Pattern Formation in Thin Polymer Films Containing Conducting Polyaniline

Jakub Haberko,[*1] Joanna Raczkowska,[2] Andrzej Bernasik,[1] Wojciech Łużny,[1] Jakub Rysz,[2] Andrzej Budkowski*[2]

Summary: In the present work knowledge the authors tried to direct the phase separation process in a thin polymer composite film to manufacture a polymer pattern via self organisation of the blend components. The Au substrate was modified by applying with a PDMS stamp a pattern of alternating stripes of a self-assembled monolayer. This in turn influenced the microstructure of the blend, allowing for the production of elongated domains repeating the pattern of the substrate. The blends studied in this work contained conducting polyaniline doped with camphorsulfonic acid or diphenyl phosphate and polystyrene. The role of the dopant was to induce electrical conductivity in polyaniline as well as to improve its solubility in common organic solvents. The microstructure of thin films was analysed using atomic force microscopy (AFM), dynamic secondary ion mass spectroscopy (dSIMS) and optical microscopy.

Keywords: conjugated polymers; polyaniline; polymer blends; self-organisation; thin films

Introduction

The process of phase separation in polymer blends has recently been intensively studied. Microstructure and phase composition of a polymer blend may affect its performance as a material for polymer electronic devices, such as light emitting diodes, transistors, photovoltaics or sensors. For example in some cases polymer light emitting diodes with vertical phase separation exhibit much higher efficiency with respect to the ones with lateral phase separation.[1] Moreover, it is possible to manufacture FET transistors via a controlled phase separation process, as described in.[2] Here spinodal decomposition leads to a semiconductor-dielectric bilayer acting as the transistor channel and gate insulator.

Among other techniques, microcontact printing is utilised to selectively change the surface energy of a substrate, which in turn allows replicating a desired polymer pattern. The authors of[3] used this technique to induce phase separation in thin polymer films containing polyvinylpyrrolidone (PVP), polystyrene (PS) and poly(methyl methacrylate) (PMMA). In this model system they observed that the proportions of polymer solution components strongly influence the process of self-organisation and, as a result, the quality of pattern reproduction. The latter is also affected by the inherent domain size in the polymer blend.

In our previous research[4] we have studied morphologies in thin polymer films spin-cast onto a homogenous substrate. The aim of the present work was to induce and effectively control phase separation in a thin composite containing a conjugated polymer (polyaniline doped with camphorsulfonic acid or diphenyl phosphate) and a conventional one (polystyrene). The goal was to obtain a desired pattern of a conductive polymer on a substrate.

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[1] Faculty of Physics and Applied Computer Science, AGH-University of Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland
E-mail: haberko@novell.ftj.agh.edu.pl
[2] M. Smoluchowski Institute of Physics, Jagiellonian University, ul. Reymonta 4, 30-059 Kraków, Poland

Experimental Part

A chloroform solution of polystyrene ($M_w = 1{,}500$ amu and $M_w = 125{,}000$ amu, PSS Mainz) and polyaniline ($M_w = 5{,}000$ amu, Aldrich) protonated with camphorsulfonic acid (Aldrich) was prepared. It was then squeezed through a teflon filter in order to remove agglomerates of undissolved PANI. The substrate was prepared by microcontact printing: a PDMS stamp was inked with an ethanol solution of 1-hexadecanethiol (CH_3-SAM) or 16-mercaptohexadecanoic acid (COOH-SAM) and then pressed against a silicon wafer covered with a thin (approx. 100 nm) layer of gold. This resulted in the formation of hydrophobic (CH_3) or hydrophilic (COOH) stripes on the substrate, divided by stripes of pure gold. Two different stamps were used: (a) a ‘‘symmetric’’ stamp whose surface consisted of a pattern of 2-micrometer wide stripes with a periodicity of 4 μm and (b) an asymmetric stamp with 12.5 μm stripes with a periodicity of 37.5 μm. In the next step the solution was spin-cast onto the substrate.

Thin polymer films thus obtained were investigated by means of Atomic Force Microscopy, Secondary Ion Mass Spectroscopy and optical microscopy.

Results and Discussion

Our results have shown that after a careful adjustment of experimental parameters it is possible to replicate a desired pattern on a substrate from a spin-cast solution of a polymer blend containing polyaniline and polystyrene. Optical micrographs of the investigated samples, collected with a Nikon metallographic optical microscope, reveal a well-defined pattern of alternating light and dark stripes over a relatively large area of the sample surface. This can be seen in Figure 1a, showing the surface of a thin film obtained from a chloroform solution containing 10 mg/ml of polystyrene ($M_w = 1500$ amu) and 6 mg/ml of PANI(CSA) ($M_w = 5000$ amu) spun-cast on a gold-covered Si wafer modified with CH_3-SAM.

The AFM images, in case of CH3-SAM covered substrates, show a difference of height of several nm to approximately 20 nm between the stripes on the sample surface. The AFM image in Figure 2a depicts the topography of the sample prepared in the same as the one in Figure 1a. The averaged cross-section from a designated region shows an average height difference between the stripes in this case. Furthermore, the magnitude of the 2D Fourier Transform of this AFM

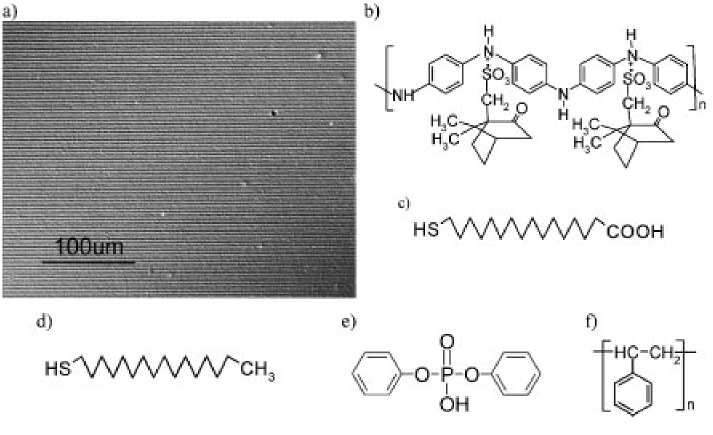

Figure 1.
a) Optical micrograph of a PANI(CSA)/PS thin film spun-cast at 1000 rpm from a chloroform solution containing 10 mg/ml PS and 6 mg/ml PANI(CSA). Chemical structure of b) polyaniline protonated with camphorsulfonic acid c) 16-mercaptohexadecanoic acid (COOH-SAM) d) 1-hexadecanethiol (CH_3-SAM) e) diphenyl phosphate and f) polystyrene.

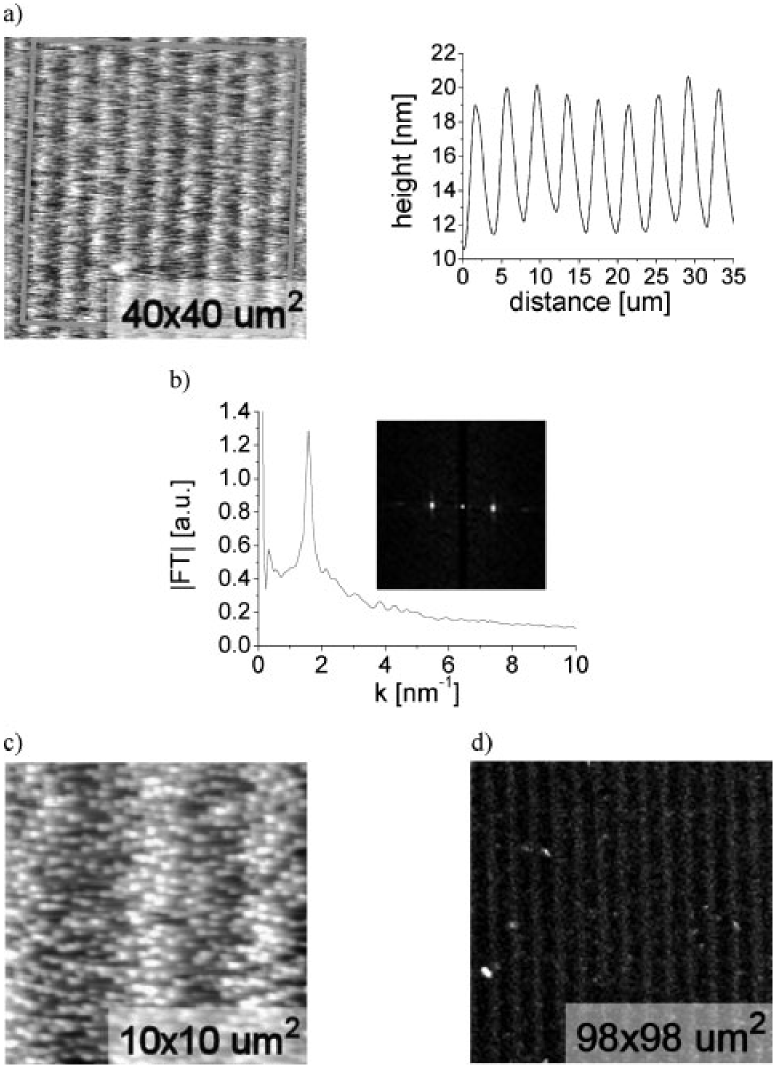

Figure 2.

a) AFM image and an averaged cross-section in a designated region of a PANI(CSA)/PS thin film spun-cast at 3000 rpm from a chloroform solution containing 20 mg/ml PS and 6 mg/ml PANI(CSA); b) 2D Fourier Transform of that image (inset) and its radial average; c) AFM image of a smaller region of the same sample showing granular morphology; d) dSIMS map presenting the intensity of secondary $^{26}CN^{-}$ ions (attesting to the presence of PANI) scattered from the sample surface. The substrate was patterned with CH_3-SAM prior to spin-coating.

image (Figure 2b inset, the peak at $k = 0$ was divided by the factor of 10 for clarity) exhibits two distinct peaks at $-k_o$ and $+k_o$. As can be seen from the radial average of the Fourier transform, $k_o \approx 1.56$ nm^{-1}, which yields the periodicity of the structure of 4.03 μm. This is in good agreement with the periodicity of grooves on the silicon stamp used for microcontact printing (4 μm). Moreover, it is important to note here that the morphology of the thin films has a hierarchic nature. The stripes are not smooth, as can be seen in the enlarged AFM image in Figure 2c. Each of them is composed of a number of column-like features, which can be also distinguished in the lower regions of the film. The features are possibly aggregates of polyaniline, whose solubility in organic solvents is relatively small compared to that of polystyrene. They might have been formed in early stages of spin coating and deposited on the substrate during the solvent evaporation. Yet basing on the experimental techniques utilised in this work one cannot say anything about the crystalline structure of the aggregates, nor about the orientation of macromolecules within them.

In order to prove that the chemical composition of the lower and higher regions of the samples is significantly different, the surface was scanned by means of a mapping mode of dynamic Secondary Ion Mass Spectroscopy. In this mode a primary Ga^+ ion beam sweeps the sample ejecting secondary ions from the surface. The intensity of chosen ions is then recorded with a mass spectrometer, which gives information about the chemical composition of the sample. Moreover,

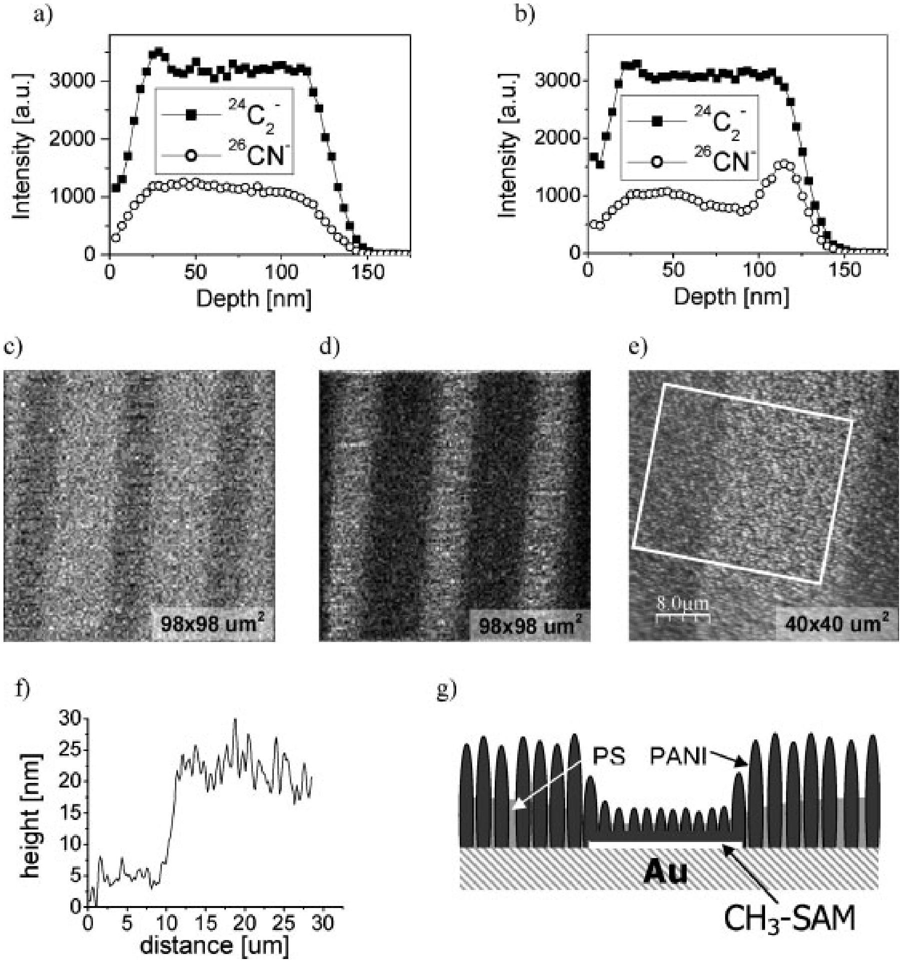

Figure 3.

PANI(DPHP)/PS thin films on a substrate asymmetrically patterned with CH_3-SAM. a) dSIMS profile (■ $^{24}C_2^-$ and ○ $^{26}CN^-$ secondary ions, the latter indicating the presence of PANI) measured on a wide stripe; b) dSIMS profile measured on a narrow stripe (please note a peak in PANI concentration); c) dSIMS map ($^{26}CN^-$ ions) measured at the depth of approx. 62 nm; d) dSIMS map ($^{26}CN^-$ ions) at approx. 108 nm; e) AFM height image; f) an averaged cross-section of the AFM image in a region designated in e); g) model of the thin film microstructure (the height scale in this picture is exaggerated with respect to the horizontal scale).

due to the primary ion bombardment, a certain layer of the sample is sputtered away revealing its deeper sections, which again can be mapped in a similar way. It is thus possible, by recording several consecutive dSIMS maps of the same sample region, to study the sample composition (or a distribution of a certain component) at different depths. In our case the intensity of $^{26}CN^{-}$ (m/z = 26) secondary ions was analyzed. Bright regions in Figure 2d correspond to a high concentration of PANI(CSA); the image shows that the phase separation process in the studied system leads to the formation of stripes with different composition.

However, in case of a symmetrically modified substrate it is difficult to differentiate between the regions on the sample which, prior to spin-casting, were covered by SAM from the ones with pure gold. In order to overcome this difficulty an asymmetric stamp was utilised. The substrate prepared in this way was then covered by spin-casting with a thin film of PANI(DPHP)/PS blend. In this case areas of SAM (narrow stripes) can be readily identified.

The AFM image (Figure 3e) shows that wide regions (polymer on Au) are higher than the narrow ones (polymer on CH_3-SAM). Moreover, the polymer layer is built of columns with a diameter of approximately 0.6 μm (>0.2 μm, the aperture of a teflon filter, which attest to the fact that the columns were created during spin-casting). The calculated RMS roughness of wide areas is significantly higher (19.8 nm) than that of the narrow ones (13.8 nm). It should also be noted here that the curvature of the contact mode AFM tips utilised in the experiments is approx. 10 nm, according to the manufacturer. Therefore, the column-like features with much larger lateral dimensions cannot be interpreted as an artifact arising from the geometry of the AFM probe.

Two dSIMS maps measured at the depth of approx. 62 nm and 108 nm (Figure 3c and 3d, respectively) show that although on the sample surface polyaniline is a dominating phase over wide stripes, the situation in lower regions of the polymer layer is reversed: close to the substrate there appears to be more polyaniline on narrow stripes. SIMS profiles taken from a wide and a narrow stripe (Figure 3a and 3b) show that while in the former case the concentration of PANI is uniform from the top to the bottom of the thin film, in the latter case the concentration of PANI is considerably higher close to the substrate. Basing on those observations a model of the thin film microstructure may be drawn (Figure 3g). The areas of CH_3-SAM are covered with a thinner polymer layer, because of poor wetting by the polymer solution. The film is composed of PANI-rich columns, which are significantly higher over clean Au. The columns are immersed in a ‘‘sea’’ of a PS-rich phase.

One of the factors influencing phase separation in the investigated polymer blend is undoubtedly the interaction of the blend components with the substrate. Modifying the substrate may significantly change the character of the pattern obtained after spin-casting. One of such modifications may be introducing water on the interface between the substrate and the polymer film. It was done by steaming a COOH-SAM-modified Si wafer with water vapour immediately before the spin-casting procedure. A thin film which was next spun-cast at 1000 rpm from a solution containing 10 mg/ml PS ($M_w = 125000$) and 6 mg/ml PANI(CSA) was characterised by a very much different pattern from the ones obtained in other cases. Elongated phase domains of the height of approx. 200 nm were formed with a dip in the middle (as seen from the cross-sections of AFM images in Figure 4. Since the features observed in this case are considerably higher than those obtained on non-steamed substrates, it cannot be excluded that the granularity of the surface is also present here, only it cannot be visible because of the higher z range. The structure here is not perfect – the stripes are damaged in several places, as seen from an optical micrograph and an AFM image. SIMS maps combined

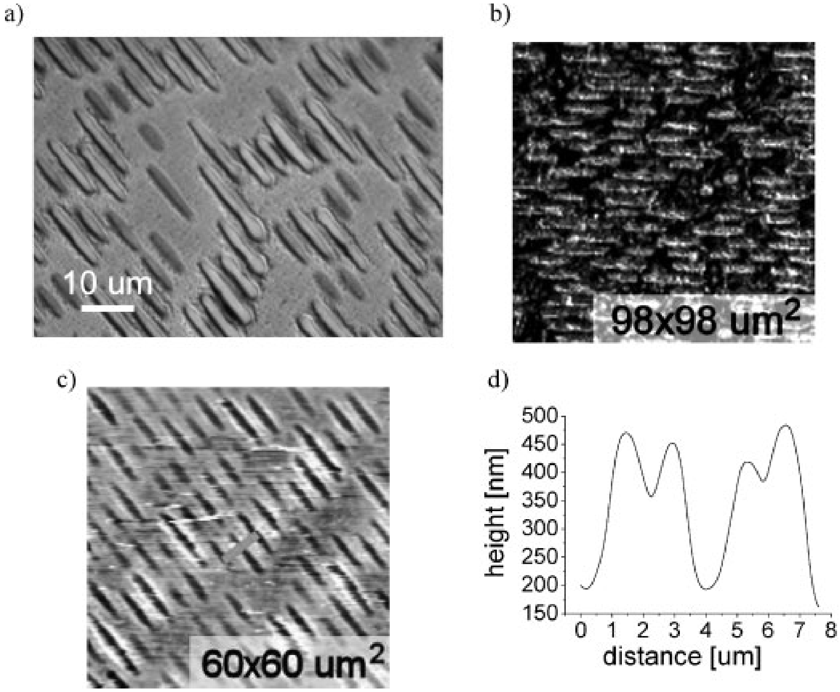

Figure 4.
a) optical micrograph (in polarised light) b) dSIMS map c) AFM image and d) its cross-section along a line designated in c) of thin film spun-cast at 1000 rpm from a chloroform solution containing 10 mg/ml PS ($M_w = 125000$ amu) and 6 mg/ml PANI(CSA). The substrate was patterned with COOH-SAM and steamed with water vapour immediately before spin-casting.

with optical micrographs show that polyaniline is in this case mostly situated in the low regions of the layer, between high domains containing little polyaniline.

Conclusions

The results of the present work show that the morphology of a thin composite film containing doped polyaniline and a conventional polymer can be controlled by deposition of a self-assembled monolayer onto the substrate via the microcontact printing technique. The thickness of the polymer film over the regions covered with SAM differs from that over pure Au substrate. There are also differences in the chemical composition of the film between these types of region, as evidenced by dynamic SIMS measurements: SIMS profiles and maps show an increased polyaniline concentration close to the substrate on CH_3-SAM covered regions and no such increase on pure gold. A model of the film morphology is proposed basing on the above results.

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