Nanostructured Stable Radical Block Copolymers for Next Generation Batteries

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Stable Radical Polymers

Polymer Architecture

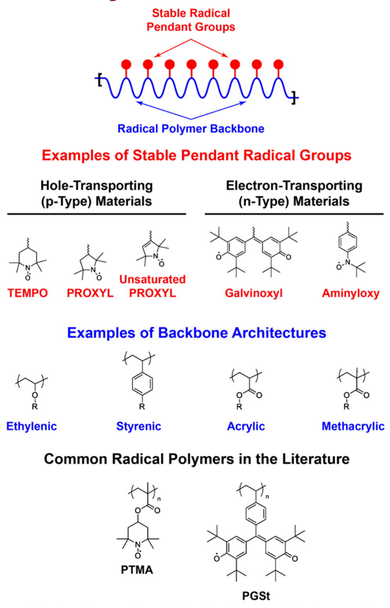


Fig 1. Example of Stable Radical Polymers[1].

Electrochemical Applications

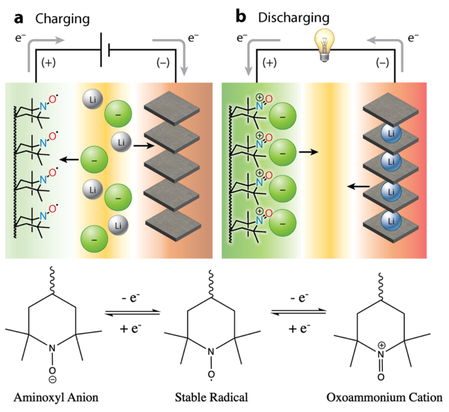


Fig 2. Redox reactions of PTMA based materials[2].

Battery Electrode Material:

- Fast Charge-Discharge Rates (owing to stable radical groups in pendant chain)[2,3].
- High energy capacity[2].

Block Copolymer Architecture

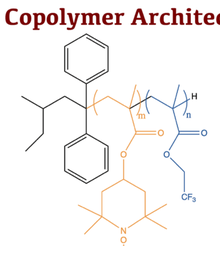


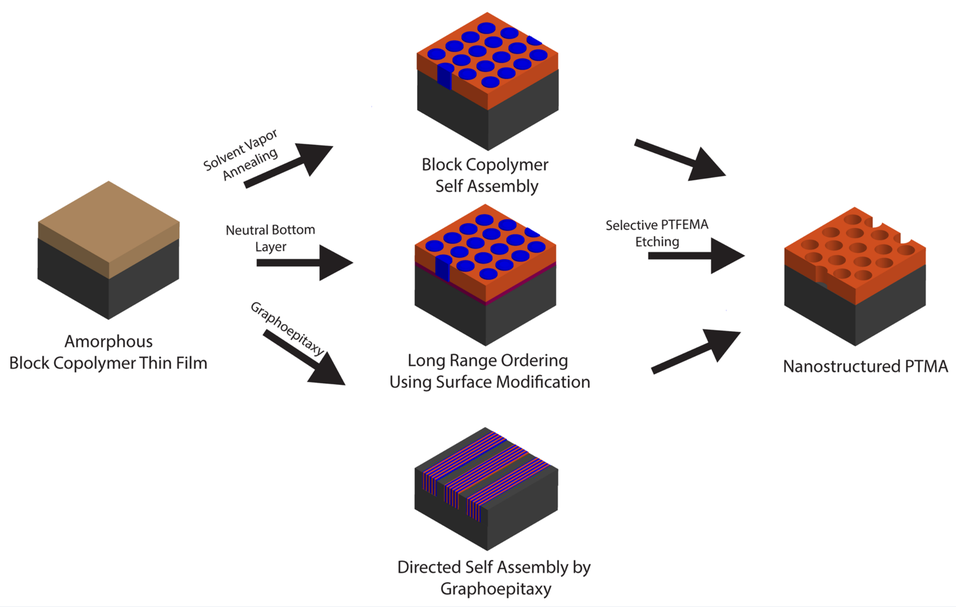
Fig 3. PTMA-PTFEMA Block Copolymers.

Block Copolymer:

- Precise placement of stable radical groups in discrete geometries[4].
- PTFEMA block is a known E-Beam sensitive material and can be etched selectively.
- Selective etching can lead to nanoporous electrodes.

Towards Nanostructured Stable Radical Polymer

Self Assembly Selective Etching



Self Assembly: Long Range Ordered Morphology

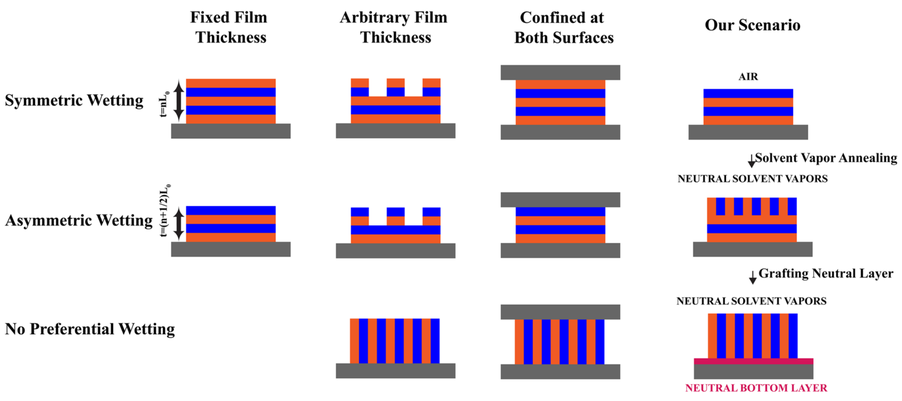


Fig 4. Summary of preferential wetting in the case of thin film block copolymers.

Challenge: Preferential Wetting

- PTMA tends to wet the silicon substrate.
- PTFEMA having low surface energy prefers air-polymer interface.
- Combination of a non preferential solvent vapor and a neutral bottom layer enables long range ordering.

Neutral Layer Grafting Process

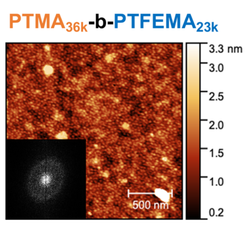
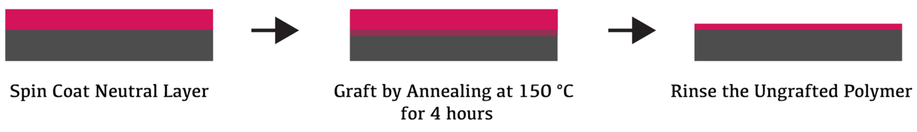


Fig 5. Cylindrical morphology in absence of Neutral Layer.



Order Disorder Characterization

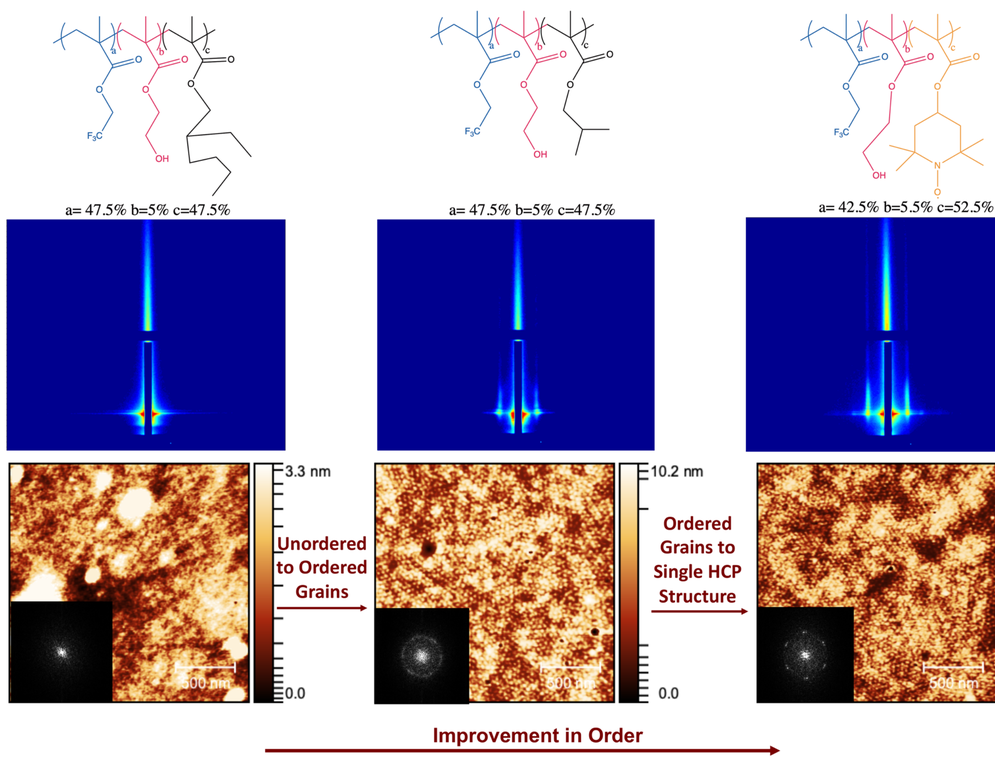
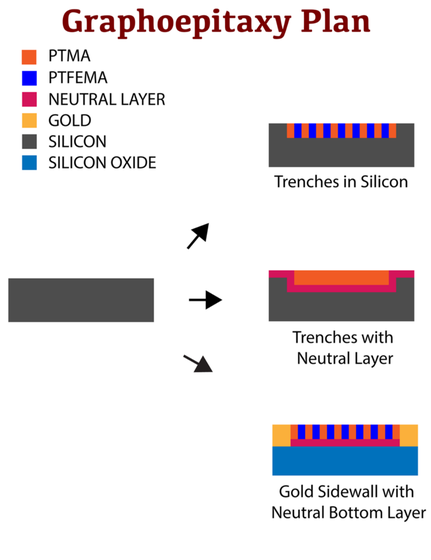


Fig 6. Summary of neutral layer structures, GISAXS and AFM data characterizing order in the block copolymers annealed for 6 hours in chloroform[5].

Directed Self Assembly: Graphoepitaxial Ordering

Graphoepitaxy Plan



SEM Images of Trench Profiles

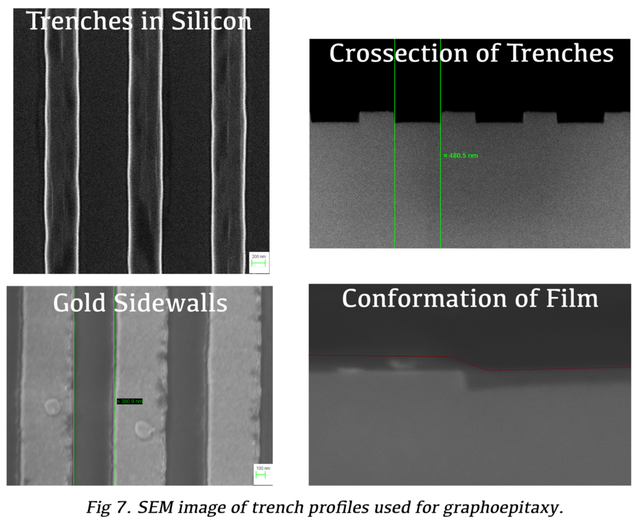


Fig 7. SEM image of trench profiles used for graphoepitaxy.

AFM Images of Block Copolymer Direct Self Assembly

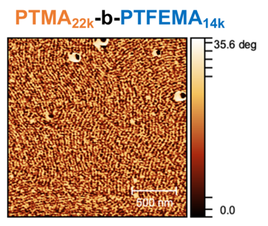


Fig 8. Lamellar morphology in presence of Neutral Layer annealed for 6 hours in chloroform.

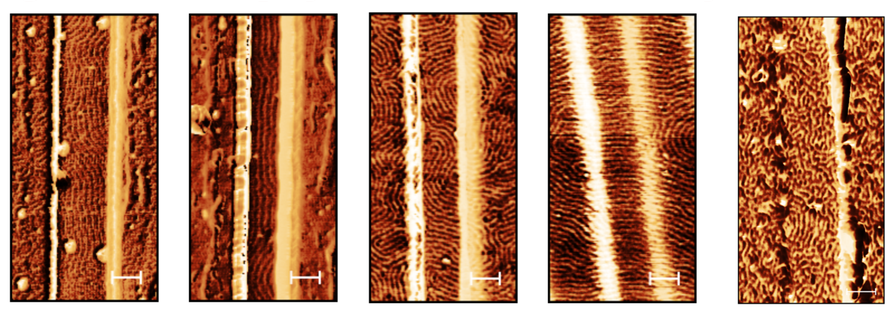


Fig 9. Graphoepitaxial direct self assembly of films annealed for 6 hours in chloroform (scale bar is 200 nm).

Width/Height Trench	3.8	3.6	3.3	3.75	5.44
Width/Height Film	2.9	1.7	2	2	3.8
Film Thickness	~50 nm	~50 nm	~50 nm	~100 nm	~50 nm
Neutral Layer	No	No	Yes	Yes	Yes
Sidewall	Silicon	Silicon	Silicon	Silicon	Gold

- A lower W/H helps in parallel alignment while the neutral layer aids in perpendicular alignment.
- Thicker films show better perpendicular alignment in agreement with literature[6].

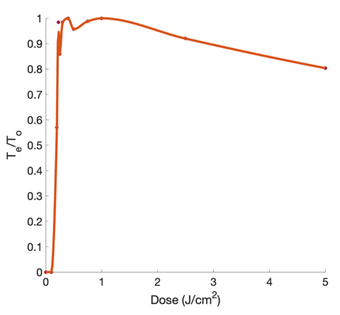
Selectively Etching PTFEMA Block

DUV Exposure

Challenge: Selective Etching

- Degrading PTFEMA without affecting PTMA.
- PTMA crosslinks under DUV irradiation.
- Post DUV radiation the polymer is rinsed with chloroform.

PTMA Crosslinking



FTIR Post DUV Exposure

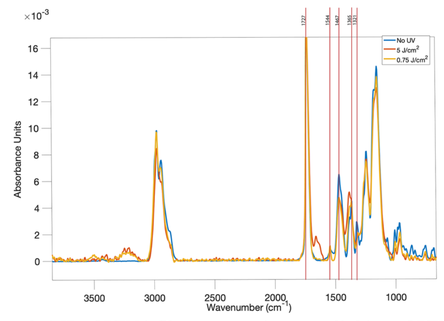


Fig 10. Variation of final thickness versus dose and FTIR of PTMA films supporting crosslinking of PTMA.

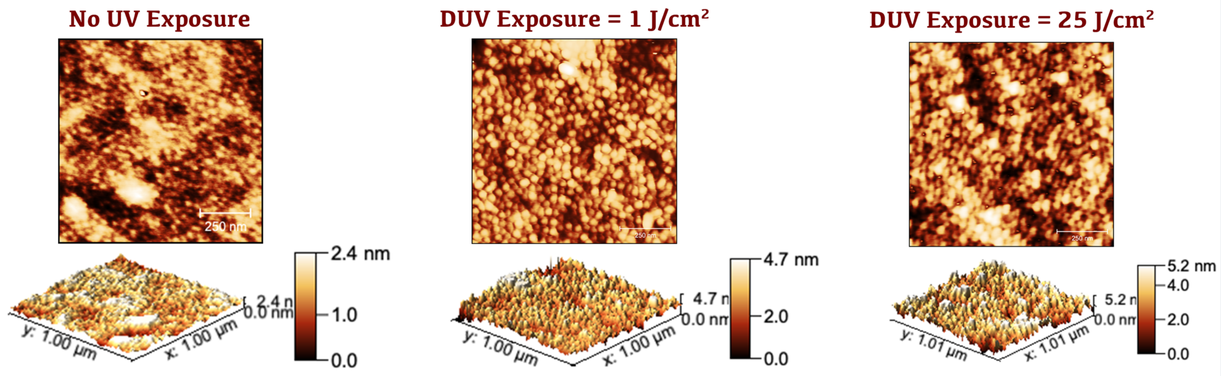


Fig 11. AFM images of the block copolymer (annealed for 3h in chloroform) after DUV exposure.

E-Beam Exposure

Exposure Dose
75 µC/cm²

Developed in
1:7 v/v of
MIBK:IPA
for 1 minute

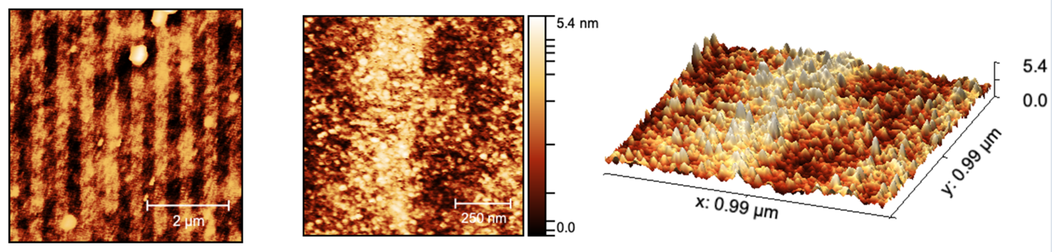


Fig 12. AFM images of the block copolymer (annealed for 3h in chloroform) after E-Beam exposure.

Conclusions

1. Successfully obtained long ranged ordered hcp stable radical block copolymers.
2. Could align lamellar blocks perpendicular and parallel (with defects) to trenches.
3. Optimized selective etching of PTFEMA using DUV and E-Beam exposure.

Future Steps

1. Currently experimenting gold sidewalls for graphoepitaxial self assembly.
2. Developing a preferential underlayer to generate defect free alignment.
3. Performing XPS to confirm PTFEMA degradation.

References

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