Electric Field Assisted Photodegradation of Spatially Confined Poly(p-phenylenevinylene)

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Abstract: The effect of electric fields on the fluorescence decay of block-copolymers containing poly(p-phenylenevinylene) (PPV) and polynorbornene (polyNBE) was measured. Electric fields of up to 200 V/μm do not perturb the fluorescence decay profiles when the average size of the PPV block is small (i.e., PPV$_3$-*block*-polyNBE$_{200}$ or PPV$_3$-*block*-polyNBE$_{25}$). It appears that for short isolated PPV segments the electric field accessible for these studies does not allow dissociation of photogenerated excitons into electron-hole pairs. For larger PPV segments, as in PPV$_{20}$-*block*-polyNBE$_{200}$, the electric field reduces considerably the fluorescence lifetime and quantum yield. In addition, irradiating the sample under an electric field changes permanently its fluorescence characteristics. Control experiments show that neither irradiation nor the field alone can degrade the polymer.

Introduction

It is widely recognized that device longevity is a major obstacle for the commercial implementation of light-emitting diodes based on emissive polymers.[1] Understanding the failure mechanisms, at the molecular level, in polymers under operating conditions provides important clues for the optimization of chemical structure, and several studies have addressed this issue.[2] In poly(p-phenylenevinylene) (PPV), defects such as hydroxyl and ketone functionalities form during the thermolytic conversion of the poly(sulfonium) precursor.[3] These functionalities decrease conjugation length and, more importantly, provide effective exciton quenching sites. Conversion under a nitrogen atmosphere containing 15% hydrogen as reducing agent diminishes the extent of backbone oxidation and increases photoluminescence (PL) and electroluminescence (EL) quantum yields. PPV prepared under reducing conditions has a PL lifetime over four times that of PPV prepared under nitrogen alone.[4] Irradiation of PPV derivatives in air also leads to the formation of carbonyl functionalities,[5] but the rate of photo-oxidation can be reduced by addition of C_{60}.[6] It appears, from independent mechanistic studies, that singlet oxygen is the chemical species responsible for the photoinduced degradation.[7]

While oxidation of polymer represents one source of instability, other problems exist. The polymer−electrode interface is unstable when highly reactive metals, such as Ca or Mg, are used. Non-emissive "dark-spot" areas appear which decrease the emitting area and increase the overall impedance of the device.[8] Incorporating an electron transport layer between the cathode and the emissive polymer layer reduces the barrier for electron injection, thus lowering operating voltages and improving device lifetime.[9] Oxygen is also known to migrate out of the transparent ITO anode, leading to polymer oxidation.[10]

Electric fields reduce the PL quantum yield of insulated PPV films.[11] Furthermore, the percentage of PL quenching (20−40% at $E_{appl} = 200$ V/μm) appears to depend on PPV preparation, orientation of chains relative to the direction of the field and film thickness.[12] Kersting and co-workers have shown that for poly(phenylphenylenevinylene) (PPPV) blended with polycarbonate the PL quenching evolves on a picosecond time scale. This time dependence suggests a field-induced exciton dissociation into electron-hole (e-h) pairs.[13] The probability of recombination is lower for e-h pairs than for excitons, consequently PL intensity decreases. Since electric fields are necessary for LED operation, this field-induced exciton breakup may constitute a limitation for electroluminescence performance.

Polymerization of paracyclophene monomers provides excellent samples of PPV.[14] The living polymerization method provides control of the average degree of polymerization, and the chains have a narrow molecular weight distribution. Soluble block-copolymers can be synthesized which allow the study of typically intractable PPV segments with standard solution techniques. Furthermore, the final conversion step to conjugated

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Photodegradation of Spatially Confined PPV

J. Am. Chem. Soc., Vol. 119, No. 23, 1997 5345

material can be accomplished in solution under mild conditions. Block copolymers of this type provide excellent samples to study the effect of chain length and interchain contacts on the PL quantum yield and lifetime.[15]

PPV   polyNBE

PPV$_x$-*block*-polyNBE$_y$
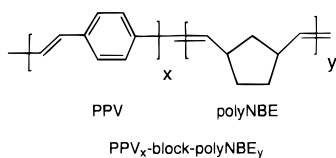
In this contribution we report the effect of electric fields on the PL and stability of PPV$_x$-*block*-polyNBE$_y$ materials. We show that the PL of short chain lengths is unperturbed under fields of 200 V/μm. Longer PPV chains, with smaller HOMO-LUMO gaps, have their PL quenched and, more importantly, degrade irreversibly when exposed to light under this field. Neither irradiation nor the electric field can independently promote the decomposition process.

Experimental Section

The syntheses of PPV$_3$-*block*-polyNBE$_{200}$ and PPV$_{20}$-*block*-poly-NBE$_{200}$ are available in the literature.[12] Samples for spectroscopic measurements were prepared by spin casting a toluene solution of 95% (by weight) PPV copolymer and 5% polystyrene (MW = 280 000) onto a 50 mm by 50 mm quartz plate. The polystyrene component is necessary to increase the viscosity of the solution and to obtain good quality films. Two layers were deposited upon the quartz plate before casting the PPV copolymers. An ITO layer was first deposited to serve as the electrode, followed by a 150 nm layer of SiO$_x$ as the charge blocking layer. On top of the PPV copolymer an 850 nm film of Pliolite OMS (a vinyltoluene−acrylate terpolymer available from Goodyear) in Isopar-G was cast to serve as the second charge insulating layer. After the sample cell was dried for 24 h under vacuum, the aluminum electrode was vacuum deposited over the Pliolite layer. In this geometry the PPV chromophores are sandwiched between layers of SiO$_x$ and Pliolite to prevent charge injection from either electrode. Both Pliolite and SiO$_x$ are excellent insulators with dielectric strengths in excess of 200 V/μm.[16] The resistance of the cell, as measured by a voltage divider using the cell and a high input impedence voltage follower, was larger than 1000 MΩ. We are thus confident that no external current flows into the cell from the electrodes during the course of the experiment. The capacitance of the assembly was found to be 710 pF, which corresponds to a distance between the two electrodes of approximately 1.5 μm. Since PPV is sensitive to oxygen, sample preparation and data collection were carried out under an atmosphere of dry nitrogen. No sample breakdown was observed at the highest field of 200 V/μm.

The second harmonic of a cw-mode locked Nd:YLF laser was used to synchronously pump a dye laser operating with pyridine 2. The dye laser output was then mixed with the fundamental frequency of the Nd:YLF laser to produce either 420- or 350-nm excitation. Films of PPV$_{20}$-*block*-polyNBE$_{200}$ were excited at 420 nm and the fluorescence collected at 550 nm, while the films of PPV$_3$-*block*-polyNBE$_{200}$ were excited at 350 nm and the fluorescence collected at 455 nm. For sample bias a home built pulsed power supply was used to apply zero field and bipolar highest field to the sample at a repetition frequency of 33 kHz. Fluorescence was detected by a SPEX 1681 monochromator equipped with a Hamamatsu 3809U microchannel plate photomultiplier tube (PMT). At a frequency of 1.9 MHz, the total intensity of light was measured at 7 μW with a Newport digital power meter (Model 815 series). Taking into account the reduction in repetition rate (33 kHz) and the laser beam area of 10 mm^2 (diverged using a cylindrical lens), the incident light intensity on the sample is calculated to be 1.2 μwatt/cm^2. The optical density of the PPV films was independently measured at 0.1 at ~420 nm. However, since the aluminum electrode acts as a mirror, the effective optical density of the cell at this

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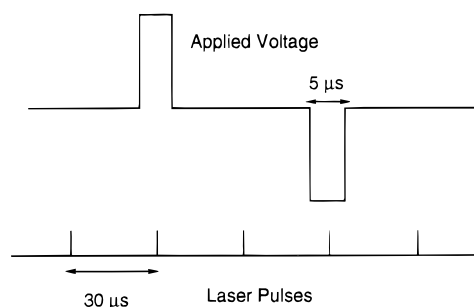

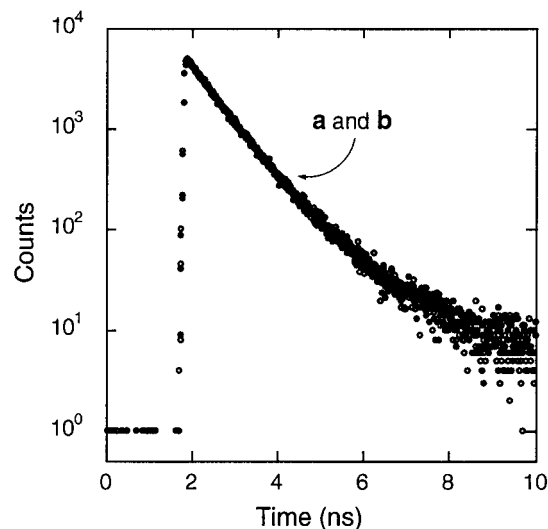**Figure 1.** Timing diagram for the applied voltage and the laser pulsed illumination.

Figure 2. Fluorescence lifetime measurements ($\lambda_{excitation}$ = 350 nm) of PPV$_3$-*block*-polyNBE$_{200}$ at (a) zero field (open circles) and (b) 200 V/μm (solid circles). The two traces are virtually indistinguishable.

wavelength during the course of the experiment is expected to be closer to 0.2. In effect, approximately 35% of the incident light is absorbed by the PPV component. Photon counts from the PMT were processed by an EG&G ORTEC TAC system and accumulated by a PC equipped with a multichannel analyzer board and an Edinburgh Instruments software package to control the measurements. Data were taken with a resolution of 16 ps per channel.

The time dependence of the sample bias and the timing of laser excitation pulses for time-resolved measurements are shown in Figure 1. Three different decay curves were collected for every applied field corresponding to positive, negative, and zero sample bias. The zero-field data at each applied field monitor changes induced in the sample. Positive and negative bias curves are identical, and were therefore averaged to a single curve before data analysis. The pulse generator supplying a bipolar square wave of up to 2500 V in amplitude was custom built, using two high voltage FET switches in a "differential" configuration.
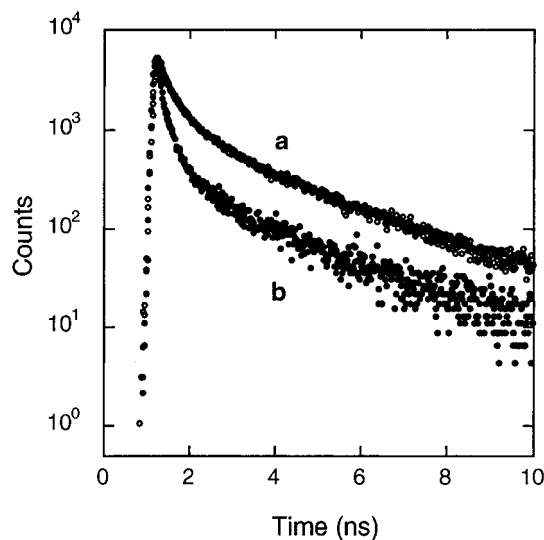
Results

It is evident from Figure 2 that the PL decay dynamics of PPV$_3$-*block*-polyNBE$_{200}$ (the subscripts refer to the average degree of polymerization) at zero field and at 200 V/μm are identical. The data collected were fitted by a double exponential function, and the results are shown in Table 1. There is also no effect of field on the PL of PPV$_3$-*block*-polyNBE$_{25}$ (see also Table 1), even after prolonged irradiation (6 h). These observations imply that for short oligomers this voltage is insufficient to split photogenerated excitons into e-h pairs.

Different behavior is observed with PPV$_{20}$-*block*-polyNBE$_{200}$. Figure 3a shows the PL decay measured for a pristine sample at zero field. Subjecting the sample to a progressive increase of applied field reveals that there is no change on PL dynamics

Table 1. Double Exponential Fits to the Fluorescence Decay after Deconvolution from the Instrument Impulse Response[a]

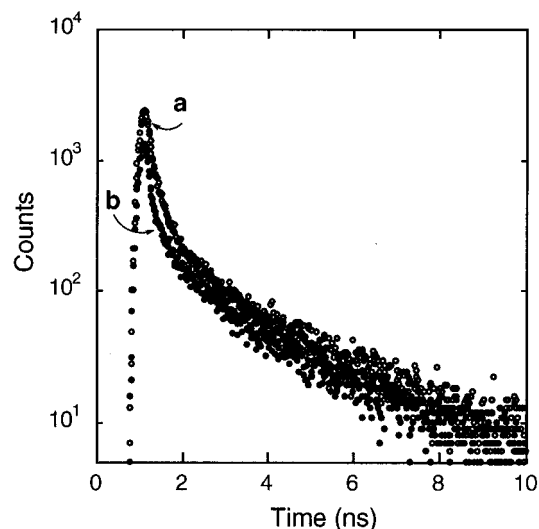| sample	E (V/μm)	τ_1 (ns)	B_1	τ_2 (ns)	B_2	$\Phi(E)$
PPV$_3$-polyNBE$_{200}$ (Figure 2a)	0	0.65	0.40	1.3	0.069	
PPV$_3$-polyNBE$_{200}$ (Figure 2b)	200	0.66	0.40	1.4	0.054	0.02
PPV$_3$-polyNBE$_{25}$	0	0.77	0.23	2.7	0.032	
PPV$_3$-polyNBE$_{25}$	200	0.77	0.23	2.6	0.033	0.003
PPV$_{20}$-polyNBE$_{200}$ (Figure 3a)[a]	0	0.32	0.14	2.3	0.029	
PPV$_{20}$-polyNBE$_{200}$ (Figure 3b)[b]	0	0.14	0.10	1.9	0.005	
PPV$_{20}$-polyNBE$_{200}$ (Figure 4a)[c]	0	0.18	0.10	2.1	0.007	
PPV$_{20}$-polyNBE$_{200}$ (Figure 4b)[d]	200	0.15	0.06	2.0	0.005	0.39

[a] The time dependence of the fluorescence intensity [$I_f(t)$] was modeled by using the following equation: $I_f(t) = B_1 e^{-(t/\tau_1)} + B_2 e^{-(t/\tau_2)}$, where τ_1 and τ_2 denote lifetimes and B_1 and B_2 are the amplitude coefficients. On the basis of three measurements, the relative error in the values of τ and B was approximately 5%. Pristine sample at zero field. [b] Zero field decay after sample was subjected to the simultaneous action of light and 200 V/μm. [c] Zero field decay during the 200 V/μm measurement. [d] PL decay at 200 V/μm.

Figure 3. Fluorescence lifetime measurements ($\lambda_{\text{excitation}} = 420$ nm) of (a) a pristine sample of PPV$_{20}$-*block*-polyNBE$_{200}$ at zero field (open circles) and (b) at zero field after the sample was irradiated with 420-nm light under a 200-V/μm field for 6 h (solid circles).

Figure 4. Fluorescence lifetime measurements ($\lambda_{\text{excitation}} = 420$ nm) of PPV$_{20}$-*block*-polyNBE$_{200}$ (a) at zero field (open circles) and (b) 200 V/μm (solid circles). Both decay traces were obtained during the course of the same experiment.

to note that no degradation is observed after irradiation with the same laser source even after 4 h. Similarly, there is no change when the sample is subjected to 200 V/μm for 4 h in the absence of light. Degradation therefore comes as a result of both external perturbations acting at the same time.

Discussion and Conclusion

In the case of PPV$_3$-*block*-polyNBE$_{200}$ and PPV$_3$-*block*-polyNBE$_{25}$ the electric field accessible for these studies is insufficient to affect photogenerated excitons. Neither intrachain nor interchain charge generation take place. The decomposition of PPV$_{20}$-*block*-polyNBE$_{200}$ by the simultaneous action of light and an electric field is unprecedented. The difference between Figure 4a and Figure 4b indicates that a field of 200 V/μm breaks up photogenerated excitons on PPV$_{20}$ segments, resulting in shorter PL lifetimes.

The exact mechanism of degradation induced by the simultaneous action of light and an electric field remains unclear. Unfortunately, because the polymer is sandwiched between two thick insulating layers it is not possible to probe the degradation products. Our current thinking is that exciton dissociation leads to the formation of charged radicals, which either alone or after interacting with another exciton or radical may result in cross-linking or bond scission reactions. Alternatively, charged radicals may react with the polyNBE companion block. One likely process is hydrogen abstraction from the doubly allylic site of the five-membered ring in the polymer repeat unit.

Regardless of the exact mechanism, the degradation of optoelectronic polymers, which requires the simultaneous action of light and an electric field, has not, to the best of our knowledge, been observed before. One possible reason is that the fields used in our experiments are higher than those typically required to observe electroluminescence.[17] Under typical LED configurations a field of 200 V/μm would probably lead to defects at the electrode−PPV interface.

It is also interesting to note that sample degradation was not observed in PPV homopolymers during electric field induced fluorescence quenching measurements.[18] It is expected that

at 33, 66, and 110 V/μm. However, PL quenching is observed at 133 V/μm. In Figure 4 the PL decay at 200 V/μm is compared against the decay at a zero field measured during the course of the same experiment. Most obvious (see Table 1) is the 39% decrease in integrated electric field induced fluorescence quenching, which is defined as $\Phi(E) = (I_f(0) - I_f(E))/I_f(0)$ (where $I_f(E)$ corresponds to the fluorescence intensity at field E). In addition, the fast component parameters decrease from $\tau_1(0) = 0.18$ ns with an amplitude coefficient of $B_1(0) = 0.10$ at zero field to $\tau_1(E) = 0.15$ ns and $B_1(E) = 0.06$ at $E = 200$ V/μm. The contribution from the longer lifetime amplitude coefficient remains virtually unaffected.

Comparison of Figure 3a against Figure 4a indicates that the zero-field PL decays more quickly after the sample has been subjected to high electric fields. This change in sample properties is permanent. The zero-field PL decay of the sample after irradiation with 420 nm light at 200 V/μm for 6 h is shown in Figure 3b. These changes in PL dynamics result in a faster initial decay rate (see Table 1). Therefore, the experimental conditions irreversibly change the sample properties.

We noticed that the PL intensity (based on the initial counts per second) decreased quickly upon application of the electric field, and reduced to close to 50% after only a few minutes. The degradation rate slows down at longer times. It is important

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more interfaces are present within a sample of PPV chains, or clusters of PPV chains, dispersed in a host medium relative to pure PPV. These confined environments are likely to be more representative of the block-copolymer films, and lead to more PPV interfaces and a higher density of trapped charges. These charges in turn are most likely responsible for the observed degradation. It is still not clear if the degradation process is intrinsic to the PPV segments or if the polyNBE (or even perhaps polystyrene) environment participates in the degradation. The possibility of phase separation between PPV- and polyNBE-rich regions further complicates the problem. Phase separation of block-copolymers containing conjugated and amorphous segments is well-known.[19] The possibility of

cooperativity between PPV chains cannot be ruled out at this stage. Experiments designed to differentiate between these possibilities are currently underway.

JA964082W

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