# Fabrication of Nanodots Using Microphase Separation of Block Copolymer

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Arranging and patterning on the nanoscale is of great importance to future efforts in data storage and nano-optical effects such as achieving negative permittivity and permeability at visible wavelengths. One way to achieve these nanoscale patterns is through the use of self-assembling block copolymer solutions. The diblock copolymer used, Polyethylene-block-Poly(ethylene glycol), was dissolved in a suitable solvent and then spin coated onto a substrate. During spin coating the diblock copolymer undergoes microphase separation to produce feature sizes on the scale of tens of nanometers. Further investigation into spin coating efficiency is researched through modification of properties such as solubility of the block copolymer, solvent volatility, and ambient humidity.

# Fabrication of Nanopatterns Using Microphase Separation of Block Copolymer

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## Nanoscale Fabrication

As electronic devices shrink in size it becomes necessary to fabricate functional devices on the order of nanometers. Current technologies of fabrication such as photolithography, E-beam lithography, and dip-pen lithography are all top-down techniques. However, by using the properties inherent in block copolymer chains it is possible to create patterned surfaces with nanoscale features. Microphase separation transition (MST) fabrication has the ability to create structures sized in tens of nanometers through a self-assembling bottom-up process that can be used to coat areas of square millimeters or centimeters.

## Microphase Separation Transition (MST)

In our diblock copolymer PE-PEG, Polyethylene-block-Poly(ethylene glycol) [*Fig. 1*], two chemically incompatible polymer chains are bonded together at their ends. In solution these two different blocks microphase separate to form periodic structures whose spacing depend on the properties of the constituent polymer blocks.

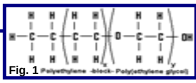


**Fig. 1** Polyethylene -block- Poly(ethylene glycol)

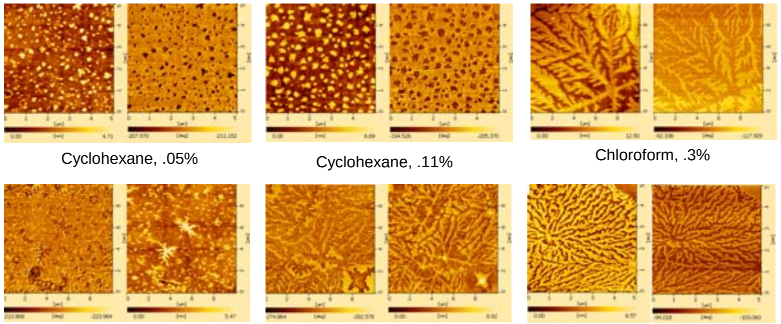
## Creating the Pattern

- Dissolve the block copolymer (PE-PEG) in a suitable solvent for both blocks. Solvents tried included: cyclohexane, chloroform, N-N-dimethylformamide (DMF), acetone, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and 1:1 mixtures of the above
  - Some solvents for one block may be nonsolvents for the other
  - Concentration of copolymer is important
    - Concentrations attempted ranged from .05 mg/ml to 1 mg/ml
- Coat a cleaned substrate with the solution using spin coating
  - Spinning conditions: Stationary dripping followed immediately by 5 seconds of 500 RPM and then 30 seconds of 3200 RPM
  - Substrate surface energy is also important
    - Slide glass was used (hydrophilic); cleaned with acetone/ethanol during sonication
    - Hydrophobic glass slides were created by cleaning and then coating with a dimethyl dichloro silane solution
- Observe the nanopatterned substrate using Atomic Force Microscopy

## Results

Many different methods were tried in our attempts to create patterned thin films of copolymer. Several variables were altered in order to observe their effects: spinning speed and length, substrate surface conditions, concentrations and solvent used, and the coating method were changed and then observed. It was found that cyclohexane and chloroform seem to be the most effective at producing nanopatterns, and that the most reliable substrate was a cleaned slide glass. However, interesting nanodot patterning was observed with cyclohexane on a hydrophobic surface only, as seen in Fig. 3a. Also, though drip casting was attempted, it was found that spin coating is necessary in order to spread the polymer evenly on the substrate.

## Effects of Varying the Concentration of Block Copolymer

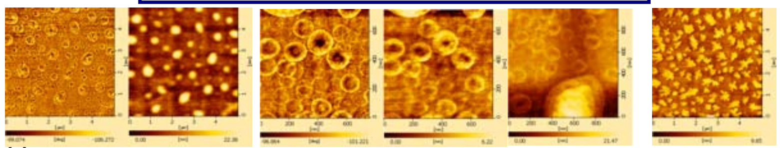


Cyclohexane, .05% | Cyclohexane, .11% | Chloroform, .3%

Chloroform, .15% | Chloroform, .3% | Chloroform, .3%

**Fig. 2** AFM images of various concentrations and solvents used for spin coating, emphasizing the two solvents chloroform and cyclohexane

## Effects of Changing the Surface Conditions



(a) (b)

**Fig.3** Solutions of cyclohexane with .3 mg/ml PE-PEG on (a) hydrophobic and (b) hydrophilic surfaces

## Conclusions

- Concentration of diblock copolymer has an effect on the size of the nanopattern as seen in Fig. 2
  - Both the size and thickness of the film is affected by the concentration
  - When little polymer is available, less concentrated solutions are unable to exhibit complex folding as seen in Fig. 2 with chloroform
- Surface conditions, specifically whether it is hydrophobic or hydrophilic, can affect the results of the spin coating as seen in Fig. 3
  - Changing the surface energy may allow opposite ends to bond to the surface of the substrate

## Application: Metamaterials and Data Storage

A possible application of these periodic structures is to plasmonic metamaterials. These metamaterials can exhibit extremely interesting effects such as negative indices of refraction and lossless transmission. For a material to be responsive to electromagnetic radiation it must have feature sizes half or less than half of the wavelength of the radiation. Therefore, structures must be have sizes less than 300 nanometers. Another possible application is data storage, due to the ability for these patterns to coat large surface areas easily.

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