The Study of the Influence of Deposition Method on Electrical and Optical Properties of PPV Polymer with High Glass Temperature

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Abstract. The paper is focused on comparison of electrical and optical properties of thin layers of copolymer with high glass transition temperature Tg-PPV (poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene], poly[2-4′-(3″,7″-dimethyloctyloxy)-1′,4′-phenyl]-1,4-phenylenevinylene] and poly[2-3″-(3″,7″-dimethyloctyloxy)-1′,4′-phenyl]-1,4-phenylenevinylene)) prepared by two different deposition methods: by spin-coating and by electrophoretic deposition. We found several differences in absorption and emission spectra using those two preparation techniques. On the other hand, the photoelectrical properties were similar.

1. Introduction

Study of organic electronics opens the way to develop new electronic applications, which are not achievable using classical semiconducting inorganic materials as silicon, gallium arsenide, etc. Thin layers of organic semiconductors could be easily deposited by simple “wet” techniques. Key role for the control of the film structure and properties plays the choice of the deposition method. This paper is focused on a comparison of two “wet” deposition methods of organic functional materials. One is the standard laboratory deposition method spin-coating (SC) and second method is the electrophoretic deposition (EPD).

While SC is a method for deposition from solution, EPD works with colloidal particles dispersed in poor solvents of deposed material. The suspension is prepared by precipitation of deposed material solution by adding poor solvents. During the process of particle formation they are charged due to the requirement that an electrochemical equilibrium with solvent has to be achieved. Then the charged particles are deposed on the electrode by applying electrical field. Whole mechanism of the EPD is not completely known yet due to the complexity of the process, but it is used in the industry for various applications [1].

In comparison with SC [2], [3] the properties of the EPD layers are more strongly influenced by the preparation conditions. On the other hand EPD allows controlled preparation of nanostructured layers [4], and a formation of multilayer stacks from materials soluble in the same solvent [5]. In comparison
with SC the EPD uses more effectively the deposed material, but consumes more of high quality solvents.

This work is focused on the study of thin layer preparation of polymeric materials for organic electronics. Poly(p-phenylenevinylene) derivatives are one group of polymeric materials with a potential application in the organic electronics. One of the well-known and described derivate is the MDMO-PPV (poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene]), which serves as model electron donor material for organic electronics. Structure of MDMO-PPV is shown on figure 1. MDMO-PPV has relatively low glass transition temperature $T_g = 45\, ^\circ C$ [6], which influences negatively the thermal stability of the active layer. Triblock copolymer of poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene], poly[2-[4′-(3′,7′-dimethyloctyloxy)-1′,4′-phenyl]-1,4-phenylenevinylene] and poly[2-[3′-(3′,7′-dimethyloctyloxy)-1′,4′-phenyl]-1,4-phenylenevinylene)], denoted here as Tg-PPV (see figure 1) with $T_g = 138\, ^\circ C$ [6, 7] seems to be a more suitable alternative.

Tg-PPV is generally synthesized for use in the organic light emitting diodes. It is distributed by Merck KGaA, Darmstadt, Germany under the commercial name PDO-123 [8].

Figure 1. Structure of the used here high Tg-PPV and more studied in the literature MDMO-PPV derivate.

2. Experimental
Films of Tg-PPV were prepared on glass substrates commercially covered with ITO (indium thin oxide) electrode (Sigma–Aldrich Co., Steinheim, Germany).

SC thin layers of polymer were deposed from chlorobenzene solution of concentration 6 g/l of Tg-PPV. The deposition was performed at rotation speed of 1000 RPM for a time of 1 min on a spin-coater KW-4A (Chemat Technology, Inc., CA, U.S.A.).

EPD was carried out from Tg-PPV suspension with a concentration of $7.74 \times 10^{-3}$ g/l. Suspension was prepared from solution of Tg-PPV in toluene by precipitation with acetonitrile. Optimal ratio of toluene and acetonitrile of 42.5 % was determined by light absorption measurements on Varian Cary 50 double-beam spectrometer. Deposition was realized under constant current condition in the range of 0.060 to 0.150 mA. Source of electrical current was Keithley 2410 Source Meter (Keithley Instruments Inc., Cleveland, OH, U.S.A.). The value of the current controls the rate of deposition. Time of deposition varied between 30 and 60 s and influenced the final film thickness.

Optical properties for quality assurance of thin layers and for suspension optimization were studied by a measurement of UV-VIS absorption spectra on Varian Cary Probe 50 UV–VIS spectrometer and fluorescence spectra on Horiba Jobin Yvon Fluorolog (Horiba Jobin Yvon S.A.S., Chilly Mazarin,
France). Liquid samples were measured in Hellma QS 10 mm quartz cuvette (Hellma GmbH, Mühlheim, Germany).

Thicknesses of layers were characterized by optical profilometer MicroProf FRT (Fries Research & Technology GmbH).

Samples for electrical characterization with semiconductor Tg-PPV thin layers were subsequently covered with aluminium electrodes by vacuum deposition. Deposition was realized in the deposition chamber U311B Tesla (Tesla, Opočno, Czech Republic).

The samples were electrically characterized in cryostat VPF-475 (Janis Research Company Inc., Wilmington, MA, U.S.A.) at 10⁻⁴ Pa at laboratory temperature by picocampermeter Keithley 6478. Current voltage characteristics were measured on samples both in dark and irradiated by LSH502 LOT Oriel xenon lamp with emission spectrum similar to the sun light (LOT-Oriel Co., Darmstadt, Germany). Intensity of the incident light of 1 mW·cm⁻² was controlled by irradiance meter X97 Gigahertz-Optik with radiometric detector head RW-3703-4 for UV-VIS range (Gigahertz-Optik GmbH, Tükenfeld, Germany).

3. Results and discussion

3.1. Optical study of suspension

A suspension concentration is a key parameter for optimal electrophoretic deposition. Suitable volume ratio of acetonitrile/toluene for suspension preparation was found by UV-VIS absorption spectrometry. Figure 2 A) shows absorption and emission spectra of Tg-PPV solution in toluene (0% acetonitrile) and after addition of 42 and 90 % volume ratio of acetonitrile. Noticeable bathochromic shift of absorption band from 476 nm to 494 nm with the increase of acetonitrile volume ratio was observed. The emission spectra behave similar, but they are more sensitive to acetonitrile addition. Bathochromic shift of emission maximum is from 549 nm to 590 nm. Generally the evaluation of the emission spectra is more difficult due to effects as fluorescence quenching, reabsorption of emitted light, changes in vibrational structure of spectra and others. On the other hand fluorescence spectra provide valuable additional information.

![Figure 2](image)

**Figure 2.** A) Absorption and emission spectra of toluene solution of Tg-PPV after addition of 0, 42 and 90 % volume ratio of acetonitrile. B) A dependence of absorption maxima position on the acetonitrile volume ratio w. Right axis is related to the first derivative of the curve. Maximum at 42.13 % of acetonitrile corresponds to the inflection point.

The position of the absorption maxima were precisely determined by taking the first derivative of the absorption spectra. The obtained values are plotted as a function of the acetonitrile volume ratio in
3.2. Optical study of thin layers
Absorption and emission spectra of Tg-PPV: solution in toluene; solution in chlorobenzene; toluene/acetonitrile suspension with 90% acetonitrile; thin EPD film produced from a toluene/acetonitrile suspension with 42.5% acetonitrile; thin SC films produced from a solution in chlorobenzene are presented in figure 3.

Figure 3. Comparison of absorption and emission spectra of Tg-PPV plot: A) solutions in chlorobenzene (Cb) and toluene (Tol) and thin layer prepared by SC, plot B) suspension prepared by addition of 90% volume acetronitrile (90% Acn) to a toluene solution, and thin SC and EPD layers.

Absorption spectra of chlorobenzene solution and thin film prepared by SC from chlorobenzene solution don’t have resolute vibrational structure. This effect is usually related to the disordered structure of polymer [9]. Both spectra showed the same position of absorption band, only thin layer absorption edge is 20 nm red shifted. This effect is related to the closer arrangement of polymer chains in the layer due to aggregation [9]. Emission spectrum of SC layer is found fully bathochromically shifted compared to the spectrum of chlorobenzene solution [10].

More differences in spectra taken from toluene solution, acetonitrile suspension and EPD layer are seen. EPD layer performs an absorption edge at 580 nm like suspension, prepared by adding of 90% volume of acetonitrile and like SC layer, but absorption maximum lies at 476 nm like in spectra, measured from solutions and SC layer. Emission spectrum of suspension and EPD layers are overlapped, only vibrational structure of spectrum is changed. Perhaps there was particularly preserved nanostructure of suspension present and particularly spill in uniform film [11]. Strict interpretation needs more investigations to be done. However, the spectra measured don’t indicate a degradation of the polymer after EPD, which may have been caused by electrical current during deposition.

3.3. Electrical study of thin layers
Several thicknesses of thin films were prepared by EPD. The aim was to prepare layers comparable to the 120 nm layer prepared by SC as a reference.

Figure 4 shows samples with best current voltages curves of SC and EPD layers. Layers were characterized in dark and under illumination with light of intensity 1 mW/cm². In dark, the EPD layers
were less conductive. The threshold voltage $V_T$, when current start strongly grow, for SC layers was around 1.1 V, whereas for SPD layers are located at much higher voltages (higher than 2 V); see figure 4. It is caused by an energy barrier for charge carries. Origin of barriers may be different: morphology of layer, bad adhesion of layers and other. Current voltage characteristics of EPD layers under illumination were on average comparable with those, taken from SC layers.

Figure 4. Comparison of current voltage characteristics measured on samples with SC and EPD layers.

Table 1. Average photovoltaic conversion parameters of three EPD layers with different thicknesses and one SC layer.

| sample | thickness (nm) | $j_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | $FF$ | $\mu$ (%) |
|--------|----------------|----------------------|--------------|------|------------|
| SP     | 120 ± 20       | $(1.2 \pm 0.7) \times 10^{-4}$ | 0.6 ± 0.2 | 0.22 ± 0.08 | $(1.8 \pm 0.3) \times 10^{-3}$ |
| EPD 1  | = 100          | $1.75 \times 10^{-4}$ | 0.52       | 0.22 | 2.02 $\times 10^{-3}$ |
| EPD 2  | 290 ± 80       | $(1.8 \pm 0.6) \times 10^{-4}$ | 0.57 ± 0.05 | 0.26 ± 0.03 | $(2.7 \pm 0.9) \times 10^{-3}$ |
| EPD 3  | 540 ± 80       | 0.09 $\times 10^{-4}$ | 0.59       | 0.21 | 0.11 $\times 10^{-3}$ |

Parameters as short current density $j_{SC}$, open circuit voltage $V_{OC}$, fill factor $FF$ and maximal photovoltaic efficiency $\mu$ were calculated from current voltages measurements taken under light exposure. Results are compared by plotting diagrams on figure 5 and summarized in table 1. Thin EPD layers (sample EPD 1 and EPD 2) have similar parameters as SC layers within the measured uncertainty. Thick layers EPD 3 (540 nm) has a reduced value of the short current density. This is an expected result, because the conductivity of the organic layers is driven by the electric field, which depends on the distance between the electrodes [12, 13].

4. Conclusion
Electrical and optical properties of thin Tg-PPV layers prepared by SC and EPD were compared. The differences in the emission spectra could be related to a nanostructure of the EPD films, while the SC films are more structureless.

Similar photovoltaic parameters of SC and EPD layers were found, only the dark-conductivity of EPD layers is lower, due to presence of higher barrier observed in current voltage curves.
Figure 5. Diagrams of average photovoltaic conversion parameters of three EPD layers with different thicknesses (see table 1) and one SC layer.

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