

Patterning Phase Separation in Polymer Films with Dip-Pen Nanolithography

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Phase separation, pattern formation, and dewetting in polymer films are classic problems receiving renewed attention because of their importance to modern topics ranging from biological adhesion to thin-film optoelectronic devices.¹ For instance, because the characteristic length scales associated with the excitations in conjugated polymers (e.g., the exciton diffusion length) are on the order of nanometers to tens of nanometers, the optimization of many polymer optoelectronic devices rests on our ability to control the nanoscale morphology of polymer films cast from solution.^{1e,2}

Although a number of approaches have been developed to control the structure of thin polymer films, there is still a need for new methods capable of generating a wide range of polymer morphologies on submicron length scales. Much fruitful effort has focused on block copolymers.³ However, simultaneous demands for optoelectronic functionality and phase-separating behavior can impose conflicting constraints on block design. Another method for controlling structure in thin polymer films is the use of surface chemistry.⁴ Several groups have used microcontact printing to define surface templates to guide the formation of micron-scale patterns in polymer films.⁵ Others have modified surfaces using techniques, including X-ray photolithography, restructuring of miscut semiconductor wafers, and randomly adsorbed nanoparticles and block copolymers.⁶ However, while some of these techniques can control polymer–surface interactions on the nanometer scale, none of them allow for the study of polymer interactions with patterned high-resolution chemical templates of controllable size, shape, composition, and spacing without access to expensive facilities.

Herein, we show that the scanning-probe technique, Dip-Pen Nanolithography (DPN),⁷ can be used as a rapid prototyping tool to generate and study nanoscale structure in thin polymer films. Although DPN has been used to write lines of conjugated polymers $< \sim 2$ molecules thick,⁸ we now show how DPN can be used to control nanoscale *phase separation* in films that are 20–60 nm thick with sub-150 nm lateral precision. Finally, we show that DPN provides a new means to study heterogeneous nucleation on surfaces and show DPN can be used to screen size-dependent interactions between films and surface features.

Figure 1A depicts our approach. An atomic force microscope (AFM) tip delivers a functional alkylthiol ink to a gold substrate with high resolution. A polymer blend is then spin-coated onto this patterned surface, and the resulting morphology is characterized with optical microscopy, AFM, and X-ray photoelectron spectroscopy (XPS).

Figure 1B shows a lateral force microscopy (LFM) image of an array of 400 nm diameter dots of 16-mercaptohexadecanoic acid (MHA) deposited on gold via DPN. Before imaging, the substrate was dipped in a 1 mM ethanolic solution of benzenethiol (BZT) to passivate the unpatterned gold. Upon this template, we spin-coated a 65/35 (w/w) blend of poly-3-hexylthiophene/polystyrene (P3HT/PS) dissolved in chlorobenzene (CB) at a total polymer concentra-

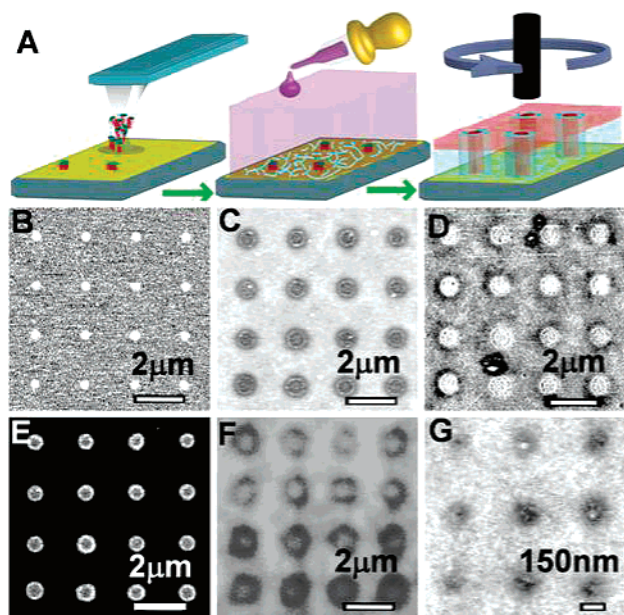


Figure 1. (A) Monolayers written by DPN are used to template phase separation in polymer blend films. (B) AFM lateral force image of MHA dots on a BZT background. (C–F) Images of P3HT/PS blend spin-coated onto this template. (C) AFM height image (5 nm z-scale). (D) AFM lateral force image. (E) Conducting AFM image (20 nA z-scale). (F) Fluorescence image. (G) AFM height image of 150 nm diameter P3HT domains (2 nm z-scale) on smaller templates at lower P3HT concentration.

tion of 10 mg/mL. PS was obtained from Aldrich (MW = 110 kDa, as reported) and P3HT from American Dye Source (MW = 55 kDa, MN = 22.8 kDa, determined by GPC). This blend of P3HT, a purple–red semiconductor, and PS, a clear insulator, provides a useful model system because the strong optical, electronic, and elemental contrast between the polymers facilitates blend characterization, while allowing us to show that the technique can be applied to the technologically important P3HT polymer.

Figure 1C–F shows that cylindrical P3HT-rich domains form on top of the MHA dots and are recessed < 5 nm in a homogeneous background (total film thickness ≈ 35 nm, as determined by AFM). Fluorescence microscopy (Figure 1F) and conducting-probe AFM (Figure 1E) confirm the composition of the domains and the fact that they extend through the entire thickness of the film. By varying pattern size and film processing conditions to limit growth after nucleation, it is possible to produce polymer patterns with features down to 150 nm in size (Figure 1F) or smaller. Features down to 50 nm can be written, but the probability of nucleation decreases with feature size (see below).

Before proposing a mechanism for the pattern formation shown in Figure 1, we summarize the following results of optical, AFM, and XPS data reported in the Supporting Information: (1) neither PS nor P3HT films of 30–50 nm thickness dewet from monolayers of BZT or MHA; (2) on BZT, PS/P3HT blend films are laterally homogeneous with a P3HT layer at the film–air interface, while

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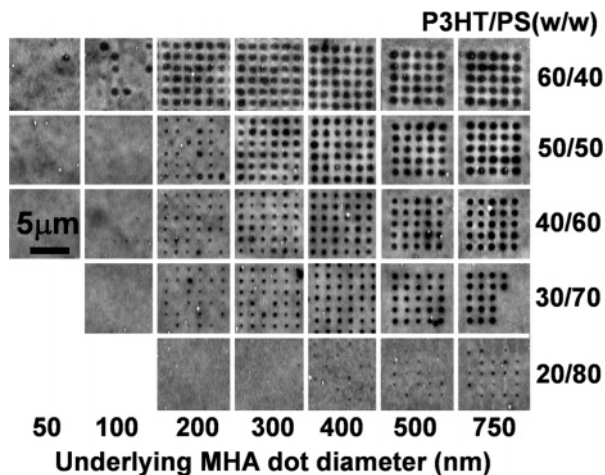


Figure 2. AFM height images (5 nm z-scale) of P3HT/PS films showing a combinatorial study of nucleation dependence on concentration and template size.

on MHA, they are laterally phase-separated; (3) the laterally homogeneous films on BZT undergo nucleated lateral phase separation upon annealing at 140 °C for 24 h; (4) PS adsorbs from dilute solution onto BZT faster than onto MHA.

We propose a mechanism for the observed pattern formation based on the known sensitivity of spin-coated film morphologies to surface chemistry.⁹ When the polymer solution is deposited on the substrate, PS preferentially adsorbs on the chemically similar BZT surface. As the solvent evaporates, the solution begins to phase-separate. On a PS/BZT surface, the interfacial energy required to form a PS/P3HT interface creates a barrier to lateral domain formation, and the film segregates vertically. The MHA/P3HT interfacial energy is lower than the PS/P3HT energy; thus, the barrier to lateral phase separation is lower, and P3HT-rich domains begin nucleating. Once nucleated, the domains continue to grow until the film vitrifies. Although experimental values for the relevant interfacial energies are not available, estimates based on group contributions¹⁰ are consistent with this picture.

Many other polymer blends exhibit either vertical, lateral, or a lack of phase separation depending on relative interfacial contact energies,¹¹ and we anticipate that our approach could be used to nucleate site-selective patterns in such systems. Indeed, guided by our model, we have successfully applied our technique to nucleate PS domains in polyvinylpyridine films using nonpolar DPN templates (Supporting Information).

Finally, Figure 2 shows how DPN can be used to study heterogeneous nucleation in thin films.¹² Five solutions with relative P3HT/PS concentrations ranging from 60/40 to 20/80 (w/w) were spin-coated onto five substrates, each having seven different grids of MHA dots of varying diameter. Three observations can be made from Figure 2. First, the final size of the P3HT-rich dots depends both on the template size and on the P3HT concentration. Second, there is a sigmoidal relationship between the area of the MHA templates and the probability that a P3HT domain will form on top of a given template. Third, the size of a dot required to guarantee nucleation of a P3HT-rich phase decreases as the P3HT composition of the blend is increased. These observations support our picture that the MHA dots serve as sites for the heterogeneous nucleation of lateral P3HT domains and demonstrate how DPN can rapidly screen nucleation kinetics with a particular materials set.

We have shown that DPN-generated surface templates offer a powerful means for controlling phase-separation and pattern formation in thin films containing conjugated polymers, without the need for masks, stamps, or extreme UV light sources. These results are important for two reasons. First, the ability to control the morphology of solution-cast polymer blends in site-specific fashion with nanoscale precision is a central problem in organic thin-film electronics. Second, our method provides a rapid means to control the size and shape of heterogeneous nucleation sites in a well-controlled manner and should facilitate the study of size- and shape-dependent nucleation in a variety of thin polymer films and other nanostructured materials.

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Supporting Information Available: XPS and AFM data of pure and blended films on multiple surfaces. AFM data of thermal annealing, polystyrene adsorption, and PS/PVP patterning. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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