Investigation of the photochemistry of the poly{*p*-phenylenevinylene} precursor system: Implications for nanolithography

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(Received 29 January 2007; accepted 19 March 2007; published online 1 May 2007)

The photochemistry of poly{*p*-phenylene[1-(tetrahydrothiophen-1-yl)ethylene chloride]} (PPTEC), a water soluble precursor of the semiconducting polymer, poly{*p*-phenylenevinylene} (PPV), has been studied both under atmospheric conditions and in environments devoid of oxygen. UV-visible spectroscopy and photoluminescence data has been used to provide a picture of the mechanistic pathways involved in UV irradiation of the PPTEC material. A new quantitative model for the effect of UV irradiation upon film morphology is presented, which leads to insights for the improved control of the characteristics of PPV nanostructures produced via near-field scanning optical lithography. © 2007 American Institute of Physics. [DOI: 10.1063/1.2727477]

I. INTRODUCTION

Near-field scanning optical microscopy (NSOM) is an established technique for characterizing surfaces on the nanoscale and microscale, with the use of commercially built instruments now widespread. NSOM is capable of imaging with light at a lateral resolution below the classical diffraction limit by illuminating through a small aperture (50–500 nm) at very close proximity (~10 nm) to the sample surface.

More recently, the NSOM instrument has been used for UV based lithography of very basic patterns on the nanometer scale.^{1–3} In particular, Riehn *et al.* used a purpose-built near-field scanning optical lithography (NSOL) instrument to achieve photolithography of poly{*p*-phenylenevinylene} (PPV).² PPV and its derivatives are important organic electronic materials with applications in polymer electronic devices such as light-emitting diodes and solar cells.⁴ Depending on morphology, PPV can also have an extremely high refractive index, making it an ideal material for fabricating photonic band gap structures and novel optoelectronic devices.⁵

The NSOL patterning process is analogous to the use of a negative photoresist. The soluble PPV precursor material, poly{*p*-phenylene[1-(tetrahydrothiophen-1-yl)ethylene chloride]} (PPTEC), [Fig. 1(a)] is spin cast onto a substrate and defined areas are exposed to UV light through the NSOM tip. UV exposure reduces the methanol solubility of the film, so after a methanol rinse only the intended pattern remains. This material is then thermally converted to PPV [Fig. 1(b)] by heating under vacuum. The insolubilization of the precursor molecule under UV exposure is attributed to the cleaving of the sulphonium leaving group from the rest of the molecule.⁶ At present, what happens to the exposed cleaving site is not well known. However, PPV is known to

be rendered insoluble during thermolytical conversion when the ratio of PPV to PPTEC monomer units reaches approximately 4.⁷

An alternative reaction pathway to the formation of the vinylene group is the process of photo-oxidation whereby the presence of oxygen results in a carbonyl bond at the cleave site.⁸ Photo-oxidation is undesirable since it reduces the conjugation length of the PPV chain and introduces impurities into the polymer structure that can act as electron traps with concomitant deleterious effects on the optical and electronic properties.⁸

In this paper we present a systematic study of the insolubilization of PPTEC. By investigating the effect of different gaseous environments upon the insolubilization process we have been able to probe the different degradative mechanisms that occur during insolubilization. We have developed a new quantitative model for the chemical mechanism of insolubilization and show that this model leads to an excel-

FIG. 1. Chemical structure of (a) the soluble precursor poly{*p*-phenylene[1-(tetrahydrothiophen-1-yl)ethylene chloride]} (PPTEC) and (b) poly(*p*-phenylene vinylene) (PPV).

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lent fit to the experimental data. Moreover, this model allows us to identify and explain the optimum UV energy dose that is found when insolubilization is carried out in air.

II. EXPERIMENT

PPV films were prepared via a variation of the Wessling method.⁹ The method used for the PPTEC synthesis is a modification of that presented by Burn *et al.*¹⁰ A constantly stirred solution of *p*-phenylenedimethylene-1,1'-bis(dimethylsulfonium) dichloride (5.0 g in 38 mL of methanol) was chilled to -5°C and nitrogen gas was bubbled through it for 1 h. Afterward in a nitrogen atmosphere 36 mL of 0.4M NaOH was added dropwise over a 20 min period. The reaction mixture was then stirred for a further hour under nitrogen before being neutralized with 0.4M HCl. The solution was then dialyzed against methanol over three days, before being condensed/diluted (with methanol) as necessary to obtain a solution capable of being spin cast to the desired thickness. The PPTEC solution thus obtained was stored in darkness at temperatures just below 0°C .

Films of the methanol-soluble PPTEC of the desired thickness (~ 50 – 100 nm) were prepared by spin casting onto 1 cm^2 sized quartz substrates. The spin speed, in the range of 1000–3000 rpm, was adjusted as necessary.

These films were irradiated with a continuous wave Melles-Griot HeCd (325 nm) laser, with the beam spread to provide a consistent dose of radiation (at a power density of approximately $1\text{ mW}/\text{cm}^2$) across the sample surface. The photoluminescence of the PPTEC film was monitored during this phase with an Ocean Optics USB2000 spectrometer at an angle perpendicular to the incident laser beam to reduce the effect of specular scattering. Samples corresponding to increasing irradiation doses (varying time exposure) were then rinsed in methanol for 20 s before being dried with nitrogen gas and thermolytically converted to PPV by baking in a vacuum better than 1 mbar at 220°C for 5 h. The thickness of the spin coated PPTEC and PPV films were measured using a Tencor Alpha-Step 500 stylus profilometer. UV-visible spectra of the final PPV films were obtained using a Cary 1E UV-visible spectrometer.

UV-visible spectra were also taken of similarly prepared samples, as well as some spun cast much thinner (~ 10 nm), irradiated with a Laser Photonics LN-300 nitrogen laser source, providing $0.367\text{ mW}/\text{cm}^2$ at 337 nm. The nitrogen laser is a pulsed laser, delivering very short (approximately 4 ns) pulses at a 20 Hz repetition rate, with peak power around 30 kW. Although the average power of the two lasers is very similar, the peak power is higher than the CW output of the HeCd laser by a factor of 10^7 .

Photoluminescence of similarly prepared samples irradiated with the HeCd laser in a nitrogen atmosphere was also monitored. The nitrogen atmosphere was maintained in a Pyramid Engineering GB5W/710/1524 glove box hooked up to a Vacuum Atmospheric Company Omni Purifier nitrogen recirculator. UV-visible spectra were taken of both samples produced (postprocessing) via irradiating in the nitrogen atmosphere and of similarly prepared samples irradiated in a

FIG. 2. UV-vis absorbance spectrum of a PPTEC film of thickness 120 nm spun out of methanol. The inset shows a magnified view of the absorbance spectrum in the wavelength range of 250–400 nm.

vacuum of 1×10^{-6} Torr. The laser light was piped into both the glove box and vacuum chamber through a modified swage lock via Cream-Optec UV50 optical fibre (50 μm core).

III. RESULTS AND DISCUSSION

The UV-visible (vis) absorbance spectrum of poly[*p*-phenylene[1-(tetrahydrothiophen-1-yl)ethylene chloride]] shown in Fig. 2 shows that significant UV absorbance only occurs at wavelengths shorter than about 360 nm. However, below this threshold wavelength, the absorbance is relatively broad suggesting that a range of UV wavelengths may promote scission of the leaving group. Indeed, a variety of UV sources have been used in the literature to cleave the leaving group, including a HeCd (325 nm) laser,² a XeCl-excimer (308 nm) laser, a high pressure mercury lamp (HBO lamp with KG4 filter), and a mercury spectral line lamp.¹¹ In addition, it has been shown that the insolubilization process is also possible by employing light in the absorption range of the pure PPTEC molecule (<260 nm), as well as in the absorption range of the stilbene units (280 to 360 nm).¹¹ As such, the emission from both the continuous HeCd (325 nm) laser source and the pulsed nitrogen (337 nm) laser source used in these studies lies well within the active absorption region of the PPTEC molecule.

Figure 3 shows the change in the final postannealed PPV film thickness resulting from in-air irradiation by UV light at 325 nm as a function of energy dose. It should be noted that no thickness reduction was noted as a result of irradiation only; only after the methanol rinse was a change in thickness observed. There are a number of observations that can be made from Fig. 3. First, given that the original PPTEC film thickness was 60 nm there is a significant thickness reduction in the postannealed PPV films following methanol rinsing and thermal conversion. Indeed, the thickest films that are measured are only around 33% of the original PPTEC film thickness. Second, a distinct maximum in the thickness variation as a function of energy dose is observed and occurs for a dose corresponding to $54\text{ mJ}/\text{cm}^2$. Finally, there is evidence for the existence of a threshold dose in that there is no measurable thickness of insolubilized film until the incident energy dose is greater than some threshold level, which from Fig. 3 appears to be about $50\text{ mJ}/\text{cm}^2$. Other authors have

FIG. 3. Variation of PPV film thickness as a function of energy dose for in air irradiation by the HeCd laser. The secondary right hand axis shows the variation of the PPV film thickness expressed as a fraction of the original PPTEC film thickness of 60 nm. Errors are based on the variation in the thickness measured across an individual scan.

also reported the existence of a minimum UV energy dose that is required before the precursor is insolubilized. Schmid *et al.* report a value of $<0.1 \text{ J/cm}^2$ for a 200 nm thick precursor irradiated using a xenon lamp,¹¹ while Riehn using a HeCd laser reports at most $\sim 0.02 \text{ J/cm}^2$ for 40 nm thick films.¹²

Figure 4 shows the UV-vis spectra for the postprocessed PPV films after exposure to the HeCd source for three different exposure doses. As expected, the UV-vis absorbance is maximized for the PPV sample exposed to the 54 mJ/cm^2 dose, in agreement with the thickness data shown in Fig. 3. Despite the fact that there is a significant variation in thickness as a function of energy dose of the final films, Fig. 4 shows that the characteristic absorbance peak of PPV, centered at 420 nm, is present in all of the processed PPTEC films over the energy dose range. Moreover, the consistency in the shapes of the spectra shown in Fig. 4 indicates that the same PPV material is produced for energy doses up to around 500 mJ/cm^2 . The inset to Fig. 4 shows that for en-

FIG. 4. UV-vis absorbance spectra for processed PPV films exposed to irradiation from a HeCd laser source at energy doses of 36, 54, and 434 mJ/cm^2 . The inset shows a comparison between the UV-vis absorbance spectra for processed PPV films exposed to irradiation from a HeCd laser source at a moderate energy dose of 54 and a high energy dose of 2352 mJ/cm^2 .

FIG. 5. Variation of peak absorbance at 420 nm with PPV postannealed film thickness. The inset shows the variation of integrated absorbance between 280 and 500 nm with PPV postannealed film thickness.

ergy doses above 2000 mJ/cm^2 , however, the characteristic PPV UV-vis spectrum is shifted to lower wavelengths indicating a reduced conjugation length.¹³

Further evidence that the chemical nature of the final processed PPV film is not significantly altered by the energy dose applied is provided by a quantitative spectroscopic analysis of the absorbance variation with energy dose. From Beer's law the absorbance of any material at a particular wavelength is proportional to the number of absorbing species,¹⁴

$$A = \epsilon bc, \quad (1)$$

where A is the absorbance, b the path length of the examining beam in centimeters, c is the concentration in mol/L, and ϵ the molar absorptivity whose units are not expressed by convention.¹⁵ Figure 5 shows that there is a linear relationship between the peak UV-vis absorbance at 420 nm for the postannealed PPV films and film thickness thus indicating that the product of the molar extinction coefficient (molar absorptivity) and the molecular density of the PPV film does not depend on the level of UV exposure. For the photoconverted PPV films overall, $\epsilon \cdot c = 2.0 \times 10^5 \text{ cm}^{-1}$ at 420 nm and, given that it is unlikely that the parameters ϵ and c vary inversely to maintain a constant product, it seems reasonable to conclude that ϵ is independent of exposure and that the final processed film is PPV irrespective of the UV exposure received.

Although it is possible to calibrate the UV-vis peak absorbance in terms of film thickness, the errors in the measured peak absorbance, which arise primarily from sample positioning imprecision, instrumental electronic noise, and stray light, result in a measurement accuracy of 5%–10%.¹⁵ A more robust indicator of thickness therefore is the integrated absorbance under the entire peak centered at 420 nm. This method is particularly useful for determining the thickness of very thin films ($<20 \text{ nm}$) due to the relatively large uncertainty associated with the profilometer measurements of these film thicknesses. Indeed, Beer's law is most applicable for very thin films when specular scattering is a minimum.¹⁵ The inset of Fig. 5 shows that there is a clear

FIG. 6. Variation of integrated absorbance with applied energy dose for samples irradiated with (a) the HeCd laser and (b) the N_2 laser in air. The initial PPTEC layer thicknesses were 60 nm (filled circles), 70 nm (filled squares), and 10 nm (open squares). The area of the plotted data points represents the experimental uncertainty of the measurement. A broken line has been drawn to guide the eye for both plots.

linear relationship between the integrated absorbance, which is defined here as the area under the absorbance peak between 280 and 500 nm, and the thickness of the PPV film.

Figure 6(a) reveals that, for 60 nm PPTEC films exposed to varying UV energy doses with the HeCd laser, the integrated absorbance (which scales with film thickness only) rises to a maximum at an exposure of 54 ± 10 mJ/cm² and then decreases for higher exposures. The existence of an optimum in the dose dependence of thickness implies an optimum in the insolubilization of the precursor film and that, subsequently, some further effect is acting to make the precursor more soluble as the UV exposure is increased. Given that the molar absorptivity of the resulting PPV is unaffected, the resolubilization most likely occurs via a mechanism that renders the affected PPTEC molecule soluble again, after having first been made insoluble by removal of the leaving group.

In order to examine the role of irradiation intensity upon the insolubilization process, a corresponding experiment using a nitrogen laser, which has a peak power 107 times greater than the HeCd, was carried out. The results are presented in Fig. 6(b) for two PPTEC films of different thickness. Interestingly, the optimum exposure, which we estimate at 60 ± 14 mJ/cm², is the same for both the 10 and 70 nm thick films. Additionally, when scaled to account for the lower PPTEC absorbance at 337 nm (a factor of 1.36) this optimum exposure dose is consistent with the result for the HeCd laser to within the error margins, demonstrating that the UV insolubilization/resolubilization process is also insensitive to irradiation intensity.

Figure 6(b) also reveals that the variation of the integrated absorbance (and hence film thickness) with energy dose appears to be insensitive to the thickness of the original

FIG. 7. Photoluminescence (PL) spectra taken during irradiation of the PPTEC film with the HeCd laser in air. The corresponding value of the irradiation energy dose (in mJ/cm²) is labeled above each PL spectra. The positions of the peak structures at 440 (A), 500 (B), and 530 nm (C) are marked on the graph. The inset shows the variation of the integrated area under the PL curve with energy dose.

PPTEC film. The absolute absorbance of both the 10 and 70 nm thick PPTEC films are actually quite low (Fig. 2) and hence the surface side of the PPTEC film will absorb a UV energy dose approximately equal to the substrate side and uniformly throughout the film volume. Therefore the similarity between the two different thickness substrates when irradiated with the nitrogen laser is evidence that insolubilization and resolubilization reaction rates are dependent only on the energy dose absorbed per volume of PPTEC and that these processes are not diffusion limited.

Figure 7 shows the photoluminescence (PL) spectra for PPTEC films following HeCd laser exposure, for increasing irradiation energy doses. The PL spectra exhibit peak structures at 440, 500, and 530 nm that appear to change in relative intensity with increasing irradiation energy dose. The peaks at 500 and 530 nm, which are characteristic features of postannealed PPV films,¹⁶ increase to a maximum around 56 mJ/cm² and then subsequently decay in magnitude with increasing energy dose. The 440 nm feature, on the other hand, decays monotonically with increasing energy dose and has almost disappeared after a dose of 168 mJ/cm². As such, we speculate that the feature at 440 nm is associated with the unreacted PPTEC material, whereas the presence of the spectral features at 500 and 530 nm suggests that PPV is being formed directly by UV irradiation. Thus, the data in Fig. 7 show that, up to the optimum dose, increasing the UV irradiation dose increasingly converts the PPTEC film directly into PPV. However, for energy doses in excess of the optimum value, increasing the energy dose then leads to a subsequent decrease in the amount of PPTEC that is converted into PPV. Thus it appears that the reduction in film thickness

FIG. 8. Variation of integrated absorbance with applied energy dose for samples irradiated with the HeCd laser in nitrogen. A broken line has been drawn to guide the eye.

seen for high energy doses in Fig. 3 actually arises from a decreasing subsequent conversion of PPTEC into PPV.

Although removing the sulphonium leaving group reduces the solubility of the precursor, it also leaves the resulting material much more reactive since with the cleaving of the C–S bond a reactive intermediary is formed. This reactive species is likely to be vulnerable to attack by atmospheric oxygen, especially given that it is well known that PPV itself is susceptible to photodegradation when illuminated by UV light.¹⁷ In particular, the C=C bond can be converted to a C=O bond thus producing a ketone side chain or terminal aldehyde, which then quenches the photoluminescence.^{9,18} As a consequence, any photooxidized PPV structures are more likely to be resolubilized since the process of breaking of the polymer backbone and lowering the molecular weight increases solubility, as does the addition of side chains to PPV.¹⁹ Thus, it seems reasonable to hypothesize that once PPTEC has been converted to PPV, which is insoluble, it begins to undergo photo-oxidative decay, which provides a mechanistic pathway for resolubilizing the PPV film. The presence of these two competing mechanisms accounts for the photoluminescence maximum and also the reduced thickness (and hence integrated absorbance) of the postannealed PPV films since the more soluble photo-oxidized chains are simply rinsed away.

In order to test the hypothesis that photo-oxidation is associated with increased solubility, irradiation of the PPTEC film was carried out in a nitrogen environment. Figure 8 shows the integrated absorbance of processed PPV films irradiated with the HeCd laser in a nitrogen environment and there are two main observations that can be made. First, under these conditions the optimal dose is more than double than that of under normal atmospheric conditions. Second, the integrated absorbance (and thus PPV thickness) does not exhibit the same rapid decay with increasing energy dose observed for UV irradiation in air (Fig. 6). There is, however, a gradual reduction, which indicates that PPV is still be removed with increasing energy dose even under nitrogen conditions. Previous work by Bullock *et al.* has shown that working in an oxygen depleted environment is not sufficient for complete photoconversion of precursor to PPV, and that prior to irradiation the film must be heated to 120 °C in the dark before being irradiated, to prevent an as yet unidentified side

FIG. 9. Photoluminescence (PL) spectra taken during irradiation of the PPTEC film with the HeCd laser in nitrogen. The corresponding value of the irradiation energy dose (in mJ/cm²) is labeled above each PL spectra. The positions of the peak structures at 440 (A), 500 (B), and 530 nm (C) are marked on the graph. The inset shows the variation of the integrated area under the PL curve with energy dose.

reaction. Thus, we speculate that the observed gradual decay observed in Fig. 8 might be attributed to the same unknown side reaction observed by Bullock *et al.*²⁰

Figure 9 shows the corresponding PL spectra with increasing energy dose. The integrated PL signal versus energy dose (Fig. 9 inset) shows the same trend as that for the integrated absorbance. There is an increase in intensity with increased duration of irradiation of the precursor, and an apparent shift to longer wavelengths (as a result of a relative increase in intensity at 530 nm) indicating the formation of a material that fluoresces more intensely than the precursor and at longer wavelengths. The peak at 530 nm is more prominent here than for the experiment conducted in air shown in Fig. 7. Once again, we attribute this behavior to the formation of PPV directly by UV illumination, since the peak at 530 nm is characteristic of PPV.¹⁶

Interestingly the data presented here also offer a possible explanation for the increase in photoluminescence intensity of PPV with continual exposure at 442 nm under vacuum observed by Ghosh *et al.* for energy doses up to ~500 mJ/cm².²¹ The reported precursor curing temperature was lower than is most commonly reported in the literature (185 °C) and we speculate here that the observed behavior is due to the laser conversion of unconverted sections of precursor polymer. The proportion of such monomer units would be small, which provides an explanation for why the increase in photoluminescence observed here is greater than that reported by Ghosh *et al.*²¹

FIG. 10. Variation of integrated absorbance with applied energy dose for samples irradiated with the HeCd laser in a vacuum (1×10^{-6} Torr). A broken line has been drawn to guide the eye.

For high energy doses ($>500 \text{ mJ/cm}^2$) the photoluminescence is seen to be quenched and shifts back to the blue end of the spectrum; a change that Fig. 8 shows is accompanied by an increase in solubility. Given the previous discussion for samples exposed in air, it would appear therefore that even for PPTEC films irradiated under nitrogen conditions, there is still some photo-oxidation occurring. While we cannot unequivocally rule out oxidation by residual oxygen or water, given that the concentration of these species in the nitrogen glovebox is below 100 ppm it seems unlikely that these are the oxidizing species. Alternatively, the photodegradation that is observed under a nitrogen atmosphere could be a result of trapped methanol solvent, which could react with the newly formed PPV to yield a methoxy derivative.²⁰ The creation of a methoxy derivative would also tend to increase the solubility of the PPV material and would therefore result in a gradual reduction in PPV film thickness with dose in an atmosphere otherwise devoid of oxygen.

In order to test this hypothesis, the exposure experiments were repeated under high vacuum conditions ($<10^{-6}$ Torr) since this should eliminate any residual methanol solvent in the film since the solvent molecules will diffuse through the thin film and desorb from the surface.²² Figure 10 shows the variation in PPV film thickness with increasing energy dose in vacuum. In contrast with the results for films irradiated in the nitrogen atmosphere (Fig. 8) there is no reduction in integrated absorbance with increasing energy dose. In this instance the integrated absorbance for postprocessed PPV appears still to be increasing for doses approaching 1000 mJ/cm^2 , supporting the hypothesis that methanol solvent trapped in the film is the cause of the reduction in the integrated absorbance observed for films irradiated in a nitrogen atmosphere. Ordinarily thermal conversion to PPV is carried out in vacuum,^{2,6,7,20} where most solvent is driven off.²² Although Bullot *et al.* discounted the possibility of trapped solvent producing a methoxy species in photoconverted PPV, their experiments were performed under vacuum conditions rather than a nitrogen atmosphere.²⁰

Given the preceding discussion, it is now possible to hypothesize a mechanism for the origin of the blueshifted spectrum observed for the highly exposed PPV sample (Figure 4 inset). This spectrum (and that of Bullot *et al.*²⁰) is reminiscent of those for short chain phenylene vinylene oligomers presented by Nguyen *et al.*,¹³ indicating a reduced

FIG. 11. Schematic diagram of the photochemistry pathways for PPTEC. (A) Formation of a reactive intermediary. (B) Formation of a vinylene linkage. (C) Formation of a ketone or methoxy side group. (D) Formation of a cross-linked polymer network.

conjugation length. Given that the shortening of the conjugation length is not accompanied by an increased solubility of the PPV chains it seems unlikely this lower conjugation arises from the formation of $\text{C}=\text{O}$, methoxy, or other side chains since these processes would all tend to increase the solubility of the PPV chains. A more probable explanation is that the high UV doses lead to cross linking of the PPV chains, resulting in polymer structures with a reduced solubility and shorter conjugation length.

The chemical processes presented thus far are summarized in Fig. 11. Initially the precursor is soluble in methanol (remembering that solubility is an average property of the polymer chain⁹). UV irradiation leads to the sulphonium leaving group being removed, producing a reactive intermediary [marked as (A) in Fig. 11]. This reactive intermediary is unstable, which results in the formation of a vinylene bond [marked as (B) in Fig. 11] and the formation of a PPV backbone. However, in air there is also a competing reaction which results in the oxidation of the vinylene bond to produce a ketone side group or, if methanol is present, a methoxy side group may be formed [marked as (C) in Fig. 11]. The formation of a vinylene group will reduce the solubility of the polymer film whereas the addition of the polar functional side groups will tend to allow the polymer to resublimize in polar solvents such as methanol. Indeed photo-oxidation, in contrast to thermal oxidation, of PPV has been shown to induce scission of the vinylene group resulting in the formation of terminal aldehyde groups,¹⁸ a process which results in breaking the polymer backbone, a lower molecular weight, and therefore more soluble material. In principle, UV irradiation in air could also lead to the direct oxidation of the reactive intermediary [pathway (A) to (C) in Fig. 11]. However, given that polymer material is left following irradiation in air and subsequent rinsing in methanol this indicates that vinylene formation is favored over direct oxidation. Thus, even if the direct oxidation pathway does exist it would appear that the rate constant for pathway (A) to (B) is much greater than that for pathway (A) to (C) (i.e., $k_1 \gg k_2$). At very high UV energy doses, the PPV conjugated structure breaks down through cross linking, which does not increase the solubility but degrades the polymer's electronic and optical properties.

In order to test the mechanistic pathways presented in Fig. 11, a quantitative model for the insolubilization of PPTEC was developed. We consider the PPTEC film to consist of discrete precursor sites that are converted into in-

soluble PPV polymer upon receiving a certain UV energy dose. Thus, the number of converted precursor sites, N , will be proportional to the total dose received, D , and to the fraction of unconverted precursor sites remaining, $(1 - N/N_0)$, where N_0 is the total number of sites in the film such that

$$N = k \left(1 - \frac{N}{N_0} \right) D, \quad (2)$$

where k is a constant of proportionality. Rearranging this expression and introducing a new constant, a , such that $a = k/N_0$ then gives

$$N = \frac{kD}{(1 + kD/N_0)} = \frac{aN_0D}{(1 + aD)}. \quad (3)$$

From the preceding discussion, we have already noted that the energy dose is effectively uniform through the thickness of the PPTEC film and thus, for a constant cross-sectional area, the fraction of converted sites, N/N_0 , is equal to the fraction of converted film thickness, T/T_i , where T_i is the initial thickness of the precursor film and T is the insolubilized film thickness. Moreover, given the existence of a threshold dose, D_{th} , then the net effective dose becomes $(D - D_{th})$ and thus Eq. (3) can be rewritten as

$$D \leq D_{th}: \quad T = 0, \quad (4a)$$

$$D > D_{th}: \quad T = \frac{T_i a (D - D_{th})}{(1 + a(D - D_{th}))}. \quad (4b)$$

Assuming that the final thickness, T , of a film exposed to an infinite dose is equal to the initial thickness, T_i , and setting $D_{th} = 20 \text{ mJ/cm}^2$,¹² we have fitted the data for the nitrogen atmosphere and obtained $a = 0.08$. To take account of the more common situation of the process conducted in atmosphere we make use of our finding that insolubilized monomers may be oxidized upon application of further energy dose. We then impose the same conditions for resolubilizing by oxidation as were imposed for insolubilization and group any unaccounted for unknowns and proportionality constants together in a second constant b , such that

$$D \geq D_{th}: \quad T = 0, \quad (5a)$$

$$D > D_{th}: \quad T = \frac{T_i a (D - D_{th})}{(1 + a(D - D_{th}))} - \left(\frac{T_i a (D - D_{th})}{(1 + a(D - D_{th}))} \right) \times \left(\frac{b(D - D_{th})}{(1 + b(D - D_{th}))} \right). \quad (5b)$$

Profilometer data show that under atmospheric conditions T is a maximum for $T = 0.34^* T_i$. This information was used to fit the combined data of Fig. 6 scaled to give an equivalent dose to that applied by the HeCd laser. Under these conditions, keeping $a = 0.08$, the best fit was found for $b = 0.04$.

Figure 12 shows that the new model provides a good fit to the experimental data for UV irradiation in both atmosphere and nitrogen environments. As such, the model fits shown in Fig. 12 provide good support for the proposed mechanism presented in Fig. 11. Moreover, this mechanism and the associated model provide insights for the application

FIG. 12. Comparison of experimental (data points) and model (solid lines) PPV film thickness as a function of equivalent energy dose for irradiation with the HeCd laser light using 325 nm light.

of NSOL to fabricate PPV nanostructures via the precursor route. Given that the light field emanating from a NSOM tip is highly inhomogeneous, for NSOL-based irradiation in oxygen-devoid environments some portions of the PPTEC film will necessarily receive a much higher energy dose than others. The model reveals that cross linking of these overexposed regions is likely to occur, resulting in a reduction in PPV conjugation length with ensuing negative effects on the optical and electronic properties of the fabricated PPV nanostructures. Our results show that for NSOL irradiation in air cross linking will not be a significant factor but oxidation will take place which will produce thinner and structurally more complicated features.

IV. CONCLUSIONS

The photochemistry of PPTEC has been systematically investigated with particular regard to its solubility with varying energy dose for lithographic applications. It was found that the thickest films of PPV irradiated in air were produced for an energy dose of $54 \pm 10 \text{ mJ/cm}^2$ at 325 nm. Increased solubility (and therefore reduced thickness) beyond this dosage was attributed to oxidation of PPV formed during irradiation. Irradiation in a nitrogen environment reduced the effects of oxidation, resulting in thicker PPV films. However, some resolubilization of the films was still observed to occur for energy doses above 500 mJ/cm^2 , which was attributed to reaction with residual methanol solvent trapped in the precursor film. Irradiation in vacuum ensured that any residual methanol solvent was eliminated and under these conditions no resolubilization was observed. For very high energy doses, a reduction in the conjugation length of the final processed PPV was observed which was attributed to cross linking of the polymer chains. A model for predicting final PPV film thickness as a function of dose applied has been presented. Such a model should prove useful when applied to lithography for PPV via the PPTEC precursor route.

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