Improved Grain distribution in polymer thin films after electric polarization

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Abstract. In this research, the effect of electric polarization on the kinematics and distribution of grain growth and grain size respectively in organic thin film of poly (2-methoxy-5-(2-ethylhexyloxy)-1, 4-phenylenevinylene) MEH-PPV conducting polymer have been studied. An atomic force microscope was used to measure the grain size of the MEH-PPV thin films. We developed surface morphological data and analyzed. The data shows major asymmetric grain growth (from spherical grains at room temperature to lingered needle like-shapes after polarization) under an application of electric field during cooling of polymer film. The grains show evidence of highly ordered, domain-oriented arrangement of MEH-PPV grains after polarization.

1. Introduction
Recently, organic semiconductor has become increasingly important in thin film technology because of their application in many areas like: organic light emitting diodes (OLEDs), organic thin film transistors (OTFTs), and organic photovoltaic devices (OPVs) [1–3]. While the grain size of organic conducting polymer is one of the important considerations in the fabrication of such devices. The grain grown mechanism helps us to understand the optical, electrical and structural properties of the thin films, thereof its use in these applications [4]. The Atomic force microscopy (AFM) is the most powerful tool to investigate the three-dimensional (3-D) information about the thin film topography. The understanding of the thin film structure which depends on grain boundaries, grain size, and film roughness would allow us to tailor electrical properties, such as the carrier mobility and stability [5]. Poly (2-methoxy-5-(2-ethylhexyloxy)-1, 4-phenylenevinylene) MEH-PPV, is being developed for use in the field of organic electronics due to its outstanding optical and electrical properties. In order to
realize the full potential of MEH-PPV for such applications, significant progress must be made for the study of grain distributions and their kinematics.

We report the grain size distribution of MEH-PPV thin films after electric polarization. It is expected to have a significant effect on the properties and grain shape distributions of the resulting polarized films in contrast to unpolarized films. In our study, ordered structures and asymmetric grain distribution in thin films of MEH-PPV are investigated by an effect of electric polarization.

2. Experimental
The MEH-PPV conducting polymer films (Sigma-Aldrich) were fabricated onto the glass substrates by a spin cast technique. Prior to any coating, substrates were ultrasonically cleaned and dried in each step at 90 K for 10 minutes. MEH-PPV polymer solution was prepared by taking 10mg/ml into the chlorobenzene solution. Thin films of polymer were prepared by spin casting of the polymer solution onto the precleaned glass substrates under the nitrogen atmosphere. Further, these films were cured under the vacuum oven at 120 °C and the thinknesses of the cured films were measured by atomic force microscopy and were estimated approximately 150 nm [3]. Subsequently, a constant electric field was applied transverse to objected polymer sample at an eminent temperature to polarize the polymer film and further cooled down to a temperature below 98 K in the presence of the applied field. Thereafter, we removed the applied field and the sample was shortened for a few minutes to eliminate the undesired charges, if they were presented. Subsequently, the morphology of the thin films was investigated with AFM using a NTMDT solver scanning probe microscope in the tapping mode. We recorded several high resolution AFM images for each sample to accumulate data of at least 3000 grains per sample, see figure 1. The grain size was determined by Watershed image segmentation processing.

3. Results and discussion
Morphology of the thin film was examined using AFM in MULTIMODE (TM) scanning probe microscope in contact mode. One dimensional (1-D) and three dimensional (3-D) morphology of the MEH-PPV thin film photographed with the AFM images are presented in figure 1 (a) and (b) respectively. This showed spherical island crystals consisting of different mono domains conventional to other PPV derivatives.

Figure 1. (a) 1-D and (b) 3-D images of the unpolarized MEH-PPV thin films.

Figure 2 (a) and (b) show 1D and 3D AFM images of polarized MEH-PPV films. The grain size was determined by WXMS software technology. The oval surface pattern of crystal domains has been formed instead of a discontinuous array of spherical microdomains under polarization. The difference
in featured elliptical size of the grains can be credited to the effect of the applied electric field under the cooling of an elevated temperature [6].

Figure 2. (a) 1-D and (b) 3-D images show the 5×5 mm² images of the film after polarization, respectively.

Further, these AFM images were used to extend our study the surface analysis of the data. For this WXM method can be employed. The grain boundary drawn in the original AFM image of figure 1 (a) and (b) is covered. The relative orientation of the short axis and long axis of the ellipse after polarization is determined. Table 1 summarizes the results obtained by AFM images. As a result of the particle shape, the average of the outline is approximately equal to about 4 times the square root of the average surface value of the MEH-PPV particles. Thus, the effect of polarization on the particle size of the MEH-PPV film is that the particle size increases due to polarization. For the quantitative analysis of the region shown in figure 2a, the square root (σ RMS), skewness (σsk), kurtosis (σ Ku) and thickness (t) of all samples were measured which is reflected in Table 1. This shows a homogeneous and flat surface with a square root roughness (σ RMS) of only 7.866 nm was observed before polarization with a thickness of 1 μm. However, after polarization, many crystal domains appeared and σRMS increased to 29.3 nm.

Table 1. Root-mean-square roughness (σrms), the Skew ness (σsk), the Kurtosis (σku) and the perimeter for unpolarized and polarized thin film.

| Parameters | Unpolarized | Polarized |
|------------|-------------|-----------|
| σrms       | 7.866       | 29.3      |
| σsk        | 0.2107      | 0.065     |
| σku        | 1.020       | -0.204    |
| Perimeter  | 0.765       | 1.275     |
As the value of the roughness of the MEH-PPV film after polarization increases, in contrast to the non-polarizing thin film, the crystallinity of the polarized sample is lowered, which leads to a more irregular intermolecular alignment/orientation. The height values $\sigma_{sk}$ and $\sigma_{ku}$ of the film indicate that a sharp peak exists on the surface according to the visual AFM image. After polarization, these values are close to the expected value of the random distribution (Gauss), $\sigma_{sk} = 0.065$ and $\sigma_{ku} = 0.20$ [7].

The quantitative analysis of these nanostructures formed after polarization, two axial lengths were measured. The domain is much bigger and appears to be a little round. Domain is not completely circular, it has eccentricity of 0.18 (eccentricity is circle ~ 0). However, the eccentricity of these nanostructures is much larger than the spherical eccentricity (eccentricity ~ 0.94). Interestingly, after polarization, the surface structure of figure 2a, undergoes an elliptical transition of the spherical region with axial lengths of 2.25 nm and 2.74 nm and the average surface characteristics were shown in Table 2. These surface structures may appear very bright after polarization [7]. It is suggested that an elongated cusp is formed after polarization. In view of the results, further elongated cuspation can be caused by reorientation of the partially vertical form of the molecule, or it can reflect a decrease in the end capping energy upon expansion of the MEH-PPV domain and elliptical structure formed.

Table 2. Lengths of minor axis, major axis, area and the eccentricity of the domains structures for both cases.

| Sample     | Minor axis (μm) | Major axis (μm) | Area (nm$^2$) | Eccentricity |
|------------|----------------|----------------|---------------|--------------|
| Unpolarized| 1.14           | 1.1            | 3500          | 0.18         |
| Polarized  | 2.25           | 2.74           | 20,000        | 0.94         |

The growth conditions, especially the polarization in the particular case strongly affects grain size of the film. The particles extend along the major axis B and increase their area. The average particle surface area increases from 3500 to more than 20,000 nm$^2$ and is increased more than 5 times due to the weak Vander-Waals bonding nature of organic molecules.

A detailed explanation of the actual surface roughness is indispensable to evaluate the topography of the surface. Various rough surfaces may have different height distributions, but generally Gaussian distributions are used for mathematical simplicity. To determine how close a Gaussian distribution the comparison must compare the data between Gaussian agreement and root mean square ($\sigma_{RMS}$) and skewness ($\sigma_{sk}$) and width $\omega$ of kurtosis ($\sigma_{ku}$). The expression of the Gaussian function of surface height fluctuation can be written as [8].

$$p(h) = \frac{\Delta Z}{\omega \sqrt{2\Pi}} \exp\left(-\frac{(h-h_c)^2}{2\omega^2}\right)$$

(1)

where, $h_c$ is the mean height, $\omega$ is the width of the distribution, $\Delta Z$ is the area under the curve.

In figure 3, the height distribution function ($p(h)$) of the MEH-PPV film in the two cases, i.e. before and after the polarization, was presented. The area under the experimental curve ($\Delta Z_{exp}$) was calculated through normalization of the total number of pixels. The curves are fitted using equation (1) and the parameters extracted from the analysis are tabulated in table 3.
Figure 3. shows the height distribution function for the unpolarized and polarized thin films.

Table 3. Parameters after fitting the height distribution for unpolarized and polarized MEH-PPV thin film.

| Parameters        | Unpolarized | Polarized |
|-------------------|-------------|-----------|
| center ($x_c$)    | 34.348      | 89.929    |
| width ($w$)       | 13.655      | 53.029    |
| area ($A$)        | 3174.3      | 2971.3    |
| average height ($f_c$) | 185.47      | 44.407    |
| variance ($\sigma^2$) | 28.3763     | 0.15285   |

4. Conclusion
From above discussion, we concluded our results on the basis of quantitative analysis of MEH-PPV thin films under two different conditions such as unpolarized and polarized. The particle size of the MEH-PPV film increases due to polarization. The surface structure of the grains enhanced to an eccentricity of 0.18 to 0.94 and a diameter of about 1.1 to 2.14 nm with a formal conversion of spherical to elliptical shape.

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