Dependence of poly(p-phenylene vinylene) morphology and time-resolved photophysics on precursor solvent

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Abstract

The effects of precursor solvent on the optical properties and morphology of poly(p-phenylene vinylene) (PPV) films are investigated using X-ray diffraction, steady state absorption and fluorescence, and picosecond time-resolved spectroscopy. Precursor films spin cast from water yield PPV films with higher average crystallite size and conjugation than films cast from methanol. These changes affect not only the steady state absorption but also the femtosecond stimulated-emission spectra, which are narrower and red-shifted in water cast films. This indicates that PPV’s short time spectral behavior is sensitive to the details of sample preparation. Fluorescence decay measurements from 100 ps to nanoseconds at temperatures ranging from 16 to 290 K are the same for both samples, however, indicating that the longer time exciton dynamics remain unaffected.

Keywords: Poly(p-phenylene vinylene); Morphology; Time-resolved photophysics

1. Introduction

Conjugated polymers are of interest for organic light emitting displays, and a great deal of effort has been devoted to improving their performance through chemical means [1]. The role of sample preparation and morphology has also been investigated, notably in the case of poly[(2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene)vinylene] (MEH-PPV) and how solvent affects its aggregation [2,3]. The unsubstituted polymer poly(p-phenylene vinylene) (PPV) has also been studied, mainly in the context of how its properties are affected by thermal conversion conditions [4,5] and the choice of precursor leaving group [6-9]. In this work we study the effects of precursor solvent on the optical properties and morphology of PPV. In contrast to MEH-PPV, PPV is a polycrystalline material, and precursor films spun using water as a solvent (referred to as H2O PPV) have an average crystallite size twice that of films spun using methanol as the solvent (MeOH PPV). Using this ability to vary the morphology, we can see how the optical properties of the material depend on the details of sample preparation. H2O PPV possesses a red-shifted, better-resolved absorption spectrum, suggesting greater average conjugation. Femtosecond pump-probe dynamics at a single wavelength can be very different between samples, due to the greater spectral broadening in the MeOH PPV. Measurements on longer timescales, however, show similar dynamics for both samples, suggesting that exciton diffusion and the final emitting state remain unaffected.

2. Experimental

The PPV samples were prepared from a precursor polymer with a tetrahydrothiophenium leaving group [6,9]. Equal amounts aqueous (p-xylenebis (tetrahydrothiophenium chloride)) solution and NaOH solution were reacted under an argon atmosphere with stirring at 0 °C. The reaction was stopped after 2 min and 30 s by adding HCl until the pH of the polymer solution was between 2 and 3. The solution was transferred to regenerated cellulose dialysis tubing (Fisher, 3500 MWCO) and dialyzed against water for 48 h changing the water every 12 h. For H2O PPV, the precursor solution was used right out of the tubing without further processing and stored in a sealed container in a refrigerator. For MeOH PPV, the water was removed from the precursor solution through dialysis for another 48 h against isopropanol, changing the solvent every 24 h [10]. After 48 h of dialysis in isopropanol the pale yellow solid was dissolved with a minimum of methanol, put in a sealed container and stored inside a freezer until use. The major
difference between the two preparations is the water removal and partial conversion that occurs before the MeOH PPV sample is redissolved in methanol. Precursor samples were spin cast on 12.5 mm diameter, 0.5 mm thick sapphire substrates at 600 rpm. The spun precursor films were converted under vacuum (<30 mTorr) at 300 °C for 3 h in a tube furnace. The converted films were transferred to a cryostat under an argon atmosphere and stored under vacuum in the cryostat. The converted films used for experiments were approximately 50 nm thick with a peak optical density of about 0.5. Infrared spectra of both samples showed no measurable absorption due to carbonyl defects [4].

For X-ray measurements, H$_2$O PPV and MeOH PPV thin films were removed from their substrates using a HF acid bath and thoroughly rinsed to remove residual salt. X-ray diffraction spectra of the unoriented samples were measured over a 2θ range of 0 to 60° using a Bruker AXS Rotating Anode Monochromator as the source of Cu Kα radiation for a Bruker AXS P4 Single Crystal X-ray Diffractometer with a Bruker AXS HI-STAR area detector. The crystallite sizes were calculated from the X-ray diffraction profile using the Scherrer equation (Eq. (1)) [11].

$$D_{hkl} = \frac{K\lambda}{\beta_{1/2}\cos \theta}$$  (1)

Using this equation, the true peak widths of the sample ($\beta_{1/2}$), the wavelength of the X-ray radiation ($\lambda$), the detection angle ($\theta$) and a shape parameter ($K = 1.0$) are all used to find the average dimension of the crystallites along the axis normal to the plane. To get the true peak widths of the sample, the instrument broadening had to be measured and then deconvoluted from the measured peaks. A lanthanum hexaboride standard (NIST SRM 660a) was used to measure the instrument broadening.

Picosecond time-resolved fluorescence measurements were taken using a streak camera (Hamamatsu, streak scope C4334). The samples were held under vacuum in the cold head of a helium cryostat where the temperature was varied from 16 to 290 K. Samples were excited at 400 nm with the beam coming in at an angle of about 20° from the sample surface normal. The polarization of the excitation beam was rotated to the magic angle (54.7°) to eliminate any rotational diffusion effects. The full-width at half maximum for the instrument response for the 5 ns sweep window used in these experiments was 50–70 ps. Excitation powers were less than 1 μW with a focal spot of about 50 μm in diameter, resulting in a maximum excitation density of $2 \times 10^{17}$ cm$^{-3}$. This is below the threshold for amplified spontaneous emission or exciton–exciton annihilation [12,13].

To measure the femtosecond emission dynamics, wavelength resolved pump-probe experiments were carried out using the amplified Ti:sapphire femtosecond laser system used for the streak camera experiments to produce 400 nm pump pulses and white-light continuum probe pulses. The temporal resolution was 150 fs. The excitation density was $\sim 10^{18}$ cm$^{-3}$, which is just below the threshold for nonlinear effects in the spectral response [2,14]. The pump and probe beams were focused collinearly into the sample with 40 and 20 μm spot sizes, respectively. After the sample the probe pulses were spectrally filtered in 5 nm windows and detected with a silicon photodiode connected to a lock-in. The differential transmittance, $\Delta T/T$, was $\sim 10^{-5}$ at the signal peak.

3. Results

The normalized X-ray data shown in Fig. 1 have the same placement for the (1 1 0), (2 0 0), and (2 1 0) peaks in the diffraction profiles for H$_2$O PPV and MeOH PPV, indicating the same unit cell dimensions for both samples. Our peak positions agree with literature values from other groups [7,15–18] but lack some of the structure seen in other PPV diffraction patterns [7,18]. The reason for this lack of structure may be the lower order present in the very thin spin cast films [19] as opposed to the thicker (by at least a factor of 10) drop cast films studied by previous workers. The (2 1 0) peak is well resolved in both patterns and shows the difference in peakwidth most clearly, so it was chosen for crystallite size calculations [16]. After subtracting the broad background, the peak was fit with a Lorentzian and Eq. (1) was used to obtain average crystallite sizes of 10 nm for H$_2$O PPV and 4 nm for MeOH PPV. This factor of two difference was consistent from sample to sample, although the absolute sizes varied by about 20%. These crystallite sizes are consistent with direct measurements using transmission electron microscopy [17] and other X-ray studies [16,20,21].

Fig. 2 shows the absorption and emission spectra for both H$_2$O PPV and MeOH PPV. The absorption spectrum of the H$_2$O PPV film is red-shifted and has sharper vibronic features than the absorption spectrum of the MeOH PPV film.

![Fig. 1. X-ray diffraction profiles for (a) H$_2$O PPV and (b) MeOH PPV. The locations of the (1 1 0), (2 0 0) and (2 1 0) peaks are the same for both samples. The signal levels for both samples were the same and only the air scatter and NaCl background have been subtracted from the data. The sharper (2 1 0) feature of the H$_2$O PPV indicates it has a larger average crystal dimension.](image-url)
Little difference, however, is seen in the fluorescence spectra of both films. The vibronic structure is due to the C–C double bond vibrations of the polymer backbone in the energy range of 1300–1500 cm\(^{-1}\) [22,23].

Similar structure is observed in the transient spectroscopy of the PPV samples. Fig. 3a shows the normalized pump-probe dynamics of H\(_2\)O PPV and MeOH PPV from 0 to 95 ps at 20 K. The spectral detection window for the data is centered at 550 nm, where the spectroscopy is dominated by stimulated-emission. The two traces are dramatically different, which is surprising given the similarity of the two samples in static measurements. The origin of this difference is clarified in Fig. 3b shows the emission spectra at 500 fs after excitation for the two samples. Both spectra exhibit the 0–1 fluorescence vibronic peak which is shifting to lower energy during the first 10 ps [14,24,25]. As this peak shifts, the signal at 550 nm declines, and in the case of H\(_2\)O PPV later recovers as the wing of the 0–0 peak shifts into the 550 nm window. This leads to the dip and recovery of the H\(_2\)O PPV signal in Fig. 3a. The MeOH PPV peak is approximately 50% broader than that of H\(_2\)O PPV, leading to greater overlap of the 0–0 and 0–1 peaks. This blurring together of the spectral features results in a less pronounced shifting effect in the 550 nm window. At higher temperatures, the difference between the two samples is less dramatic due to increased spectral broadening in both samples.

At longer times (>100 ps), the emission spectra of the two samples become similar, as measured using a picosecond streak camera [26]. We have examined the decay rate of the overall excited state population to see if non-radiative rates are affected by sample preparation. The inset to Fig. 4 shows the room temperature fluorescence decay of H\(_2\)O PPV as an example of a typical decay and fit. The dashed line represents an exponential fit that is used to describe the exciton dynamics during the first nanosecond of the decay. The long-time decay is nonexponential due to carrier recombination [27], and no attempt was made to fit it. We assume that the first nanosecond of the decay is dominated by exciton diffusion to quenching defects in the film [27–29] and can be described using a simple diffusion-reaction...
model [30] which adds a second rate constant to the decay. The radiative decay time of PPV is held constant at 1.2 ns [27,31] and the non-radiative rate \( k_{nr} \) due to quenching is allowed to vary in the fits (Eq. (2)).

\[
y = A \exp \left[ -\left( k_t + k_{nr} \right) t \right]
\]  

(2)

Fig. 4 shows an Arrhenius plot of the variation of \( k_{nr} \) with temperature. The absolute rates are very similar, and the slopes of linear fits to the data yield activation energies of 180 cm\(^{-1}\) for H\(_2\)O PPV and 200 cm\(^{-1}\) for MeOH PPV. These values are identical to within the experimental uncertainty of 30 cm\(^{-1}\).

4. Discussion

From the X-ray data, we can see that H\(_2\)O PPV has larger crystallites than MeOH PPV by roughly a factor of two. The origin of this difference is unclear, but may be the result of different conformations of the precursor polymer in water versus methanol. The precursor is a polyelectrolyte and if its Cl\(^-\) counter-ions are solvated by water molecules, the polymer will act as a chain of positive charges and extend. Coulomb repulsion has been shown to be a powerful force for increasing average conjugation in related phenylene vinylene polymers in solution [32]. In less polar methanol, the counter-ion will be more closely associated with the polymer chain, which cancels out some of the Coulomb repulsion and makes the chain more likely to fold back on itself. Previous workers have shown how variations in preparation conditions can result in more conjugated PPV [22,33], attributing this increased conjugation to greater chain ordering before final conversion to PPV. It is likely that this increased conjugation also leads to the formation of larger crystalline domains due to increased local order.

The increased conjugation that leads to increased crystallinity also leads to changes in the spectroscopic properties. Previous workers [22,33] have observed that increased conjugation leads to sharper, more red-shifted absorption spectra, but our work shows that these effects extend to the transient spectroscopy as well. Both the absorption and short time transient emission spectra are sharper and red-shifted in H\(_2\)O PPV as compared to MeOH PPV. The energy shift of the absorption spectrum is determined by the ground to excited state energy difference, which decreases as the exciton becomes delocalized over many repeat units [23,34]. The spectral broadening is influenced by the coupling of the electronic transition to molecular vibrational degrees of freedom. As this coupling becomes smaller, the Huang–Rhys parameter decreases and higher-lying vibronic transitions become less pronounced. Temperature-dependent measurements show that as conjugation increases the Huang–Rhys coupling decreases for both high and low frequency vibrations, leading to narrower absorption and fluorescence spectra [14,35]. Similar effects would be expected in the transient emission: more conjugation leads to weaker vibronic coupling and sharper spectra [36]. We note that an alternative explanation for the broadening of the absorption spectrum is that there is less inhomogeneous broadening in the H\(_2\)O PPV sample. This static effect would not explain the broadening observed in the transient spectroscopy, however, which is due to homogeneous effects like vibronic coupling. Over time, as the exciton relaxes and vibrational energy is randomized, the shape of emission spectrum is determined by coupling to the ground state. The fact that the long-time spectra for these two samples are so similar suggests that the ground state has similar vibrational structure in both. It would then appear that the excited state properties of PPV molecules are more strongly affected by changes in conjugation and ordering than the ground state.

One important consequence of the differences in spectral shape on the femtosecond to picosecond timescale is that caution must be used when comparing time-resolved data taken for separate samples. Although the two 550 nm traces shown in Fig. 3 look completely different, this difference is not due to profound differences in the dynamics, since both are red-shifting on similar timescales and have the same behavior at delays greater than 100 ps. Instead, the difference is due to the difference in peak-widths: a narrow peak shifting through a 5 nm spectral window causes a sharper temporal response in that window than does a broader peak. The fact that differences in sample preparation can lead to different widths in transient spectral features which are evolving in time means that the time-dependent absorption or emission at a single wavelength can appear to be sample dependent, even though the overall spectral evolution is actually quite similar from sample to sample.

The narrowing and red-shift of the absorption and transient emission spectra are basically local effects, confined to a single molecule. The non-radiative decay of the fluorescence, on the other hand, is usually attributed to exciton migration to defects [28,29]. Other workers have estimated the diffusion length of the singlet exciton to be on the order of 10 nm [28,37], which is similar to the average size of the crystallites in the polymer films. It is possible that this motion can be interrupted by crystal boundaries, and if this were the case, we would expect to see differences in the activation energy for exciton diffusion, with the less crystalline sample having a higher activation energy. The data in Fig. 4 show that this is not the case, since both the absolute decay rates and the activation energies are the same to within the experimental error. Apparently, the quenching process in PPV is not strongly affected by the size of the crystalline domains in the polymer. One explanation for this is that the fluorescence is dominated by exciton dynamics in the amorphous regions of the polymer. A second possibility is that the excitons are not diffusing from crystallite to crystallite, but rather within a single crystallite. Of course, if the density of quenching defects is sufficiently high, so that even within a nanometer domain there is at least one defect, then we would not expect to see a strong effect due to morphology on
length-scales greater than a nanometer. From IR absorption we confirm that our samples have undetectable levels of CO defects, the most common type of quenching defect [28], but that does not rule out the presence of other defect types, perhaps at crystalline grain boundaries.

5. Conclusion

Different precursor solvents can result in PPV films with different degrees of conjugation and crystallinity, and also differences in spectral shape, both in steady state and time-resolved optical experiments. An example of how this affects the transient spectroscopy is shown in Fig. 3, where the decreased spectral broadening in H$_2$O PPV leads to very different transient behavior at 550 nm than in MeOH PPV, despite the fact that the overall dynamics are similar. Longer time fluorescence measurements at various temperatures yield identical results for both polymers, with the conclusion that such variations affect mainly the short time molecular photophysics, and not longer time phenomena like exciton diffusion to quenching defects.

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References