Poly(*p*-phenylene vinylene) Prepared by Chemical Vapor Deposition: Influence of Monomer Selection and Reaction Conditions on Film Composition and Luminescence Properties

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ABSTRACT: The influence of reaction conditions and monomer selection on the resulting film composition and luminescence properties of poly(*p*-phenylene vinylene) (PPV) prepared by chemical vapor deposition is investigated. Greater aliphatic hydrocarbon incorporation into the polymer is observed when α,α′-dibromo-*p*-xylene is used as the starting monomer, as compared to α,α′-dichloro-*p*-xylene. This difference has implications for the peak photoluminescence output of the resulting PPV films, with the Br-PPV shifted to higher energies compared to Cl-PPV. From X-ray photoelectron spectroscopy, temperature-dependent infrared spectroscopy, and Raman spectroscopy, the reaction pathway for aliphatic hydrocarbon incorporation into the polymer chain is determined to be fragmentation of the monomer during the pyrolysis step.

Introduction

Conjugated polymers that exhibit electroluminescence, such as poly(*p*-phenylene vinylene) (PPV) and its derivatives, are attractive materials for use as the active element in light emitting diodes[1] (LEDs) and optically pumped lasers[2,3] due to their excellent mechanical properties and ease of processing compared to inorganic semiconductors. In addition, the peak emission color from this class of organic semiconductors can readily be tuned across the visible spectrum through chemical modification of the polymer backbone with spacer units and/or side chains, which effect the conjugation length and band gap of the polymer. Thin films of PPV are usually incorporated into devices by processing a sulfonium-based polyelectrolyte precursor polymer from solution, followed by a thermal conversion step. This method can have problems of side reactions with solvents or residual oxygen during polymer synthesis and thermal conversion, which leads to the incorporation of luminescence-quenching oxidative defects into the polymer.[4,5] An alternative, less-developed synthesis method for processing PPV is fabrication by chemical vapor deposition (CVD) of *p*-xylene derivatives.[6,7] CVD of PPV would have the advantage of elimination of side reactions with solvents and oxygen during film fabrication, as well as the potential to control the architecture and composition of the polymer layer on the molecular level. In our ongoing research of CVD of PPV, we have demonstrated facile, highly reproducible synthesis of unoxidized polymer,[8] and incorporated the films into single layer devices that exhibit low turn-on voltages and good brightnesses.[9]

The CVD process for fabrication of PPV is similar to that used for vapor-phase preparation of parylene.[10] In fact, α,α′-dihalo-*p*-xylene, the monomer most often used for CVD of PPV, can also be used to synthesize parylene if the pyrolysis is carried out in the presence of a metal promoter such as copper turnings or mossy zinc.[11,12] CVD of PPV has also been demonstrated from α,α-dihalo-*p*-xylenes[13] and 1,9-dihalo[2.2]paracyclophanes,[7] which are analogues of typical monomers used for vapor processing of parylene. However, the effect of monomer choice and deposition conditions on the resulting PPV polymer film composition and luminescence properties is not well understood. In particular, aliphatic hydrocarbon incorporation into the PPV polymer backbone is consistently observed with the CVD process. This is an important concern, since the additional sp^3-hybridized CH$_2$ segments interrupt the conjugated π-bond structure of the polymer backbone, which can potentially influence the energy band gap and peak emission wavelength of the film. It has been suggested that these hydrocarbon segments originate from incorporation of *p*-xylylene, generated from side reactions of the monomer pyrolysis, to form parylene-like segments in the polymer chain.[13] However, the presence of *p*-xylylene as a product of α,α′-dihalo-*p*-xylene pyrolysis *in the absence of metal promoters* has not been detected directly. In one study, less aliphatic hydrocarbon incorporation was observed when unsymmetrically substituted α,α-dihalo-*p*-xylene, which should not be able to form *p*-xylylene during pyrolysis, was used as the starting monomer, as compared to the analogous symmetrically substituted monomer.[13] However, the tendency of these two compounds to undergo alternative side reactions such as fragmentation at the relatively high pyrolysis temperatures used was not investigated. It is not unreasonable to expect the dihalo-*p*-xylenes to undergo fragmentation reactions at the pyrolysis temperatures of 600−900 °C typically used for CVD of PPV. Fragmentation of *p*-xylene has been observed in vapor-phase synthesis of parylene, due to the high furnace temperatures required to convert the starting monomer to *p*-xylylene.[10,14] The significant extent to which the fragmentation reaction occurs motivated the introduction of [2.2]paracyclophanes[15] and α,α′-dibromo-*p*-xylenes (used in conjunction with a metal promoter[11,12]) as monomers for CVD of parylene, since both of these compounds can be pyrolyzed to *p*-xylylene at lower temperatures, resulting in fewer side reactions.

In this report, we present an investigation of the influence of CVD monomer choice and growth conditions

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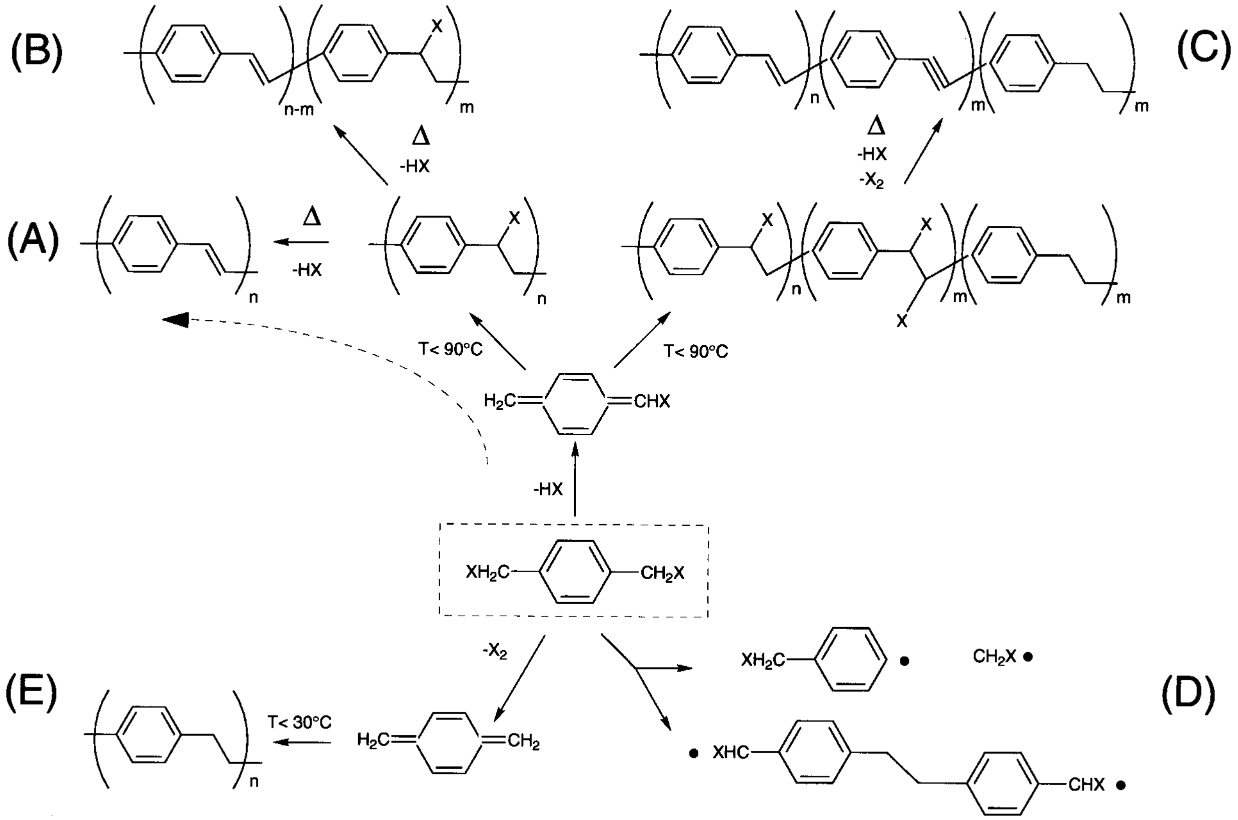
Scheme 1. Pathways for (A) Pyrolysis of α,α′-Dihalo-*p*-xylene To Form Pristine PPV (Highlighted by Dashed Arrow), and Aliphatic Hydrocarbon Incorporation into CVD PPV by (B) Incomplete Conversion of Halogenated Precursor Polymer, (C) Misalignment of Halo-*p*-xylylene during Polymerization, (D) Incorporation of Fragmentation or Dimerization Products of Monomer Pyrolysis, and (E) Incorporation of *p*-Xylylene (X = Cl, Br)



on the resulting PPV polymer layer composition and luminescence properties. This is achieved by varying the temperatures of the deposition surface and furnace during film synthesis. Several possible side reactions of the CVD monomer during pyrolysis and deposition are considered, and the source of aliphatic hydrocarbon incorporation into the polymer chain is determined. Our study focuses on α,α′-dihalo-*p*-xylenes as starting monomers for the CVD process, since these materials are readily available commercially. The results of this work provide insights into the optimal reaction conditions for PPV deposition, as well as future design of CVD monomers and polymers for tuning the peak emission wavelength of the luminescent polymer film.

Experimental Section

Materials. Both α,α′-dichloro-*p*-xylene and α,α′-dibromo-*p*-xylene (97%) were purchased from Aldrich and used without further purification. Typical deposition surfaces used were silicon metallized with 2000 Å of aluminum.

Polymer Chemical Vapor Deposition. The system used for fabrication of thin films of PPV by CVD has been described previously.[8] Typical deposition rates were 2−3 Å/s, at a pressure of 0.05 Torr. For film growth above room temperature, the temperature of the sample surface was controlled by radiative heating from the chamber walls. For deposition below room temperature, the sample temperature was controlled by cooling the sample holder with liquid nitrogen. Once the precursor polymer had been deposited, the samples were transferred to a separate chamber where they were converted at 250−270 °C and 10^{-6} Torr for several hours.

Film Composition and Optical Characterization. All infrared reflection absorption spectroscopy (IRRAS) studies were conducted with a Nicolet 800 spectrometer on samples approximately 1000 Å in thickness. Photoluminescence (PL) spectra were measured with a SPEX fluorimeter at an excitation wavelength of 350 nm. Raman spectroscopy was performed with a 647.1-nm krypton ion laser line on aluminized silicon surfaces coated with approximately 3000 Å of polymer. The poly(2,5-dibutoxy-1,4-phenylene acetylene) (DBuOPPA) used as a standard for the Raman studies was provided by Z. V. Vardeny of the University of Utah, and was prepared into thin films by spin coating from tetrahydrofuran (THF). The total Raman sample acquisition times for the standard and CVD polymer were 1 and 1600 s, respectively. X-ray photoelectron spectroscopy (XPS) was performed using a monochromatic Al Kα (1486.6 eV) radiation source and a chamber with a base pressure of 10^{-10} Torr.

Results and Discussion

Ideal pyrolysis of α,α′-dihalo-*p*-xylene to form a halogenated precursor polymer to PPV, which is subsequently converted to the fully conjugated polymer, is shown in Scheme 1A (note that this and the following schemes are not elementary reactions). Since the structures of the UV−vis, IRRAS, and PL spectra of films prepared by this method have been shown to be predominantly characteristic of PPV, Scheme 1A is the primary reaction taking place during pyrolysis and polymer deposition.[6−8] To illustrate the effect of monomer selection on final film composition and luminescence properties, the IRRAS spectra of CVD PPV prepared from α,α′-dichloro-*p*-xylene (Cl-PPV) and α,α′-dibromo-*p*-xylene (Br-PPV) at a pyrolysis temperature of 675 °C and a deposition temperature of 25 °C are shown in Figure 1. Both films exhibit residual CH_2 stretching at 2950 cm^{-1} after thermal conversion, with the effect more pronounced in the Br-PPV spectrum. This difference has implications for the PL output from

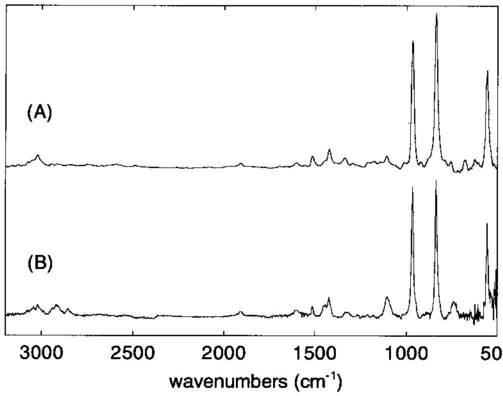


Figure 1. IRRAS spectra of (A) Cl-PPV and (B) Br-PPV prepared at a pyrolysis temperature of 675 °C and surface deposition temperature of 25 °C.

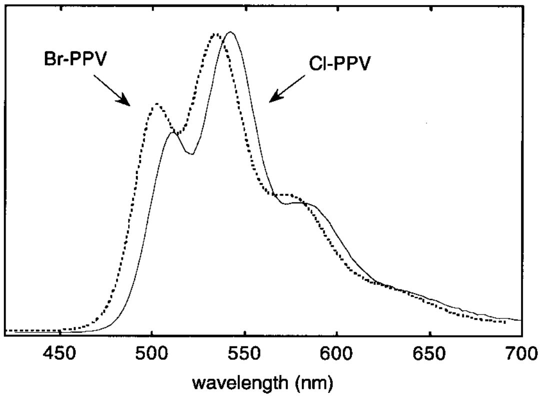


Figure 2. Photoluminescence spectra from the Br-PPV (dashed line) and Cl-PPV (solid line) films.

the two polymers, as shown in Figure 2. The peak PL from the Br-PPV film is 533 nm, which is blue-shifted compared to the Cl-PPV peak PL of 542 nm. This shift to higher energies in the Br-PPV polymer is consistent with the enhanced hydrocarbon incorporation observed with IRRAS, since the additional aliphatic segments would interrupt the delocalized structure of the π-bonded electrons more frequently, leading to a shorter overall conjugation length and larger band gap in the polymer film. Therefore, the choice of α,α'-dihalo-*p*-xylene CVD monomer can influence the film composition and, consequently, the luminescence properties of the deposited polymer.

Since one of the potential advantages of polymer CVD is control of the film composition on the molecular level, it is important to understand the underlying mechanism of the CH_2 incorporation into the polymer layer. Side reactions during the monomer pyrolysis, polymer deposition, or thermal conversion steps could all lead to the incorporation of aliphatic hydrocarbon segments into the polymer backbone. Of these three stages, the simplest mechanism for CH_2 incorporation is incomplete conversion of the precursor polymer to PPV, as shown in Scheme 1B. This would result in residual halogenated aliphatic segments in the final polymer film. To test for the presence of these segments in the converted polymer layer, the halogen content of the film was measured with XPS. This analysis showed 1.5 wt % residual chlorine in the Cl-PPV, but only trace amounts of bromine in the Br-PPV. Since greater aliphatic hydrocarbon stretching was observed in the IRRAS spectrum of Br-PPV compared to Cl-PPV (Figure 1), the XPS data suggests that the mechanism shown in Scheme 1B is not the source of aliphatic hydrocarbon incorporation into the polymer backbone. This was further confirmed by the observation that the final CH_2 signal in the IRRAS spectra of both polymers does not diminish at higher conversion temperatures or longer conversion times. Thus, we conclude that incomplete conversion of the polymer film is not a pathway for incorporation of the aliphatic hydrocarbon segments into the polymer chain, and that the source of the residual CH_2 segments must be side reactions that occur during the deposition or pyrolysis steps.

One possible side reaction that could occur during condensation polymerization of the CVD monomer is shown in Scheme 1C, in which some fraction of the halo-*p*-xylylene pyrolysis product does not orient head-to-tail before polymerization. The deposited copolymer would then consist of the precursor polymer to PPV, as well as segments of parylene and a precursor polymer of poly(*p*-phenylene acetlyene) (PPA).[16] If active, this pathway would incorporate aliphatic segments *as well as* carbon−carbon triple bonds into the polymer backbone after thermal conversion. Consequently, the significance of this mechanism can be determined by testing for the presence of carbon−carbon triple bonds in the polymer film. Although selection rules do not allow symmetrically substituted carbon−carbon triple bonds to be detected with infrared spectroscopy, the group is active in Raman spectroscopy. Resonance Raman spectroscopy was performed on both the Br-PPV and Cl-PPV films, and the spectra were compared to that of poly(2,5-dibutoxy-1,4-phenylene acetylene) (DBuOPPA) in the region of the carbon−carbon triple bond Raman peak. This analysis showed that neither of the CVD polymer films exhibited a significant carbon−carbon triple bond signal. Therefore, we conclude that misalignment of halo-*p*-xylene during condensation polymerization of the CVD monomer is not a significant source of aliphatic hydrocarbon incorporation into the polymer backbone.

Pathways D and E of Scheme 1 represent side reactions that could occur simultaneously with Scheme 1A during monomer pyrolysis, to form copolymers of PPV and the side reaction byproducts after thermal conversion. In Scheme 1D, the starting monomer fragments into hydrocarbon radicals or recombines in the gas phase to form species such as biradical dimers, which can then incorporate into the polymer chain. In Scheme 1E, chlorine or bromine gas is eliminated instead of hydrochloric or hydrobromic acid during pyrolysis to form *p*-xylylene, the reactive monomer used for CVD of parylene. It has been shown that Scheme 1E does occur with high yield if a metal promoter is placed in the pyrolysis tube,[11] but it is unknown if the reaction would occur to a lesser extent in the absence of such a promoter. However Scheme 1E would not be a significant pathway for aliphatic hydrocarbon incorporation at substrate temperatures above the *p*-xylylene critical condensation temperature of 30 °C.[15] In contrast, halo-*p*-xylylene would continue to deposit on the surface until its critical condensation temperature of approximately 85 °C was reached.[8] Therefore, by depositing the polymer at temperatures above and below 30 °C and comparing the amount of aliphatic hydrocarbon incorporation into the film, we were able to determine the significance of Scheme 1E during monomer pyrolysis. Figures 3 and 4 show the IRRAS spectra of Br-PPV and Cl-PPV films deposited above and below

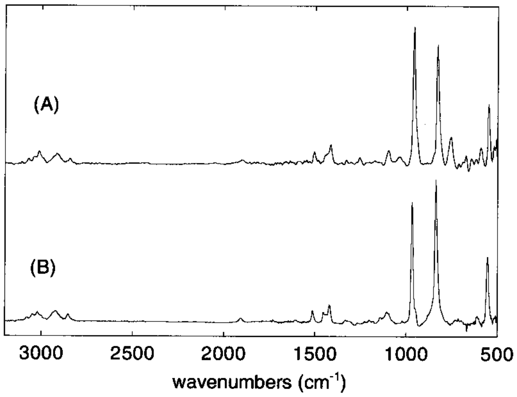


Figure 3. IRRAS spectra of Br-PPV prepared at surface deposition temperatures above and below the critical condensation temperature of *p*-xylylene: (A) $T_{\text{deposit}} = 38$ °C; and (B) $T_{\text{deposit}} = 9$ °C.

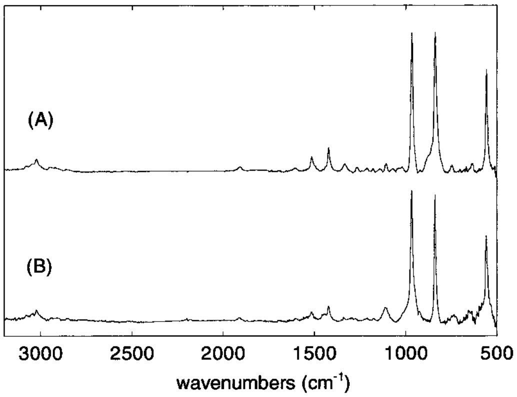


Figure 4. IRRAS spectra of Cl-PPV prepared at surface deposition temperatures above and below the critical condensation temperature of *p*-xylylene: (A) $T_{\text{deposit}} = 60$ °C; and (B) $T_{\text{deposit}} = 13$ °C.

the critical condensation temperature of *p*-xylene. Although both polymers show residual aliphatic hydrocarbon content at temperatures above 30 °C, the signal is not enhanced in the IRRAS spectra at lower deposition temperatures. In addition, the PL spectra of these films (not shown) do not exhibit a shift in peak luminescence as a function of temperature. From this we conclude that simultaneous formation and copolymerization of *p*-xylylene with halo-*p*-xylene is not a significant reaction pathway during CVD PPV deposition.

It is therefore likely that incorporation of fragmentation or dimerization byproducts of monomer pyrolysis into the polymer chain (Scheme 1D) is the source of residual aliphatic hydrocarbon segments in the CVD polymers. The fact that Br-PPV exhibits more hydrocarbon incorporation compared to Cl-PPV most likely reflects a difference in the degree of fragmentation of the two monomers during pyrolysis, which is consistent with the observation that a greater amount of soot is formed on the furnace tube during pyrolysis of α,α′-dibromo-*p*-xylene compared to α,α′-dichloro-*p*-xylene.[6] To confirm the significance of the fragmentation reaction pathway, the effect of pyrolysis temperature on the amount of hydrocarbon incorporation into the polymer film was investigated. Figure 5 shows the relative IRRAS peak area of the CH_2 signal in Cl-PPV, deposited at a surface temperature of 60 °C, as a function of furnace temperature. These data clearly show an enhancement in CH_2 incorporation at higher pyrolysis temperatures. The PL spectra of Cl-PPV polymer fabricated at the highest pyrolysis temperature of 950 °C (not shown) exhibited a significant blue shift in peak luminescence (533 nm) compared to polymer prepared at lower furnace temperatures. This type of shift in peak PL with increasing CH_2 incorporation is analogous to the effect observed in the Br-PPV. However, the intensity of the PL spectra from the high pyrolysis temperature sample was visibly lower than that from samples of Cl-PPV and Br-PPV prepared at lower pyrolysis temperatures. The cause for such quenching in photoluminescence is not clear at present, but it does highlight the significance of monomer and furnace temperature selection on CVD polymer quality.

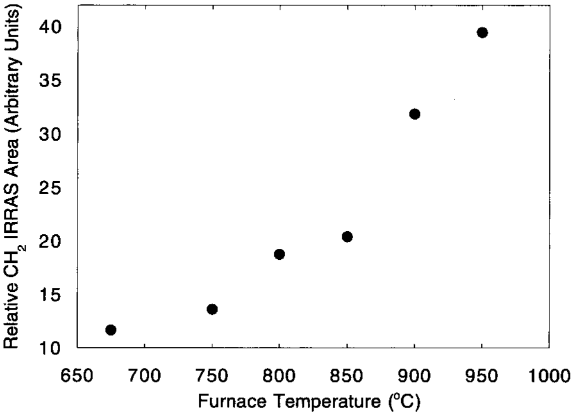


Figure 5. CH_2 IRRAS peak area as a function of furnace temperature for Cl-PPV. The CH_2 signal was normalized to the intensity of the symmetrically substituted ring mode at 1420 cm^{-1} to account for small variations in sample thicknesses.

Conclusions

The influence of pyrolysis conditions and monomer choice on the resulting film composition and luminescence properties of poly(*p*-phenylene vinylene) (PPV) prepared by chemical vapor deposition was investigated. Greater aliphatic hydrocarbon incorporation into the polymer was observed with α,α′-dibromo-*p*-xylenes compared to α,α′-dichloro-*p*-xylenes. This difference was manifested in the peak photoluminescence output of the resulting PPV films, with the Br-PPV shifted to higher energies compared to Cl-PPV. From X-ray photoelectron spectroscopy, temperature-dependent infrared spectroscopy, and Raman spectroscopy, the reaction pathway for aliphatic hydrocarbon incorporation into the polymer chain was determined to be incorporation of fragmentation byproducts of the CVD monomer pyrolysis.

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