Self Assembled Heterojunction Solar Cell Active Layers: CFN/USB/CAT Collaboation

Supported in part by the SensorCat program at NYSTAR,NSF-MRSEC

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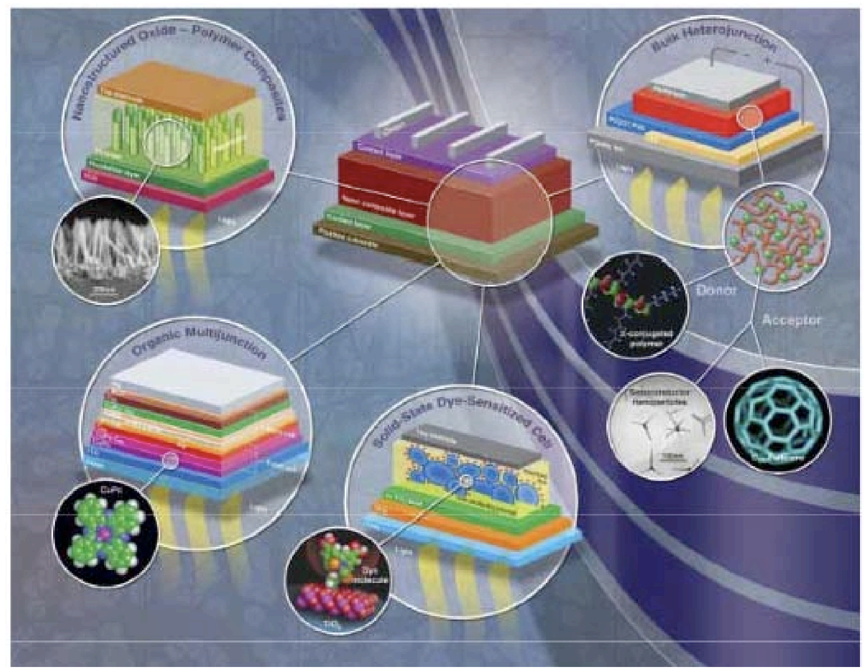
NIST National Institute of Standards and Technology

STONY BROOK UNIVERSITY

Center for Functional Nanomaterials

Solar Cells

- 1st generation:
  - Large area, high quality, single junction
  - Typical silicon solar cells- efficient, but very expensive
- 2nd generation:
  - Thin film cells
  - CIGS-CIS, DSC and CdTe
- 3rd generation:
  - Multijunction PV cells
  - Organic solar cells



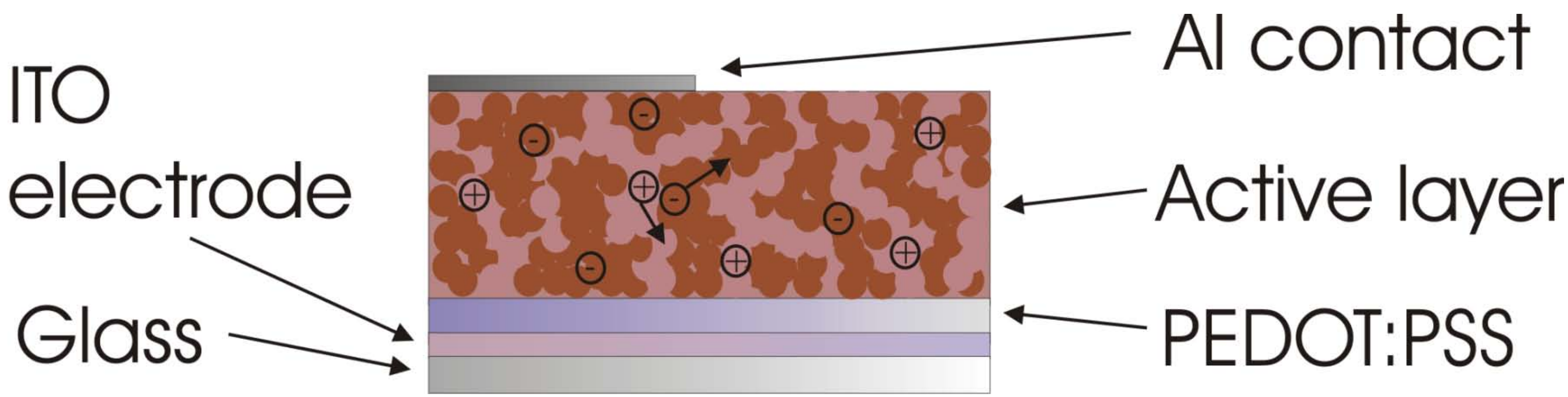
January 2005 *Materials Research Society Bulletin*

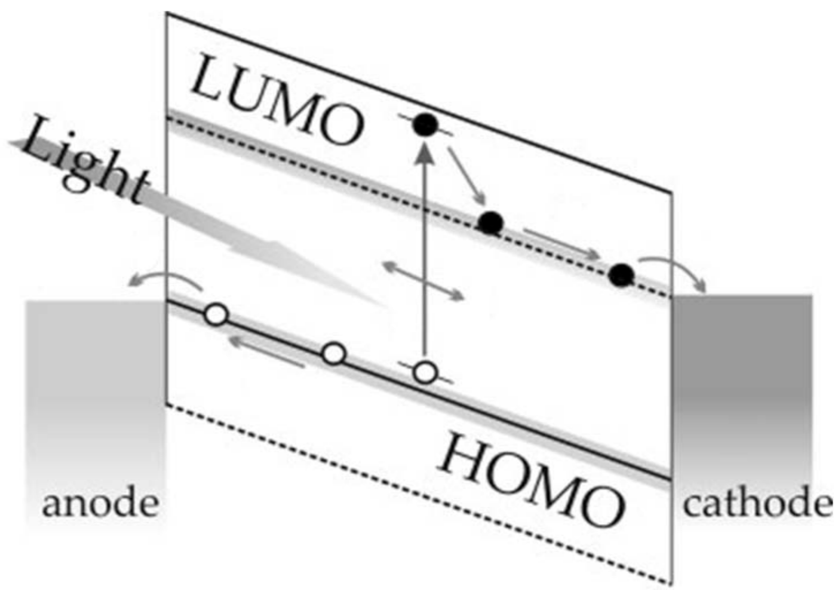
Objectives

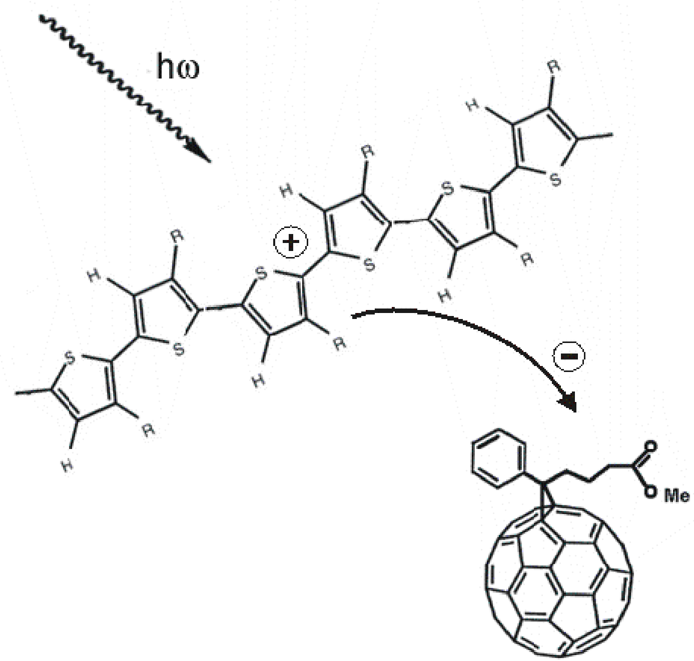
1. Morphological control of the P3HT and PCBM phases used in current BHJ solar cells to achieve a more precisely organized and efficient structure.

2. Investigate the physical properties of the materials, as received from the supplier, so that we may determine if new materials or functionalization is required to achieve a novel, successful BHJ solar cell structure

Current State-of-the-Art BHJ Solar Cell



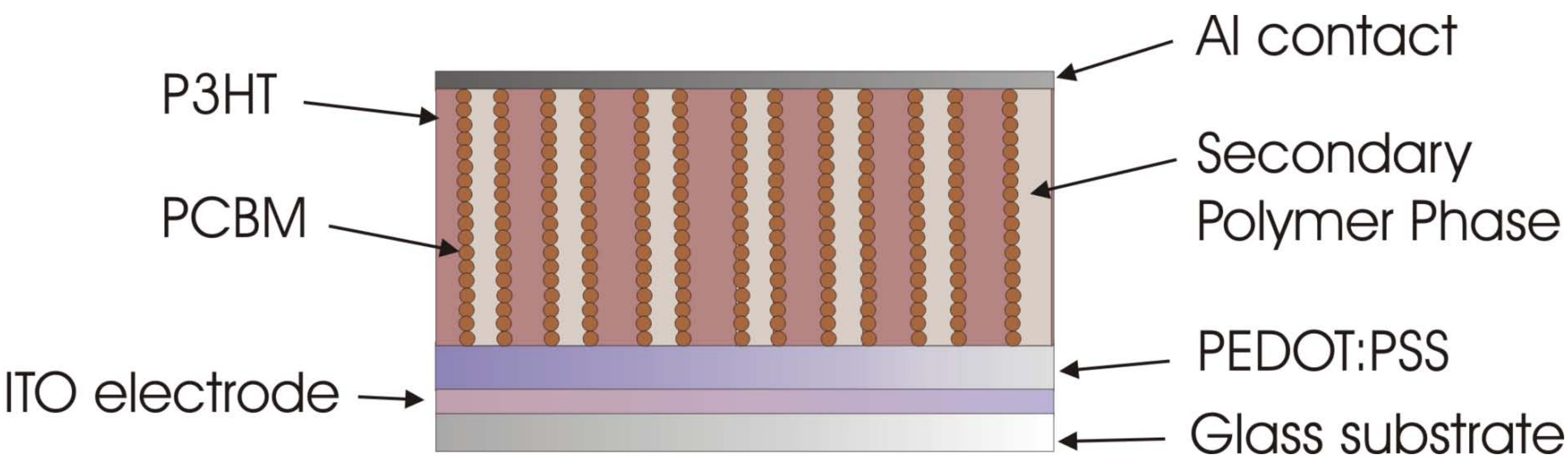




Blom et. al., Adv. Mat. 2007, 19, 1551-1566

Proposed Structure

- Improved UV-vis absorption efficiency due to increased polymer content
- Control over domain size and interface width to improve exciton dissociation efficiency
- Improve carrier transport by creating columnar domains – shorter path: less scattering, trapping

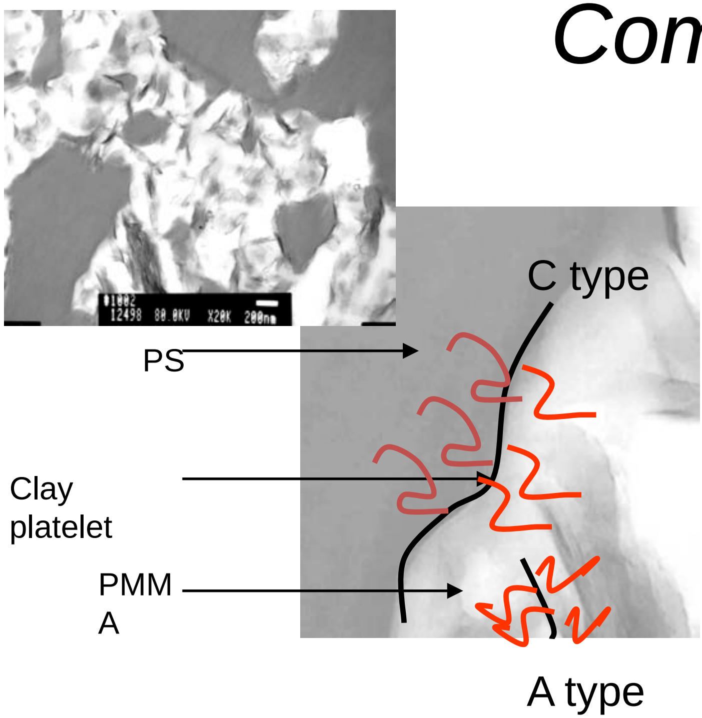


• Fillers at Blend interfaces

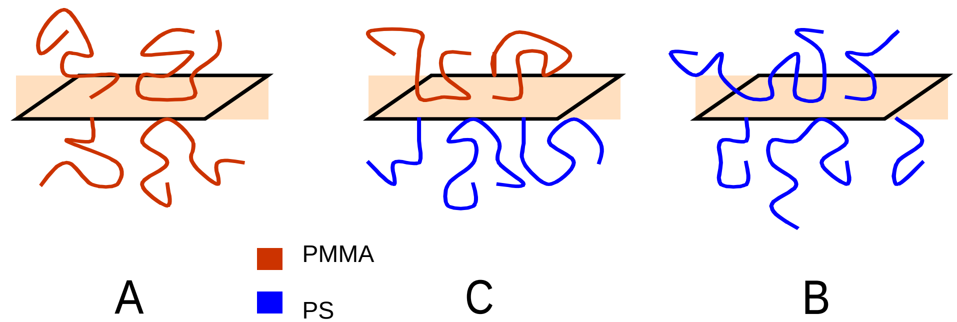
- Interfaces have unfavorable energy.
- Both phases interact with the filler.
- Both Ea, Eb have to be less than Eab
- Key to the use of nanofillers: Fillers will migrate to the interface and lower the energy of the system
  - Fillers must migrate to the interface between the two polymers
  - Fillers must provide mechanical reinforcement across the interface
  - Low concentrations of fillers should provide desired effect

Compatibilization Model

M. Si et al Macromolecules, 2006



Three types of in-situ graft absorption on clay



Equilibrium morphology can be determined by by balancing the reduction in interfacial energy with the increase in bending energy:

$$F = \gamma(n-m)l^2 + \gamma' ml^2 + mF_{bending}$$

Energy penalty of putting C type platelets in either of the phases

Interfacial energy of the platelet covered domains

Bending energy of the platelets due to interfacial curvature.

γ: the interfacial energy between the two polymers,

γ': is the interfacial energy when platelets are at the interface,

n: the total number of clay platelets of C

m: the number of clay platelets of C, contributing interfacial energy reduction

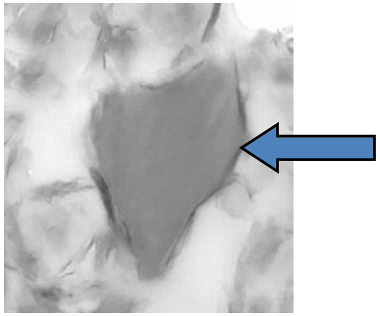
l^2 : the surface area of the platelets

r: the radius of domains

Compatibilization Theory

Assumption: all the domains are fully covered by the clay platelets and the blend has equal amount of each phase, we can derive an expression for *m*:

$$F_{bending} = \frac{Eh\ \zeta^4}{4l^2} \qquad (\zeta \approx l^2/r) \qquad m = 3V/2rl^2$$



E :Young's modulus, *h*: thickness of a platelet, ζ: displacement of the platelet for small deformations, V: system volume

Minimize free energy with respect to *r*,

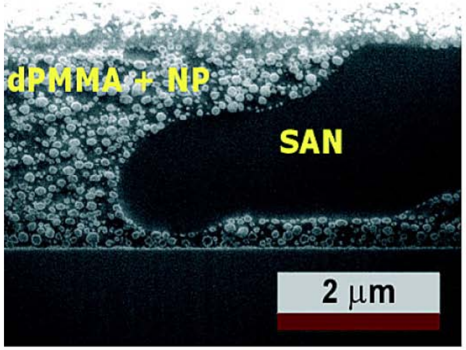
d*F*/d*r* = 0

$$r = \alpha l \qquad \alpha = \left(\frac{5Eh}{4(\gamma - \gamma')}\right)^{1/4}$$

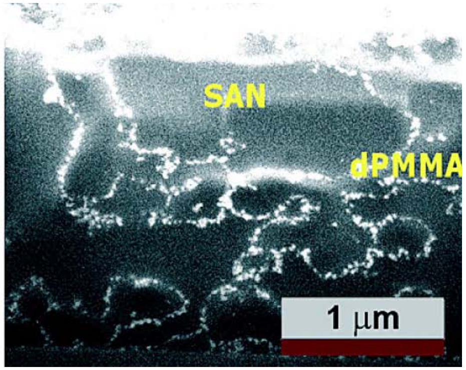
- Let γ = 2mN/m, *E* ~ 1GPa, $\gamma >> \gamma'$,then α ~l, the domain size is the magnitude of clay platelet size, which is similar to the diameter of the domains: 400-600 nm (TEM)
- Larger γ , smaller *r*, more efficient compatibilizing.

M. Si et al Macromolecules, 2006

• Nanoparticles in Blends



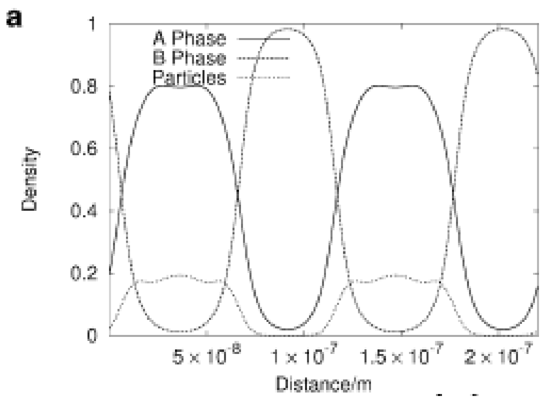
vs.

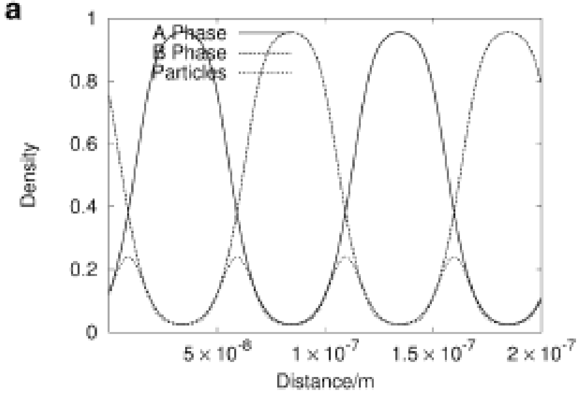


NP Partition into dPMMA

NP Segregation to interface

Chung, et. al., Nano Lett., **2005**, 5(10), 1878-1882.





Buxton, et. al., Macromolecules., **2003**, 36, 963.

Nanoparticles can stay in one phase or segregate to the interface

• Simulation parameters

- δ was introduced to enhance repulsive interactions between the monomers. When $\delta<1$, repulsion increases, leading to phase separation.

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \delta\left(\frac{\sigma}{r}\right)^{6}\right]$$

- The simulation box was held at $2L_x=2L_y=L_z=32\sigma$.
- The temperature of the simulations was held constant at 1.1 ($T_g \approx 0.5$).
- The temperature of the system was dissipated by the two walls.
- Before shear, the system was equilibrated to avoid any residual stresses.
- Attractive force between polymer and filler was fixed with $\varepsilon_{fp}=2.0$ for both A and B polymers ($N=64$).

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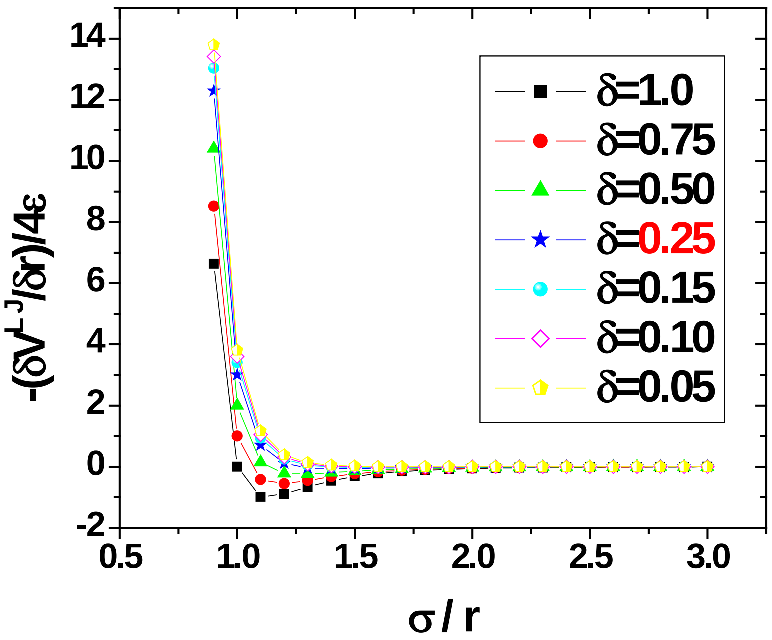
• Simulation parameters

- We manipulated the system by controlling values of:
  - filler size – s
  - filler concentration – ϕ_f
  - interaction parameter – δ
  - wall velocity – v

s	ϕ_f	v	δ
0.25	0.02	0.12	0.10
1.00	0.05	0.24	0.25
		0.48	0.50
			0.75



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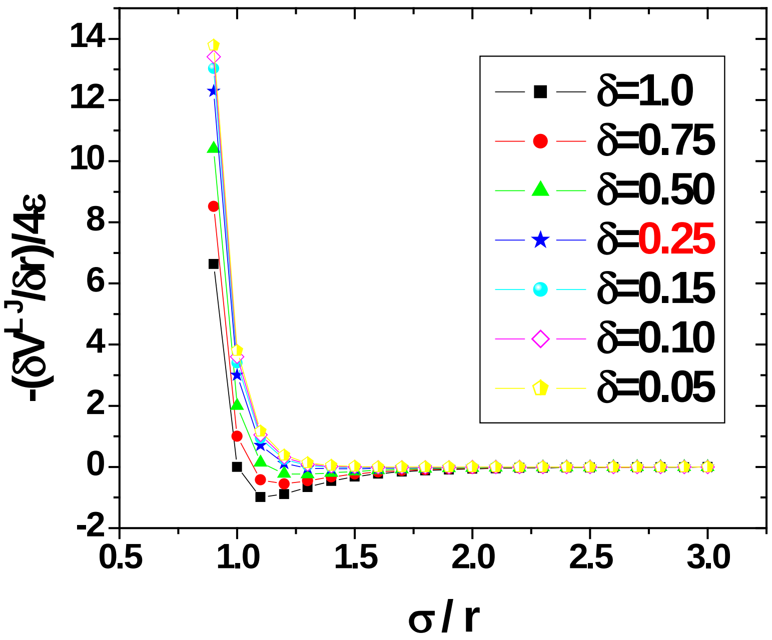
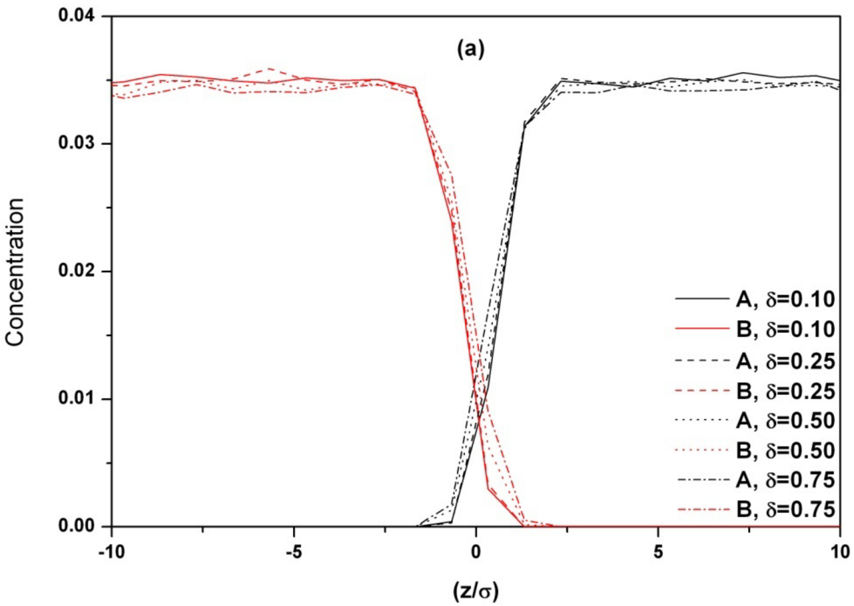
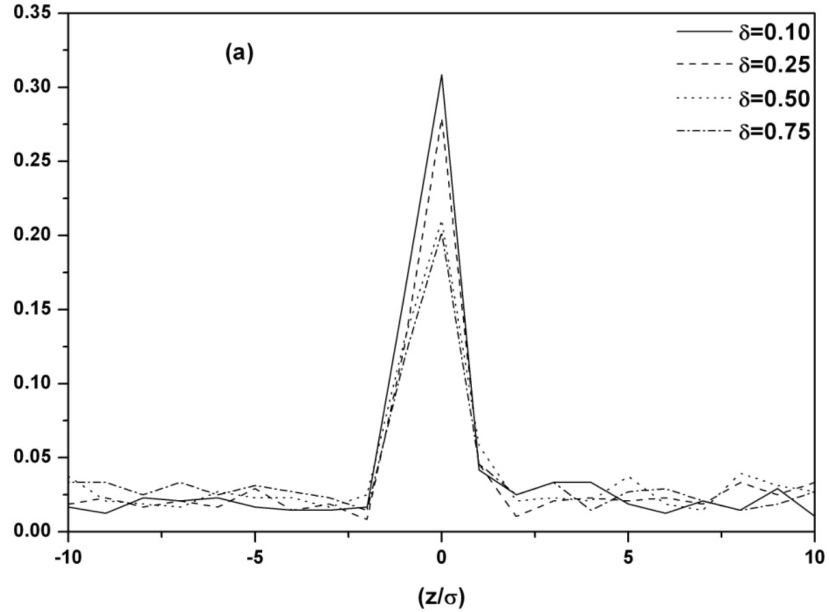


Equilibrium profiles

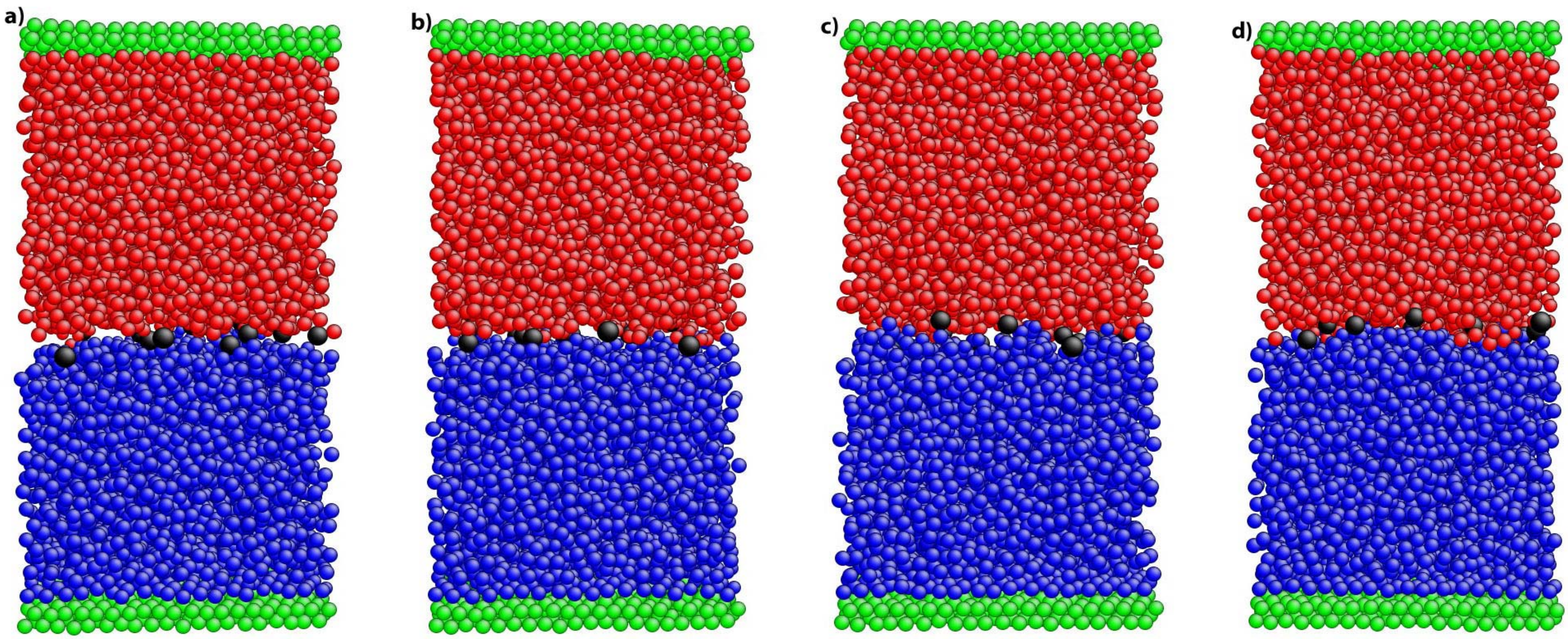




- Nanoparticle segregation increases with increase in repulsion between phases

Creating polymer blends

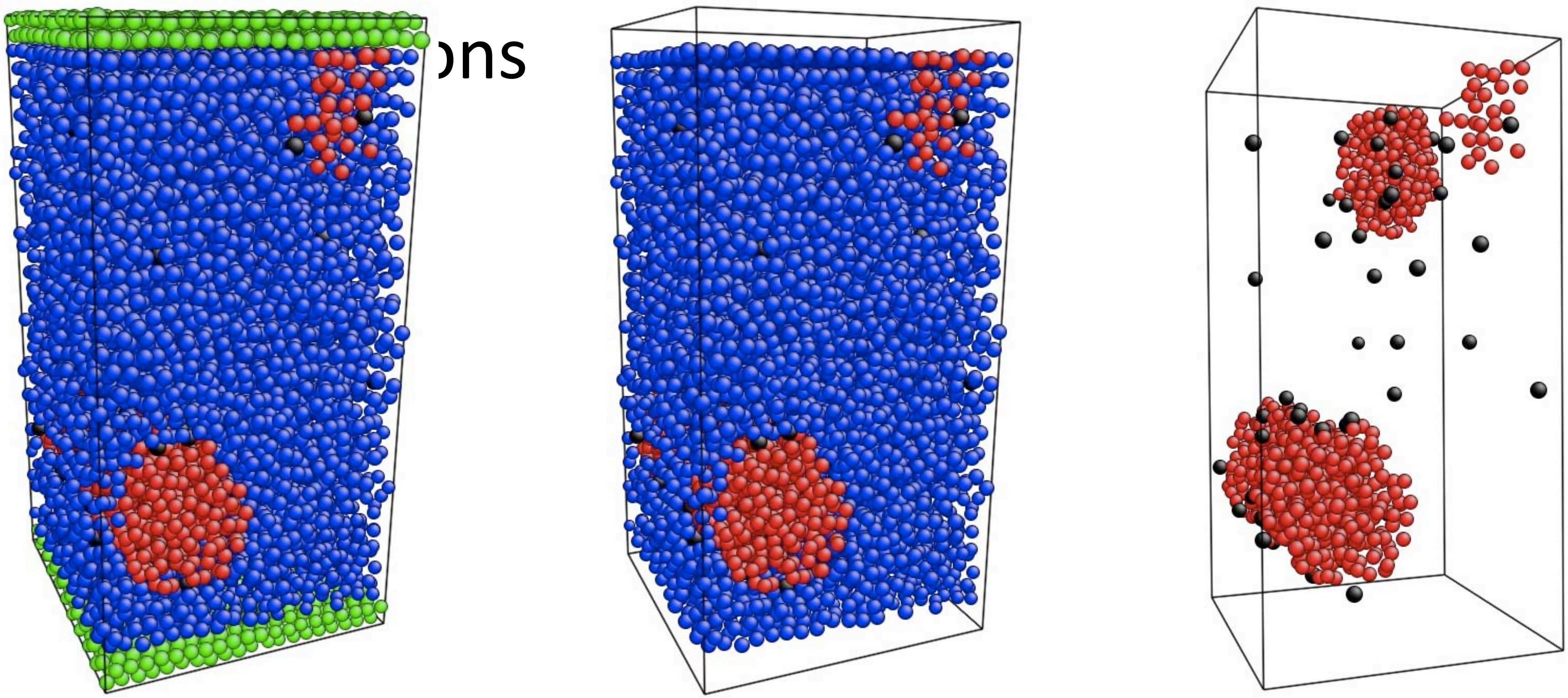
By adjusting the δ term, we were able to force varying degrees of phase separation.



(a) δ=0.10 **(b)** δ=0.25 **(c)** δ=0.50 **(d)** δ=0.75

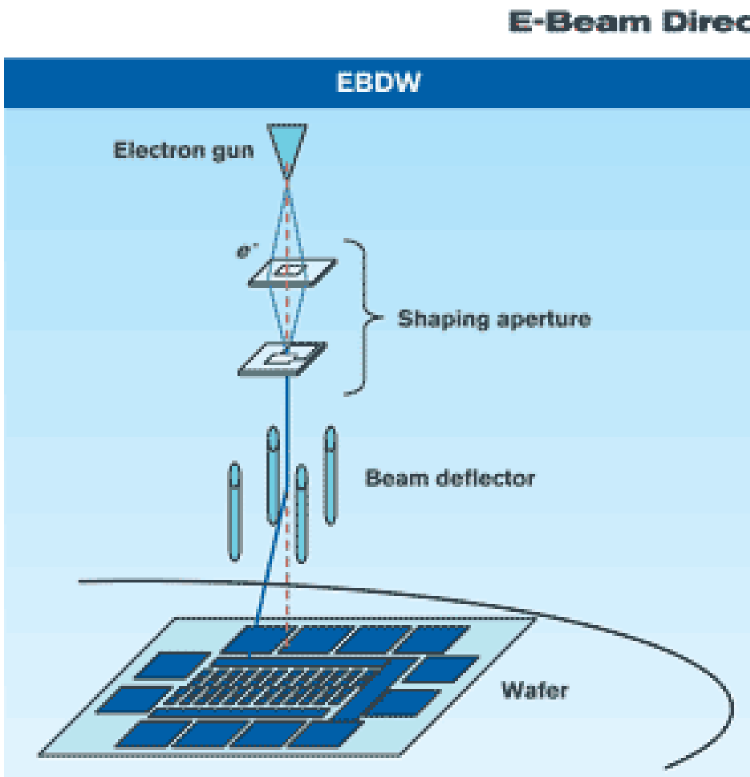
Non planar interfaces

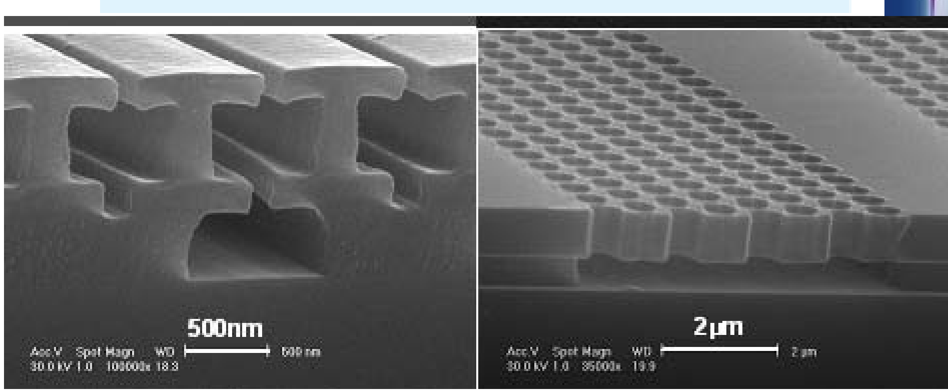
- Fillers can also segregate even if the interface is not planar -- solar cell [illegible]ons



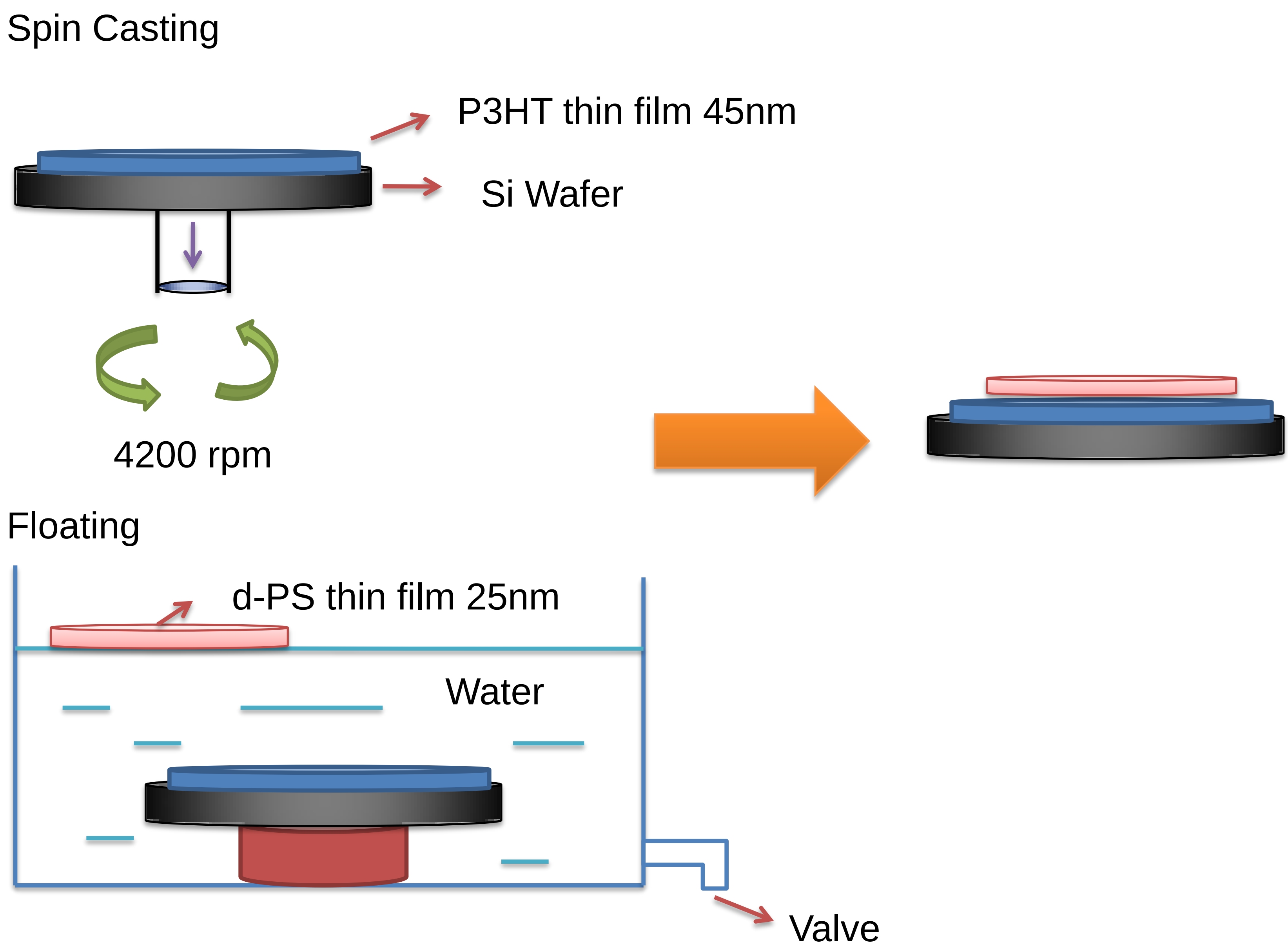
E-Beam Lithography

- •. One wafer throughput
- Slow: Up to 150 hours to process.
- Ideal for complex patterns
- Research vs commercial applications

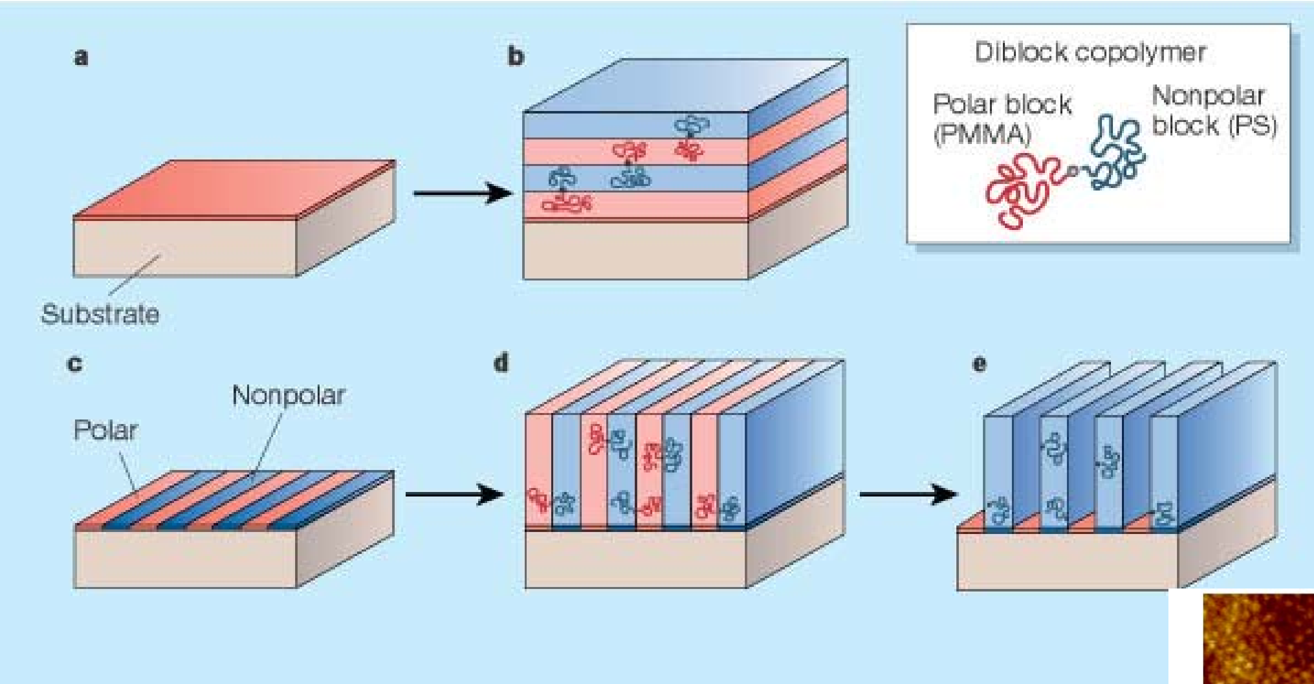


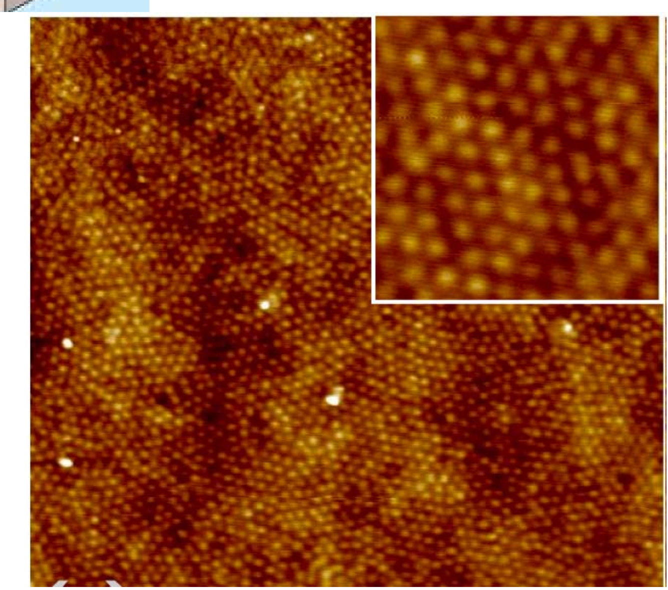


Sample Preparing



Polymer self assembly

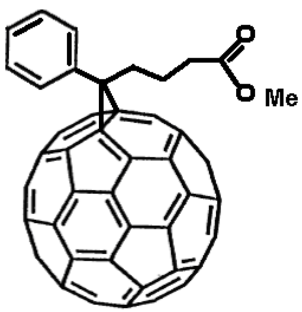




Richard Register, Nature 2004

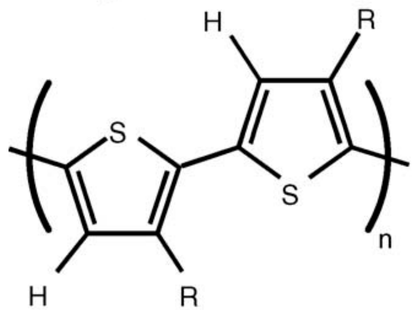
Materials and Methods

PCBM



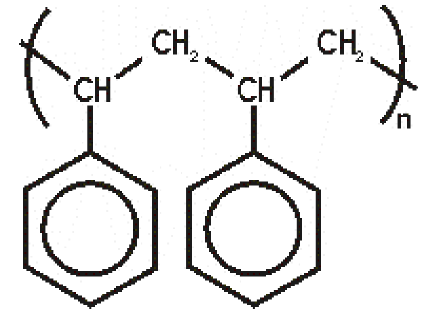
American Dye Source

P3HT (R=C_6H_{13}), **32 kD**



American Dye Source

PS, 65 kD



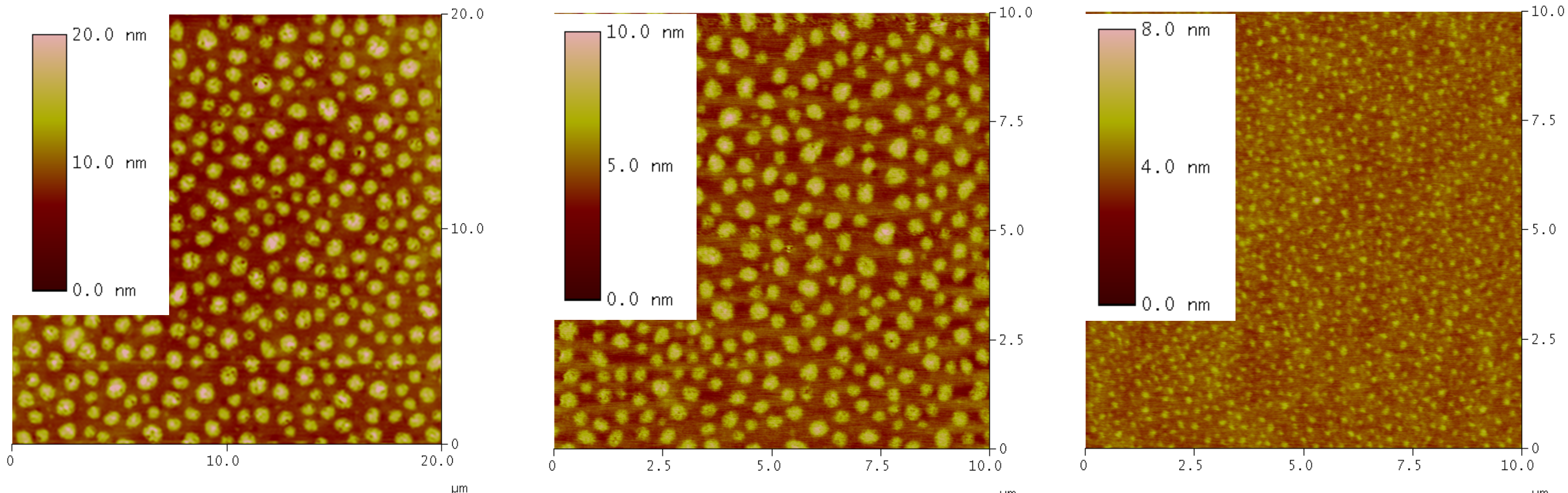
Pressure Chemical

Solution preparation: 1 – 8 wt% polymer and PCBM in chlorobenzene with varying ratio by wt% depending on experiment

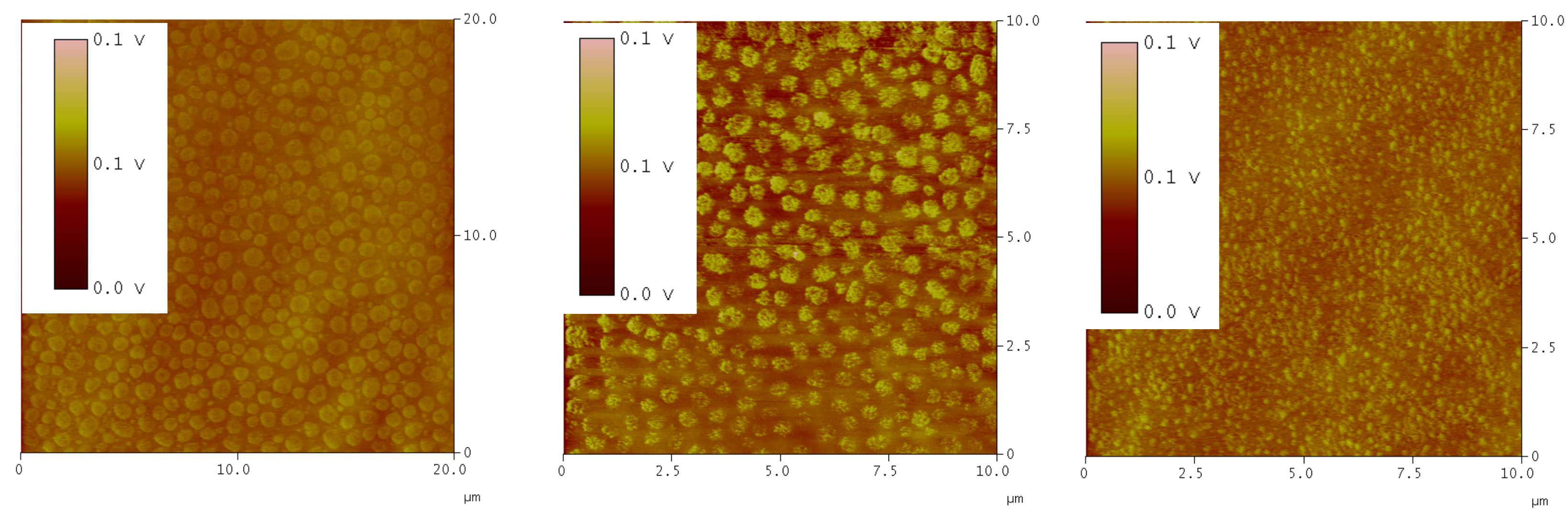
Thin film preparation: Spin casting method on hydrophilic and hydrophobic Si, copper TEM grids, glass slides

Thin film analysis: AFM, TEM

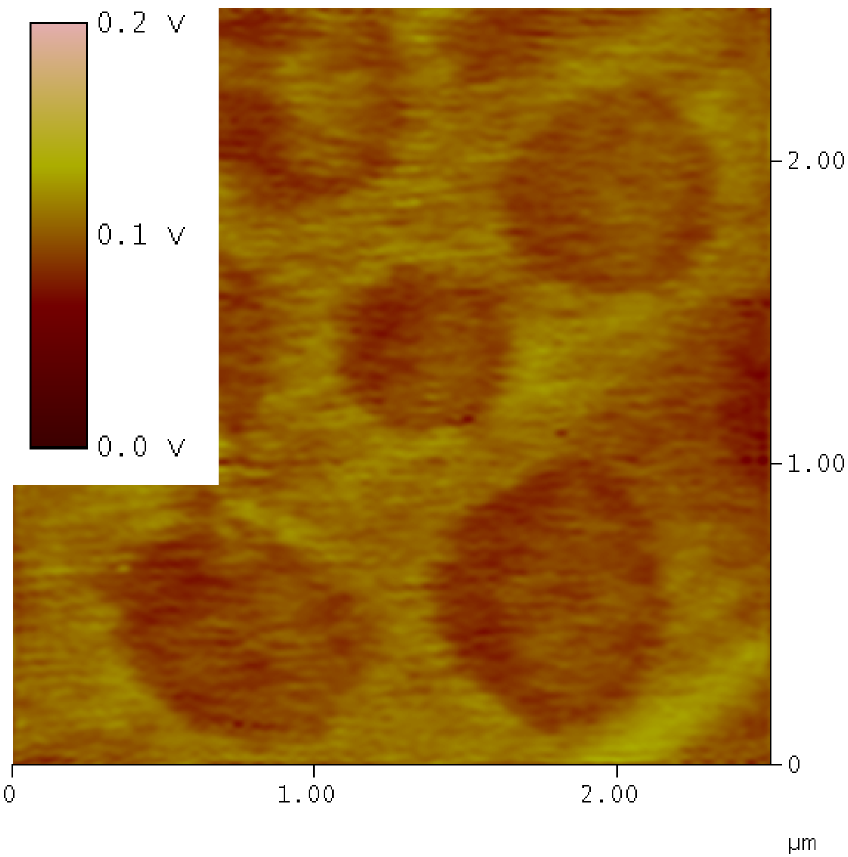
14:1 PS:P3HT Surface Morphology via AFM



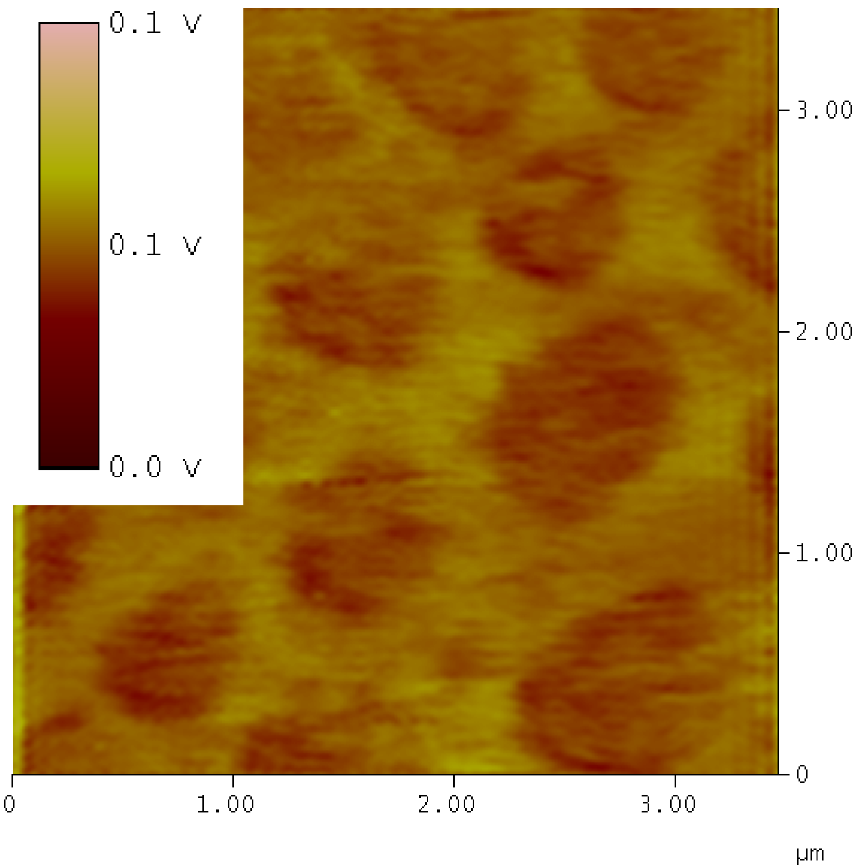
2500 RPM – 7.5 wt% | 4000 RPM – 7.5 wt% | 2500 RPM – 3.75 wt%



14:1:1 PS:P3HT:PCBM Lateral Force AFM

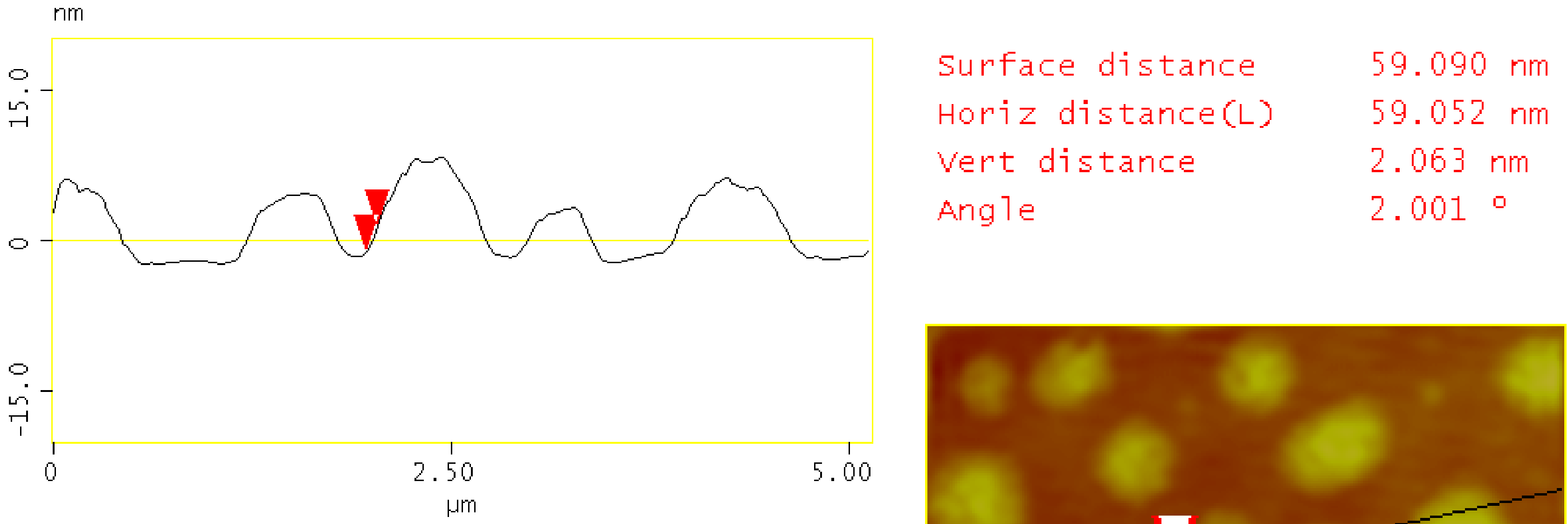


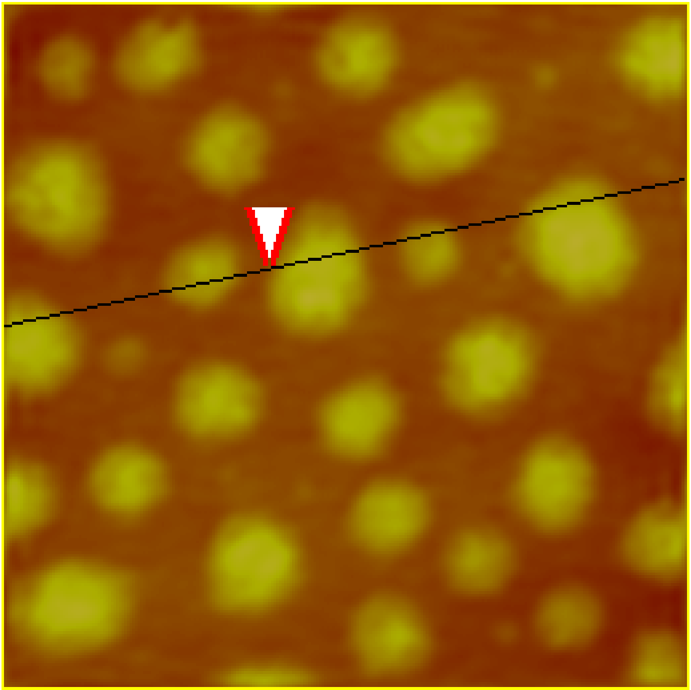
With PCBM



Without PCBM

Polymer-polymer interfacial tension from AFM contact angle measurement





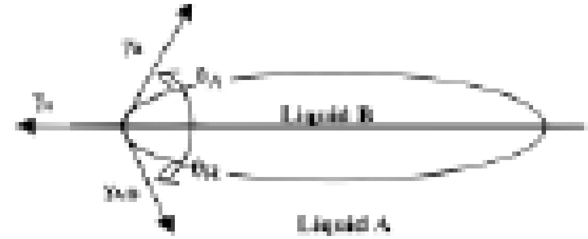
Solid-liquid interface:

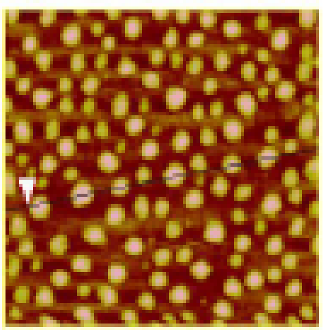
$$\gamma_{PS/P3HT} = \gamma_{PS} - \gamma_{P3HT} \cos\theta$$

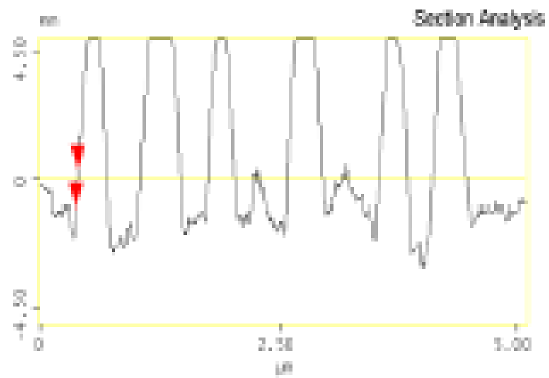
γ_{PS} = 40.6 dyn/cm
γ_{P3HT} =36 dyn/cm
γ_{PCBM} = 50.2 dyn/cm

Interfacial energies fromContact angle goniometry

$$\gamma_A - (\gamma_{A/B} + \gamma_B \cos\theta_A) = 0;$$







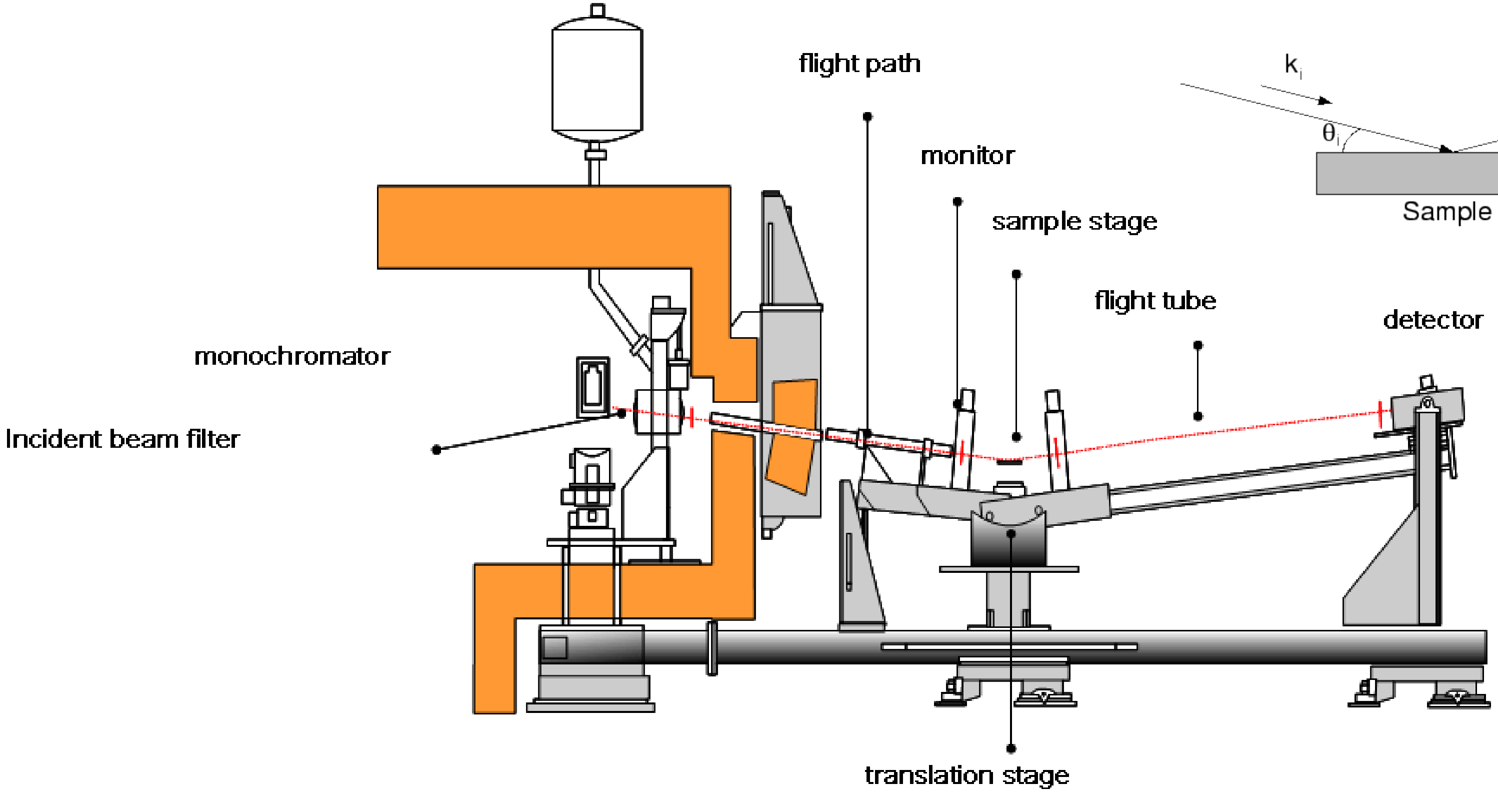
γ_A=40.2 dyn/cm θ_A=3.533

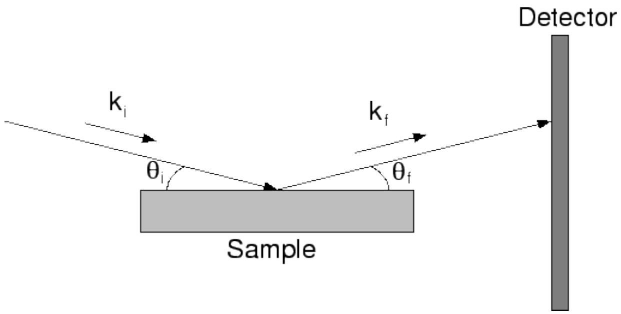
γ_B=36.0 dyn/cm

$$\gamma_A - (\gamma_{A/B} + \gamma_B \cos\theta_A) = 0$$

Sample Description	Without PCBM				With PCBM			
	Contact Angle (θ)	Interfacial Tension $\gamma_{A/B}$ (dyn/cm)	Domain Length (nm)	Thickness (nm)	Contact Angle (θ)	Interfacial Tension $\gamma_{A/B}$ (dyn/cm)	Domain Length (nm)	Thickness (nm)
62 K M_w PS: P3HT	3.89 ± 0.775	4.283	246 ± 8.9	84.4 ± 6.87	2.72 ± 1.062	4.241	260 ± 29.0	75.7 ± 2.84
123 K M_w PS: P3HT	7.49 ± 1.498	4.507	295 ± 16.8	96.8 ± 8.00	2.86 ± 0.352	4.245	295 ± 55.4	97.8 ± 4.79

Neutron Reflectometer*





*Thanks Dr. Sushil Satija, Dr. Bulent Akgun from NIST Center for Neutron Research these two schemes come from NCNR's website http://www.ncnr.nist.gov/instruments/ng7refl/instrumentfeatures.html and http://www.ncnr.nist.gov/programs/reflect/NR_article/index.html

Helfand-Tagami theory

$$\sigma = \left[\frac{a^2}{3\pi\chi} + \frac{1}{4\pi a\rho}\sqrt{\frac{6}{\chi}}\ln\left(\frac{q_{\max}^2}{q_{coh}^2 + q_{\min}^2}\right)\right]^{1/2}$$

$$a \approx 6.7\text{Å}$$

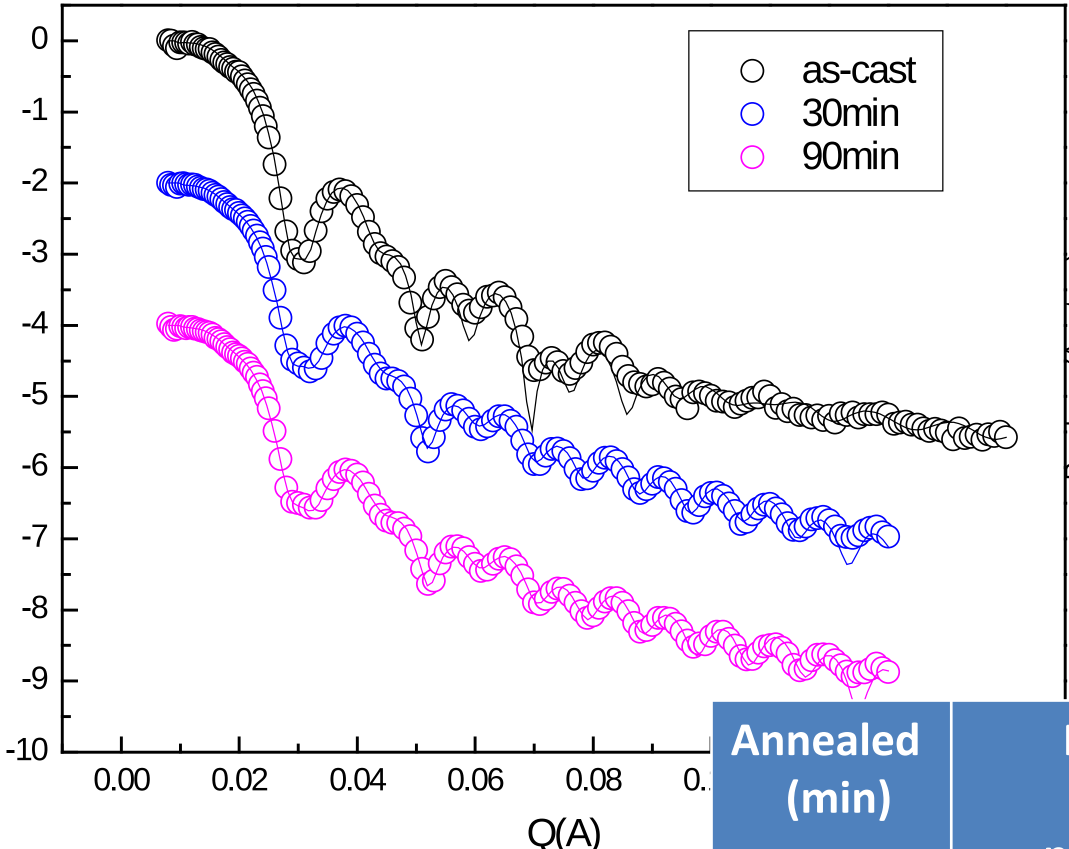
Interfacial tension between polymers at equilibrium point is 83 Å

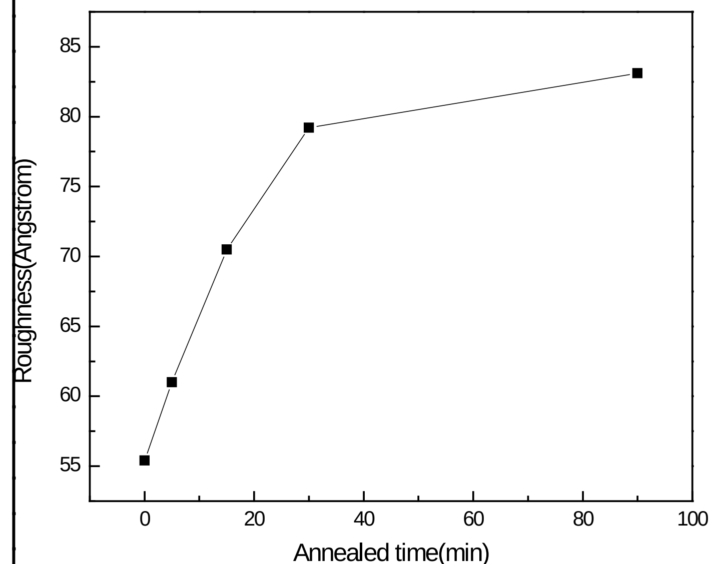
Flory-Huggins interaction parameter between the two polymers:

$$\chi \approx 6.92\times10^{-4}$$

$$(\gamma_{INT} = \left(\frac{kT}{a^2}\right)\sqrt{\frac{\chi}{6}})$$

Neutron Reflectivity



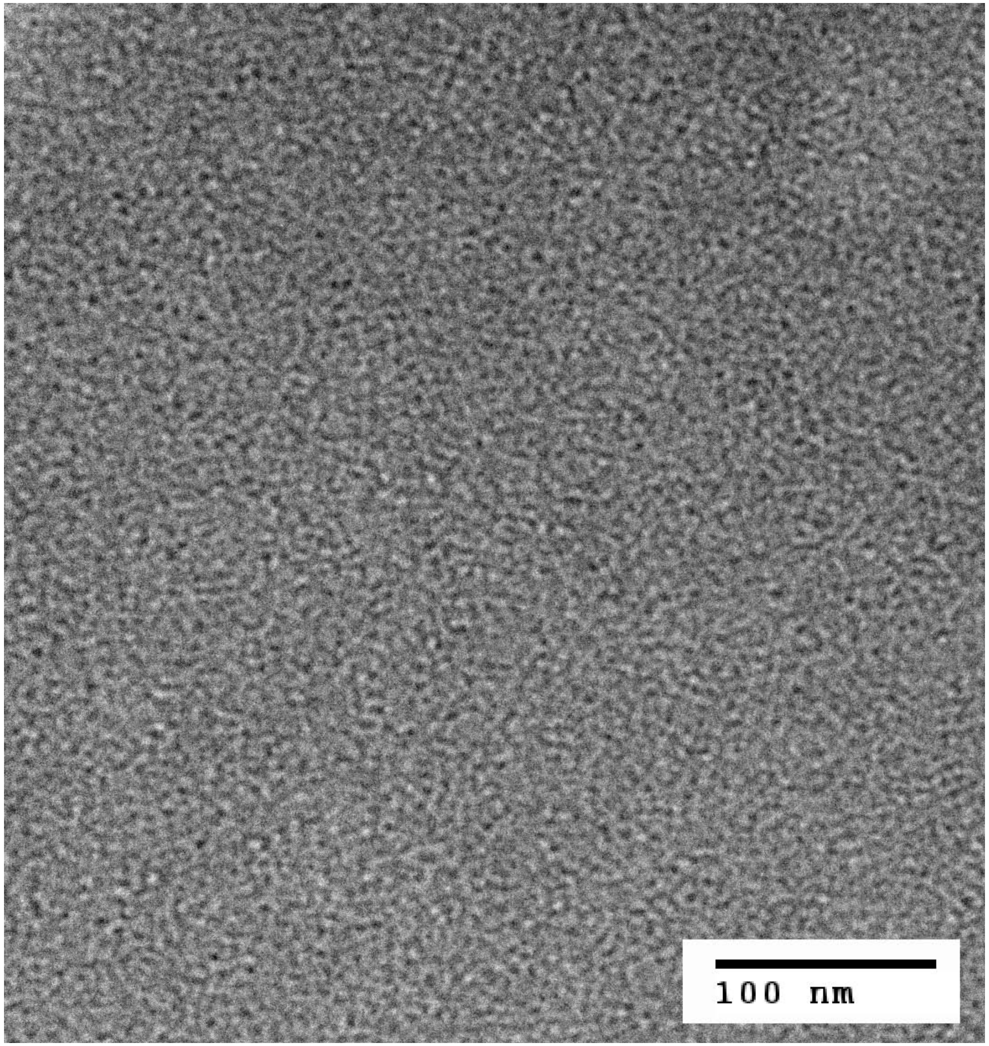


Annealed (min)	Roughness between polymers (Å)	Thicknes s of PS(Å)	Thickness of P3HT(Å)
0	55.4	265.5	443.2
5	61.0	259.9	439.9
15	70.5	259.7	443.9
30	79.2	260.2	440.0
90	83.1	257.2	428.4

PCBM Effect on PS:P3HT Interfacial Tension

Sample	Annealed	PCBM	Substrate	Contact Angle	$\gamma_{PS/P3HT}$
14:1 PS:P3HT	72 hr	No	hydrophilic	1.32	**4.61**
14:1 PS:P3HT	72 hr	No	hydrophobic	1.508	**4.612**
14:1 PS:P3HT	0 hr	No	Hydrophilic	1.251	4.609
14:1 PS:P3HT	0 hr	No	Hydrophobic	1.1952	4.608
14:1:1 PS:P3HT:PCBM	0 hr	Yes	Hydrophilic	1.441	4.610
14:1:1 PS:P3HT:PCBM	0 hr	Yes	Hydrophobic	1.156	4.607
14:1:1 PS:P3HT:PCBM	72 hr	Yes	Hydrophilic	0.936	**4.605**
14:1:1 PS:P3HT:PCBM	72 hr	Yes	hydrophobic	0.848	**4.604**

PCBM nanoparticle distribution in P3HT



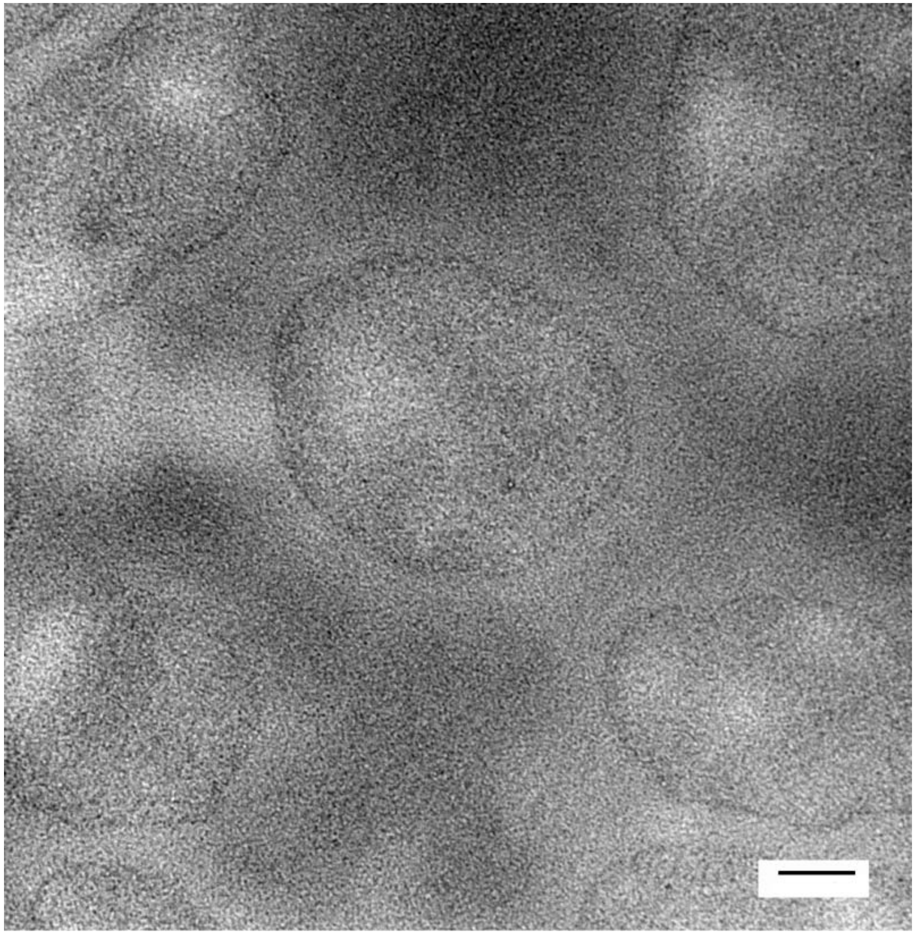
80 kV electron beam energy

1:1 PCBM:P3HT by weight at 1 wt% in chlorobenzene

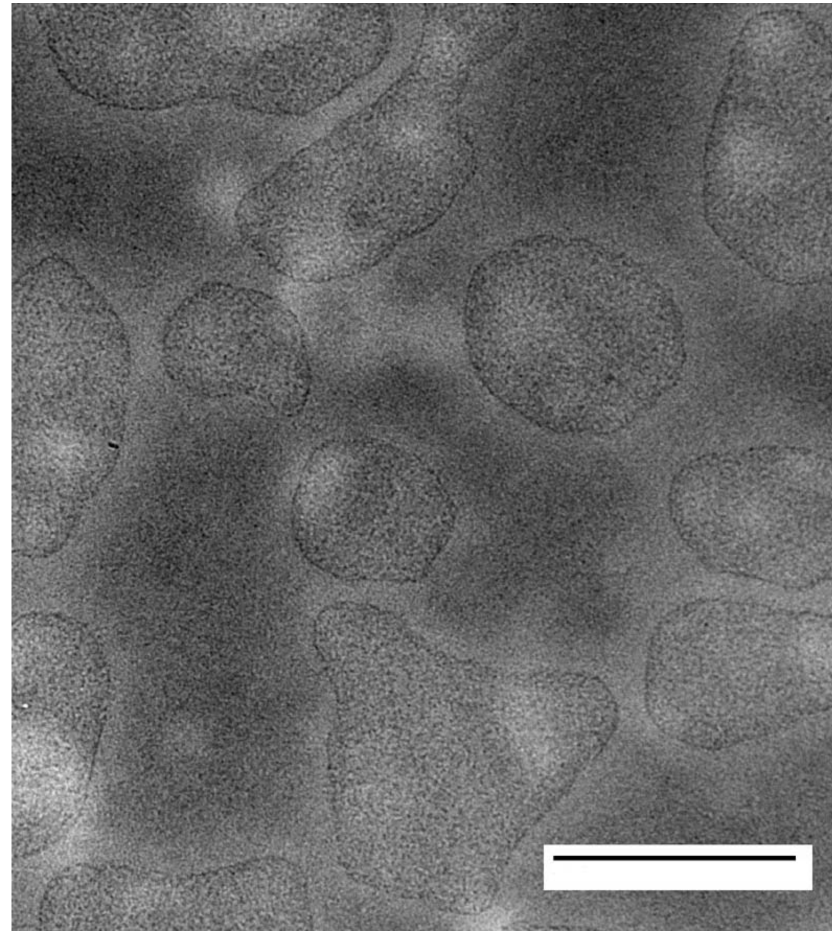
Spin cast at 2500 RPM onto glass

Floated from water surface onto copper TEM grids

PCBM distribution in PS:P3HT



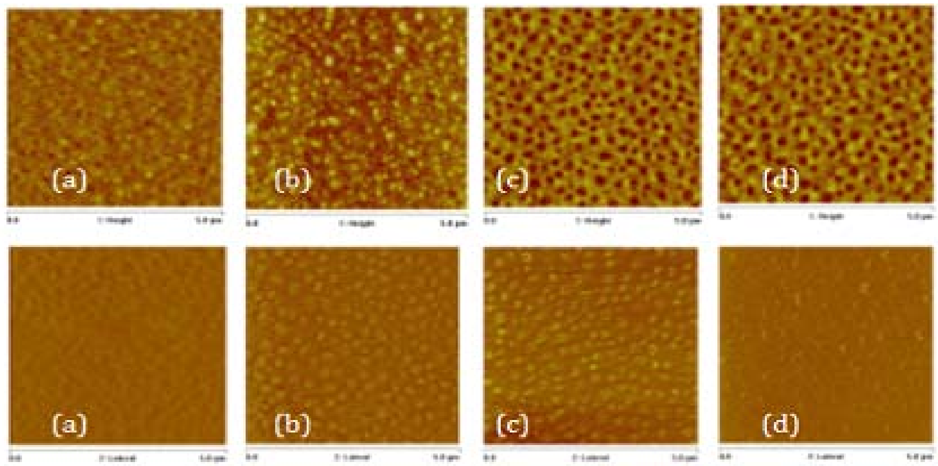
Scale bar = 100 nm



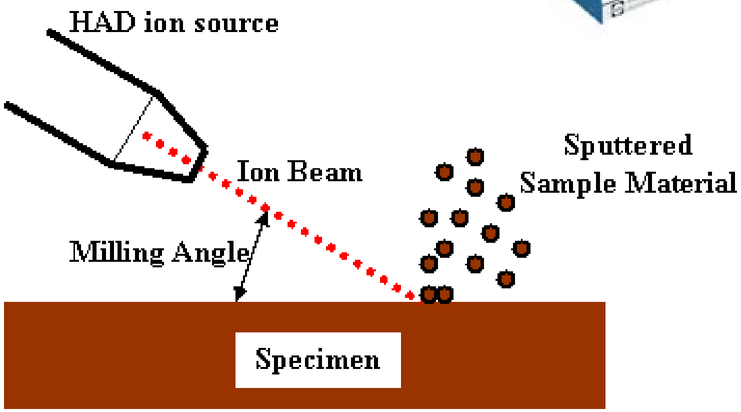
Scale bar = 500 nm

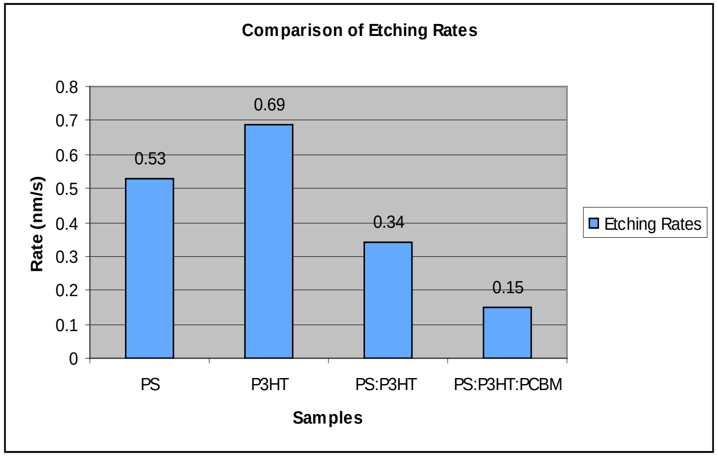
1 wt% 1:1:0.2 PS:P3HT:PCBM in chlorobenzene, spin cast at 2500 RPM onto glass, floated from water onto copper TEM grids

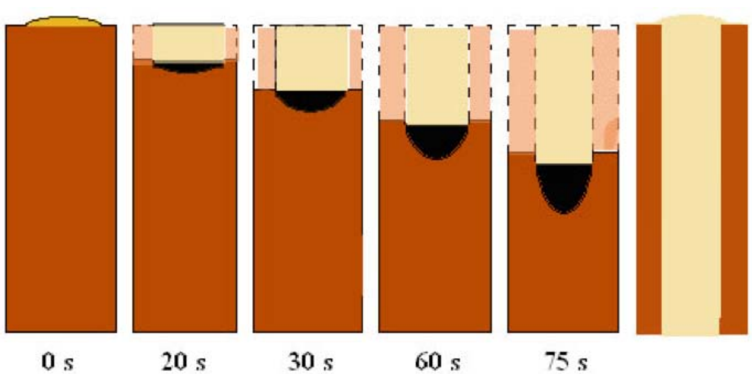
3D: Columnar Structures



Sputtering Technique:







Summary

1. A solar cell structure based on nanoparticle confinement in polymer blend thin films was proposed

2. PCBM nanoparticles did not prefer either polymer phase

3. The particles reduced the interfacial tension between the two polymers – we conclude that they are drawn to the interface.

4. PCBM was confined to the polymer-polymer interface in a PS:P3HT blend film to form a conductive pathway

Fabricate the Device and Test it!