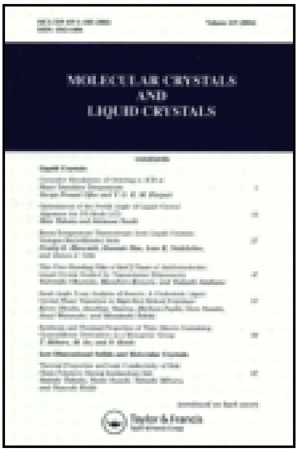


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Thermal and Photochemical Origin of Carbonyl Group Defects in Poly-(P-Phenylenevinylene)

Fotios Papadimitrakopoulos [a] , Ming Yan [a] , Lewis J. Rothberg [a] , Howard E. Katz [a] , Edwin A. Chandross [a] & Mary E. Galvin [a]

[a] AT&T Bell Laboratories, Murray Hill, NJ, 07974

To cite this article: Fotios Papadimitrakopoulos , Ming Yan , Lewis J. Rothberg , Howard E. Katz , Edwin A. Chandross & Mary E. Galvin (1994): Thermal and Photochemical Origin of Carbonyl Group Defects in Poly-(P-Phenylenevinylene), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 663-669

To link to this article: http://dx.doi.org/10.1080/10587259408039307

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 663–669
Reprints available directly from the publisher
Photocopying permitted by license only

THERMAL AND PHOTOCHEMICAL ORIGIN OF CARBONYL GROUP DEFECTS IN POLY-(*P*-PHENYLENEVINYLENE)

FOTIOS PAPADIMITRAKOPOULOS, MING YAN, LEWIS J. ROTHBERG, HOWARD E. KATZ, EDWIN A. CHANDROSS and MARY E. GALVIN
AT&T Bell Laboratories, Murray Hill, NJ, 07974.

Abstract The thermal stability of poly(*p*-phenylenevinylene) (PPV), along with its ability to form flexible devices, has sparked a considerable amount of research in the area of polymer light emitting diodes (LEDs). The presence of carbonyl groups as defects in the PPV structure has been reported elsewhere.[1] An increase in carbonyl groups correlates well with a dramatic reduction in the photoluminescence and electroluminescence of this polymer. We have discovered that these carbonyl defects can be introduced thermally as well as photochemically. This paper reports the mechanisms for the thermal and photochemical oxidation of PPV. Although PPV is thermally quite stable, its hydroxy containing defects present in the precursor polymer are very susceptible to reaction with traces of oxygen at the elevated temperatures used in thermal conversion, resulting in the formation of ketone based carbonyl impurities. In addition, pristine PPV is very unstable in the presence of light and oxygen. The photooxidation of PPV involves the cleavage of the vinyl double bond and the formation of terminal aldehyde groups. These results have important implications for the stability of this polymer in LEDs, where elevated temperatures or light create highly reactive charged species.

INTRODUCTION

The 1990 discovery of poly(*p*-phenylenevinylene) (PPV) based light emitting diodes[2] (LEDs) has triggered a considerable amount of research on polymeric light emitters. Although much of the work has concentrated on device improvement and new light emitting polymers,[3] little effort has focused on a fundamental understanding of the interplay between polymer synthesis, polymer defects and luminescence.[4] The insoluble and intractable nature of PPV requires a two step synthesis.[5] First, a soluble precursor polymer is made, followed by thermal conversion of the precursor at elevated temperatures in vacuum or under an inert atmosphere such as argon. The generation of carbonyl groups during thermal conversion in the presence of oxygen has been reported by Murase et *al.*[6] to result in shorter conjugation and lower conductivity. Ultraviolet irradiation in air has also been reported to lead to carbonyl formation and decreased fluorescence.[7]

Realizing the critical role of carbonyl groups as effective photoluminescence (PL) quenchers, much of our early work concentrated on minimizing their formation.[1] For this reason, the thermal conversion of the precursor was performed under a reducing atmosphere (a commercial grade forming gas with 85% nitrogen and 15% hydrogen) to generate a high quality PPV sample, with a five fold improvement in the PL yield[1] and PL decay lifetime[8], and a ten fold increase in the electroluminescence (EL) yield.[1] Companion studies show that many literature results in PPV can be explained on the basis of oxidation defects.[8,9]

Here we report the infrared (IR) analysis and mechanisms for the carbonyl formation mentioned above. We show that the concentration of carbonyl impurities as created by thermal and photochemical oxidation mechanisms relates inversely to the PL of PPV. Issues such as the effects of the conversion atmosphere and conjugation as well as electroluminescent device lifetime are discussed in light of the present results.

EXPERIMENTAL

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) and molecular sieves. The synthesis of the PPV precursor has been described elsewhere[1] Thin films (~1000 Å) of the precursor polymer were prepared by spinning a 1% methanol solution of the precursor onto fused silica slides and double polished *(100)* silicon wafers.

Thermal Conversion - Thermal conversion of the precursor to PPV was performed in an oven at elevated temperatures (200 - 300 °C) in a continual purge with one of the following atmospheres. Gas purities are as provided by the supplier.

i) Industrial Research Grade Argon - 99.997% purity - more than 1 ppm O_2 content.[10]

ii) Forming Gas - a mixture of 85% N_2 of 99.998% purity and more than 1 ppm O_2 with 15% hydrogen of 99.5% purity and more than 10 ppm O_2.[10]

In order 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 (25 °C for 1 hr followed by a 5 hr increase to the conv. temp. which was maintained for 6 hr). 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.[11]

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. The sample was on a silicon substrate and was held at 45 degrees 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.

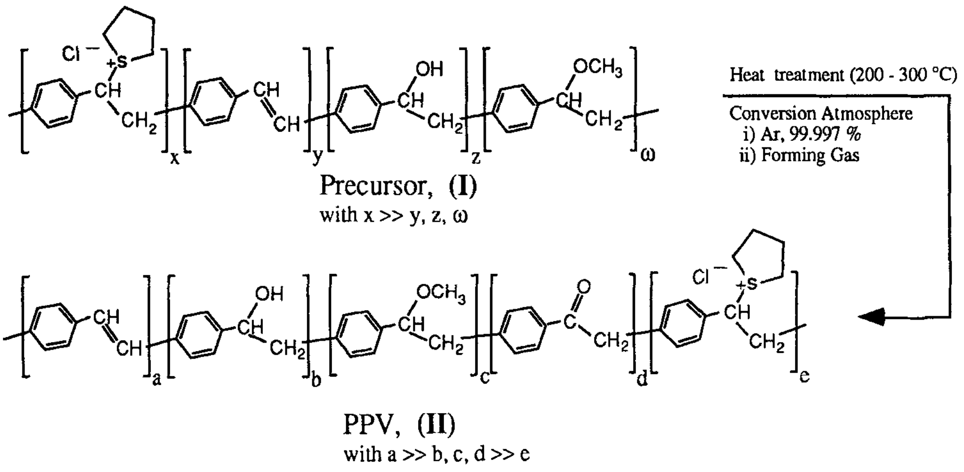
Fluorescence data were obtained from a Spex Fluorolog-2 spectrofluorometer with a Xe lamp as a source and a GaAs photomultiplier detector. Front face fluorescence data were collected on 1000 Å PPV films on silicon, which were loaded into a 1 mm thick quartz cuvette under N_2. The excitation wavelength was 400 nm. Correction for thickness variations (c.a. 150 Å) was made using thickness values measured on a Dektak profilometer. UV-VIS absorption spectra were obtained with a Hewlett Packard 8425A diode array spectrometer from 1000 Å PPV films made on fused silica slides.

For the photooxidation experiments, we used a variety of light sources that cover the entire absorption envelope of PPV. The photoxidation data presented here, were obtained with a blue-green filtered Xe lamp, although these results are essentially the same for a 248 nm excimer laser and a 400 nm HeCd laser. The light power for the Xe lamp was measured with a Coherent 2010 power meter to be about 10 mW/cm^2.

RESULTS AND DISCUSSION

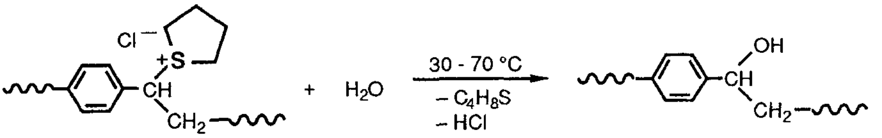
Thermal oxidation - The state of chemical purity of PPV, synthesized via the precursor polymer pyrolysis route has been addressed by other researchers.[4-6] Scheme I illustrates the chemical composition of the precursor polymer (**I**) and thermally converted PPV (**II**), based on IR, X-ray photoelectron spectroscopy (XPS), Rutherford back scattering (RBS) and Secondary ion mass spectroscopy (SIMS) analysis. FTIR analysis of the precursor (**I**) indicate the absence of carbonyl groups, providing the synthesis is performed in the absence of UV and blue light.[7] During the thermal conversion of the precursor (**I**) to PPV (**II**) a number of eliminations have been reported to occur. The tetrahydrothiophene unit is almost completely eliminated at 200 °C for these 1000 Å films, resulting in sulfur concentration of less than 0.006 atomic %. The hydroxy groups require much higher temperatures (>250 °C) to eliminate.[5] According to Burn et *al.*,[11a] the elimination of the methoxy groups generally requires the addition of HCl catalyst. Some HCl is, however, generated during the elimination of tetrahydrothiophene that may contributes slightly to methoxy elimination.[11,1]

The two likely sources of carbonyl groups in PPV (**II**) are the double bonds and the hydroxy (OH) groups. Both have been reported to be oxidatively sensitive in other organic compounds.[12,13] Prolonged exposure (for more than two days) in Ar 99.997%,



Scheme I. Chemical structure and defects of PPV (II) and its precursor (I)

at 300 °C, of a sample previously converted at 300 °C in forming gas, showed insignificant increase of carbonyl content, indicating that the vinyl bonds are quite stable up to 300 °C. On the other hand, the same experiment with a sample first converted in forming gas at 200 °C, showed substantial increase of carbonyl content. The above data suggest that the OH groups are the source of carbonyl groups, since the 200 °C converted sample contains more OH groups than the 300 °C one.[1] In light of these results we investigated the conditions that maximize the OH content. Similar to the methoxy substitution reported by Halliday et *al.*,[11b] careful heating of the precursor in its aqueous solution facilitates nucleophilic substitution. This reaction



proceeds slowly below 50 °C, while above 60 °C, the solution gels within a few hours. Figure 1a shows that both hydroxy and carbonyl content in the 300 °C converted polymer increase as a function of thermal treatment of the aqueous precursor solution at 50 °C. The decrease in the integrated photoluminescence caused by carbonyl formation[1,9] is shown in Figure 1b.

This decrease is in agreement with previous findings.[1] The small but reproducible blue shift of the PL spectrum, caused by the increase of OH content, indicates a smaller average conjugation length. According to Zhang et *al.*,[14] the decreased conjugation length should increase the luminescence due to the decreased exciton mobility to quenching sites. The present data indicate the opposite because the increased quenching site concentration overpowers the decreased exciton mobility.

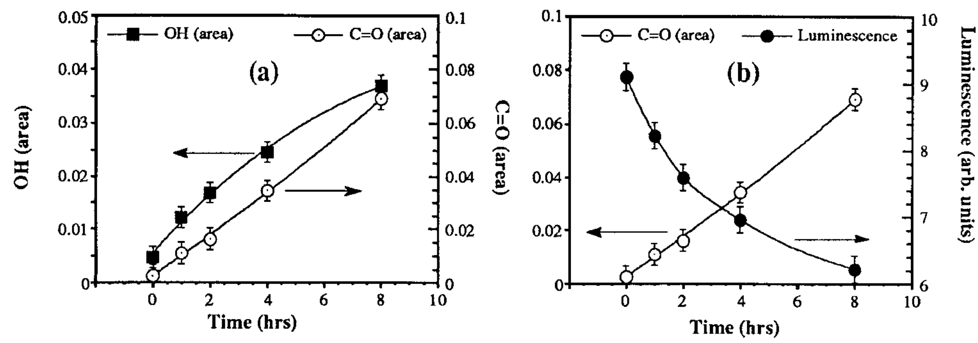


Figure 1. Hydroxy, carbonyl and integrated photoluminescence of ~1000 Å PPV films converted at 300 °C in Forming gas, as a function of thermal treatment of the aqueous precursor solution at 50 °C.

Photochemical oxidation - The photochemical oxidation mechanism for PPV is somewhat different. Evidently, the most sensitive unit in PPV is the vinyl group. The photooxidation behavior of polyacetylene $[(CH)_x]$ provided the initial clues to the possible byproducts. Gibson et *al.*[12] indicated that photooxidation of $(CH)_x$ proceeds through chain scission to yield two terminal aldehyde groups. Applying this to PPV, we decided that a suitable low molecular weight model compound should contain a terminal aldehyde group. Stilbene-4,4'-dialdehyde[15] (StAld) shown in Figure 2 was chosen based on availability. Figure 2 illustrates the difference IR spectra of PPV as a function of lamp exposure and compares them with the corresponding pristine PPV spectrum and the solution and solid spectra of StAld. The growing peaks correspond well with those of the StAld model compound (1693 cm^{-1} aromatic aldehyde C=O stretch, 1602 and 1567 cm^{-1} 'quadrant' ring stretch, 1390 cm^{-1} aldehyde CH in plane rock, 1207 cm^{-1} phenyl-C(aldehyde) stretching mode and 1165 cm^{-1} aromatic aldehyde mode of unknown origin). The negative peaks correspond well with the disappearance of the pristine PPV spectrum (1516 and 1423 cm^{-1} *p*-substituted phenylene semi-circle stretches, 965 cm^{-1} *trans*-vinylene CH out of plane bend and 837 cm^{-1} *p*-phenylene CH out of plane bend). At the late stages of oxidation, a shoulder at 1720 cm^{-1} becomes quite prominent. The origin of this shoulder is still unclear. Higher oxidation products of aldehydes, such as esters and anhydrides, could explain its higher frequency and evolution.

The PL intensity of these PPV films is shown in Figure 3 as a function of irradiation. In air, we see a dramatic decrease in PL intensity, due to the resulting carbonyl incorporation in the polymer. On the other hand, the PL intensity remains

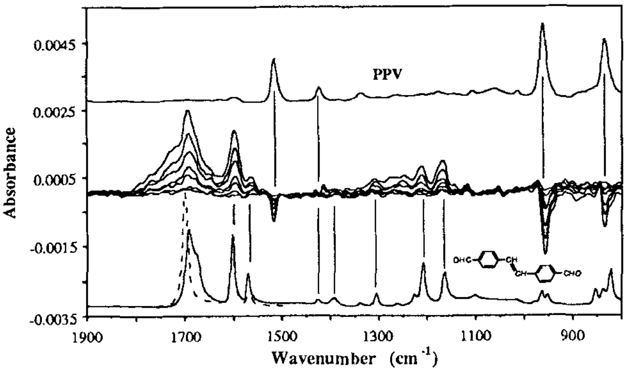


Figure 2. Difference FTIR spectra (middle) for varying degrees of photooxidation. The positive growing peaks are compared with the corresponding spectra of StAld model compound (bottom) (solid line for solid, and broken line for solution in THF). The negative growing peaks are compared with the pristine PPV spectrum (top) converted at 200 °C in Forming gas.

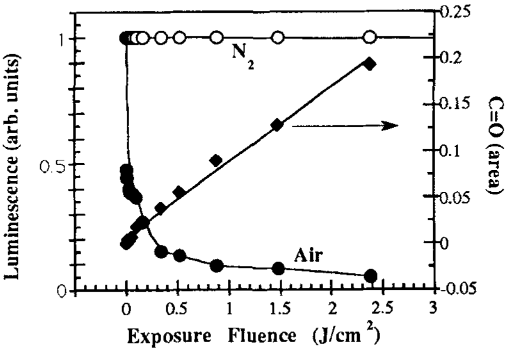


Figure 3. Overall effect of carbonyl content (♦) on the integrated photoluminescence of a 1000 Å PPV film against the lamp exposure, for photooxidation in air (•). The integrated PL in nitrogen (o) is also included.

virtually constant when the irradiation is performed in an inert atmosphere.

The PL decay as a function of carbonyl content shows the same trend as that of the thermally converted samples.[1] The PL spectra show only an intensity decrease upon progressive light exposure, while the vibronic peak positions are unchanged. This is in agreement with the fact that carbonyls act simply as effective photoquenchers, and most of the excitons that are in their vicinity (within 50 Å) are fated to decay nonradiatively.

CONCLUSIONS

1) The thermal oxidation of PPV occurs predominately through the residual hydroxy groups which oxidize to ketones at elevated temperatures in the presence of traces of oxygen.

2) The photochemical oxidation of PPV occurs at the vinylene bond and results in chain scission with terminal aldehyde formation.

3) The present study indicates that PPV is quite stable in the absence of oxygen. Carbonyl impurities, formed by thermal or photochemical oxidation, act as effective PL quenchers. Therefore the long term stability of PPV based LEDs could be achieved in the absence of carbonyl forming environment.

ACKNOWLEDGMENTS

The authors wish to thank A. Dodabalapur, K. Konstandinidis, R. L. Opila and T. M. Miller for stimulating discussion and suggestions.

REFERENCES

1. Papadimitrakopoulos, F.; Galvin, M. E.; Kim, H. H.; Konstadinidis, K.; Miller, T. M.; and Chandross E. A.; In *Polymer Preprints* **1994**, *35 (1)*, 414; *ibid.* submitted to Chemistry of Materials.
2. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P.L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
3. a) Greenham, N. C.; Moratti, S. C.; Bradley, D.D.C.; Friend, R. H.; Holmes, A. B. *Nature*, **1993**, *365*, 628. b) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. Nature **1992**, *357*, 477. c) Yang, Z.; Sokolik, I.; Karasz, F.E. *Macromolecules* **1993**, *26*, 1188.
4. Hsieh, B. R.; Antoniadis, H.; Abkowitz, M. A.; Stolka, M. *Polymer Preprints* **1992**, *33*, 414; Burn, P. L.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Holmes, A. B. *Synth. Metals* **1991**, *41-43*, 261.
5. Lenz, R. W.; Han, C. C.; Stenger-Smith, J. S.; Karasz, F. *Polym. Sci.: Part A: Polym. Chem.* **1988**, *26*, 3241.
6. Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1984**, *25*, 327.
7. Yoshino, K.; Kuwabara, T.; Iwasa, T.; Kawai, T.; Onoda, M. *Japanese Journal of Applied Physics* **1990**, *29*, L1514.
8. Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller T. M. *Phys. Rev. Lett.* **1994**, *72*, 1104.
9. Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller T. M. submitted to Phys. Rev. Lett..
10. Air-Products *Electronics Speciality Gas Catalog*; **1992**.
11. a) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1993**, *356*, 47. b) Halliday, D. A.; Burn, P. L.; Bradley, D. D. C.; Friend. R. H.; Gelsen, O. M.; Holmes, A. B.; Kraft, A.; Martens, J. H. F.; Pichler, K. *Adv. Mater.* **1993**, *5*, 40;
12. Gibson, H. W.; Pochan, J. M. *Macromolecules* **1982**, *15*, 242.
13. Müller, P The Chemistry of ethers, crown ethers, hydroxy groups and their sulfur analogues, Part 1, Chapter 12, Patai, S. editor, **1980**, J. Wiley & Sons Ltd., NY.
14. Zhang, C.; Braun, D.; Heeger, A. J. *J. Appl. Phys.* **1993**, *73(10)*, 5177.
15. Katz, H. E.; Shane, S. F.; Wilson, W. L.; Schilling, M. L.; Ungashe, S.; submitted for publication.