

Confined Crystallization of Polymers

Nanoscale confinement of polymers is present in many systems of scientific and technological importance. Examples include polymer thin films supported on substrates and polymer nanocomposites. The structure and dynamics of confined polymers is vastly different from that of bulk polymer systems, as interfaces play a dominant role at these spatial lengthscales. In this thesis work, I will study the mechanisms of crystallization in polymers confined by inorganic materials. In such systems, polymer-surface interactions dictate the kinetics and conformations of polymer chains and thus influence the nucleation and growth of polymer crystals. I will probe and tune these interactions, study the resulting crystalline structures, and assess the subsequent physical properties.

Thin films: I will first study the crystallization of ultrathin (< 100 nm) polymer films on various substrates. In this quasi-2D geometry, crystal growth is typically diffusion-limited rather than nucleation-limited. As a result, the observed crystal morphologies include dendrites, seaweeds, compact structures, and faceted regular shapes¹. Due to the confined nature of these films, the crystal lamellae may preferentially adopt flat-on orientations, in which the chain axis is perpendicular to the substrate, or edge-on orientations, in which the chain axis is parallel to the substrate². In ultrathin films, polymer-substrate interactions determine the surface adsorption and diffusion of polymer chains and thus determine the crystallization kinetics and film morphology³⁻⁵. In addition, geometric matching at the molecular scale between the polymer crystal and substrate may induce epitaxial growth. It was demonstrated by Wittmann and Lotz that due to the flexible nature of polymer chains, ultrathin films with a lattice disregistry below $\sim 10\%$ relative to the underlying substrate may grow epitaxially⁶.

Crystallization, epitaxy, and meso/macroscale structure formation in ultrathin polymer films has been studied using common deposition methods such as spin coating or drop casting^{1,7}. In this research project, I will study these phenomena using a unique method of physical vapor deposition: matrix-assisted pulsed laser evaporation (MAPLE). In MAPLE, a dilute polymer solution is rapidly frozen and then irradiated with a pulsed laser under vacuum. Absorption of laser energy by the solvent generates an ablation plume consisting of polymer solution droplets. While in transit to and after landing on the substrate, the solvent evaporates, leaving behind a dry mass of macromolecules tens to hundreds of nanometers thick⁸. Subsequently, the viscous polymeric liquid spreads to form a ‘precursor layer’ whose thickness is on the order of the polymers’ radii of gyration⁹ before eventually crystallizing. Since film formation in MAPLE deposition occurs by the consolidation of a multitude of polymer globules and their associated precursor layers, this work presents a unique opportunity to elucidate the mechanisms of crystallization in macromolecular assemblies exhibiting multiple simultaneous confinements.

I have begun by studying a model system: poly(ethylene glycol) (PEG) atop muscovite mica. Standard methods of thin film deposition create uniform films which only induce confinement in the direction perpendicular to the substrate. In these geometries, crystallization of PEG atop mica typically results in the flat-on orientation of lamellar crystals^{7,10,11}. My preliminary work employing MAPLE deposition has demonstrated that under multiple simultaneous confinements, PEG will undergo epitaxial crystallization with the underlying mica substrate. My experimental results show that the nucleation of edge-on crystals within the confined globules is preferred. The crystallization proceeds outwards into the precursor layer and results in epitaxially arranged needle-like morphologies as shown in Figure 1.

To further understand the mechanisms of confined epitaxial crystallization on mica, I will perform phase-field simulations in collaboration with Prof. Mikko Haataja’s group. We will

modify code written by a past PhD student, Dr. Alta Fang, to incorporate an anisotropic free energy of crystallization to account for epitaxial effects. Preliminary simulations will model 2D crystallization in a comparatively thick globule region which extends out into the thin precursor layer. To perform code validation we will simulate and compare crystal morphologies at various crystallization temperatures.

It has been shown that a charge-complex forms between ether groups in PEG and potassium ions in solution and that the strength of the interaction is dictated by the extent of hydration^{12,13}. I suspect that this same charge complexation is responsible for the observed epitaxial arrangement of PEG crystals atop mica. Therefore, to elucidate this mechanism, I have formed a collaboration with Prof. Ian Bourg's group to perform molecular dynamics (MD) simulations of PEG crystals atop mica under various states of hydration. To validate the simulation results, I will perform crystallization experiments in a humidity-controlled environment.

Once the theoretical framework of has been thoroughly developed, I will deposit functional materials such as PEG block copolymers and functionalized PEGs.

Nanocomposites: Ultrathin films supported on inorganic substrates are often viewed as model nanocomposites because in both systems, polymer chains lie within several hundred nanometers from an interface¹⁴. In the second phase of this research project I will extend the work described in the above section to study crystallization in polymer nanocomposites (PNCs). In particular, I will study the crystallization of polymer-filled graphene oxide sacks. These sacks will be formed by aerosol evaporation synthesis, in which a suspension of graphene oxide and the polymer of interest are ultrasonically aerosolized. The aerosolized microdroplets are subsequently dried in a flow-through furnace and collected on a substrate. It has been shown that due to the graphene oxide sheets' relatively low diffusion coefficients in suspension, the sheets will preferentially adsorb at the air-solvent interface during evaporation¹⁵. On the other hand, polymer chains have a higher diffusion coefficient and will preferentially stay in the bulk solvent phase. Thus, solvent stripping and microdroplet collapse are expected to result in a polymeric core wrapped with graphene oxide sheets. Depending on the size of the initial graphene oxide sheets and the concentration of both constituents, particles ranging in size from ~100 nm to several microns may be generated. Graphene and graphene oxide are known to induce epitaxial crystallization in polyethylene (PE)^{16,17}; therefore, I will use PE as a model polymer. I will assess the crystalline orientation within the graphene-wrapped polymers using TEM and AFM together with ultramicrotomy. Additionally, the phase-field code mentioned previously is currently being converted into three dimensions. Once this is complete, we will employ the code to simulate crystallization within these graphene-wrapped polymer nanoparticles. At a later stage, we will employ the knowledge gleaned from these experiments to synthesize graphene-wrapped polymer nanoparticles with functional materials such as conjugated polymers.

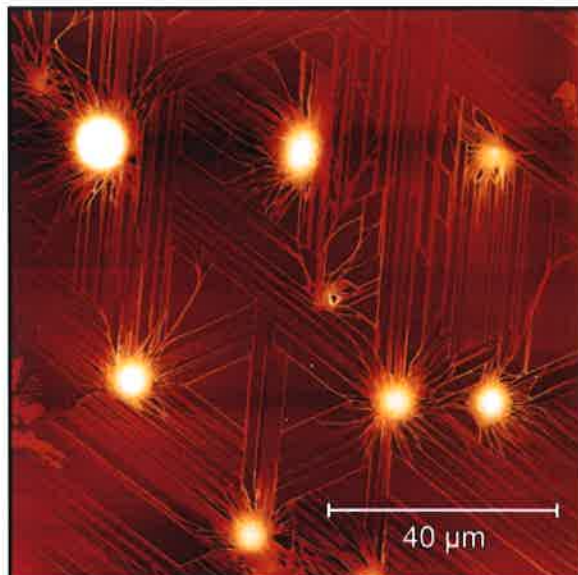


Figure 1: Tapping mode AFM images of PEO needles, 5 – 10 nm in height, grown epitaxially atop mica by MAPLE.

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