The Role of Carbonyl Groups in the Photoluminescence of Poly(*p*-phenylenevinylene)

F. Papadimitrakopoulos, K. Konstadinidis, T. M. Miller, R. Opila,
E. A. Chandross, and M. E. Galvin*

AT&T Bell Laboratories, 600 Mountain Ave., Murray Hill, New Jersey 07974

Received February 23, 1994. Revised Manuscript Received May 20, 1994®

This paper reports that carbonyl moieties are present as defects, formed during the thermal conversion of a precursor to poly(*p*-phenylenevinylene) (PPV), a polymer used in light-emitting diodes. The increase in carbonyl groups can be correlated with a dramatic reduction of PPV photoluminescence. We have discovered that if the conversion is carried out in a reducing atmosphere, e.g., 15% hydrogen in nitrogen, the amount of carbonyls is substantially reduced and the photoluminescence intensity of the polymer increases as much as 5-fold. These results also have important implications for theories, advanced by other authors, of the effect of conjugation length or chain alignment on photoluminescence and electroluminescence in these systems.

Introduction

The discovery in 1990 that poly(*p*-phenylenevinylene) (PPV) could be used to fabricate a light-emitting diode[1] (LED) has spawned a considerable amount of research. Much of this work has been devoted to the discovery of alternative polymers[2–6] and to improving the performance of these devices.[6,7] When PPV is sandwiched between indium-tin oxide (ITO) and metal electrodes, device efficiencies of 0.05%[1] and 0.01%[8] photons/electron have been achieved with calcium and aluminum, respectively, as the metal electrode. If an electron-transport layer is inserted between the metal electrode and the polymer, device efficiencies are increased to 0.8% with calcium.[7] While these efficiencies are lower than those achieved with evaporated organic films,[9–11] the thermal stability of these polymers coupled with their ability to form flexible devices[6] has fostered an interest in light-emitting polymers for display applications.

Although considerable research has concentrated on discovering new polymers, the effort aimed at understanding the interplay between polymer synthesis, polymer defects, and luminescence has been small. This relationship is emphasized here. We chose to concentrate on PPV for two reasons. It and its derivatives have yielded the highest reported LED efficiencies thus far. Additionally, Hsieh and co-workers at Xerox[12] have reported some preliminary research on the defects produced in the synthesis of PPV, which provided a good framework for our investigations.

The great similarity between the electroluminescence and photoluminescence spectra of PPV[3,6,7,13,14] suggests that the light-emitting species are identical in both cases. This implies that increasing the photoluminescence yield of PPV will result in improvements in electroluminescence efficiency, assuming that other variables such as charge injection, transport, and combination are not the limiting aspects of electroluminescence. As support for this concept, we note that Tang *et al.*[9] improved both photoluminescence and electroluminescence in aluminum tris(8-oxyquinolinate) (Alq_3) based devices by doping the Alq_3 with various fluorescent dyes. Since there are fewer variables to control in studying photoluminescence than electroluminescence, we concentrate on how defects produced during polymer synthesis affect photoluminescence. A later paper will deal with the correlation between these defects and electroluminescence.

The insoluble and intractable nature of PPV requires a two-step synthesis.[15] First, a monomer is polymerized to form a soluble precursor polymer. The precursor polymer is then spin-coated onto a substrate and converted into PPV at elevated temperatures (200–300 °C), in vacuum or under an inert atmosphere such as argon. Hsieh and co-workers have noted that this synthetic route can lead to the incorporation of some chemical defects such as hydroxyl groups into the PPV

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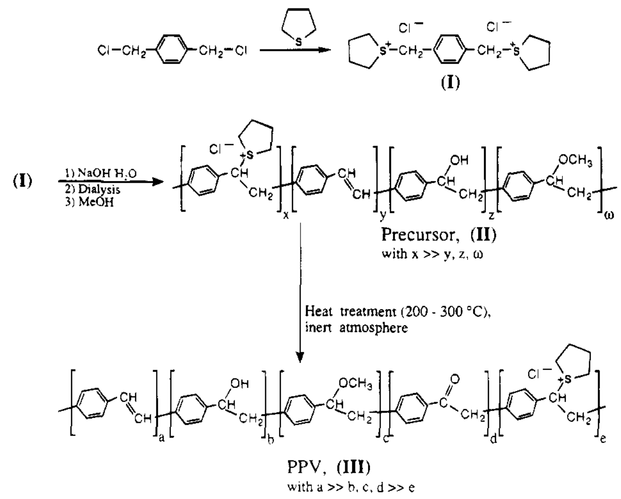
chains,[12] but they do not mention carbonyl groups. Murase *et al.*[16] reported that carbonyl groups, formed during thermal conversion in air, resulted in PPV with reduced conjugation length and lower conductivity when oxidized. Ultraviolet irradiation in air of the precursor to PPV is also reported to lead to carbonyl formation and decreased fluorescence.[17] The last two studies were, however, completed prior to the discovery that PPV could be used in light-emitting diodes. More recent studies have ignored the role that carbonyl groups might play in device electroluminescence efficiencies. Intersystem crossing to nonluminescent triplet states is a common phenomenon in carbonyl compounds.[18]

Here we report that traces of molecular oxygen in the conversion atmosphere, combined with prolonged exposure to elevated temperatures results in carbonyl formation and reduced photoluminescence. Improving the vacuum or minimizing the oxygen levels in the inert gases used during conversion is not a completely effective way to eliminate carbonyl formation. We have developed a novel, simple way to suppress the formation of carbonyl defects: conversion of PPV precursor in an atmosphere of commercial grade forming gas (a mixture of 85% nitrogen and 15% hydrogen). Considerable emphasis is given here to relating the concentration of carbonyl impurities to the photoluminescence of PPV and to the influence of hydrogen in minimizing carbonyl formation. The identity and relative levels of other impurities present in PPV and its precursor are also addressed. This technique of converting a precursor in a reducing environment to limit carbonyl formation should be beneficial for many polymer systems, especially those whose electronic properties are of interest, including the preparation of poly(thienylenevinylene).

Experimental Section

Materials. All chemicals were obtained from Aldrich. The reaction and spinning solvents were bubbled overnight with argon which had been passed over Oxiclear catalyst (Fisher Scientific). The *p*-xylylenebis(tetrahydrothiophenium chloride) monomer (**I**) was purified by dissolving it in a minimum amount of water, filtering to remove insoluble impurities, and precipitating it in cold acetone.[19] The white powder obtained was carefully filtered, dried in argon, and briefly stored at −40 °C away from room light prior to polymerization. The precursor polymer was synthesized according to Scheme 1 by adding an equimolar aqueous NaOH solution to a 0.25 M aqueous solution of monomer **I** cooled to 1 °C. The polymerization was quenched by the addition of 1 N HCl solution (to pH 7) as soon as the viscosity of the solution rose substantially (usually after 5−15 min). The solution was then dialyzed against distilled water through a SPECTRA/POR membrane with 6000−8000 molecular weight cutoff and stored in a freezer. The precursor polymer (**II**) was precipitated from its aqueous solution by isopropyl alcohol, filtered and washed with anhydrous ethyl ether, and dried under a stream of dry, O_2 free argon. If isopropyl alcohol alone did not precipitate the precursor polymer, a solution of NH_4Cl in isopropyl alcohol was used to facilitate precipitation. The polymer was then washed with a 3:1 isopropyl alcohol:water mixture to remove adventitious salt. Thin films of the precursor polymer were prepared by spinning a 1% methanol solution of the precursor onto fused silica or silicon wafers.

Scheme 1. Synthesis of PPV



Thermal Conversion. Thermal conversion of the precursor to PPV (**III**) was performed in an oven at elevated temperatures (200−300 °C) under vacuum or in a continual purge with one of the following three atmospheres (gas purities are as provided by the supplier): (i) Industrial research grade argon (argon), 99.997% purity, more than 1 ppm O_2 content.[20] (ii) Research purity argon (high-purity argon), 99.9999% purity, less than 0.5 ppm O_2 content.[21] (iii) Forming gas, a mixture of 85% N_2 of purity 99.998% and more than 1 ppm O_2 and 15% hydrogen of purity 99.5% and more than 10 ppm O_2.[20]

To ensure reproducible results, the oven temperature was kept at ±1 °C with respect to the following ramp and soak program of a programmable temperature controller. The sample was introduced and purged at 20 °C for 1 h, heated linearly over a period of 5 h to the desired conversion temperature, held at the conversion temperature for 6 h, and then cooled slowly to room temperature. The initial purging and slow heating ramps were introduced in order to allow residual methanol to evaporate slowly. This should minimize the reaction of methanol with the precursor polymer.

Characterization Techniques. Infrared (IR) spectroscopic data were obtained from a Mattson RS-1 Fourier transform infrared spectrometer using a liquid N_2 cooled wideband HgCdTe detector at 4 cm^{-1} resolution. Thin PPV films (1000 Å) were made on one side of a double polished *(100)* silicon wafer. The sample was held at 45° with respect to the incident IR beam in order to increase the sampling path length and to eliminate the interference fringes from the double polished wafer. This resulted in alteration of peak intensities as compared to those published in the literature. For example, the intensity of the 1516 cm^{-1} band decreases almost by a factor of 2 relative to the 0° tilt due to the parallel orientation of the PPV units with respect to the surface of the substrate. A minimum of 200 scans were signal averaged. The FTIR spectrum of the silicon wafer was included into the spectrometer's background to ensure minimum signal contribution from the silicon substrate. All IR spectra were normalized with respect to the area of the 1516 cm^{-1} band to account for small thickness variations (±150 Å).

Fluorescence data were obtained from a Spex Fluorolog-2 spectrofluorometer with a Xe lamp as a source and a GaAs photomultiplier detector. Front-face excitation fluorescence data were collected for 1000 Å PPV films made on fused silica slides or silicon wafers which were loaded into a 1 mm thick fused silica cuvette under argon. The excitation wavelength was 400 nm. Thickness variations of ±150 Å, measured on a Dektak profilometer, were corrected for by normalization.

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UV–vis absorption spectra were obtained with a Hewlett-Packard 8425A diode array spectrometer from 1000 Å PPV films made on fused silica slides.

X-ray photoelectron spectroscopy (XPS) experiments were performed in a PHI (Perkin-Elmer) Model 5600 spectrometer equipped with a monochromatic source. Aluminum Kα X-rays were excited at 400 W of power. The size of the analysis area was 800 × 800 μm^2. For high-resolution core level spectra the analyzer pass energy was set at 11.75 eV and the energy step at 0.05 eV. Under these conditions the fwhm of the Ag $3d_{5/2}$ peak is 0.57 eV. Spectra were collected at two photoelectron takeoff angles, 45° and 10°, corresponding to a sampling depth of about 40 and 10 Å, respectively. To avoid exposure to atmospheric oxygen, the samples were transferred from the glovebox to the XPS spectrometer using a PHI vacuum-transfer vessel filled with argon. The atomic composition of the sampling volume was determined from the integrated area of the core level peaks taking into account known sensitivity factors. No charge neutralization was necessary; however, in some cases the energy scale had to be slightly corrected by setting the main hydrocarbon C 1s peak to 284.8 eV.

Results and Discussion

As stated in the Introduction, the chemical purity of PPV synthesized via the precursor polymer pyrolysis route has been addressed by other researchers.[12,15,16,22] Scheme 1 includes some of the defects which have been reported to exist in PPV or its precursor. Very weak hydroxyl absorption in the infrared suggests the presence of a small amount of species b; species c is expected to be formed in a similar manner during polymerization; and an upper limit of 0.01% has been determined for e. Of these, the carbonyls, not present in the precursor, can be luminescence quenchers, and therefore, we concentrated on trying to reduce carbonyl formation. Note, in a 10^{-6} Torr vacuum, a common condition for the thermal conversion of the precursor polymer to PPV,[23] oxygen reaches the surface at a rate of 1/5 of a monolayer/s,[24] and, therefore, a 1000 Å polymer film could undergo significant reaction with oxygen during the 2–6 h conversion to PPV. Speculating that carbonyl moieties arise from oxidation or other radical processes, that occur during the thermal conversion step, we chose to convert the polymer in a reducing atmosphere, i.e., forming gas.

XPS is a surface technique, probing 10–100 Å, that is useful for analyzing the composition of thin polymer films. Studies of our films converted at elevated temperatures revealed that sulfur was not present even for the lowest temperature conversions. Rutherford backscattering (RBS) analysis indicated that only minute concentrations (<0.01 atomic %) of sulfur were present in the bulk of the film, proving that the tetrahydrothiophene unit is almost completely eliminated from thin films of the precursor at 200 °C. Other elements such as sodium and chlorine were present in minute concentrations (<0.01 atomic %). The only elements observed in significant concentrations were carbon and oxygen.

Figure 1 plots the atom percent of surface oxygen, as determined by XPS for a depth of about 40 Å, for three different atmospheres at three temperatures. These data are important in several respects. At 200 °C the samples from the three atmospheres are very similar in surface oxygen content, varying between 2.4% and 3.0%. This is considerably lower than the 17% reported by Hsieh and co-workers.[25] Some of this difference may be attributable to the handling of the samples. When our sample was exposed to the atmosphere prior to XPS analysis, the surface oxygen increased to 17%. As the temperature of conversion is increased to 300 °C, the surface oxygen content decreases monotonically and reaches its lowest value for samples converted in forming gas. This decrease suggests that one of the oxygen containing defects listed in Scheme 1 is being eliminated at higher temperatures. A logical choice is the hydroxyl group through simple dehydration. According to Holmes,[26] the elimination of methoxyl groups generally requires the addition of HCl catalyst. Some HCl is, however, generated during the elimination of the tetrahydrothiophene and could contribute to a loss of methoxyl units which might explain some of the oxygen decrease. It is difficult, however, to understand why this would have a temperature dependence above 200 °C when the tetrahydrothiophene and HCl are completely eliminated by that temperature and the samples are under a continuous purge which should remove HCl from the oven. The elimination of carbonyls is unlikely, forcing us to return to dehydration as a possible explanation. Since the XPS data could not be deconvoluted, we turned to IR analysis to further study this decrease in surface oxygen.

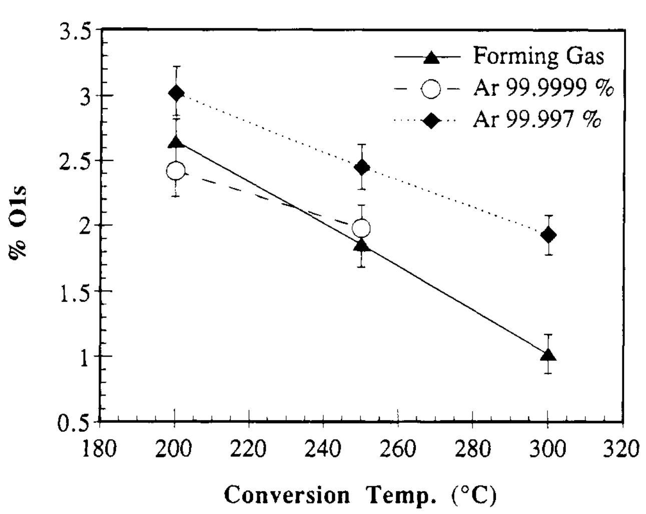

Figure 1. Surface oxygen content (% O 1s) as a function of conversion temperature and atmosphere, obtained from a 45° XPS surface analysis of 1000 Å PPV films.

Figure 2 shows plots of two regions of the IR spectra of samples converted in argon at three temperatures. Note that in contrast to other researchers who use thick films for IR,[23] these spectra are taken on 1000 Å films and are, therefore, indicative of what occurs in the electroluminescent device configuration. Since IR samples the bulk properties of a material, it might not detect the high concentration of carbonyls arising from thermal oxidation of the surface of thick PPV films. A complete assignment of the IR peaks is given in Table

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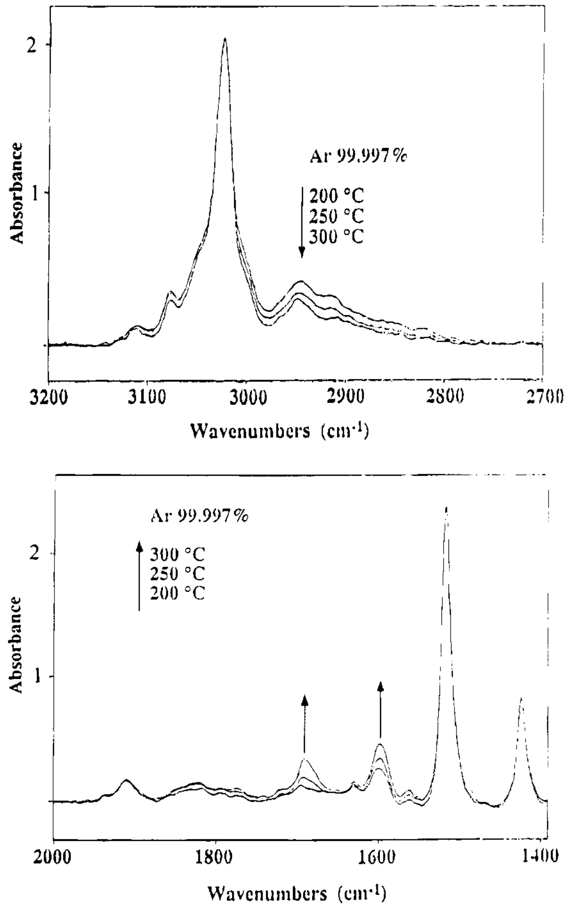

Figure 2. (a, top) FTIR spectra of the CH stretching region for three 1000 Å PPV films converted under argon at 200, 250, and 300 °C. (b, bottom) FTIR spectra of the 200−1400 cm^{-1} region (carbonyl) for the same three films.

Table 1. Infrared Band Frequencies, Relative Strengths, and Assignments for Thermally Converted PPV

peak frequency ν (cm^{-1})	rel strength	assignment
3109	vw	aromatic CH stretch
3075	v	
3048	v	
3023	s	*trans*-vinylene CH stretch
2947	w	aliphatic CH stretch[a]
2918	w	
2852	w	
1910	w	overtone of the *trans*-vinylene CH out-of-plane bend[c]
1690	w	*trans*-conjugated C=O stretch[27]
1595	w	"quadrant" ring stretch[b]
1561	vw	
1516	s	*p*-phenylene "semicircle" stretch
1423	m	

[a] The modes at 2947, 2918, and 2852 cm^{-1} are assigned to the saturated hydrocarbon groups within the PPV chain. The 2947 and 2853 cm^{-1} modes originate from the CH_2 stretch (out-of-phase stretch) and CH_2 stretch (in-phase stretch), respectively, while the 2918 cm^{-1} mode could possibly assigned to the CH or CH_3 stretches.[28] [b] Although for para-substituted phenylene with the same substituent the "quadrant stretching" modes are infrared inactive, the nature of these bands originate from the loss of the center of symmetry due to different substituents or conformational irregularities of the PPV chain.[27] [c] The *trans*-vinylene CH out-of-plane bend mode is observed at 964 cm^{-1}.[27]

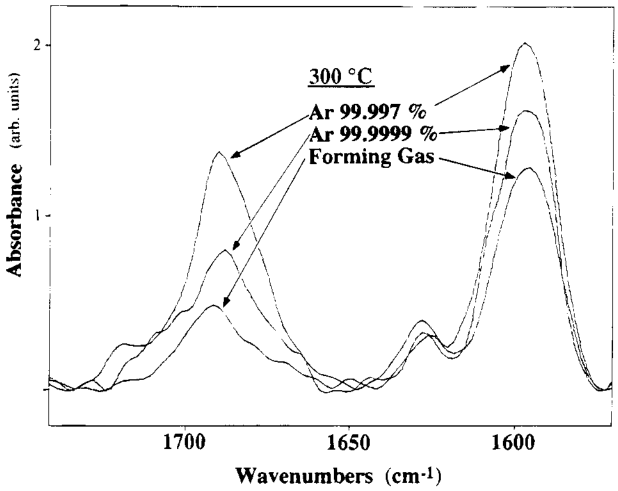

Figure 3. FTIR spectra of the carbonyl region for three 1000 Å PPV films converted at 300 °C under three different atmospheres.

1. In Figure 2a, we concentrate on the aliphatic CH stretch modes (2947, 2918, and 2852 cm^{-1} (not clearly shown here)). As the temperature of conversion is increased, these intensities decrease as well. The magnitude of this decrease can not be attributed to the loss of tetrahydrothiophene, since XPS and RBS revealed that this group was eliminated even in the 200 °C samples. Instead, these data are consistent with the dehydration of the precursor polymer at elevated temperatures. The carbonyl region of the IR spectra is plotted in Figure 2b. The band at 1690 cm^{-1} is assigned to the carbonyl stretch and corresponds well with the 1695 cm^{-1} carbonyl mode of deoxybenzoin, a low molecular weight analog of the proposed carbonyl impurity in PPV. The 1595 cm^{-1} peak is indicative of substituent perturbations[27,28] on the absorption intensity of *p*-phenylene rings and, therefore, should increase with carbonyl formation. Both the 1690 cm^{-1} and the 1595 cm^{-1} bands increase with conversion temperature, suggesting that the samples are more heavily oxidized at higher temperatures. The decrease in surface oxygen with increasing temperature, as measured by XPS, must be due to loss of the hydroxyl or methoxyl groups, since IR analysis shows that carbonyls increase with temperature. The fact that the lowest surface oxygen content was obtained at 300 °C with forming gas led us to speculate that forming gas decreases carbonyl formation.

Figure 3 displays the carbonyl and ring stretch modes for samples converted at 300 °C in three different atmospheres. When high-purity argon (99.9999%) is used instead of "ordinary" argon (99.997%), the amount of carbonyls decreases significantly. The lowest carbonyl content is, however, found in the samples converted in forming gas even though this atmosphere has the highest content of oxygen. To quantify these data better, we calculated the area under the carbonyl peak. This involves a few steps. First, the spectra are normalized to the 1516 cm^{-1} stretch (not shown in Figure 3) to remove variations due to thickness difference. Second, it is necessary to resolve the weak carbonyl peak from the baseline noise, and this introduces some error into the calculations. The results are, however, qualitatively significant and are plotted for three temperatures and three atmospheres in Figure 4.

In all the atmospheres the carbonyl content increases with increasing conversion temperature. At 200 °C there is little difference between amounts of carbonyls

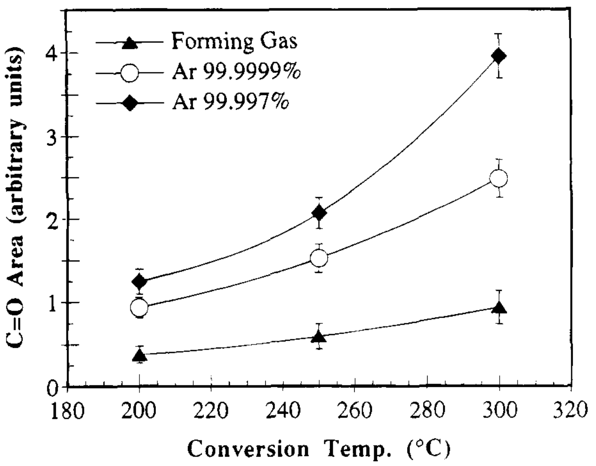

Figure 4. Effect of conversion temperature and atmosphere on the carbonyl content (area under 1695 cm^{-1} peak) of PPV films.

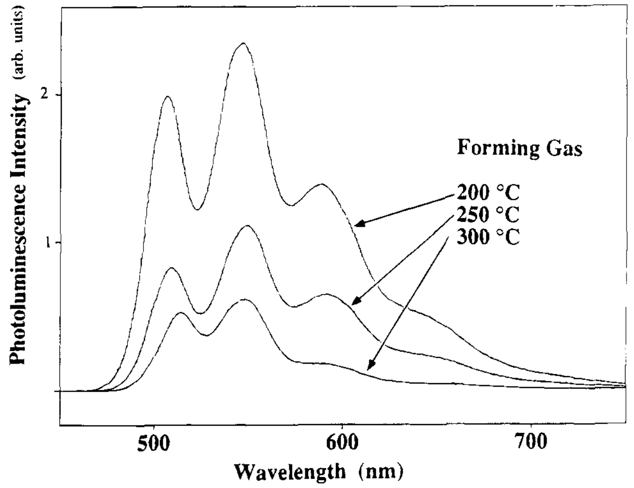

Figure 5. Photoluminesence spectra of a 1000 Å PPV films converted under forming gas at 200, 250, and 300 °C, respectively (400-nm excitation wavelength).

formed in either of the two argons, while the forming gas product is distinctly lower in carbonyl content. The differences attributable to the atmospheres are more pronounced at higher temperatures. Decreasing the amount of oxygen in the argon reduces carbonyl formation by approximately 40%. The greatest protection against carbonyl formation is afforded with forming gas, where the carbonyl content is reduced by a factor of 5. Since the forming gas is relatively high in oxygen content, we conclude that the reducing atmosphere created by the hydrogen affords the polymer the highest protection against thermal oxidation.

The effect of carbonyls on the photoluminescence of the polymer is demonstrated in Figure 5. As the conversion temperature increases, there is a corresponding decrease in photoluminescence and a red shift in the highest energy band of the electronic spectra. At first this shift would appear to conflict with the fact that increasing conversion temperature results in an increase in the carbonyl concentration. The red shift indicates an increase in conjugation length, while carbonyls decrease conjugation length. XPS offers the resolution to this conflict. Remember that the surface oxygen and, therefore, hydroxyl group concentration decreased with increasing temperature. The increase in conjugation created by dehydration outweighs the decrease due to carbonyl formation. This is entirely consistent with the conclusion drawn from the XPS results.

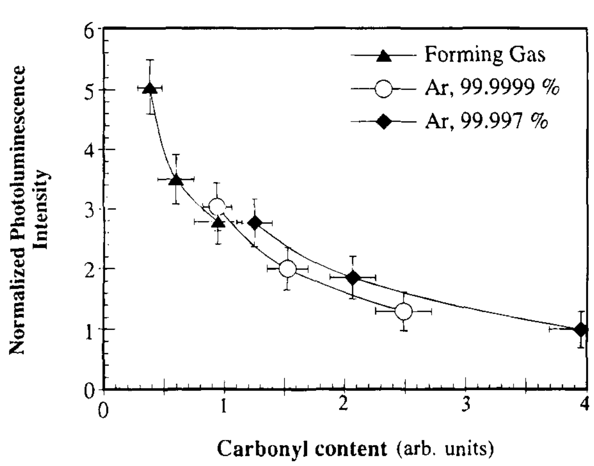

Figure 6. Overall affect of carbonyl content on the photoluminesence of 1000 Å PPV films.

The decrease in photoluminescence which accompanies carbonyl formation is more dramatically presented in Figure 6, where the photoluminescence intensity is plotted against the carbonyl content for all three atmospheres and temperatures. The rapid decrease in luminescence with increasing amounts of carbonyl is entirely consistent with but does not prove that carbonyls are detrimental to sample luminescence. For comparison, we point out that the photoluminescence of a sample converted in a 10^{-3} Torr vacuum was an order of magnitude lower than that of our sample with the poorest luminescence. We are currently investigating the electroluminescence efficiency of devices made from PPV samples converted in forming gas. Preliminary data indicate it also increases significantly.

In addition to providing a better route to PPV, our work is significant in another way. Many researchers have reported that partially converted polymer has higher photoluminescence and electroluminescence efficiencies than does fully converted PPV. Some elaborate reasons have been advanced to explain why a decrease in conjugation increases efficiency. For example, Zhang and co-workers[29] report that as the conjugation length of PPV increases, the electroluminescence and photoluminescence yields decrease. They attribute this to "larger excitation mobility resulting in more rapid motion and greater possibility of interaction, e.g., with quenching sites, that lead to nonradiative decay". We point out that the partially converted PPV is obtained by heating the samples to between 160 and 210 °C under nitrogen. Fully converted PPV is obtained by heating the precursor under vacuum to 300 °C. These different conditions could lead to very different carbonyl contents and, therefore, very different luminescence. Energy migration to traps in these systems is expected to be an important factor, amplifying the effect of even minor concentrations of quenchers. If increasing conversion to higher conjugation lengths is accompanied by increased quencher content, the result-

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ing diminution of luminescence is expected to be even more dramatic. The beneficial effects of increasing conjugation while avoiding carbonyl formation are supported by the recent work of Rothberg and co-workers.[30] They report that the photoluminescence lifetimes in PPV samples, converted in forming gas, have increased to the values observed in solutions of PPV oligomers[31] and are well beyond any previously reported for PPV films.

Holmes and co-workers[23,26] recently reported improved photoluminescence in PPV via a new synthetic route which they suggest preorders the chains prior to complete conversion of the precursor. They named this route the "tent frame precursors". They contend that it leads to large-scale ordering of the final polymer and that this ordering increases photoluminescence. Their conversion temperature never exceeds 220 °C, and the carbonyl concentration in these polymers should, therefore, be lower than in conventional PPV, resulting in higher luminescence efficiency. It is our contention that many of these results should be reexamined in light of our work.

Conclusions

We have shown that the concentration of carbonyl moieties in PPV greatly affects the photoluminescence of this polymer. The data suggest that carbonyls act as one type of quenching site, although we prefer not to speculate about the quenching mechanism at this time. Other types of quenchers are probably present. The temperature to which the precursor polymer is heated to form PPV plays a critical role in carbonyl formation. Lower temperatures afford lower carbonyl content and higher photoluminescence efficiencies. The largest reduction in carbonyl formation is achieved by converting the precursor in a reducing atmosphere, i.e., forming gas. It is, therefore, evident that the present data strongly suggest that reevaluation of many theories on the effect of conjugation length or chain alignment on the luminescence of PPV is in order. We believe that our work also has implications for other polymer systems, especially those whose electronic properties are of interest, including the thermal conversion of a precursor to form poly(thienylenevinylene) (PTV). It has been reported that this polymer can be used in the production of thin-film transistors. We suggest that if, forming gas were used to convert the precursor to PTV, the resulting polymer would have fewer carbonyls and, therefore, exhibit higher carrier mobility.

Acknowledgment. The authors thank Lewis Rothberg, Ananth Dodabalapur, and Helen Kim for useful discussions.

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