

# Structures in Multicomponent Polymer Films: Their Formation, Observation and Applications in Electronics and Biotechnology

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Several strategies to form multicomponent films of functional polymers, with micron, submicron and nanometer structures, intended for plastic electronics and biotechnology are presented. These approaches are based on film deposition from polymer solution onto a rotating substrate (spin-casting), a method implemented already on manufacturing lines. Film structures are determined with compositional (nanometer) depth profiling and (submicron) imaging modes of dynamic secondary ion mass spectrometry, near-field scanning optical microscopy (with submicron resolution) and scanning probe microscopy (revealing nanometer features). Self-organization of spin-cast polymer mixtures is discussed in detail, since it offers a one-step process to deposit and align simultaneously domains, rich in different polymers, forming various device elements: (i) Surface segregation drives self-stratification of nanometer lamellae for solar cells and anisotropic conductors. (ii) Cohesion energy density controls morphological transition from lamellar (optimal for encapsulated transistors) to lateral structures (suggested for light emitting diodes with variable color). (iii) Selective adhesion to substrate microtemplates, patterned chemically, orders lateral structures for plastic circuitries. (iv) Submicron imprints of water droplets (breath figures) decorate selectively micron-sized domains, and can be used in devices with hierarchical structure. In addition, selective protein adsorption to regular polymer micropatterns, formed with soft lithography after spin-casting, suggests applications in protein chip technology. An approach to reduce lateral blend film structures to submicron scale is also presented, based on (annealed) films of multicomponent nanoparticles.

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## 1. Introduction: solution deposition of conjugated polymer blends

The discovery and development of conjugated polymers [1], i.e. chains of alternating single and multiple covalent bonds raise strong hopes of modern technology. This is not merely because of their semiconducting or conducting properties, exhibited by pure or doped conjugated macromolecules, but *also* due to their easy solution-based processing. In contrast to metals or silicon, conjugated polymers can be dissolved and re-

trieved with unchanged composition after solution evaporation. Therefore, it is very common to deposit polymer (semi)conductors from their solutions. Fast deposition of uniform polymer films onto a rotating substrate, called *spin-casting*, has been already implemented on the manufacturing lines [2].

Mainstream strategies to produce organic (opto)electronics are based on additive deposition of various functional polymers [3]. However, spin-casting of polymer mixtures seems technologically more attractive as it offers a *one-step procedure*, provided that the domains of various polymers could self-organize to form different elements of (opto)electronic devices.

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Here we discuss several self-organization processes in spin-cast multicomponent films, which supplemented by soft-lithography techniques, might result in the specific structures intended for (opto)electronics. An extension of this approach to biotechnology is also demonstrated.

## 2. Structure formation processes, their observations and applications

### 2.1. Surface segregation drives self-stratification (for solar cells and anisotropic conductors)

Spontaneous formation of lamellar structures in polymer blend films is called self-stratification. It can be applied to form extended heterojunctions, i.e. interfaces between *n*-type (with larger electron affinity) and *p*-type macromolecules (with lower ionization potentials). Heterojunctions considerably enhance dissociation of electron-hole pairs (excitons) created by light in solar cells, increasing their power conversion efficiency (PCE) [4, 5].

Effective self-stratified heterojunctions (with PCE  $\approx$  3.5%) are formed during spin-casting of a polyfluorene copolymer (APFO-3, *p*-type) mixed with the fullerene derivative (PCBM, *n*-type) [6, 7]. Corresponding lamellar film structures are revealed by dynamic secondary ion mass spectrometry (dSIMS), as an oscillating depth profile of APFO-3 composition (Fig. 1). In dSIMS technique a primary ion beam ( $\text{Ga}^+$ , 5 keV, 2 nA) is used to sputter the film and to induce secondary ions, which are mass-resolved to yield concentration profiles with the depth resolution (standard deviation  $\delta$ ) of 5 nm [8].

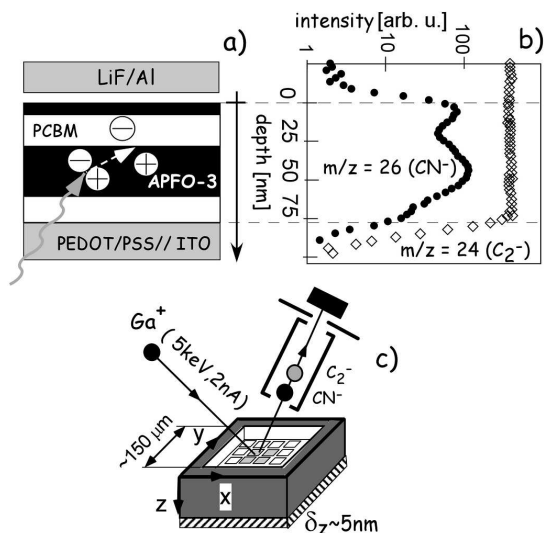


Fig. 1. Lamellar structure formed in spin-cast mixtures of *p*-type (APFO-3) and *n*-type (PCBM) macromolecules (a), revealed as oscillating APFO-3 composition (solid circles) vs. depth profile (b) by the profiling mode of dSIMS (c). In contrast, blend composition ( $\diamond$  in (b)) is constant.

Composition waves normal to the film surface are formed readily during spin-casting only when the composition of binary polymer blend allows for an easy access to the unstable (spinodal) region of the phase diagram [6, 7], with the quench enabled by solvent extraction from the 3-component film. This indicates spontaneous spinodal phase separation as the responsible self-organization mechanism. Composition waves, formed by spinodal decomposition, are directed not randomly as in the bulk material, but normally to the surface, driven and ordered by surface segregation [9].

Surface segregation in one component of the polymer blend can be induced by its lower surface tension or specific substrate interactions. In addition to these two forces driving the surface-directed phase decomposition (observed earlier in annealed blends [9]), self-stratification in spin-cast films is driven by the solubility difference of dissolved polymers. The less soluble polymer is easily depleted from the film solution directly to the substrate. All three driving forces were concluded for the spin-cast blends of dielectric polystyrene (PS) mixed with conducting polyaniline doped with camphorulfonic acid (PANI(CSA)) [10]. Structure of resulting anisotropic lamellar conductors (thickness, number of lamellae) is controlled by spinning speed and polymer molecular weight.

### 2.2. Cohesion energy controls transition from lamellar to lateral structures (for encapsulated transistors and light emitting diodes)

One of the most studied conjugated polymer families are polythiophenes (PTs). This is due to their (commercial availability and) superior charge mobility (up to  $0.6 \text{ cm}^2/(\text{V s})$ ). Mixtures of PTs with dielectric polymers can be used to spin-cast structured films for diverse device designs [11, 12]. Lamellar structures can be applied to produce field-effect transistors (FETs) with self-encapsulated layer protecting from environmental conditions, or with a (deposited) hygroscopic layer sensing gases. In turn, lateral (quasi-2D) structures were proposed to fabricate light emitting diodes (LEDs) with variable color, nanoLEDs or anisotropic (semi)conductors.

The first systematic morphological studies of PT mixtures with an insulating polymer have just been performed for poly(3-alkylthiophene)s (P3ATs), with different head-to-tail regioregularity and alkyl chain length, blended with polystyrene (PS) [12]. P3AT exhibits fluorescence, so lateral domains rich in P3AT can be identified with fluorescence microscopic techniques. In near-field scanning optical microscopy (NSOM), fiber exciting fluorescence is attached to the probe of scanning probe microscope (SPM) — scanned at constant distance above the film surface. Therefore, fluorescence (or light reflection/transmission) images revealed with lateral resolution of some 100 nm are combined with topographic information (Fig. 2), allowing an easy film structure determination, confirmed independently by dSIMS.

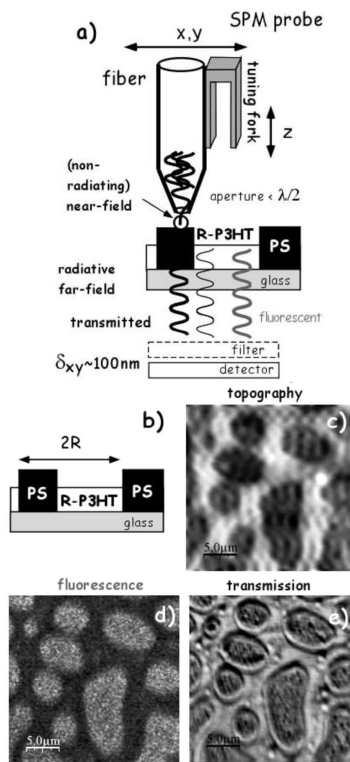


Fig. 2. NSOM (a) reveals fluorescence (d) and light transmission (e) images combined with topographic information (c), used to determine the lateral structure (b) of spin-cast (PS/R-P3HT) blend. R-P3HT is the most commonly used P3AT polymer.

Lamellar and lateral structures determined, besides the minor dewetting morphology, for the blend films spin-cast from the solutions of five solvents, containing PS mixtures with four different P3ATs, can be consistently arranged according to their cohesion energy density  $\delta^2$ . Morphological transition from lateral to lamellar structures is induced by the changed cohesion energy density: increased for P3ATs and decreased for the solvents [12]. This can be explained with Young's theory of contact angle phenomena, applied to the transient interface between the layers of P3AT-rich phase and solvent-rich PS solution – formed during the late stage of spin-casting prior to (possible) lateral structure formation.

### 2.3. Selective adhesion to substrate micropatterns organizes lateral structures (for plastic circuitries)

To produce polymer-based circuitries for electronic devices, the deposition of polymers must be controlled spatially on a micron scale. This can be achieved with reactive techniques, such as area-selected electropolymerization or photochemical patterning, and non-reactive approach using dissolved molecules (usually printed). Only the non-reactive strategy is simple and versatile enough to allow a mass production [3]. The most attractive non-reactive approach employs the *one-step* spin-casting,

in which the blend domains of different polymers are guided by selective adhesion to the substrate micropatterns (Fig. 3), printed earlier with self-assembled monolayers (SAM) (e.g. alkanethiols and chlorosilanes for Au and  $\text{SiO}_x$ , respectively).

The combination of soft-lithographic substrate patterning and blend spin-casting have been demonstrated and examined thoroughly [13, 14] for the model dielectric mixtures of poly(vinylpyridine) (PVP) – selectively segregating to gold substrate regions not protected by SAM pattern. Topographical images, recorded with SPM (Fig. 3), reflect lateral film structures aligned by substrate microtemplate. To confirm that 2D domain structure extends from the surface through the film to the substrate, submicron dSIMS tomography is applied (Fig. 4), characterized by lateral and depth resolution of  $\delta \approx 260$  nm and 14 nm, respectively [8]. Indeed, almost identical dSIMS maps of PVP distribution are recorded for successive depth  $z$  in the studied films.

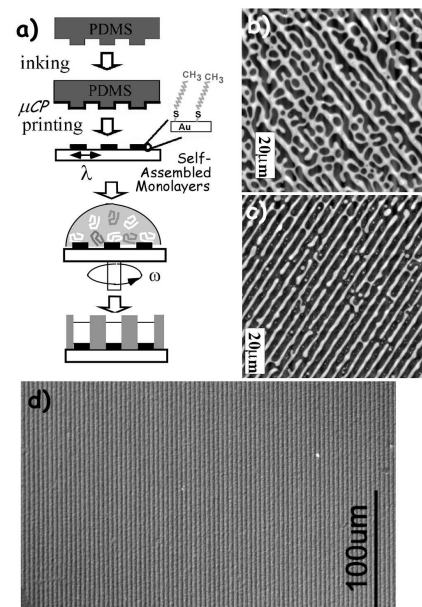


Fig. 3. Chemical substrate micropatterns (with periodicity  $\lambda$ ), printed with SAMs on gold (a), are replicated by lateral structures of spin-cast blends PVP/PBrS (with inherent domain scale  $2R$ ), for  $2R \sim \lambda/2$  (b) and  $2R \sim \lambda$  (c), and PANI(CSA)/PS (d), revealed by SPM (b)–(c) and optical microscopy (OM) (d).

Patterns can be transposed from the substrates into the spin-cast films for judiciously chosen systems, defined by the polymer mixture, the solvent and the patterned surface. The quality of pattern-directed film structures depend on the length-scale commensurability (Fig. 3b) between the blend ( $2R$ ) and the pattern ( $\lambda$ ) [13], as well as on the match between blend composition and patterned area fraction [14]. The patterns replicated by film morphology can be optimized with spin-coating conditions (tuning the domain scale  $2R$ ) or with changed pattern periodicity  $\lambda$ . Pattern-guided alignment can be ob-

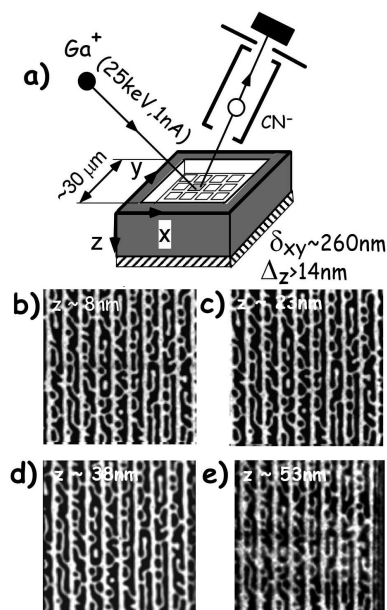


Fig. 4. The imaging mode of dSIMS (a) reveals maps of PVP distribution recorded at distance  $z \approx 8$  (b), 23 (c), 38 (d) and 53 nm (e) from the surface of PVP/PBrS blends spin-cast on the micropattern Au/SAM with  $2R \sim \lambda/2$  (corresponding to Fig. 3b, another spot). PBrS is partly brominated PS.

tained even for the domains with the scale ( $\lambda/2$ ) [13] or even the periodicity ( $\lambda/2$ ,  $\lambda/3$ ) smaller than  $\lambda$  [14].

Recently, the studies on pattern-aligned spin-cast blends have been extended to the mixtures of conjugated polymers, including the pair of conducting PANI(CSA) and insulating PS [10]. Chemical SAM microtemplates on Au substrate can be replicated over very broad areas ( $\gg 100 \mu\text{m}$ ) due to selective adhesion but also due to solution wetting modified by the pattern (Fig. 3d).

#### 2.4. Breath figures decorate selectively lateral domains (for devices with hierarchic structure)

Casting polymer films from the solution evaporating in a humid ambience results in the formation of air bubbles, often ordered hexagonally and embedded in polymer matrix (Fig. 5a, b). Cooling of solution surface, caused by solvent evaporation, enables condensation of water droplets which are trapped in the polymer film and evaporate to form air bubbles. Such breath figures with the size ranging from 200 nm to  $20 \mu\text{m}$  can have numerous applications, such as picoliter beakers or surfaces for cell growth [15].

Unfortunately, breath figure formation by *direct solvent evaporation* (Fig. 5a, b) is slow (it takes  $\approx 5$  min), requires high relative humidity ( $\text{RH} > 40\%$ ) — undesired in high-tech laboratories — and results in polymer films with varied thickness. These disadvantages can be removed, when the breath figures are created in dry atmosphere ( $\text{RH} < 40\%$ ) during the fast ( $\approx 5$  s) *spin-casting* of uniform polymer films from solutions containing small

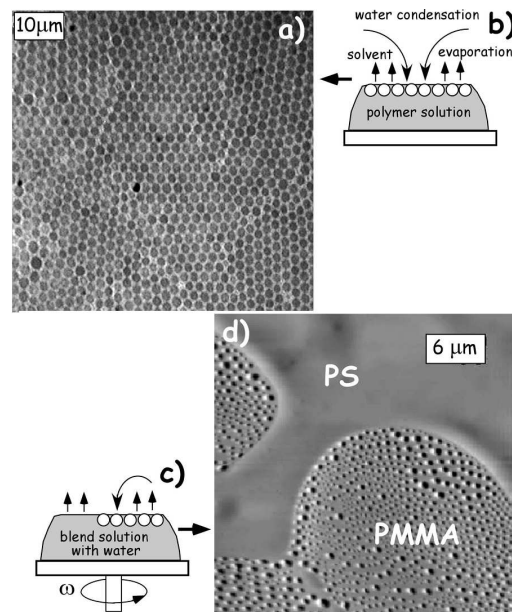


Fig. 5. Breath figures (imprints of condensed water droplets) formed by direct solvent evaporation (b) from P3AT solution (a), and obtained after spin-casting (c) of PS/PMMA blend and resulting in *hierarchic structure* (d). Micrographs are recorded with OM (a) and lateral-force mode of SPM(d).

(6–9 wt.%) amount of water. Studies performed for spin-cast films of polar poly(methyl methacrylate) (PMMA) show that water added to the (tetrahydrofuran) solution has much stronger impact on resulting breath figures than the water originating from ambient moisture [16]. In contrast, no air bubbles are observed in spin-cast films of non-polar PS.

These observations lead to the suggestion that the breath figures in the spin-cast blends of PMMA and PS should appear selectively in the lateral domains of polar PMMA, which would accumulate water present in solution. Resulting hierarchic structures with two length scales: submicron due to breath figures and tens of microns large due to lateral domains, have been indeed observed (Fig. 5c, d). They are suggested for several applications, including waveguides based on photonic crystals, displays based on structured LEDs or plastic circuitries integrated with picoliter sensors [16].

#### 2.5. Selective micromolding of regular polymer patterns (for protein microarrays)

Protein microarrays consist of large numbers of proteins distributed in densely packed spots with size  $< 250 \mu\text{m}$  [17]. They are expected to be commonly used to perform numerous parallel assays, detected with fluorescence, aimed to determine the presence (analytical chips) or activity (functional chips) of proteins.

One of the strategies used to form protein microarrays is based on non-specific and selective protein adsorption to surface patterns of homogeneous polymer coatings.

The polymer patterns, used to test selective protein attachment, are fabricated with self-organization, breath figure formation or soft-lithography: obtained surface patterns are disordered, partly ordered or completely regular, respectively.

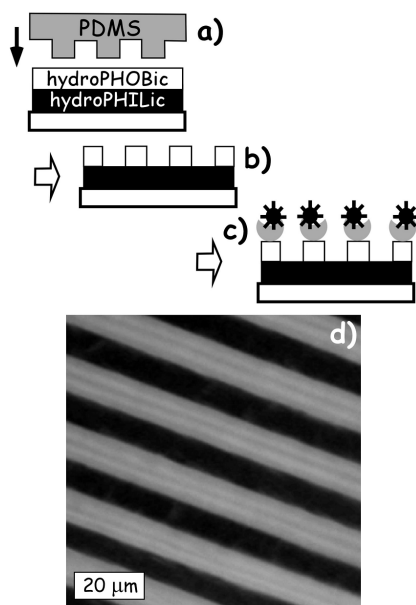


Fig. 6. Selective adsorption (c) of proteins (fluorescently labeled lectins), recorded by fluorescence microscopy (d), to *regular surface patterns* of hydrophobic and hydrophilic polymers (b) prepared with selective micromolding of initial bilayers (a).

The simplest approach to polymer patterns is to fabricate lateral structures in the spin-cast films of the binary mixtures of hydrophilic and hydrophobic polymers. Such step must be often supplemented by cross-linking, as the hydrophilic polymers, used to form areas with no protein binding, can be dissolved in aqueous protein solutions. The same is true for soft-lithographic approach to regular polymer patterns (solvent-assisted micromolding): the patterned elastomer stamp, wetted with selective solvent, is put into contact with the bilayers of successively spin-cast hydrophilic and hydrophobic polymers (Fig. 6). Both methods are tested for fluorescently labeled lectins [18].

#### 2.6. Films of blend nanoparticles with submicron structures (for optoelectronics)

Since the self-organization of polymer blend domains is a very fast process, the size of formed lateral film structures falls usually in the range of 1 to 10  $\mu\text{m}$ , reflecting the *late stages* of this process. However, some optoelectronic applications would require the blend film structures to be reduced to submicron scale. For instance, in order to generate charge in solar cells the excitons, appearing in absorber domains and characterized by the diffusion range of 10–20 nm, must reach the interface (heterojunction) with another domains.

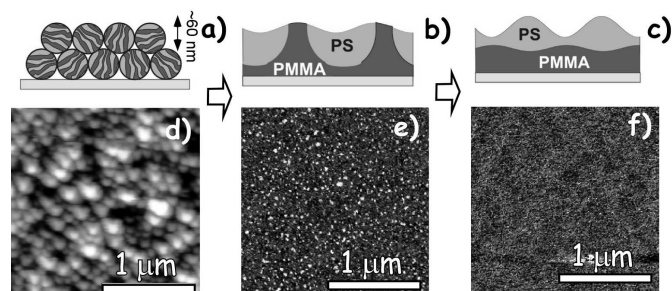


Fig. 7. Micrographs recorded with atomic (d) and lateral (e), (f) force modes of SPM, revealing evolution (a), (b), (c) of *submicron structures* of annealed blend films of PS/PMMA nanoparticles.

To study the *early stages* of self-organization in polymer blend films, one should start with the film structures reduced to submicron scale, e.g. based on blend nanoparticles [19], prepared using mini-emulsification process [20]. Morphological coarsening of such films, composed of model nanoparticles of PS mixed with PMMA, is initiated by annealing at temperatures elevated above polymer glass point (Fig. 7). Initial nanoparticles merge to form *continuous* film with distinct submicron (10 to 200 nm) surface domains, visible due to the frictional contrast of SPM. Then the dispersed surface domains disappear due to hydrodynamic flow to wettable substrate resulting in lamellar film structure, which is formed directly in the spin-cast blends.

### 3. Conclusions

To determine unequivocally multicomponent films structure, SPM, yielding topography, must be combined with techniques revealing phase domain structure, such as nanometer depth profiling and submicrometer tomography modes of dSIMS or submicrometer imaging provided by NSOM.

TABLE

The relations between structural types of multicomponent films, their formation processes and potential applications.

Structural type	Formation process	Potential application
lamellar	self-stratification	solar cells, transistors
lateral	cohesion energy effects	light emitting diodes
pattern-replicating	selective adhesion	plastic circuitries
hierarchic	selective droplet imprinting	integrated picoliter sensors
regular pattern	selective micromolding	protein chip technology
reduced lateral	annealing of nanoparticles	optoelectronics

Different structural classes, determined by specific self-organization and soft-lithographic processes, can be applied in various applications. These relations are described in Table.

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