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Optical Absorption, Luminescence, and UV-Excited Optically Detected Magnetic Resonance (UV-ODMR) Study of Poly(P-Phenyleneethynyleneaniline) (PPEA) Derivatives

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OPTICAL ABSORPTION, LUMINESCENCE, AND UV-EXCITED OPTICALLY DETECTED MAGNETIC RESONANCE (UV-ODMR) STUDY OF POLY(*P*-PHENYLENEETHYNYLENEANILINE) (PPEA) DERIVATIVES.

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Abstract The absorption, photoluminesence (PL), and X-band (9.35 GHz) ODMR spectra of several PPEA derivative films is described and discussed. The absorption of the solutions and films peak at 390 - 415 and 415 - 422 nm, resp. The intense PL of the solutions and films peak at 425 - 450 and 450 - 490 nm, resp. Interestingly, the vibronic structure of the PL of the solutions is clearer than that of the films. The ODMR excited at $254 \leq \lambda_{ex} \leq 400$ nm includes the following familiar features: (i) a narrow polaron resonance at $g \approx 2.002$ and (ii) full- and half-field triplet exciton powder patterns. However, the widths of the polaron and full-field triplet powder pattern resonances are ~30 and ~1500 G, resp., as compared to 10 - 15 and 600 - 900 G, resp., of other π-conjugated polymers. The results are discussed in relation to structural disorder and defects in these polymers.

INTRODUCTION

Rapid advances in the development of π-conjugated polymer-based LEDs[1-8] and the present challenges to improve their stability and efficiency provide a strong motivation for basic studies of their photo- and device-physics. The various types of optically detected magnetic resonance (ODMR) techniques have proven to be powerful tools in providing insight into these materials and devices.[9-14] However, the photoluminescence (PL)-detected magnetic resonance studies reported to date have all employed visible laser sources to excite relatively low-gap polymers, and novel higher-gap systems were inaccessible for such investigations. This paper describes UV-excited ODMR measurements on new π–conjugated poly(*p*-phenyleneethynyleneaniline) (PPEA)-type polymers. The properties of these polymers are compared to those of poly(*p*-phenyleneacetylenes) (PPAs),[15] which have been previously characterized by absorption, PL, and

ODMR obtained by visible excitation, have been utilized as the emissive layer in LEDs.[7,8] The results suggest that the films contain a high density of structural defects. These defects are suspected to stabilize polarons that can recombine to form singlet excitons, but also quench these excitons. The possibility that they quench triplet excitons as well is also discussed. Some speculative suggestions on the nature of these defects are discussed in light of the the PL and ODMR of these polymers.

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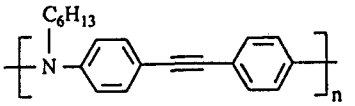
EXPERIMENTAL PROCEDURE

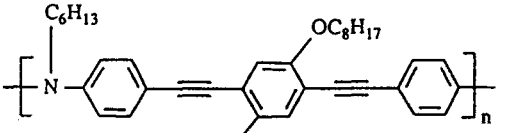
Figure 1 shows the structure of the PPEA-type polymers studied in this work. PPEA (Fig. 1a) was synthesized by a modified Heck coupling reaction[16] of diiododiphenyleneamine[17] and diethynyldiphenyleneamine. The diethynylene PPDEA (Fig. 1b) was synthesized by the oxidative coupling reaction[18] of diethynyldiphenyleneamine.

The filtered output from an Oriel short-arc Hg lamp was reflected from mirrors blazed at 248, 308, and 353 nm to selectively excite the samples at these bands. Other details of the ODMR system, which has been used extensively with an Ar^+ laser for excitation in the visible range, are described in previous reports.[9-11,14]

poly(*p*-phenyleneethynyleneaniline)
(PPEA)



poly(di(phenyleneethynylene)aniline)
(PDPEA)



poly(phenylenedi(ethynylene)aniline)
(PPDEA)

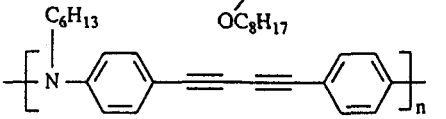


Figure 1. *Structure of the poly(p-phenyleneethynyleneaniline) polymers*

RESULTS

The results of molecular weight, optical absorption and fluorescence measurements are summarized in Table I. As clearly seen, the peak emission $\lambda_{e,max}$ of the efficient PL is in the blue region of the visible spectrum. However, the onset of absorption $\lambda_{a,o}$ is in the violet region, and the peak absorption $\lambda_{a,max}$ is in the near UV. Figure 2 shows the PL spectra, excited at ~353 nm. The striking observation is that while the emission of all the films is structureless, the PPDEA solution exhibits some structure and in the spectrum of the PDPEA solution it is pronounced. The splitting between the peaks in the former and between the two high-energy peaks in the latter is ~0.257 eV, consistent with C≡C stretch vibration.

Table I. *The weight-average molecular weight M_w, polydispersivity (P.D.), and onset of optical absorption ($\lambda_{a,o}$), peak absorption ($\lambda_{a,max}$), and peak emission ($\lambda_{e,max}$) wavelengths (in nm) of the solutions and films studied in this work (see Fig. 1).*

polymer	M_w	*P.D.*	*state*	$\lambda_{a,o}$	$\lambda_{a,max}$	$\lambda_{e,max}$
PPEA	$5x10^4$	1.5	solution	430	389	550
			film	430	390	550
PPDEA	$7x10^4$	1.4	solution	450	399	590
			film	450	417	650
PDPEA	$6x10^4$	2.4	solution	465	415	520
			film	465	415	590

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The ESR of undoped PPEA was undetectable, suggesting an upper limit of ~10^{-9} spins per repeat unit; upon exposure to iodine, the spin density increased to ~$3x10^{-6}$ per repeat unit; the derivative peak-to-peak ESR linewidth was a relatively wide 14 G.

The narrow total PL-detected polaron resonance of PDPEA films excited at ~353, ~308, and ~250 nm at 10 K is shown in Figure 3. As clearly seen, the resonance is excitation-wavelength λ_{ex}-independent, similar to the behavior of PPAs but in contrast to the UV-ODMR of poly(3-alkylthiophenes) (P3ATs) and poly(*p*-phenylenevinylenes) (PPVs) described elsewhere in this volume.[19] In addition, the full width at half maximum is $\Delta H_{1/2} \approx 30$ G, as compared to 10 - 15 G in P3ATs[9] and PPVs.[10]

The full-field triplet exciton powder-pattern resonance of PPEA and PDPEA at λ_{ex} ~ 353 and 250 nm is shown in Figure 4, and the half-field resonance in the latter, at λ_{ex} ~ 353 and 308 nm, is shown in Figure 5. Several observations are noteworthy: (i) The widths of the full-field patterns are 1200 - 1500 G, i.e., much broader than

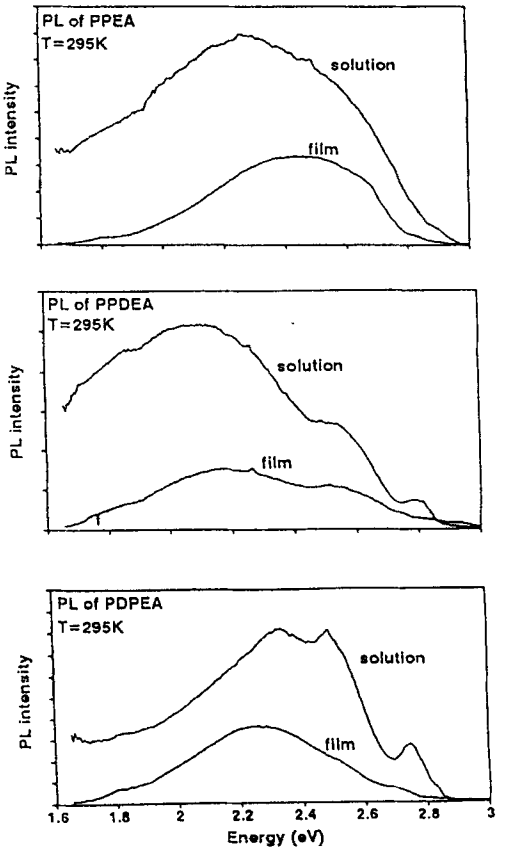

Figure 2. *The room temperature PL spectra of PPEA, PPDEA, and PDPEA films and solutions excited at ~353 nm.*

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those of P3ATs[9] and PPVs,[10] and even broader than those of PPAs.[11] (ii) In PDPEA, the half-field resonance excited at ~353 nm suggests that two distinct triplet excitons affect the dynamics of the luminescent singlet excitons. (iii) Excitation at ~308 nm then apparently generates a drastically lower population of the narrower, higher-field exciton. (iv) Finally, excitation at ~250 nm apparently yields a very low density of triplet excitons which affect the PL. This latter observation is consistent with similar UV-ODMR measurements on P3ATs and PPVs described elsewhere in this volume.[19]

DISCUSSION

The salient observations described above offer several interesting, but at present tentative, suggestions on the nature of these polymers:

(i) The structure of the PL of solutions (Fig. 2) is consistent with the C≡C stretch vibration energy. However, since very few progressions are observable, the assignment of this structure to that vibration mode is clearly speculative. Still, the general observation of greater structure in solutions rather than films is striking. It may be argued that the triple bond-based backbones are much more rigid than double bond-based chains and the solvent consequently induces fewer dynamical structural defects which disrupt the conjugation. Casting onto films may then induce far more static structural defects than in the more flexible double-bonded backbones, which may relax during the casting process.

(ii) Similar to PPAs[11] but in contrast to PPVs[10] and P3ATs,[9] the narrow PL-enhancing polaron ODMR (Fig. 3) is very

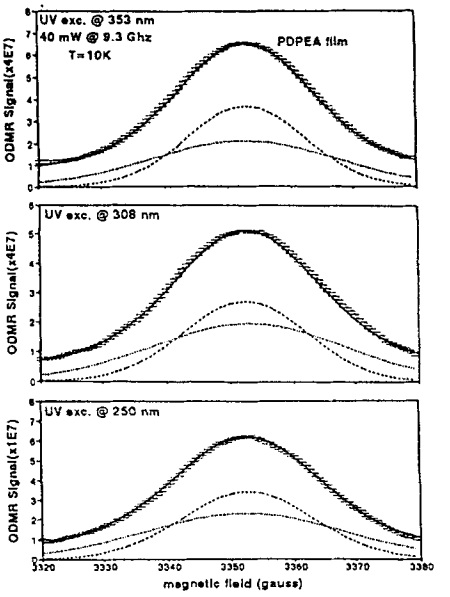

Figure 3. *The narrow total PL-detected polaron resonance of PDPEA films excited at ~353, ~308, and ~250 nm at 10 K.*

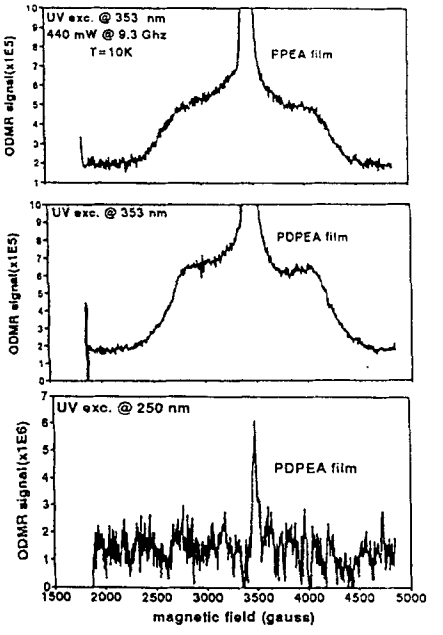

Figure 4. *The full-field triplet exciton powder-pattern ODMR of PPEA and PDPEA excited at ~353 and ~250 nm at 10 K.*

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wide ($\Delta H_{1/2}$ ~ 30 G) and short λ_{ex} does not induce a PL-quenching resonance. This behavior is also consistent with a large density of structural defects in the films, if these structural defects stabilize polarons and thus enhance their steady-state population. Although higher energy neutral and charged excitations are photogenerated at short λ_{ex}, the high density of these structural defects may relax a large number of these excitations into polaron states similar to those generated at visible λ_{ex}, resulting in λ_{ex}-independent polaron ODMR.

(iii) The ~1500 G width of the full-field triplet exciton powder pattern ODMR is also consistent with a large density of structural defects, if it is assumed that the triplet excitons may become stabilized by these structural defects. If this scenario is vindicated, it would explain the broad distribution of triplet zero-field splitting parameters in general and of the parameter E which indicates the deviation from axial symmetry in particular, which result in the broad relatively structureless pattern.

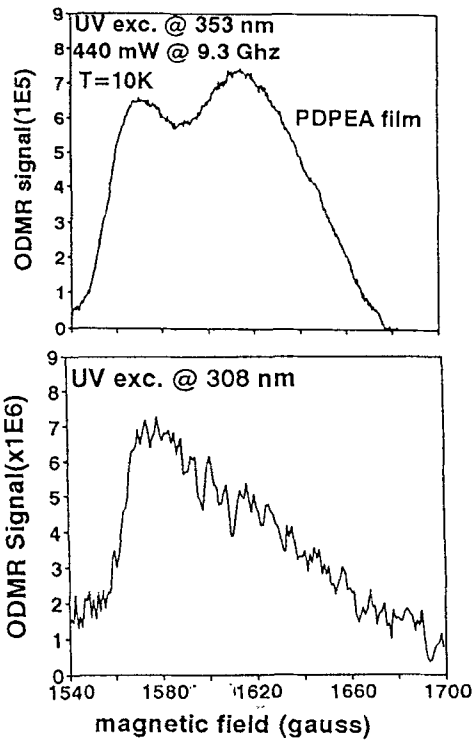

Figure 5. *The half-field triplet exciton ODMR of PDPEA excited at ~353 and ~308 nm at 10 K.*

Finally, the drastic reduction in the intensity of the triplet exciton pattern at short λ_{ex} is similar to the behavior of PPVs and P3ATs.[19] It is suspected that the major triplet exciton generation mechanism is intersystem crossing from the (rigid) singlet 1^1B_u exciton which is the dominant photogenerated excitation at longer λ_{ex}. Thus, short λ_{ex} generates higher-energy excitations and the quantum yield of the 1^1B_u exciton, which is the source of both the PL and the 1^3B_u triplet excitons, sharply decreases. The observed reduction of the PL at short λ_{ex}, which is indeed observed in other systems as well as in the PPEAs,[19] is clearly consistent with this scenario.

SUMMARY AND CONCLUDING REMARKS

In summary, the absorption, photoluminescence (PL), and UV-excited optically detected magnetic resonance (ODMR) spectra of poly(*p*-phenyleneethynyleneaniline) (PPEA), poly(di(phenyleneethynylene)aniline), (PDPEA), and poly(phenylenedi(ethynylene)aniline) (PPDEA) was described and discussed. The PL spectra of solutions were generally more structured than those of films, probably due to a high density of structural defects in

the latter. The UV-ODMR yielded a strong relatively broad PL-enhancing polaron (p^+, p^-) resonance at all excitation wavelengths $\lambda_{ex} \geq 250$ nm. This behavior is consistent with stabilization of polaron by the structural defects. The observed polaron resonance is consistent with either p^+ - p^- fusion into the luminescent 1^1B_u singlets, or with their elimination as nonradiative 1^1B_u quenching centers.. The full-field triplet exciton resonance is also very broad, but unobservable at short λ_{ex}, consistent with triplet generation by intersystem crossing from the 1^1B_u exciton and stabilization by these defects.

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