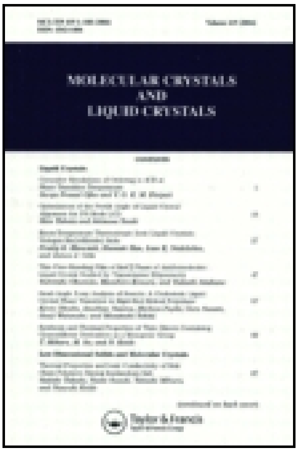

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Excited States in Polymers of Different Dimerization

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EXCITED STATES IN POLYMERS OF DIFFERENT DIMERIZATION

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Abstract Investigations of the excited states of a planar poly(*para*-phenylene)-type ladder polymer are presented. In this system dimerization due to ring rotation angles is completely suppressed. We compare these results to investigations on poly(*para*-phenylene) and poly(*para*-phenylenevinylene).

INTRODUCTION

17 years after the discovery that polyacetylene (PA) can be doped to high conductivity[1] the properties of conjugated polymers in their undoped state attract increasing attention. The electroluminescence (EL) of poly(*para*-phenylene) (PPP)[2] and poly(*para*-phenylenevinylene) (PPV)[3] is exploited in polymer light emitting diodes (LED). In the case of PPV the well-established precursor route[4] yields materials, which lack vibrational structure in the absorption spectra. Low *inter*- and *intra*-chain order serve as an explanation for this obeservation[5]. Considerable progress was made in this field by using ''tent frame precursors''[6] to produce rigid rod conjugated segments which result in large changes in the electronic structure. For PPP the invention of a precursor route[7] allowed the preparation of high quality films with a compact, non-fibrous morphology, while the ''classical'' methods (Kovacic[8], Yamamoto[9], electrochemical[10] and vacuum deposition[11]) result in a granular or fibrillar morphology. In PPP an increase of the torsion angle (20-30°,[12-14]) between successive phenyl rings is known to increase the gap. And even in the nearly planar PPV (7±6°,[12]) the freezing out of small ring torsions is used as an argument to explain the red shift of the absorption peaks[6], which amounts to about 0.05eV between room temperature and liquid-helium temperature. Therefore we expect an increase of the

intrachain order and a decrease of the gap by planarizing PPP. Aside from cycloaddition reactions the transformation of a linear precursor into a two-dimensional system by subsequent ring closure[15] was recently shown to be an adequate approach in the synthesis of ribbon structures[16]. Ring closure of a polyphenylene via a Friedel Crafts type reaction resulted in the first soluble, processable polyphenylene possessing *planar* π-systems[17].

EXPERIMENTAL

The synthesis of the PPP-type ladderpolymer (LPPP) is described in Ref.17 comprehensively. Films were cast on KBr from a toluene solution - the choice of KBr enables us to perform optical spectroscopy on the *same* sample between 370 and 50000cm^{-1}. To measure the Photoinduced Absorption (PIA) of the samples we used the standard pump and probe technique, utilizing a dispersive and a Fourier Transform setup, alternatively. $FeCl_3$ in a solution of acetonitrile was used for p-type doping, with the polymer films prepared on silicon.

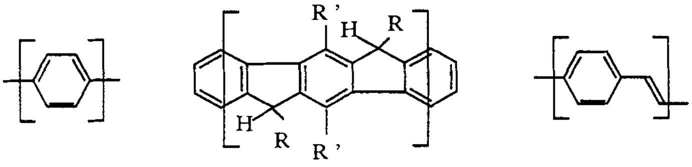

FIGURE 1 Structure of PPP, LPPP and PPV (left to right); R'=C_6H_{13}, R=-1.4-C_6H_4-$C_{10}H_{21}$.

RESULTS AND DISCUSSION

Absorption and Fluorescence

In Figure 2 we show the optical density(OD) and the photoluminescence (PL) spectra of a thin LPPP-film. The onset of the interband

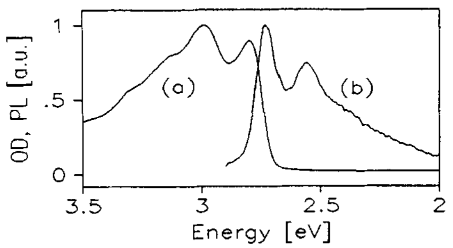

FIGURE 2 OD (a) and PL (b) of a thin LPPP-film.

absorption (E_{ao}) is at about 2.69eV while the *dominant* absorption peak (E_{ad}) is found at 2.79eV. The onset (E_{po}) and the first peak of the PL (E_{pl}) are found at 2.81 and 2.72eV, respectively. E_{ad}, E_{po} and E_{pl} are normalized to E_{ao} and compared to other materials in Table I. One can see that LPPP, PPP and PPV are quite similar in PL (E_{po}, E_{pl}) but LPPP and improved PPV show a different behaviour in the absorption compared to standard PPV and PPP(E_{ad}).

TABLE I Optical properties of LPPP, PPV and PPP.

Material	E_{ao} [eV]	E_{ad}/E_{ao}	E_{po}/E_{ao}	E_{pl}/E_{ao}
LPPP	2.69	1.037	1.045	1.011
standard PPV1[18]	2.32	1.29[u]	1.078	1.034
standard PPV2[19]	2.36	1.21[u]	1.051	1.004
improved PPV[6]	2.27	1.079	1.004	1.048
PPP[20,21]	2.85	1.281[u]	1.026	1.012

[u]...unstructured absorption

The shape of the absorption spectra in improved PPV and LPPP are very similar except for the strong tailing below the gap in PPV. For three dimensional crystalline PA theory predicts a gap of 1.1eV while the gap for one-dimensional PA, is 1.5eV[22]. This three dimensional effect might be responsible for the tailing in improved PPV, for which electron diffraction measurements show an interchain coherence length[6] of 45Å. In LPPP no crystallinity was observed (long sidechains) and the absorption spectra in film and solution match perfectly.

Photoinduced Absorption Spectra

Figure 3 shows the PIA spectra of an as prepared LPPP-film and a photo-oxidized sample. For the intact film we observe three broad features centered at 690, 1050 and 1500cm^{-1}. The latter two show modes at 1600, 1494, 1380, 1325, 1257, 1197, 1140, 1104, 1078, 1004cm^{-1} whereas the signal noise is too high to detect a structure for the broad peak at 690cm^{-1}. Two wide features are found which we assign to electronic transitions due to their large full width at half maximum

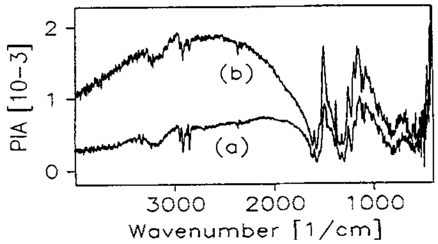

FIGURE 3 PIA of a LPPP-film: (a) as prepared, (b) degraded.

(FWHM): the first peaking at 0.26eV with its onset at 0.20eV. The second has its onset at about 0.6eV and shows a 5 times higher intensity at 1.24eV than the peak of the first (Figure 4). Upon photo-oxidation the broad feature at 690cm^{-1} moves up by about 30cm^{-1} and increases its FWHM from 70 to 100cm^{-1}. Some IR modes shift (1494→1504cm^{-1}, 1380→1384cm^{-1}, 1197→1199cm^{-1}, 1140→1152cm^{-1} and 1104→1108cm^{-1}) and the peak of the lower lying electronic transition moves from 0.26eV up to 0.33eV (the onset remains constant).

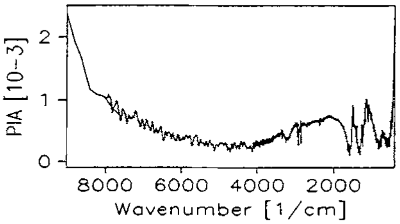

FIGURE 4 PIA of a LPPP-film.

Upon photo-oxidation the absorption spectrum of the LPPP shows the same qualitative change, as it was found by comparing improved PPV to the standard material[6]. This would indicate a loss of intrachain order. Moreover, we find the electronic PIA shifting towards higher energies accompanied by an increase of its intensity[23] relative to the vibronic PIA by a factor of 2. The first fact would indicate a decrease of conjugation length while the second is an evidence for an increase in the defect mass[24] of the photogenerated species. The latter can be explained as reduced mobility along the chain due to reduced conjugation.

Kinetics of the Photoinduced Absorption

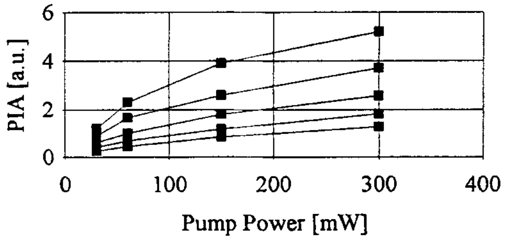

FIGURE 5 Kinetics of PIA of a LPPP-film. The signal increases with increasing τ_c (here: τ_c=6,12,23,47,94ms).

The kinetics of the PIA was investigated by varying the intensity p_i and the chopping period (τ_c) of the pump beam. To describe the results in Figure 5 in a comprehensive way we use the following relation:

$$I = (A\tau_c^B)p_i^{(C\tau_c^D)} \qquad (1)$$

A and C are normalizing constants depending on the units of I, p_i and τ_c. The physical meaning is contained in B and C. A steady increase of the PIA signal (I) at 0.26eV is observed, when increasing the chopper period from 6 to 94ms (B=0.65). Therefore, we conclude that the lifetime of the photogenerated defects is longer than 100ms. For the dependence of the PIA on pump beam intensity we found a $p_i^{0.65}$-behaviour which is expressed by C=0.57 and D=-0.031. A zero D-value means that the choice of τ_c does not influence the p_i-dependence of the PIA. This is seen for *trans*-PA where we found D to approach 0 for increasing oxidation of the sample and for decreasing conjugation in unoxidized samples. The value found for LPPP corresponds to PA of a mean conjugation length of five double bonds. For the LPPP we find a conjugation length of approximately 9 phenyl rings[25].

PIA Dependence on Pump Wavelength and Temperature

We recorded the excitation spectra of the PIA at two distinct quantum energies of the probe beam - at 0.26 and at 0.62 eV. It was seen that the onset of efficient production of photo-defects is redshifted by about 0.1eV with respect to the interband transition spectrum[23]. The temperature dependence of the PIA signal (probe at 0.26eV) is shown in Figure 6. The PIA in LPPP - compared to PA - shows a lower threshold temperature where the signal starts to decrease rapidly with increasing temperature (140K vs 200K).

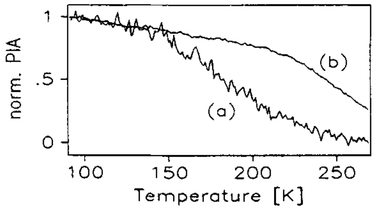

FIGURE 6 Temperature dependence of the PIA at (a) 0.26 eV in LPPP and at (b) 0.4eV in *trans*-PA[26].

Doping Induced Spectra

In Figure 7 we show the net change in absorbance of a doped LPPP-film with respect to the pristine material compared to the PIA of a undoped LPPP. Doping of the material should result in charged defects with a higher defect mass on the chain. The qualitative similarity to the

PIA spectrum shows that the photogenerated states are also charged. Some quantitative differences are found however: the doping induced IR-modes shift up in frequency compared to the photoinduced ones. The onset of the electronic peak does not change while the peak moves from 0.26eV to 0.43eV. The oscillator strength of the electronic transitions relative to the vibronic ones increases by a factor of two (see photo-oxidation)[23]. We also want to emphasize that the spectra of the doped LPPP film did not show any sign of the electronic transition with the onset at 0.6eV that was observed in the PIA (Figure 4). Therefore this PIA feature is not related to *charged* defects.

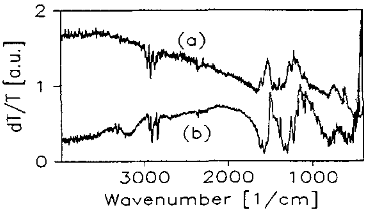

FIGURE 7 Doping induced absorption of a LPPP-film (a) compared to PIA (b).

Time Resolved Photoluminescence Measurements

In order to discuss the nature of the photogenerated species, created immediately after excitation, we performed time resolved luminescence measurements that are described in detail elsewhere[27]. There is a clear evidence for at least two processes appearing on the ps-timescale. One with τ_1 of about 80ps, the other with τ_2 of about 500ps. The decay of the luminescence was measured at emission wavelengths between 450 and 620nm. With increasing wavelength increasing rise-times are observed and the relative weight of the τ_2-component also rises. This means that the spectral composition of the photoluminescence emission shifts towards the red with time. A similar behaviour is seen for PPV[28].

Discussion of the defect states

In Table II we present a comparison of the photo- and doping induced defects found in optical experiments in a LPPP, PPV and PPP. $E^{h\nu}_{\omega 1}$ and $E^{h\nu}_{\omega 2}$ denote the photoinduced ($h\nu$) transitions between the band and defect levels according to the Fesser Bishop Campbell model[35] while the superscript p-d stands for p-type doping. In the framework of this model the ratio ω_o/Δ_o of the distance between midgap and the defect states divided by half the gap plays an important role - therfore it is provided in brackets below the energy values of the defect states.

It is seen that ω_o/Δ_o increases from PPV via PPP to LPPP. Within the mentioned model this implies that the confinement of the defect states increases in the same order.

TABLE II Defect states of LPPP, PPV, PPP.

Material	LPPP	PPV^{s}1	PPV^{s}2	PPV^k	PPP
$E_{\pi-\pi^*}$ [eV]	2.79	2.8	3.2	2.65	3.4
$E^{h\nu}_{\omega 1}$[eV]	0.26	0.6	-	0.4	-
	(0.81)	(0.57)	-	(0.70)	-
$E^{h\nu}_{\omega 2}$[eV]	-	1.6	-	1.6	-
	-	(0.14)	-	(0.21)	-
$E^{p-d}_{\omega 1}$[eV]	0.43	-	0.9	0.8	0.55
	(0.69)	-	(0.44)	(0.40)	0.68
$E^{p-d}_{\omega 2}$[eV]	-	-	2.3	2.0	2.5
	-	-	(0.44)	(0.51)	(0.47)

PPV^{s}1:Ref.19, PPV^{s}2:Ref.29, PPV^k:Ref.30, PPP: Refs 12,31-34

CONCLUSION

We have presented results concerning the excited states in LPPP emphasizing the influence of large intrachain order which is responsible for the similarity between LPPP and improved PPV in the shape of the interband transition. For LPPP we observe only one transition caused by *charged* defects which we assign to strongly confined bipolarons with lifetimes of the order of 0.1s.

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