chains parallel to the substrate. Further, x-ray reflectivity measurements confirm the anisotropic structure of the thin polymer films and that the chains

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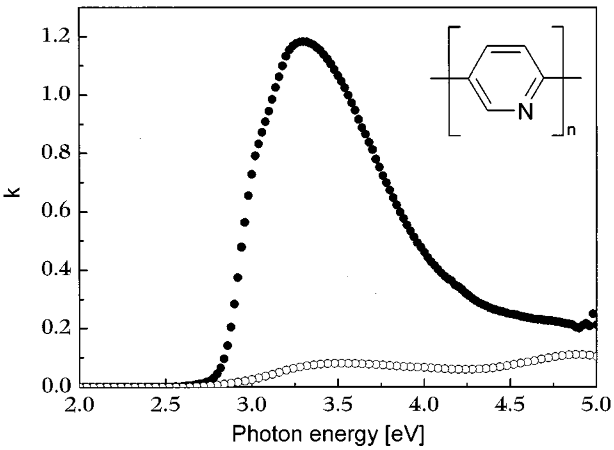

FIG. 1. The imaginary part of the complex refractive index (proportional to the absorption coefficient) measured in a thin disordered film of PPY with the polarization of the incident light in the plane of the substrate (filled circle) and perpendicular to it (open circle). After Pettersson *et al.* (Ref. 10). Inset shows the repeat unit structure of PPY.

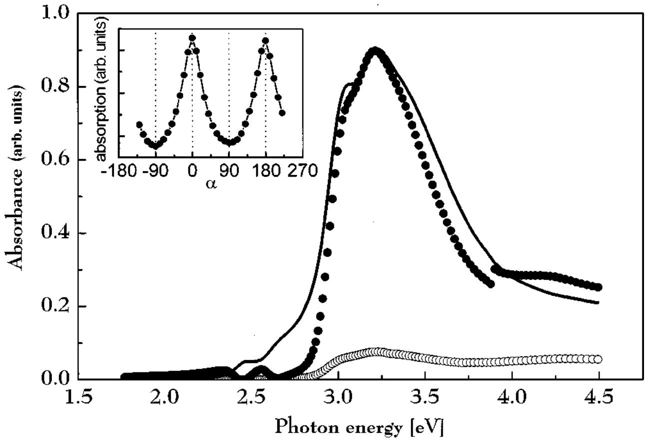

FIG. 2. Absorption spectrum of stretched PPY for light polarized parallel (filled circles) and perpendicular (open circles) to the stretch direction. The absorption spectrum of a disordered (spin cast) film is shown for comparison (solid line). The angular dependence of the maximum absorption at 3.3 eV is depicted in the inset.

do not π stack, rather the pyridly rings sit over the neighboring inter-ring C-C bond with the plane of the rings perpendicular to the substrate.[11] These findings are directly attributable to the rigid rod nature of the PPY.

This recent work, using EA to probe the effects of polymer chain alignment in PPY, has enabled us to identify a highly delocalized excitonic species, and ascribed then to interchain Wannier excitons. As these are created by photoexcitation, this result indicates that interchain photoexcitation may not necessarily yield charge separated, polaronic states.

II. EXPERIMENT

To produce oriented films, PPY was cast on polyvinyl alcohol films (PVA films), which were stretched under gentle heating to elongation ratios between 10:1 and 20:1. After cooling (under tension) the PVA-PPY samples could be removed from the stretching rig as freestanding films without losing their orientation. Two interdigitated gold electrodes (finger spacing 160 μm) were vacuum deposited on to the films. These allow the application of electric fields of up to 60 kV/cm in the plane of the film. For measurements with the electric field applied perpendicular to the plane of the film, we used the standard device configuration for polymer LED's, the PPY film was spun onto an ITO-coated glass substrate and a semitransparent gold electrode evaporated on top. The experimental apparatus for the electroabsorption measurements has been described previously.[2] Absorption measurements where conducted using a Lambda 19 absorption spectrometer (Perkin Elmer).

III. RESULTS

Figure 2 shows the absorption spectrum of a stretched oriented film of PPY (on PVA) for polarization of the incident light parallel and perpendicular to the stretching direction. It can be seen that the absorption drops more than one order of magnitude when light is polarized perpendicular to the stretch (chain) orientation direction. At 3.3 eV both spectra reach their maximum absorbance, here we observe an absorption anisotropy ratio of 13 for a stretch ratio of ca. 10:1. In the inset of Fig. 2 the angular dependence of the peak absorption at 3.3 eV is depicted. The curve is very symmetric with respect to zero degrees indicating the well-ordered structure of the stretched films.

To illustrate the effect the increased order in the PPY films has to the line shape of the absorption spectrum, Fig. 3, shows the scaled spectra for both directions of polarization along with the absorption of a disordered film produced by spin casting. Despite having very different absorption magnitudes the two spectra of the stretched film exhibit very similar line shapes with similar distribution of vibronic modes. The deviation in the higher energy part of the spectrum is due to an increasing influence of the absorption of the substrate (PVA) material. This contribution does not depend on light polarization and therefore becomes more apparent in the scaled spectrum.

An interesting point can be seen when comparing the absorption spectra of the oriented sample with the nonoriented

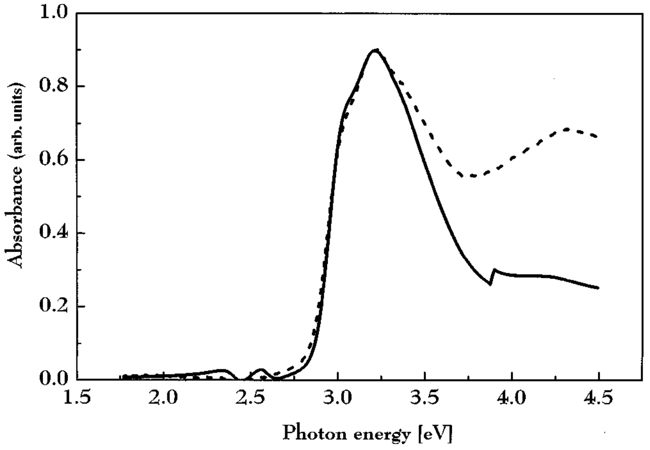

FIG. 3. Absorption spectrum for light polarized parallel and perpendicular (dashed line) to the stretch direction of an oriented PPY film scaled to demonstrate the constancy in line shape.

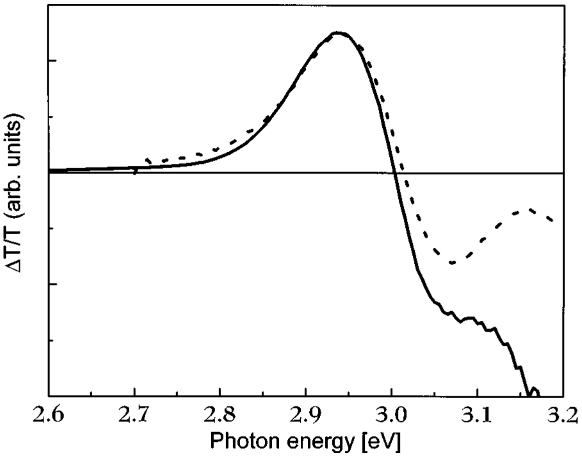

FIG. 4. Electroabsorption spectrum of a stretch oriented PPY film with the electric field applied parallel to the stretch direction (solid line). The spectrum of a disordered film is depicted as a dashed line for comparison.

sample (Fig. 2). Clear line narrowing can be observed as a result of the orientation process. In particular, the transition probabilities for transitions in the low-energy tail region of the absorption seem to be significantly reduced resulting in a sharpening of the onset. On the other hand, the low-energy shoulder at about 3 eV does not become more pronounced in the oriented film.

In the electroabsorption experiment there are two vectors that can be rotated with respect to the stretching direction, the externally applied electric field, and the electric-field vector of the polarized light. Figure 4 shows the electroabsorption spectrum of a stretched oriented PPY film with both the applied electric field and the polarization of the light being parallel to the stretching direction. Also depicted is the scaled EA spectrum of a disordered (spin cast) film. In the oriented spectra a slightly narrowed main feature around 2.9 eV can be observed. As a result the spectrum of the ordered sample crosses the zero line at a photon energy 10 meV lower than that of the disordered sample. Apart from this sharpening the line shapes of both spectra look almost identical, indicating a common origin of the EA response for the ordered and the disordered system. In the high-energy region, again, the PVA substrate material increasingly contributes to the signal.

If the polarization of the light is rotated out of the parallel direction while keeping the electric field applied along the chains, the electroabsorption signal is found to decrease. In Fig. 5 the angular dependence of $\Delta T/T$ is depicted. Again, the signal is symmetrical with respect to zero degrees and reaches its minimum when the light is polarized perpendicular to the chain direction. However, the electroabsorption anisotropy ratio $\Delta\alpha(\parallel)/\Delta\alpha(\perp)$ is determined to be only 3. This is more than four times lower than the measured linear absorption anisotropy of 13.

To measure the electroabsorption for the applied electric field aligned off parallel to the polymer chains, two methods were used. First the interdigitated electrodes were evaporated with the shadow mask rotated to certain angles to the stretching direction. The maximum EA signal measured at a photon energy of 2.9 eV is depicted in Fig. 6, for different directions of the applied electric field. The incident light was polarized in the chain (stretch) direction, which was always found to produce the largest signal. The signal decreases constantly and no electroabsorption signal was detectable when the field was applied perpendicular to the stretch direction.

In the second arrangement a thin (ca. 100 nm) spin cast PPY film was sandwiched between ITO and semitransparent gold. This allows the application of relatively high electric fields. At a field of 500 kV/cm, which is ten times higher than in the planar configuration using the interdigitated electrodes, the magnitude of the sandwich cell EA at 2.9 eV is less than a third of the maximum planar EA. Taking into account the quadratic voltage dependence of the electroabsorption signal, this indicates an EA anisotropy of 100–1000 with respect to the direction of the applied electric field. Figure 7 shows the EA spectrum for a sandwich cell and compares it with the scaled spectrum of a PPY film measured in planar configuration using the interdigitated electrodes. It is remarkable that, despite the huge difference in magnitude of the signals and the distinct electrode arrange-

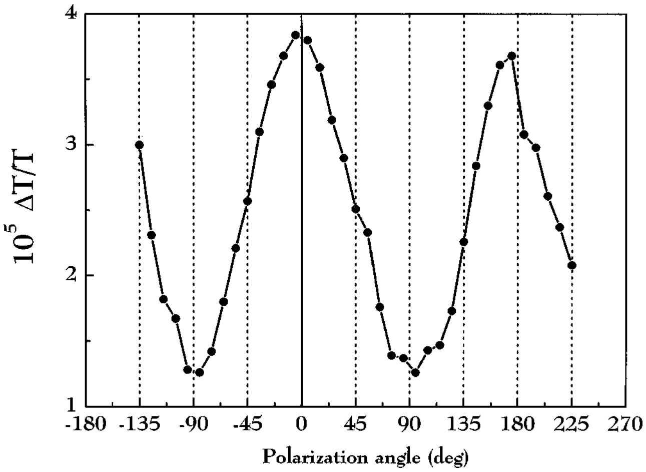

FIG. 5. The dependence of the electroabsorption signal on the angle between the polarization of the incident light and the applied electric field (applied parallel to the stretch direction), measured at a photon energy of 2.9 eV.

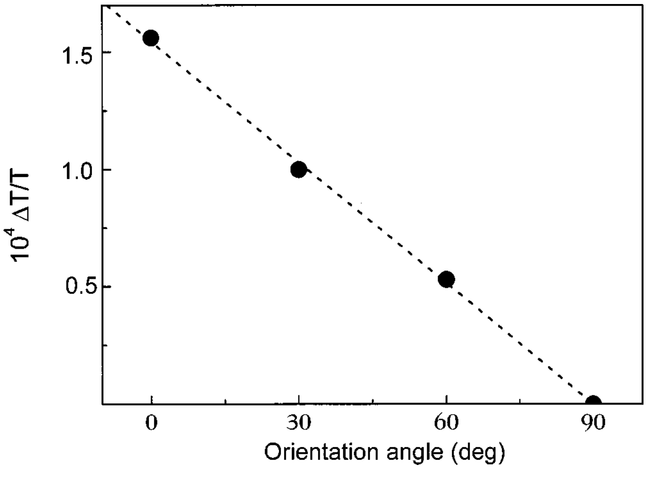

FIG. 6. The effect on the EA signal measured in the planar electrode configuration for a stretched oriented film using different orientations of the applied electric field with respect to the chain orientation.

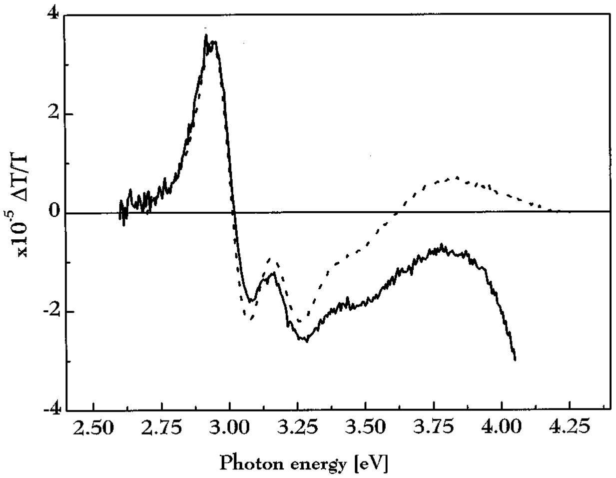

FIG. 7. Electroabsorption spectrum of a spun PPY film in a sandwich electrode configuration (between ITO and Al), applied field 500 kV/cm. The spectrum of a disordered film (measured in plane) is depicted as a dashed line for comparison.

ments in the two configurations, both spectra exhibit almost identical line shape. This in conjunction with the angular dependence on the stretched films suggests that the electric-field component parallel to the chain direction always interacts with the same species.

IV. DISCUSSION

The line narrowing of the first allowed transition in the absorption spectrum is expected for a sample with increased order. Similar effects were observed in oriented samples of other conjugated polymers.[12,13] In the poly(phenylenevinylene) derivative MEH-PPV reduced disorder gave rise to a steeper onset of the absorption and to an improved resolution of the vibronic features. This sharpening of the absorption edge is also observed in the spectrum of the oriented PPY films and indicates that the low-energy shoulder of the absorption band at about 3.0 eV corresponds to the lowest, i.e., the vibronically relaxed energy state. In contrast to all other conjugated polymers the energetic position of the absorption maximum and its shoulder are independent of both stretching and the polarization of the incident light (Fig. 3). In poly(octylthiophene), for example, the absorption peak blue shifts by almost 0.5 eV when changing the light polarization from parallel to perpendicular and the stretching itself causes an energy shift of 0.1 eV.[12,13] The authors explained this behavior with an increase of the conjugation length upon stretching. Although the stretched-oriented PPY films exhibit a far larger absorption anisotropy ratio (Fig. 2), no shift or significant redistribution of the vibronic components can be observed. This can be explained by the rigid-rod-like nature of the PPY chains, and the fact that the polymer chain has no bulky alkyl side groups introducing torsional distortion to the polymer backbone, reducing effective conjugation. A high degree of crystallinity, which was revealed in x-ray powder-diffraction measurements by Monkman *et al.*,[14] implies efficient packing of the polymer chains. Therefore even in disordered (spin cast) films of PPY there is high degree of order in the neighborhood of each chain. Since this microscopic order and the rigidity of the polymer chains are both unaffected by stretching the conjugated π-electron system does not experience a change of its energy levels and so the band center for intrachain processes does not alter on orientation. A degree of line narrowing is apparent, however. This, we believe, is due to the increased interchain ordering of the film either by increased ordering of the individual crystallites and/or orientation of the amorphous regions within the film. As ellipsometery shows that nonstretched films have a high degree of order in planes parallel to the film substrate, we assume that orientation primarily affects the intraplane ordering in the film. We believe that the small features seen between 2.2 and 2.6 eV in the absorption spectrum of the oriented film are artifacts from the absorption spectrometer.

The electroabsorption response of disordered films of PPY have been discussed in detail previously.[2] Therein the strong low-energy feature around 2.9 eV was recognized to arise from a nonlinear stark shift of the first allowed optical transition due to a change in polarizibility between the ground and the excited state. A fit of the EA spectrum to a linear combination of the absorption signal and its first and second energy derivative allowed the exact determination of the shift by separating the effects involved:

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

Thus using the linear coefficient of the first derivative the calculation of the average change in polarizibility upon transition from the ground state to the excited state $\langle\Delta\vec{\alpha}\rangle$ was possible:[15,16]

$$k\Delta E=\frac{kF^2}{2}\langle\Delta\vec{\alpha}\rangle.$$

From the results of the electroabsorption anisotropy of the stretched sample the average change in polarizibility can now be separated into its two components, parallel and perpendicular to the polymer chains. Thereby it is important to note that the line shape and peak positions of the electroabsorption spectrum does not change upon stretching (Fig. 4) and that the linear stark effect is still negligible. Therefore the equations above can be applied to the EA data for polarization of the incident light parallel and perpendicular to the polymer chains. We thus obtain

$$\langle\Delta\vec{\alpha}\rangle_{\parallel}=5.4\times10^{-37}\,\mathrm{C/(V/m)},$$

$$\langle\Delta\vec{\alpha}\rangle_{\perp}=25\times10^{-37}\,\mathrm{C/(V/m)}.$$

The polarizibility of an energy state denotes the capability of an electron system to redistribute its charges under the influence of an external electric field forming an electric dipole. The values obtained for $\langle\Delta\vec{\alpha}\rangle_{\parallel}$ and $\langle\Delta\vec{\alpha}\rangle_{\perp}$ mean that for excited states generated by light polarized perpendicularly to the chains the *change* of this capability upon excitation is about five times larger. Thus the question arises whether these perpendicular excited states are created at the few chains that could not be oriented by the stretching process or are they an intrinsic part of the excited state of the oriented chains. The first alternative can be excluded since this corresponds to the configuration where the electric field is applied perpendicular and the light polarized parallel to the stretching direction. This situation was seen to give rise to no electroabsorption signal within the accuracy range of the experiment (Fig. 6) although far more chains are addressed. Therefore the relatively high EA signal for light polarized perpendicularly and electric field parallel to the chain direction is assigned to be a perpendicular component with low oscillator strength $[\alpha(\|)/\alpha(\perp)=13]$ but very high polarizability *in the* chain direction. This, together with the fact that charge-transfer excitons in the oriented film are still negligible (no significant contribution of the second absorption derivative to the EA signal) suggests the creation of Wannier-like excitons in the following way. A photon with polarization perpendicular to the chain direction leads to the transfer of an electron to a neighboring chain. This aids the separation of the electron from its correlated hole as the influence of the hole is effectively reduced due to the Coulomb screening when the electron is located on the neighboring chain. The same electric field could then separate electron and hole to a larger extent as compared to the intrachain Frenkle exciton, which would explain the high polarizibility of these Wannier exciton states. We know from photoconductivity experiments[2] that only negatively charged species are mobile in PPY, thus we assume that the hole is strongly localized on its chain (at its photogeneration site) whereas the electron will be able to delocalize to a greater extent on its neighboring chain, but still remain correlated to the hole. We envisage the electron being able to run up or down the neighboring chain producing a much more weakly bound exciton. This interpretation would also mean that the small absorption for light polarized perpendicular to the stretching direction originates from such interchain transitions rather than from imperfections of the alignment.

When the electric field was applied perpendicular to the polymer chains very low electroabsorption was measured for either polarization direction of the incident light. In the stretched samples no signal at all could be detected (Fig. 6) and in the sandwich cell experiment, where far higher electric fields were used, the EA response was 100–1000 times smaller then in the planar configuration. This allows two conclusions: First, the off-axis component of the excited state polarizibility is very small or, more exactly, does not differ greatly from the ground-state polarizibility. This is consistent with the general picture that the displacement of charges along the chains is much easier than perpendicular to them. The second conclusion becomes obvious when one remembers that the sandwich cells are produced by simple spin casting of PPY in formic acid solution. The very high EA anisotropy again mirrors the high degree of alignment of the polymer chains in the plane of the substrate, as determined by both ellipsometery and x-ray reflectivity. As the shape of the EA spectrum measured in the sandwich cell configuration is very similar to that measured in the standard planar configuration we assume that the very high applied field, 500 kV/cm, picks out chains which are not perfectly aligned parallel to the substrate. Thus we are really observing a very weak on-chain EA signal component in the sandwich cell geometry.

V. CONCLUSIONS

We have carried out absorption and electroabsorption measurements on stretched oriented and spin cast samples of the rigid rod conjugated polymer, poly(2,5-pyridinediyl). The absorption spectrum of the stretched film has been found to exhibit a relatively large anisotropy with respect to the light polarization indicating the majority of generated dipole moments to be aligned along the polymer chains. On the other hand, the anisotropy ratio of the electroabsorption has been found to be much lower. We have presented an explanation for this apparent conflict by assigning the comparably large off-chain electroabsorption signal to originate from highly delocalized excited states with high polarizibility in the chain direction, i.e., Wannier excitons, generated by transferring one electron to a neighboring chain.

The electroabsorption spectrum of spin cast PPY films in a sandwich electrode configuration together with the results from ellipsometery measurements reveal a high degree of parallel alignment of the polymer chains on the substrate. The very high applied field in this case picks out a weak on-chain EA contribution from misaligned polymer chains. The high degree of alignment in stretched films and intrinsic in-plane orientation on substrates is a direct consequence of the rigid rod nature of the PPY.

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[1] T. W. Hagler, K. Pakbaz, K. F. Voss, and A. J. Heeger, Phys. Rev. B **44**, 8652 (1991).

[2] F. Feller and A. P. Monkman, Phys. Rev. B **60**, 8111 (1999).

[3] M. Liess, S. Jeglinski, Z. V. Vardeny, M. Ozaki, K. Yoshino, Y. Ding, and T. Barton, Phys. Rev. B **56**, 15 712 (1997).

[4] G. Weiser and A. Horvath, Chem. Phys. **227**, 153 (1997).

[5] S. Dailey, M. Halim, E. Rebourt, L. E. Horsburgh, I. D. W. Samuel, and A. P. Monkman, J. Phys.: Condens. Matter **10**, 5171 (1998).

[6] D. D. Gebler, Y. Z. Wang, J. W. Blatchford, S. W. Jessen, L. B. Lin, T. L. Gustafson, H. L. Wang, T. M. Swager, A. G. MacDiarmid, and A. J. Epstein, J. Appl. Phys. **78**, 4264 (1995).

[7] L. E. Horsburgh, A. P. Monkman, and I. D. W. Samuel, Synth. Met. **101**, 113 (1999).

[8] F. Feller and A. P. Monkman, Appl. Phys. Lett. **76**, 664 (2000).

[9] T. Yamamoto, T. Maruyama, Z. H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A Fukuda, and K. Kubota, J. Am. Chem. Soc. **116**, 4832 (1994).

[10] L. A. A. Pettersson, H. Kariis, G. Greczynski, L. E. Horsburgh, and A. P. Monkman (unpublished).

[11] E. J. Samuel, A. P. Monkman, L. Pettersson, L. E. Horsburgh, K. E. Aasmundtveit, and S. Ferrer (unpublished).

[12] T. Danno, J. Kürti, and H. Kuzmany, Phys. Rev. B **43**, 4809 (1991).

[13] S. Luzzati, P. Elmino, and A. Bolognesi, Synth. Met. **76**, 23 (1996).

[14] A. P. Monkman, L. E. Horsburgh, M. E. Vaschetto, P. D. Hatton, H. D. Burrows, W. Brown, and L. Pettersson (unpublished).

[15] F. Rohlfing and D. D. C. Bradley, Chem. Phys. **227**, 133 (1998).

[16] L. Sebastian, G. Weiser, and H. Bassler, Chem. Phys. **61**, 447 (1981).