Polymer Bulletin 45, 129-135 (2000)

Polymer Bulletin

Synthesis of substituted poly (arylene vinylene) films by vapor deposition polymerization

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Received: 18 May 2000/Revised version: 21 July 2000/Accepted: 28 July 2000

Summary

An efficient method for the synthesis of PPV based polymers, poly (2,5-dimethyl-1,4-phenylene vinylene) (DMe-PPV) and poly (2,5-dimethoxy-1,4-phenylene vinylene) (DOMe-PPV) were developed using 2,5-dimethyl-1,4-bis (chloromethyl) benzene and 2,5-dimethoxy 1,4-bis (chloromethyl) benzene via vapor phase pyrolysis and followed by vapor deposition polymerization. The structure of polymer films were confirmed by FT-IR, solid state NMR and elemental analysis. Thermal gravimetry analysis reveals that the precursor polymer films form a conjugated polymer after thermal conversion at 250°C. The optical and electrical properties of the polymer films were investigated by UV-Vis absorption and photoluminescence spectroscopies. Electroluminescent devices were fabricated using these polymers.

Introduction

Since the first discovery of electroluminescence (EL) in poly (1,4-phenylene vinylene) (PPV) by Burroughes (1) in 1990, PPV based polymers have attracted great attention to scientists. But, the synthesis, analysis and application of these materials are limited by their solubility. In order to overcome this problem various substituted PPV derivatives were synthesized using different kinds of precursor routes(2-4) and solution-processible poly(phenylene vinylene)s were reported (5-7). Generally PPV films are incorporated into electronic devices by processing different precursor polymers from solution and converted to the final conjugated form through thermal elimination. Therefore the contamination and residual oxygen in solvents may cause oxidation of vinylene groups then forming the carbonyl defects in polymer films. These defects shorten the conjugation length and influence the polymer conductivity, as well as optical properties. However, it should be pointed out that, almost all soluble PPV derivatives used in multi-layer EL devices are processed from solvents and that may cause swelling or dissolution of the already deposited layer and forming space charge at the interfaces between polymer layers.

In this communication, by circumventing the use of solvent, we report a more efficient and clean treatment condition for the fabrication of substituted poly (arylene vinylene) light emitting devices. We modified the traditional CVD method first used by Gorham (8-12). Attention was focused on the synthesis of poly (2,5-dimethyl-1,4-phenylene vinylene) (DMe-PPV) and poly (2,5-dimethoxy-1,4-phenylene vinylene) (DOMe-PPV) films

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from 2,5-dimethyl-1,4-bis(chloromethyl)benzene and 2,5-dimethoxy-1,4-bis(chloromethyl) benzene via vapor phase pyrolysis (FVP) and followed by vapor deposition polymerization (VDP) . Different from traditional precursor routes, uniform pinhole free thin film was obtained by vapor deposition polymerization. In addition, contamination of polymer films by impurities in the solvent was excluded by solvent free reaction conditions. Other advantages over the other methods are, VDP process is compatible with traditional inorganic semiconductor technology, and one can integrate these technologies for organic and inorganic materials in hybrid devices.

Experimental

Material

2,5-dimethyl-1,4-bis (chloromethyl) benzene (1A) (Lancaster) was further purified by sublimation under reduced pressure. The 2,5-dimethoxy-1,4-bis (chloromethyl) benzene (2A) was synthesized using a modified literature procedure (13). A stirred solution of 1,4-dimethoxy benzene (5.0 g, 36 mmol) in 150 ml dioxane was cooled to 0°C and treated with 30 ml of concentrated HCl and subsequently with 4 g of (144 mmol) formaldehyde. The reaction mixture was refluxed overnight, cooled, decanted the supernatant liquid, and the waxy residue was washed twice with aqueous sodium hydroxide (5%). To this residue 100 ml of hexane was added, warmed and filtered when it was hot. The filtrate was cooled in ice-bath and the white precipitate formed was filtered, washed with hexane and finally purified by sublimation. Yield: 6.1g (72.1%). mp. 117°C.

Vapor Deposition Polymerization (VDP)

The apparatus for VDP process is shown in Fig. 1. The system was slightly modified from the conventional one used for CVD by reducing the length and changing the pathway from horizontal to vertical to avoid the carbonization ashes. The system consists of a vaporization chamber, pyrolysis zone, deposition zone, cold trap, and a high vacuum pump. The pyrolysis zone is heated by a tube furnace. In synthesizing polymer films, de-gased, dried argon gas controlled by a mass-flow controller (MFC) was used as a carrier

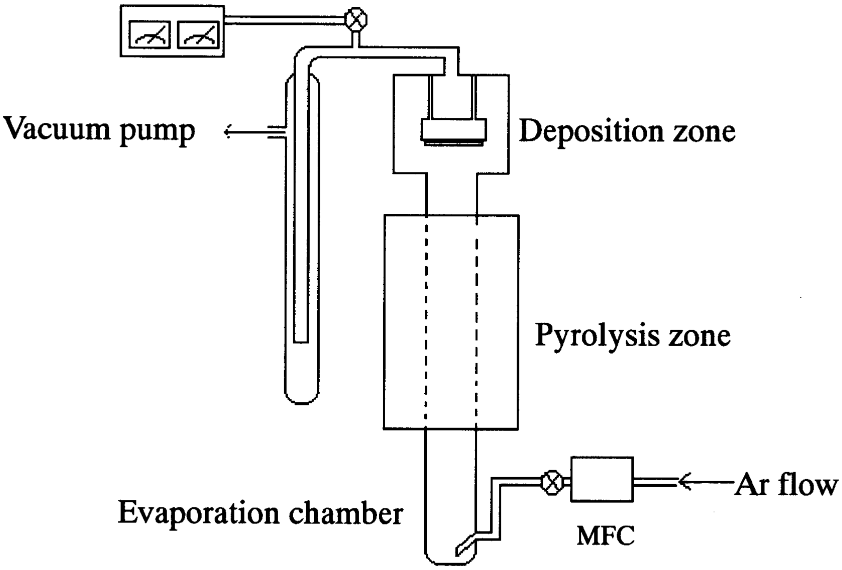
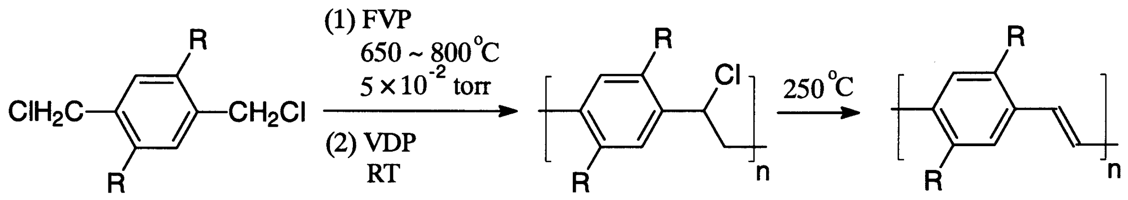


Figure 1. Schematic diagram representing the apparatus for the Vapor Deposition Polymerization (VDP)



1A : R = CH_3
2A : R = OCH_3

1P : R = CH_3
2P : R = OCH_3

Scheme 1

gas. The substrate is mounted on a temperature controlled glass holder, and is oriented perpendicular to the argon gas flow so that the polymerization can take place by the condensation of reactive intermediates on the substrate. When the temperature of the pyrolysis zone, which was slowly heated by tube furnace reaches around 650°C, 1g of monomer (1A or 2A) already placed in vaporization section was heated to their respective sublimation temperature by oil bath. The monomer was converted to the reactive intermediates between pyrolysis zone, and deposited on the preheated substrate to form a yellowish precursor polymer film. The substrate temperature was kept around 90°C to collect the deposition of the precursor polymer film and the whole system was operated at low pressure. The conversion of the precursor film to conjugated polymer was done by annealing it at 250°C (Scheme 1).

Device fabrication

ITO glass sheets with a resistance of 20Ω/□ were purchased from Merck Display Technologies Ltd. and cut into 3x3 cm squares. Polymer 1P was deposited on the ITO glass using the VDP method for single layer device, and the top aluminum electrode was then evaporated over emission layer 1P under a pressure below 10^{-6} torr at a rate of 3 nms^{-1} and thickness of the film was controlled between 100-150 nm.

Measurements

The infrared reflection absorption spectroscopy(IRRAS)studies were complemented with a Nicolet 520 FT-IR spectrometer. UV-Vis and PL spectra of the precursor polymer and final polymer films were obtained from Shimadzu UV-1601 spectrophotometer and RF-5301PC spectrofluorophotometer respectively. Thermogravimetric analysis (TGA) was performed using a Seiko system. 5 ~ 10 mg precursor polymer and final polymer were analyzed between 30 and 650°C under nitrogen with a heating rate of 10°C min^{-1}.

Results and discussion

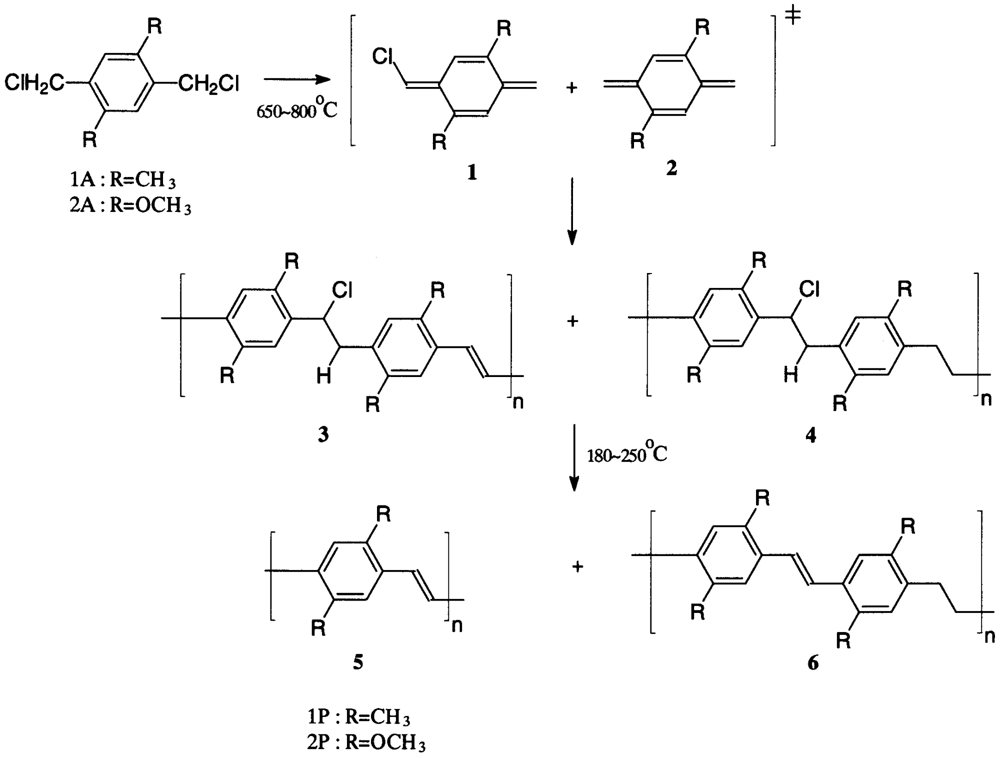
Investigations on evaporation, pyrolysis and polymerization temperatures have been carried out to determine the optimum processing temperature. The best pyrolysis temperatures for these reactions were determined from the thin film morphology (SEM), photoluminescence intensity and elemental analysis. The result reveals that optimal evaporation temperature for monomer 1A is 70 °C under $5x10^{-2}$ torr and the best pyrolysis temperature is 750°C. Little carbonaceous deposits were found in the heating section of the quartz piping of the oven during pyrolysis process of 1A. For 2A lower pyrolysis temperature 600-650°C and a evaporation temperature of 90 °C under $5x10^{-2}$

torr were observed as the best one. At the same time appreciable amounts of carbonaceous residues were also observed in the oven. Under typical conditions for both 1A and 2A, a film growth rate of 1nm/min was observed when the substrate temperature was kept at 90 °C. This growth rate allows the formation of a practical film thickness (100 nm) for polymer LEDs.

Characterization of conjugated polymers DMe-PPV (1P) and DOMe-PPV(2P)

The precursor polymer had a strong absorption peak at 690 cm^{-1} attributed to the non-eliminated chlorine (C-Cl) in the polymer chain. This absorption peak gradually disappeared during heat treatment under argon and a new peak emerged at 963 cm^{-1} which was assigned to the out of plane bending of the trans-vinylene C=C–H after annealing at 250°C and a peak around 2950 cm^{-1} assigned to the aliphatic CH declined and a trans vinyl group grew at 3050 cm^{-1}. The same trend was observed for the DOMe-PPV polymer films. All these data concretely supports the formation of the double bond. Interestingly no carbonyl peak was observed in our process.

Scheme 2 represents the proposed mechanistic pathway for the synthesis of polymers. In the recent polymerization mechanistic study by Munzel (14) for these kind of polymerization, the existence of an reactive intermediate of quinoid structure was proposed. In our scheme also halogenated quinodimethane **1** was proposed as the main quinoid species, which can be formed from 1A or 2A under the reaction conditions and in the similar way dehalogenation reaction may also occur in both monomers, providing a quinodimethane intermediate **2**. The formation of **6** as a side product were also observed with both monomers. Elemental analysis of the precursor polymer 1P film obtained at different temperatures were investigated and found that there are two species **3** and **4** in



Scheme 2. Proposed mechanism for DMe-PPV/DOMe-PPV polymerization

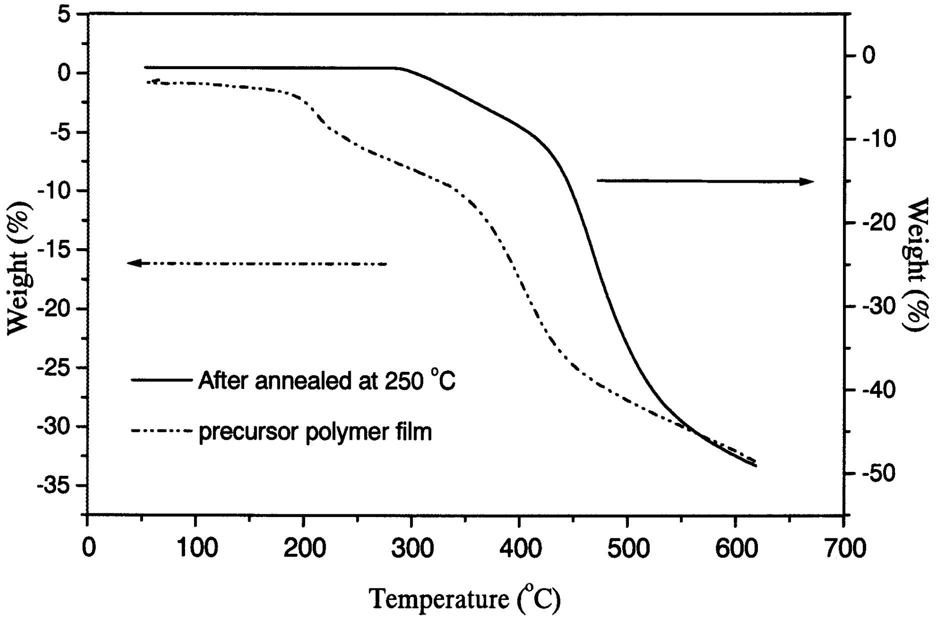


Figure 2. The thermal stability of DMe-PPV film in Nitrogen

scheme 2 and it was also observed that major product was **5** and minor was **6** under the pyrolysis temperature kept at 750°C.

Thermal elimination to polyconjugated polymers

Thermal analysis of the elimination reactions of the precursor polymers were studied by thermogravimetry (TG) with a heating rate of 10°C/min and the TG thermograms are shown in Fig. 2. Appreciable weight loss was found from 200°C to 250°C attributed to the dehalogenation of the precursor polymer. The total weight loss during the thermal elimination / conversion process was found to be 15 % (expected weight loss 22 %). This may be due to the presence of some conjugated parts in the precursor polymer films. From the Fig. 2 the thermal decomposition temperature for precursor polymer and the same polymer annealed at 250°C were found to be same around 400°C.

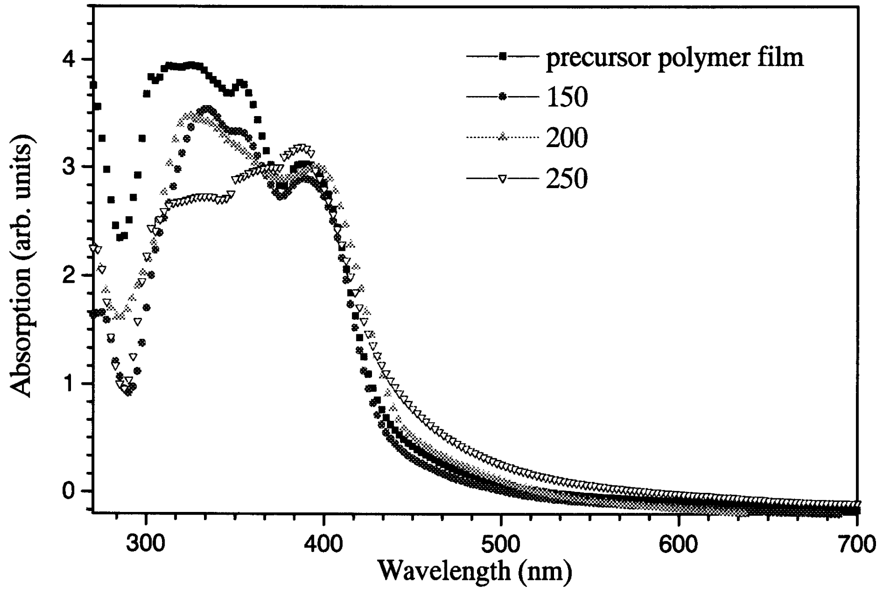


Figure 3. The optical absorption spectra of DMe-PPV thermally converted at different conversion temperatures

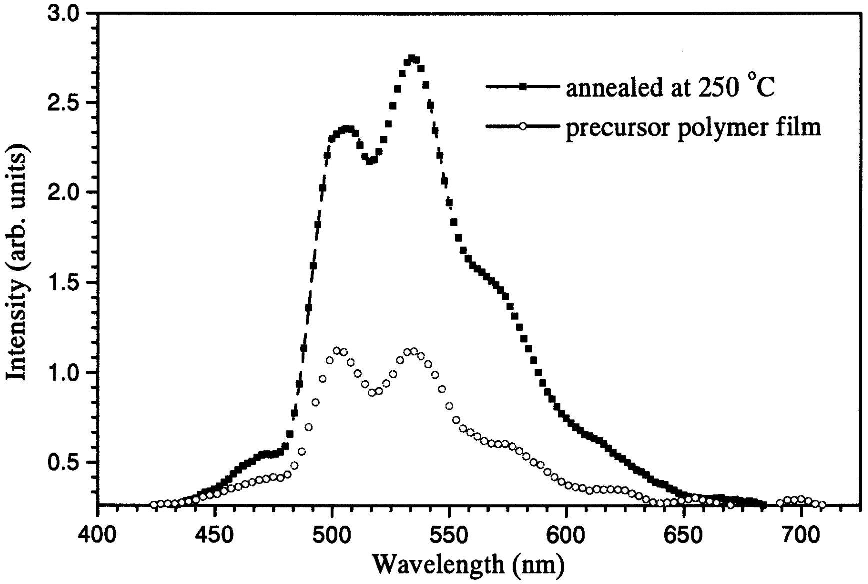


Figure 4. The emission spectra of DMe-PPV precursor film and thermally converted at 250 °C

Optical and electronic properties of poly-arylenevinylene films

The colors of the precursor films of DMe-PPV and DOMe-PPV were light yellow and orange, respectively. Fig. 3 shows the UV spectra of the precursor film and final polymer film after the heat treatment at different temperatures under nitrogen flow. The precursor has shown two absorption peaks at 324 nm and 396 nm. After the heat treatment at 250°C for 10 hrs, the peak centered at 324 nm changes into a broad peak at 396 nm with initial slope starting at 460 nm (2.2 eV).

Fig. 4 compares the photoluminescence spectra for DMe-PPV before heat treatment and after 250°C conversion temperature. It was observed that polymers with non-conjugated segments have a zero-photon peak at approximately 507 nm and the one-photon peak at 534 nm. After annealed, with increasing conjugation, there is a considerable enhancement in oscillator strength in the green, seen in the increased strength of the one-photon peak.

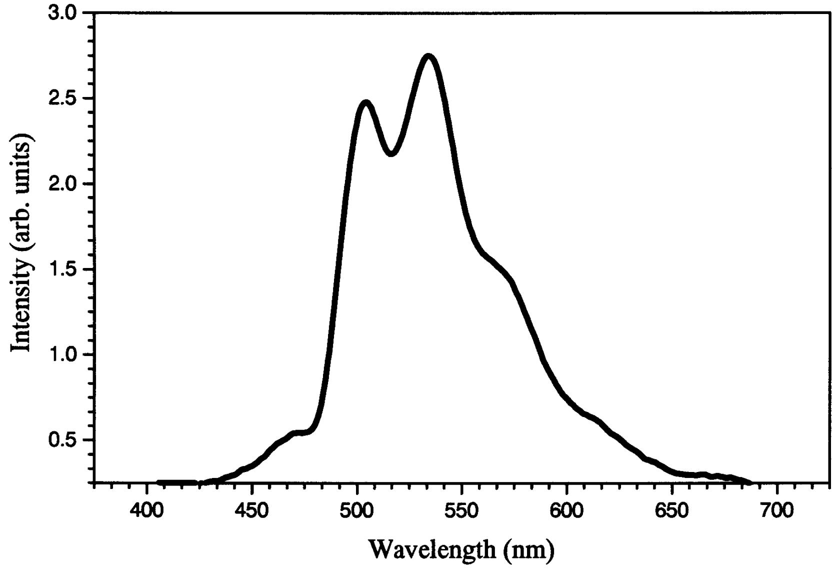


Figure 5. The EL spectra of ITO/DMe-PPV/Al device

In Fig. 5 the emission spectrum of a ITO/DMe-PPV/Al device is presented and it was noticed that the maximum of the emission is slightly red shifted in comparison with PL spectra of 1P. The optical and electrical properties of the polymer device will be discussed elsewhere.

Conclusion

Avoiding the use of solvent, a practical and an efficient vapor deposition polymerization method was developed for the first time for the disubstituted PPV derivatives. This method can be extended to other substituted PPV based polymers. Parameters for the evaporation, pyrolysis and polymerization temperatures were optimized for the monomers 1A and 2A. Dimethyl substituted monomer provided good results when compared to the dimethoxy substituents. Consequently electroluminescent devices were fabricated using 1P as the luminescent polymer and it emitted a bright green light. No carbonyl defect was found in the polymer film 1P and 2P. So our method can be compared to any of the best methods available in the literature due to very thin film forming properties of polymer, non-usage of solvents and it paves a way for the fabrication of multi-layer polymer LEDs.

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