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Controllable Molecular Doping and Charge Transport in Solution-Processed Polymer Semiconducting Layers

By Yuan Zhang, Bert de Boer, and Paul W. M. Blom*

Dedicated to the memory of Professor Bert de Boer, who passed away January 2009.

Here, controlled p-type doping of poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene) (MEH-PPV) deposited from solution using tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) as a dopant is presented. By using a co-solvent, aggregation in solution can be prevented and doped films can be deposited. Upon doping the current–voltage characteristics of MEH-PPV-based hole-only devices are increased by several orders of magnitude and a clear Ohmic behavior is observed at low bias. Taking the density dependence of the hole mobility into account the free hole concentration due to doping can be derived. It is found that a molar doping ratio of 1 F4-TCNQ dopant per 600 repeat units of MEH-PPV leads to a free carrier density of $4 \times 10^{22} \text{ m}^{-3}$. Neglecting the density-dependent mobility would lead to an overestimation of the free hole density by an order of magnitude. The free hole densities are further confirmed by impedance measurements on Schottky diodes based on F4-TCNQ doped MEH-PPV and a silver electrode.

doping is still challenging due to the intrinsic instability of n-type dopants in air, pioneering work has been performed utilizing alkali metals, cationic salts, or organic materials with a low ionization potential.^[8–14] In organic light-emitting diodes (OLEDs) based on evaporated, small molecules it has recently been demonstrated that doping of the hole and electron transport layers strongly reduces their operation voltage.^[15,16] Furthermore, the use of doped injection layers makes the OLEDs less sensitive to the work functions of the anode and cathode.

In conjugated polymers stabilized doping in light-emitting electrochemical cells has been realized, where the doping is formed electrochemically and subsequently stabilized either by a chemical reaction or by lowering of the temperature.^[17–19] However, for standard (non-

ionic) solution-processed polymer-based light-emitting diodes (PLEDs),^[20] doped charge transport layers are hardly applied. A major bottleneck is that often already in solution charge transfer between the host polymer and the dopant occurs, leading to aggregation and precipitation of the active components. So far highly-doped layers based on an aqueous suspension of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) have been used as a hole injection layers. However, putting a highly-doped injection layer in direct contact with the emitting layer can result in considerable luminescence quenching via direct energy transfer.^[21] Therefore, intermediate hole transport layers, of which the doping content can be controlled, are highly desirable. Simultaneous with our submission another report of Yim et al. appeared online in which p-type doping of various conjugated polymers has been realized.^[22] The next challenge is to address how many of the added dopant molecules do actually ionize and how many charge carriers are actually generated in the conjugated polymers. For this we use the model system poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene) (MEH-PPV) and (p-type) dope this polymer with F4-TCNQ. Recently, the dependence of the hole mobility μ_h on the charge-carrier density in a PPV-derivative has been investigated by a combined study on polymeric diodes and field-effect transistors.^[23] It has been demonstrated that the hole mobility is constant for charge carrier densities typically $<10^{22} \text{ m}^{-3}$ and strongly increases with density for charge carrier densities $>10^{22} \text{ m}^{-3}$. The enhancement of the mobility at higher bias voltages in space-charge limited (SCL) diodes at room temperature has been shown to be entirely due to

1. Introduction

The successful development of semiconducting electronic devices is largely due to the ability to tune their electronic properties by doping. The field of organic electronic devices was boosted tremendously with the discovery in 1977 that the conductivity of polyacetylene can be enhanced over many orders of magnitude by p-type doping.^[1] A decade ago, p-type doping of thin films of evaporated organic molecules as vanadyl- or zinc phthalocyanine was realized by co-sublimation of the matrix and the acceptor tetrafluoro-tetracyanoquinodimethane (F4-TCNQ).^[2–4] Next to a strong increase of the conductivity it was demonstrated that also the electronic structure of the interfaces is modified upon doping.^[5,6] The shift of the Fermi-level and the corresponding space-charge formation induced by (p-type) doping, resulted in an enhanced hole injection into the matrix.^[7] Although n-type

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the increase of the charge-carrier density.^[24] However, at lower temperatures the field dependence of the mobility becomes increasingly more important. Therefore, a transport model has been developed that incorporates both the effect of charge-carrier density and electric field on the mobility.^[25] Evidently, the strong dependence of the mobility on charge-carrier density will also play a dominant role in the analysis of doped layers where the charge-carrier density can be varied over orders of magnitude. From the analysis of the current density–voltage (J – V) characteristics we ascertain that we can controllably dope MEH-PPV with F4-TCNQ. A doping ratio of (1:600) leads to a free hole density of $\sim 4 \times 10^{22} \text{ m}^{-3}$. Using different doping concentrations, the obtained free hole density is observed to scale linearly with the host-acceptor ratio. Capacitance–voltage (C – V) measurements on Schottky diodes based on doped MEH-PPV and silver blocking electrodes confirmed the free carrier densities as obtained from the J – V measurements. Neglecting the effect of the charge-carrier density dependence on the mobility would have led to an overestimation of the free carrier density from the J – V measurements by an order of magnitude.

2. Results and Discussion

2.1. Current–Voltage Characteristics of Hole-Only (HO) Devices of MEH-PPV Doped with F4-TCNQ

HO devices were constructed to study the effect of p-type doping by F4-TCNQ on the transport properties of MEH-PPV. Patterned indium tin oxide (ITO) substrates were used as bottom contact, which were cleaned by a 20 min ultraviolet–ozone treatment. Next a PEDOT:PSS layer was spin-coated on top of the cleaned ITO in air. Spin-coating of the (doped) MEH-PPV was carried out in a nitrogen environment. Doping was achieved by mixing the F4-TCNQ acceptor and the MEH-PPV host with designed molar ratios in toluene, after separately being filtered in advance. Due to the relatively small dielectric constant of MEH-PPV ($\epsilon_r \approx 2.4$) and toluene, the Coulomb interaction between the ionized charges on the host and on the acceptor in solution leads to the formation of aggregates immediately after mixing, resulting in unprocessable solutions. However, aggregation could be prevented by adding a small amount of a polar solvent such as methanol or dimethyl sulfoxide (DMSO) to the solution. After spin-coating the organic layer, Au was thermally evaporated as a top contact to avoid electron injection. The J – V characteristics were measured using a Keithley 2400 SourceMeter under inert (nitrogen) atmosphere.

The charge transport properties of undoped PPV-derivatives have been extensively studied in order to understand the fundamental phenomena that govern the operation of these devices. It has been demonstrated that the hole current in PLEDs is SCL. At low bias voltages, at room temperature, the hole mobility (μ_h) is constant,^[26] and the J – V characteristics follow Child's law given by^[27]

$$J_{\text{SCLC}} = \frac{9}{8} \epsilon_0 \epsilon_r \mu_p \frac{V^2}{d^3} \quad (1)$$

wherein $\epsilon_0 \epsilon_r$, μ_p and d are the permittivity, hole mobility at low voltage and thickness of the polymer layer, respectively. From the

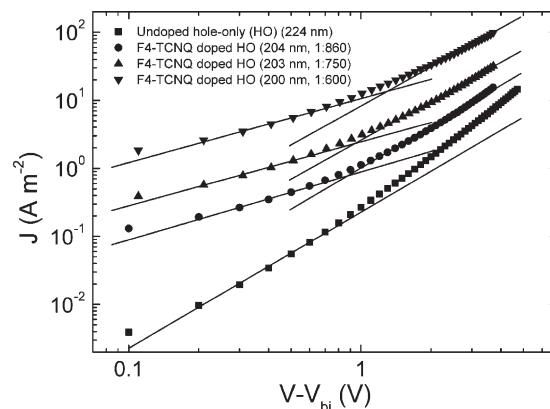


Figure 1. Current density versus voltage characteristics of MEH-PPV HO devices for various dopant:host molar ratios. At low bias voltage the current density increases by 1–3 orders of magnitude with increasing doping concentrations. The solid lines with slope of 1 and 2 denote the Ohmic and the space-limited current, respectively.

slope of the log J –log V plot of the undoped MEH-PPV HO device shown in Figure 1, a clear quadratic dependence of current on applied voltage is observed. The deviation at higher voltage originates from the charge-carrier density dependence of the mobility,^[24] which will be addressed below.

Upon addition of p-type doping free holes are introduced into the semiconductor. At low voltages these additional free holes, often the termed background density, p_0 , will largely outnumber the charges that are injected from the contacts, which are responsible for the SCLC as has been observed in undoped PPV.^[26] Since the positive charge of this background density p_0 is compensated by the negative charge of the corresponding acceptors, and therefore does not contribute to the built-up of space charge, an Ohmic-like current will flow at low voltages, given by^[27]

$$J_{\Omega} = qp_0\mu_p \frac{V}{d} \quad (2)$$

where q is the magnitude of electron charge, p_0 the free hole density, μ_p the hole mobility at low voltage, and d is the thickness of the polymer layer. For increasing bias more and more charges will be injected from the contacts and space charge starts to accumulate in the semiconductor. At a certain voltage the amount of background charge from the dopant will be equal to the injected space charge, or in other words, the SCLC will become equal to the Ohmic current. This transition voltage is then given by

$$V_T = \frac{8}{9} \frac{qp_0d^2}{\epsilon_0\epsilon_r} \quad (3)$$

Clearly, V_T is proportional to the background hole density from the doping. In Figure 1 the J – V characteristics of undoped and doped MEH-PPV films are shown for different host-acceptor ratios. The applied voltage V is corrected for the built-in voltage V_{bi} , that for the undoped films originates from the difference in

the work function of the bottom (ITO) and top (Au) electrodes. For lightly doped samples ($<10^{17} \text{ cm}^{-3}$) the same value can be used since the hole Fermi-level is then still about 0.4 eV below the center of the Gaussian density of states, which for MEH-PPV is located around -5.3 eV .^[23] As a result the Fermi-level closely aligns with the Au electrode (-4.8 eV), so band bending effects can be neglected. For higher doping levels a Schottky diode will be formed and the resulting band bending will affect V_{bi} . For the undoped MEH-PPV, the J - V plot demonstrates the quadratic behavior at low bias voltages ($<1 \text{ V}$), indicated by the solid line with slope 2 in the $\log J$ - $\log V$ plot. Upon addition of doping a clear linear dependence appears, as expected from Equation 2. Furthermore, the transition voltage V_T clearly shifts to higher voltages for increasing dopant content. The observed shifts of V_T clearly exceed variations between samples of different batches, all the measurements shown in Figure 1 were performed on the same solution of MEH-PPV for accuracy. Upon the addition of F4-TCNQ, the current of the HO device based on MEH-PPV is increased by about three orders of magnitude in the low bias regime. A remarkable result, however, is that not only the linear part increases upon doping, as expected from Equation 2, but also the SCL quadratic behavior given by Equation 1 at voltages above the transition voltage V_T . This clearly indicates that also the mobility of the free holes increases due to the doping with F4-TCNQ.

2.2. Modeling of the I - V Characteristics of HO Diodes Based on Doped MEH-PPV

Recent studies have demonstrated that the hole mobility MEH-PPV is dependent on the charge-carrier density p , the applied electric field E , and temperature T .^[23,24] The density dependence of the mobility dominates the SCL J - V characteristics at room temperature, whereas the field-dependence becomes more important at low temperature. From a numerical solution of the master equation for hopping transport in a disordered energy system with a Gaussian density of states a charge transport model has been developed by Pasveer et al. that takes both effects into account.^[25] It has been demonstrated that the mobility can be described as:

$$\mu_p(T, p, E) \approx \mu_p(T, p) f(T, E) \quad (4)$$

$$\text{with } \mu_p(T, p) = \mu_0(T) \exp\left[\frac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})(2pa^3)^\delta\right] \quad (5)$$

$$\mu_0(T) = \mu_0 c_1 \exp(-c_2 \hat{\sigma}^2) \quad (6)$$

$$\delta = 2 \frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln(\ln 4)}{\hat{\sigma}^2} \quad (7)$$

$$\mu_0 = \frac{a^2 v_0 e}{\sigma} \quad (8)$$

$$\text{and } f(T, E) = \exp\left\{0.44(\hat{\sigma}^{3/2} - 0.22) \left[\sqrt{1 + 0.8\left(\frac{Eea}{\sigma}\right)^2} - 1\right]\right\} \quad (9)$$

where $\hat{\sigma} \equiv \sigma/K_b T$ and σ are the width of the Gaussian, and a is the lattice constant. In our case a μ_0 of $6.4 \times 10^3 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, σ of 0.143 eV and a of $1.5 \times 10^{-9} \text{ m}$ well describe the J - V characteristics of the undoped MEH-PPV. These results are also consistent with earlier work on poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV), that exhibits similar transport properties as MEH-PPV. In Figure 2 the J - V characteristics of Figure 1 are represented, together with the numerically calculated characteristics using the field- and density dependent mobility. The field- and density dependent mobility is included in the calculation of the SCL current by solving the coupled equations^[25]

$$J = p(x) e \mu[T, p(x), E(x)] E(x) \quad (10)$$

$$\frac{dE}{dx} = \frac{e}{\epsilon_0 \epsilon_r} p(x) \quad (11)$$

$$\text{and } V = \int_0^L E(x) dx \quad (12)$$

where x is the distance from the injecting electrode, and L is polymer thickness. It is demonstrated that the value of p_0 that is used to fit the linear low voltage range also automatically describes the high voltage SCL regime. This is a strong indication that indeed the density dependence of the mobility is responsible

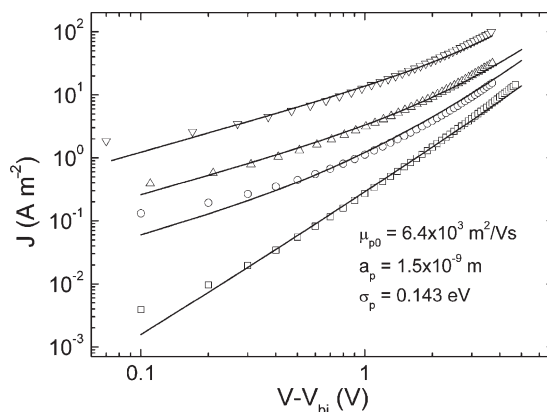


Figure 2. Current density versus voltage characteristics of MEH-PPV HO devices for various dopant:host molar ratios. Also included (solid lines) are the numerically calculated current densities taking into account a model that describes the charge-carrier density dependent hole mobility.^[25]

for the increased SCL currents upon doping. In Figure 3 the dependence of the obtained background density p_0 is plotted versus the amount of doping. As expected, a linear relation between the molar host-dopant ratio and p_0 is obtained. Remarkably, the intercept at zero doping concentration is not zero, indicating that a certain amount of doping is required before it becomes active. This is a subject of further study. For unintentionally doped MEH-PPV the free carrier density is estimated to be 10^{16} – 10^{17} m^{-3} . By varying the ratio, p_0 can be varied and controlled over one order of magnitude. The doping ratio of 1:600 that still leads to a processable solution induces a free hole density of $\sim 4 \times 10^{22}$ m^{-3} in the MEH-PPV. Based on the molecular weights of F4-TCNQ and the repeat unit of MEH-PPV, for a 1:600 ratio, we can estimate that the number of dopant molecules per volume unit is $\sim 4 \times 10^{24}$ m^{-3} considering a mass density of MEH-PPV of 1×10^6 g m^{-3} . Taking into account that a conjugated segment of MEH-PPV or its effective conjugation length is ~ 12 repeat units, we can conclude that only 1.0% of the dopants are effective and ionized. An intrinsic assumption that we have made is that the charge transport parameters of the undoped MEH-PPV are not affected by the presence of the negatively charged acceptors.

It has been suggested, both experimentally^[28] and theoretically,^[29] that doping of disordered organic semiconductors may create additional deep Coulombic traps of the opposite polarity, which might strongly suppress the carrier hopping rate and mobility.

2.3. Impedance Spectroscopy on Schottky Diodes Based on Doped MEH-PPV and Silver

To independently determine the ionized doping density we employed impedance spectroscopy on doped MEH-PPV Schottky diodes with a silver top contact and an ITO bottom contact. The ITO was not coated with a PEDOT:PSS layer, since the counter ions in the PEDOT:PSS would have interfered with the low-frequency part of the capacitance measurements. Due to the difference in work function of silver (4.3 eV) and the HOMO level of MEH-PPV (5.3 eV), a depletion region was expected to form at the polymer/Ag interface. For sufficiently high doping levels the width of this depletion region will be thinner than the device thickness. In that case the capacitance of the depletion region will vary with the applied voltage. The well-known relation between

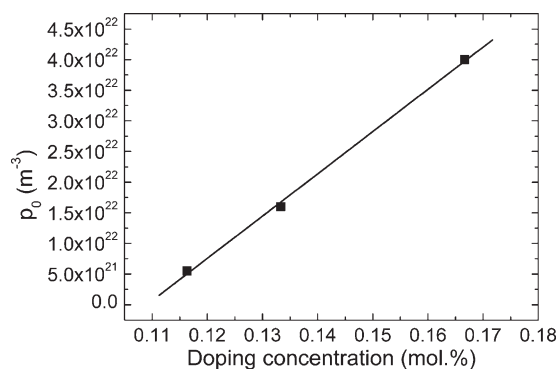


Figure 3. Background hole density due to doping, p_0 , as a function of the molar doping ratio.

the variation of the capacitance C with voltage V for a given ionized dopant density, N_D , is^[30]

$$\frac{1}{C^2} = \frac{2(V_{bi} - V - kT/q)}{q\epsilon_s N_D}, \text{ or } N_D = \frac{2}{q\epsilon_s} \left[-\frac{1}{d(1/C^2)/dV} \right] \quad (13)$$

with W the width of the depletion region. As a result from the slope of C^{-2} - V the density N_D can be determined. As a first step the forward J - V characteristics of the F4-TCNQ:MEH-PPV/Ag Schottky diode were analyzed, as shown in Figure 4a. Above the built-in voltage of ~ 0.5 V the forward bias becomes SCL and p_0 can be obtained by modeling the J - V characteristics, similar to Figure 2. For the F4-TCNQ:MEH-PPV Schottky diode considered here, a p_0 of 1.2×10^{22} m^{-3} is obtained.

For the impedance measurements on the same device an alternating voltage with a magnitude of 100 mV has been added to the applied reverse DC bias that was varied from 0 to -0.5 V. At each DC bias voltage, a frequency scan was made ranging from 10 Hz to 20 MHz to collect the impedance data of the device. By modeling the device as a parallel RC circuit for the depletion

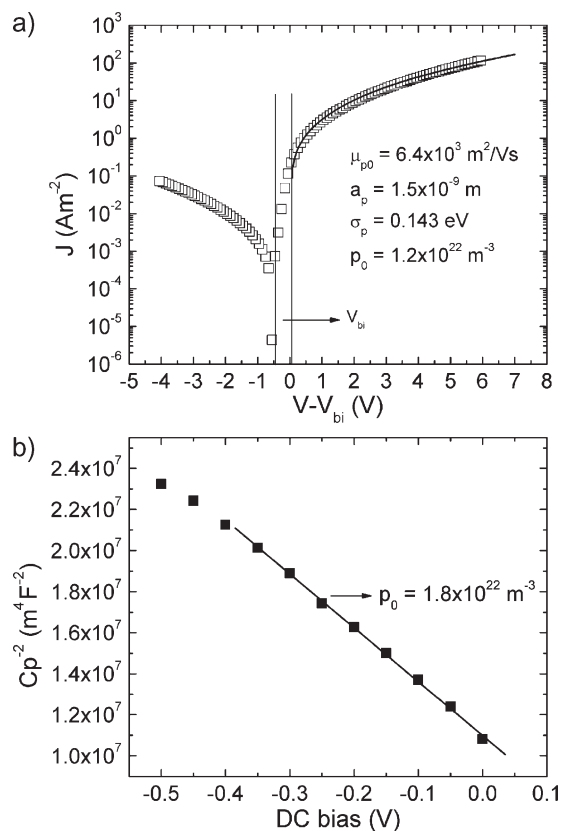


Figure 4. a) Forward bias current–voltage measurement of a F4-TCNQ:MEH-PPV/Ag Schottky diode. The solid line is a fit with the charge-carrier density dependent hole mobility. b) Capacitance versus reverse bias plot of the same device. From the slope, a density N_D of 1.8×10^{22} m^{-3} is obtained, in close agreement with the 1.2×10^{22} m^{-3} as obtained from the J - V characteristics.

region, in series with another parallel RC circuit for the bulk semiconductor, the value for the capacitance of the depletion region (C_p) was obtained at each applied bias. The resulting dependence of C_p^{-2} versus V is shown in Figure 4b. From the slope a value of $1.8 \times 10^{22} \text{ m}^{-3}$ is obtained for N_D . The relatively good agreement between these two independent methods confirms our analysis and interpretation using the charge-carrier density dependent mobility. As can be seen from the quadratic parts in Figure 1, the mobility increases by about one order of magnitude from the undoped MEH-PPV to the doped MEH-PPV using a doping ratio of 1:600. Thus, by neglecting the charge-carrier density dependent effect on the mobility and assuming a constant mobility, the values for p_0 would be overestimated by an order of magnitude when Equation 2 is directly applied to the linear J - V regime. Furthermore, the agreement also shows that the presence of dopant ions does not significantly change the mobility in the doping range studied here. The realization and analysis of controllably doped MEH-PPV films is an important step forward toward the use of doped charge transport layers in polymer-based multilayer light-emitting diodes and solar cells.

3. Conclusions

We have investigated p-type doping of MEH-PPV by blending it with F4-TCNQ. Controllable doping with F4-TCNQ in solution could be realized by the addition of a polar co-solvent. The resulting spin-coated layers demonstrated a doping-induced free carrier density p_0 up to $4 \times 10^{22} \text{ m}^{-3}$. At low bias voltage a linear regime in the current-voltage characteristics appears, followed by a transition to SCLC at higher bias, when the space-charge from the injected holes becomes dominant. At low bias the current density increases by 1–3 orders of magnitude with different molar doping ratios. In order to describe the full J - V characteristics of the doped MEH-PPV devices at room temperature, the charge-carrier density dependence of the hole mobility should be taken into account. The background carrier density p_0 is further confirmed by impedance spectroscopy measurements on F4-TCNQ:MEH-PPV/Ag Schottky diodes.

4. Experimental

The polymer matrix MEH-PPV was synthesized using the Gilch method and purified as described previously [30].

F4-TCNQ serving as p-type dopant was purchased from Sigma-Aldrich and used without further purification.

The MEH-PPV HO devices were prepared on patterned ITO substrates provided by Philips Research. All the substrates were first scrubbed to remove ITO spikes and then ultrasonically cleaned sequentially with ultrapure (18.2 M Ω) water, acetone and 2-propanol. A 20 min treatment of UV-ozone was carried out before the PEDOT:PSS layer was spin-coated. The MEH-PPV and F4-TCNQ were both dissolved in toluene with a concentration of 6 mg mL $^{-1}$ and 0.5 mL mg $^{-1}$, respectively. After being stirred on a hot plate at 70 °C for \sim 12 h, the solutions were filtered separately. PTFE media syringe filters with pore sizes of 5.0 and 0.2 μm were used for filtering the MEH-PPV and F4-TCNQ solutions, respectively. Blending of the two solutions was done in nitrogen atmosphere. In order to prevent aggregation, 30 μL of DMSO was added to the blended solutions. The films were prepared by spin-coating using a Karl-Suss spin coater. First, the solution was spread using a spin speed of 300 rpm for 5 s, then the film

was spun with 2500 rpm for 45 s. Finally, Au (for HO devices) or Ag (for Schottky diodes) with a thickness of 60–80 nm were deposited as top contacts using thermal evaporation under a chamber pressure of 8×10^{-7} mbar. All the measurements were done under inert atmosphere. A Keithley 2400 SourceMeter was used for the current-voltage (I - V) measurements and a Solartron SI 1260 impedance analyzer was used for the capacitance-voltage (C - V) measurements. A Veeco Daktak 6 stylus profiler with a typical accuracy of 5 nm was used to measure the polymer thickness. We have measured the whole area of the polymer film and different samples using the same solution and spin-coating program. The thickness is found to vary between \sim 5 and \sim 10 nm.

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