

NANOSTRUCTURED CONJUGATED POLYMERIC SYSTEMS FOR PHOTOVOLTAIC APPLICATIONS

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Abstract. In this work, conjugated block copolymer polyfluorene/polyaniline (PF/PANI) has been studied as a potential candidate for photovoltaic applications. We used two techniques based on nanoimprint lithography (NIL) for phase alignment of this block copolymer blend PF/PANI, polyaniline being the donor and polyfluorene - the acceptor phase. In the first technique, metallic nanostructures induce nanostructuring in the polymer layer, whereas in the second technique, the PF/PANI is directly patterned with a stamp. The electrical and photoelectrical properties of the polymeric systems were studied and the morphology was characterized by AFM and SEM.

1. INTRODUCTION

In the last decade, investigations into the physical properties of organic semiconductors have shown that these materials have several interesting features as regards applications in photoelectrical devices [1]. Of crucial importance to the fabrication of polymeric based solar cells is the requirement of a bicontinuous partition of the donor and acceptor phases to allow effective charge separation and transport to the electrodes. Block copolymers are extremely attractive as candidates for photovoltaic applications as they can phase separate in the 50-200 nm scale and allow the possibility of fine tuning the donor-acceptor energy levels.

Conjugated block copolymer polyfluorene/polyaniline (PF/PANI) is a novel attractive system for photovoltaic applications [2]. It consists of the conjugated homopolymers polyfluorene (PF) and polyaniline (PANI). The conjugated polymer PANI acts as the donor, whereas PF is the acceptor. The light absorption is caused by a $\pi-\pi^*$ transitions with a maxima at ca. 385 nm for PF and ca. 550 nm for PANI [2]. To obtain a nanostructure formation within the polymeric blend, two experimental techniques based on nanoimprint lithography (NIL) have been

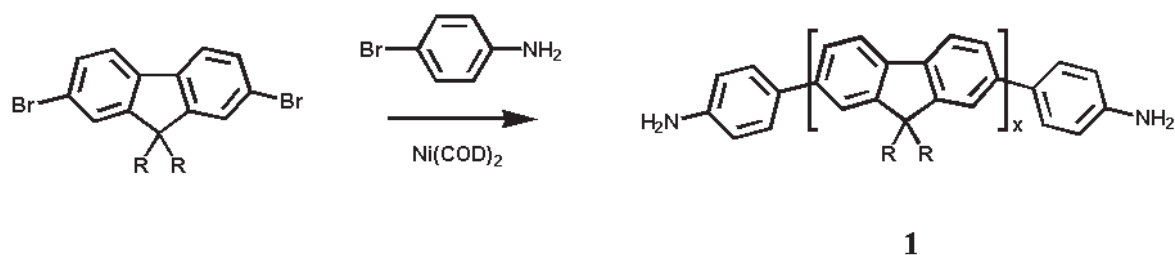
used in this work: (i) metallic nanostructures induce a nanostructuring of the polymer layer; and (ii) the PF/PANI is directly patterned by NIL. Two point photoelectrical measurements, atomic force microscopy (AFM) and scanning electron microscopy (SEM) have been used to visualize the different phases of PF/PANI.

2. EXPERIMENTAL TECHNIQUE

2.1. Synthesis of conjugated rod-rod block copolymers

We have developed an improved synthetic route towards 4-aminophenyl end-functionalized polyfluorenes and PF/PANI block copolymers wherein, we have switched from the initially used aryl-aryl cross coupling reaction according to Suzuki to the Yamamoto aryl-aryl coupling procedure. The advantage of the Yamamoto route is that it allows the use of unprotected 4-aminophenyl derivatives as endcappers instead of a 4-nitrobenzene derivative, which must be reduced in an additional reaction step. Moreover, the novel method guarantees a complete end-functionalization of the PF block. The one-step synthesis of 4-aminophenyl end-functionalized

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Scheme 1. Synthesis of the 4-aminophenyl-terminated PF prepolymers **1** after Yamamoto (R: 2-ethylhexyl).

polyfluorenes was achieved by the use of unprotected 4-bromoaniline as the end-capper (Scheme 1).

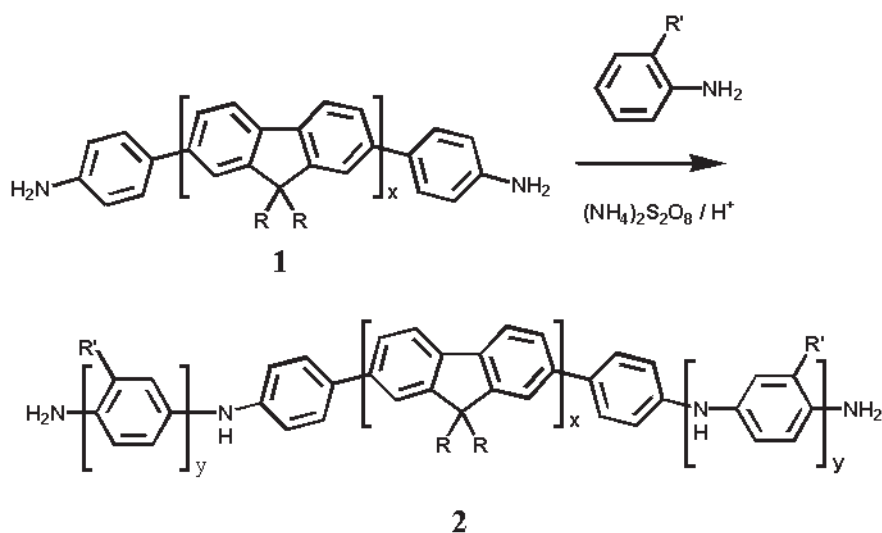
In general, the molecular weight of the polyfluorene prepolymer **1** can be controlled by modifying the bifunctional dibromofluorene/4-bromoaniline feed ratio.

By increasing the amount of the monofunctional end-capping reagent in the reaction mixture, the molecular weight of the coupling product decreases. In our first coupling reactions, 15% of the 4-bromoaniline 'end-capper' was used. The presence of 'end-cappers' in the prepolymer chains was proven by elemental analysis and ¹H-NMR spectroscopy. In relation to the molecular weight of prepolymer **1** (GPC analysis) an integration of the ¹H-NMR 'end-capper' signals allows for an estimation of the degree of end-functionalization with 4-aminophenyl units. The analysis indicates that the PF chains are completely terminated with 4-aminophenyl functions. In contrast, the degree of end-functionalization when following the initially used Suzuki cross cou-

pling method was estimated to be only 1-1.2 nitrophenyl end groups per prepolymer chain indicating that chain termination via debromination/deboronation is competing with the attachment of the 4-aminophenyl 'end-capper' [2].

The second reaction step of our improved PF-b-PANI synthesis then involves the oxidative coupling of the NH₂-terminated prepolymer **1** with 2-undecylaniline (reagents: (NH₄)₂S₂O₈/H⁺). The AB-type character of the aniline monomer guarantees the formation of PF/PANI block copolymers **2** during this reaction step without crosslinking, branching or multiblock formation (Scheme 2).

The undecyl-substituted aniline monomer was chosen because of the increased solubility of the corresponding, alkylated PANI building block [3]. In contrast to the insoluble unsubstituted polyaniline, the poly(2-undecylaniline) homopolymer is slightly soluble in several polar organic solvents (e.g. THF), but insoluble in toluene [3]. Based on this, the homocoupled side product poly(2-undecylaniline), which is also formed remains as an insoluble resi-



Scheme 2. Synthesis of the poly(9,9-dialkylfluorene)-b-poly(2-alkylaniline) (PF-b-PANI) block copolymer **2** (R: 2-ethylhexyl; R': n-undecyl).

Table 1. Molecular weights of the 4-aminophenyl end-functionalized PF prepolymer **1** and the PF-b-PANI block copolymer **2** (GPC, PS calibration with RI, and UV-Vis detection at 390/540 nm).

	<i>Prepolymer 1</i>		<i>Block copolymer 2</i>		
	<i>RI detection</i>	<i>UV detection</i> (390 nm)	<i>RI detection</i>	<i>UV detection</i> (390 nm)	<i>Vis detection</i> (540 nm)
M_n	7900	10400	33000	36900	25300
M_w	32400	33500	57600	57200	52700
M_p	34900	34800	50600	50600	52800

due during an extraction of the reaction product with toluene. The toluene soluble block copolymer was further extracted with acetone to remove any remaining starting products and short chain oligomers.

The molecular weight M_n of the block copolymer **2** is increased with respect to the prepolymer **1** (in our example: M_n (**1**): 10400; M_n (**2**): 36900). However, the peak molecular weight M_p is only moderately increased (**1**: 34800, **2**: 50600), in accordance with the low degree of polymerization of the PANI blocks. The elemental analysis of PF-b-PANI (N-content) corresponds to an average PANI block length of 7-8, which is in agreement with the observed increase of M_p . According to the degree of polymerization of the PF block (x: ca. 25), a molar PF/PANI ratio of ca. 1.7 results, corresponding to a weight ratio of ca. 3. The more pronounced increase of M_n is a consequence of the partial fractionation during the work-up of **2** (washings with acetone). Indeed, the acetone washings contain some low molecular weight material (M_n : 1000-2000). Further proof that the PANI blocks are really covalently attached to the PF blocks is obtained from a GPC analysis with a parallel UV-Vis detection of the distinctly different absorption maxima of the PF (390 nm) as well as the PANI block (540 nm), and RI detection (control experiment; Table 1). The identical peak molecular weights M_p indicate, that the absorbing species at 390 and 540 nm, respectively, correspond to molecules with nearly identical molecular weights. Also considering the low molecular weight of the poly(2-undecylaniline) homopolymer which is formed as side-product (M_n : < 5000) these results are strong proof for the presence of the expected PF/PANI block copolymers **2**.

2.2. Fabrication of nanoelectrode arrays and morphology investigation technique

To fabricate nanostructured layers of novel polymeric materials for photovoltaic applications, electron-beam lithography (EBL) and nano-imprint lithography (NIL) have been used. NIL on electrically active organic materials provides a way to obtain pronounced nanostructuring and to controllably enhance the interface area between an electron acceptor and electron donor material.

On this background, a nanostructure formation in the polymer layer could be induced, with Ti-Au electrodes on SiO_x , being prepared by EBL. These metal structures were used as pre-patterned substrates. The Ti/Au electrodes had a width of ca. 40 μm and the array of interdigitated structures is fabricated on an area of about 1600 μm^2 .

Nanoimprint lithography is a parallel process characterised by high throughput and low-cost. It makes use of mechanical deformation of a polymer layer under a temperature and pressure cycle [4,5]. This technique is well defined for PMMA and experiments with conjugated polymers are in progress [6], making it possible to pattern polymers in the nanometer scale. The patterned polymer could be used as a mask for metal lift-off or as a patterned substrate. To use it as a mask the residual polymer layer, unavoidable for physical reasons, has to be removed, e.g. in a plasma etching step. With respect to the application in photovoltaics, the printing of one of the two components of a photovoltaic cell is an option currently under investigation.

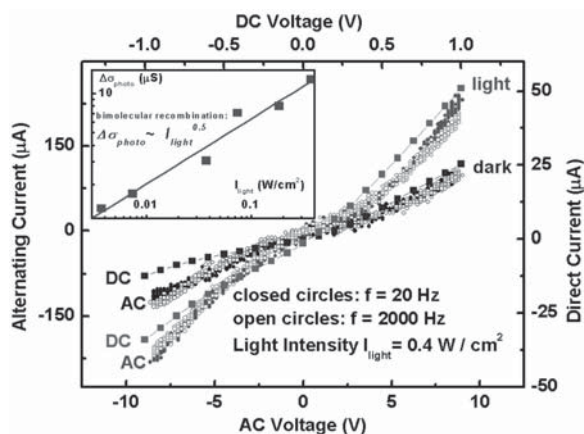


Fig. 1. Dark and illuminated DC and AC current-voltage (I-V) characteristics and photoconductivity versus white light intensity (inset) of the spincoated block copolymer PF/PANI on a metallic structure with 400 nm electrode spacing.

2.3. Electrical and photoelectrical measurements

Electrical and photoelectrical properties of the system under study have been investigated in direct current (DC) and alternate current (AC) regimes with the help of the Keithley Model 6517A Electrometer in the former case and Tektronix TDS420 Digitizing Oscilloscope in the latter. All the electrical measurements were carried out in air, at room temperature and under dark conditions or white light illumination (tungsten lamp, 12 V, 20 W; maximal measured intensity of the sample illumination: $I_{\text{light}} = 0.4 \text{ W/cm}^2$). The sample was placed into the shielded cell and the electrodes were contacted with Au-covered tungsten microprobes (mounted in the Probeheads from Suss MicroTec Test Systems GmbH) or Ag-paste. The dependence of the photoconductivity of the spin-coated block copolymer PF/PANI on a metallic structure with 400 nm electrode spacing upon the white light intensity was measured at the constant voltage ($U = 1 \text{ V}$) with the help of the “grey” optical filters.

3. RESULTS AND DISCUSSION

3.1. Electrical and photoelectrical properties of PF/PANI block copolymer

As can be seen from Fig. 1, the current-voltage (I-V) characteristics of the sample under study are almost independent of the sign and the frequency

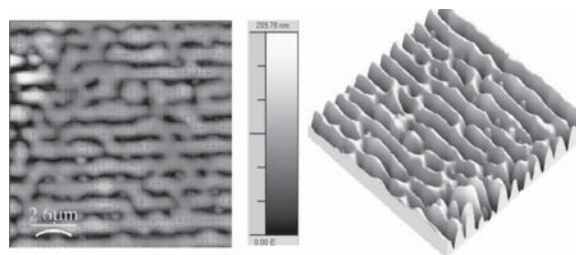


Fig. 2. AFM image of a spincoated PF/PANI block copolymer on a SiO_x substrate with the interdigitated metal (Ti/Au) electrodes (lines and spacings $\sim 500 \text{ nm}$). Microphase separation in the polymer layer is induced by the nanoelectrode array.

of the applied voltage (up to $\sim 10 \text{ kHz}$) both in dark and under white light illumination. It should be emphasized, that under the above-mentioned conditions one could obtain rather high photoconductivity values ($\Delta\sigma_{\text{photo}}/\sigma \sim 10^5$ for the as-prepared PF/PANI samples). The dependence of the photoconductivity of the spin-coated block copolymer PF/PANI on a metallic structure with 400 nm electrode spacing upon the white light intensity in the range from 0.004 to 0.4 W/cm^2 (Fig. 1, inset) follows the power law: $\Delta\sigma_{\text{photo}} \sim I_{\text{light}}^{0.5}$. The experimental data plotted in the double logarithmic scale are approximated by a straight line with the slope ~ 0.5 and the correlation coefficient $r = 0.998$. Thus one can conclude that the almost “ideal” bimolecular recombination of the charge carriers (electrons and holes) takes place without significant influence of any traps, supporting the assumption that the conjugated block copolymer PF/PANI has some potential for the photovoltaic applications.

3.2. Microphase separation in the polymer layer induced by the nanoelectrode arrays

To observe a microphase separation in the polymer layer induced by the nanoelectrode arrays, Ti/Au-electrodes were previously fabricated on a SiO_x -substrate by EBL (see Section 2.2). Afterwards, PF/PANI was dissolved in tetrahydrofuran (THF). Typically, 10 mg PF/PANI was dissolved in 1 ml of THF. After filtration, a PF/PANI solution was spincoated on top with 500 – 6000 rpm for 30 – 60 seconds. Fig. 2 shows an AFM scan of the surface of a PF/PANI film spun on an electrode array at 6000 rpm for 30

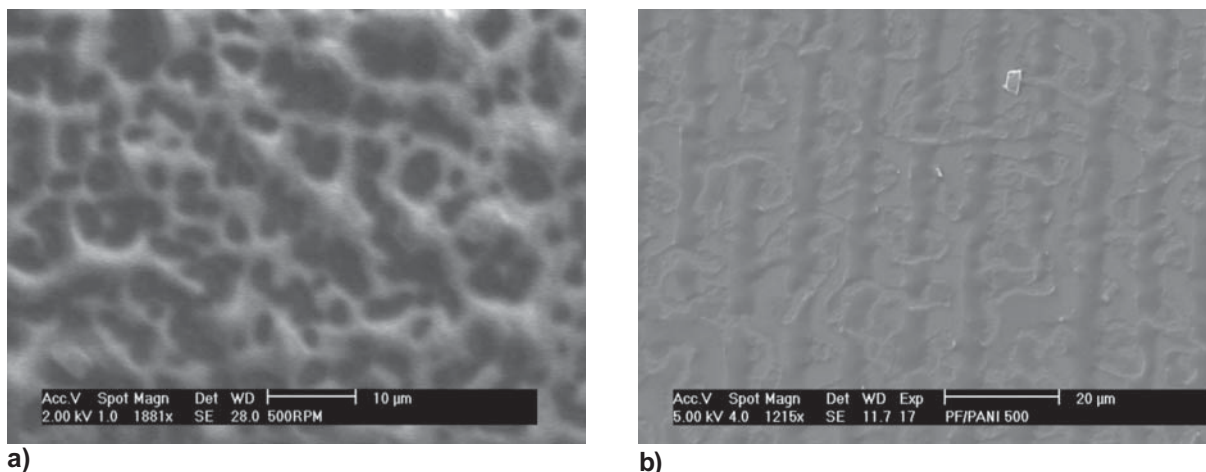


Fig. 3. SEM images of a PF/PANI block copolymer spincoated on a SiO_x – substrate (500 rpm, 60 s), before (a) and after (b) nanoimprinting. Parameters of the NIL process: 40 bar, 150 °C, 8 min. Period of the structure: 8 µm.

seconds. The formation of surface-induced microstructures is obvious. The interdigitated structure causes a parallel alignment of PF/PANI stripes (in the surrounding parts of the sample, the orientation of the domains is arbitrary).

3.3. Morphological investigations of nanoimprinted conjugated block copolymers

In the second technique, the PF/PANI spincoated on a SiO_x -substrate was directly patterned with a stamp. Fig. 3 (a, b) demonstrates SEM images of the sample before and after the nanoimprinting, respectively (parameters of the NIL process: applied pressure $p = 40$ bar, temperature $T = 150$ °C, time duration $t = 8$ min). One can easily see the distinct formation of parallel nanostructures after NIL into the randomly structured as-prepared polymer layer.

4. CONCLUSIONS

In summary, the improved method towards PF/PANI block copolymers represents a straightforward synthetic procedure, which enables the preparation of gram amounts of the block copolymers, due to the facile separation of the PANI homopolymer (formed as a side-product in the second reaction step) by a simple extraction with toluene. Moreover, the novel method leads to a nearly complete end-functionalization of the polyfluorene prepolymers

and, thereby, to the formation of PANI-PF-PANI tri-block copolymers.

To induce a well-aligned microphase separation of PF/PANI block copolymer, two techniques based on nanolithography were used. We have used metallic interdigitated structures on monocrystalline substrates produced by e-beam lithography (EBL) and nanoimprint lithography (NIL). The morphology of the conjugated block copolymer PF/PANI has been investigated. A defined orientation of the microphases has been observed on metallic interdigitated structures with a parallel arrangement of the resulting polymer stripes. The formation of nanosized patterns has been also observed after a NIL process into spin coated polymer layers.

A next step could be the imprinting of the conjugated block copolymers followed by spincoating of a second polymer on top of the imprinted pattern. The objective is to generate defined bilayer structures of donor and acceptor polymers.

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