

Self-Assembly at Supercritical Pressures: Top-down Meets Bottom-up Approaches to Nanotechnology

L.G Kaake*

Department of Chemistry, Simon Fraser University, Burnaby, BC, V5A1S6, Canada

*Corresponding author: lkaake@sfu.ca

1. Introduction

A fundamental gap in manufacturing techniques exists and limits the development of nanotechnology. Top-down approaches to nanofabrication are exemplified by photolithography, whereby monolithic materials are patterned, etched, and deposited to create structures with incredible resolution, fidelity, and reproducibility. Bottom-up approaches to nanoscale ordering are exemplified by the living organisms, which exhibit staggering complexity both in chemical structure and the concerted mechanisms responsible for function. These mechanisms have had the benefit of eons of evolution to combat entropy which fights against the fidelity and reproducibility of structure formation. However, these techniques have remained largely distinct, limiting the complexity of materials that can be formed via top-down processes, and the reproducibility and fidelity of man-made structures formed via solution-phase self-assembly. We seek to address this challenge by leveraging the unique properties of supercritical fluids.

We have developed a method of depositing non-volatile materials at supercritical pressures that leverages non-monotonic saturation solubility with respect to temperature. This technique, which we have termed physical supercritical fluid deposition, (p-SFD) allows material to be deposited without requiring in-situ chemical reactions.¹⁻⁴ This allows the deposition of materials that are synthesized and characterized ex-situ, where qualities like chemical purity and molecular weight can be more easily controlled. To date, we have used this technique to deposit two popular thiophene based semiconducting polymers^{1,4} as well as isotactic polypropylene, a semicrystalline aliphatic polymer.^{2,3} We investigated the relationship between the morphology of deposited polymer films with respect to pressure and solvent composition and have put forward a two-step model of film formation that stresses the role of the Rayleigh number in the self-assembly process.^{2,3} We also demonstrated a method for coupling this process with photolithography, allowing us to leverage the fidelity and reproducibility of top-down manufacturing while maintaining the complexity afforded by solution-phase self-assembly.¹

2. Materials and methods

A custom pressure cell was constructed from a block of BeCu and was fitted with sapphire windows allow in-situ UV-Vis measurements. The following solvents were investigated in the course of this research: pentane, pentane:toluene mixtures, novoc 7100, solstice, novoc:toluene mixtures, and solstice:toluene mixtures. Owing to the flammability of many of the solvents, special precautions were taken to eliminate oxygen from the cell. Three polymers were studied and are depicted in figure 1a. Depositions were carried out by holding the temperature of the vessel exterior at or just below the peak in the saturation solubility and resistively heating the substrate by passing current through an indium tin oxide (ITO) thin film on a glass substrate.

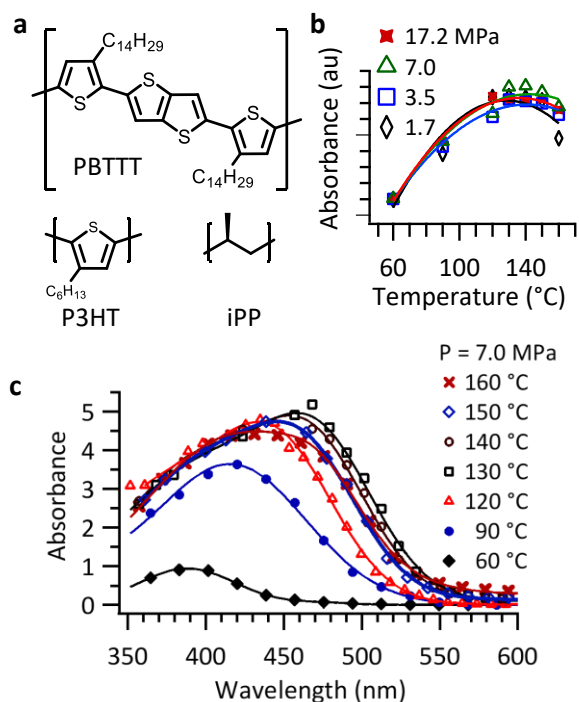


Figure 1. Compounds and representative results. a) polymers studied b) integrated absorbance from c, plotted as function of temperature. c) absorbance vs. wavelength for PBT at several temperatures at a pressure of 7.0 MPa.

3. Results and discussion

Figure 1a shows the chemical structure of a semiconducting polymer and spectra collected at a 7.0 MPa for several values of pressure (figure 1c). The spectra were integrated to measure solution concentration (figure 1b). A peak in the isobaric solubility is observed, showing decreasing solubility with increasing temperature at the highest temperatures studied. This solubility behavior is central to our implementation of the p-SFD technique in which material is deposited from a saturated solution onto a heated substrate. Figure 2a and 2b display AFM images of films of PBTtT grown from pentane:toluene solutions at 3.5 and 10 MPa, respectively. The two images show very different morphologies, which we attribute to a pressure dependent slope of the saturation solubility with respect to temperature.

Figure 2c shows an optical microscope image of a patterned film of PBTtT deposited of a thin film of poly(methyl methacrylate) (PMMA). The underlying ITO film was etched into 5 μm lines with standard photolithographic techniques. By addressing the ITO lines inside the cell and passing current through them, they served as resistive heating elements to control the deposition of material onto PMMA. The ultimate resolution of the technique has not been reached; we suspect that at least one order of magnitude improvement is possible.

4. Conclusions

We demonstrate physical supercritical fluid deposition as a means of thin film formation. The technique relies on the solvation properties involatile solutes in fluids held above their critical pressure, specifically a non-monotonic isobaric saturation solubility with respect to temperature. This allows us to precipitate materials onto heated substrates, forming thin films without the need for in-situ chemical reactions. Resistive heating is a simple and technologically relevant means of increasing substrate temperature relative to the solution bulk. Importantly, conductive traces can be patterned with photolithography, where they can direct the deposition of material with high resolution. This connects the most popular means of top-down nanoscale control (photolithography) with bottom-up nanotechnology (solution-phase self-assembly).

Control over polymer self-assembly has focused on the effect of pressure, solvent choice, and choice of polymer. The Rayleigh number of the fluid during deposition exerts an important influence. Co-solvents increase the motion of material on the substrate following precipitation. Taken in sum, the results hint at a wide field of inquiry that seeks to produce high performance materials, nanoscale structures, and electronic devices on curved and flexible substrates using the unique solvation properties of fluids in the vicinity of their critical point.

References

1. Yousefi, N.; Maala, J. J.; Louie, M.; Storback, J.; Kaake, L. G., *ACS Appl Mater. Interfaces* **2020**, *12* (15), 17949-17956.
2. Yousefi, N.; Saeedi Saghez, B.; Pettipas, R. D.; Kelly, T. L.; Kaake, L. G., *Mater. Chem. Front.* **2021**, *5* (3), 1428-1437.
3. Yousefi, N.; Saeedi Saghez, B.; Pettipas, R. D.; Kelly, T. L.; Kaake, L. G., *New J. Chem.* **2021**, *45* (26), 11786-11796.
4. Yousefi, N.; Pettipas, R. D.; Kelly, T. L.; Kaake, L. G., *under review* **2021**.

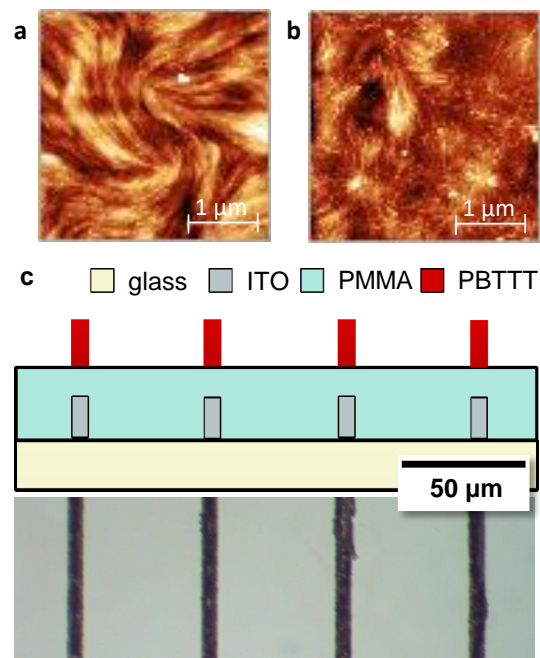


Figure 2. Deposited films of PBTtT. a) AFM image of PBTtT film deposited at 3.5 MPa. b) AFM image of PBTtT film deposited at 10 MPa. c) optical microscope image of a patterned PBTtT deposition.