Polymer Film Microstructures via Surface-Directed Condensed Droplet Polymerization

CNF Project Number: 2784-19
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Primary Source(s) of Research Funding: National Science Foundation (CMMI-2144171)

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Primary CNF Tools Used: ABM contact aligner

Abstract:

Non-spherical polymer particles exhibit unique flow dynamics that enhance drug delivery by improving permeation through blood vessels walls. However, traditional synthetic methods are complex and inefficient. We developed a facile and scalable method called condensed droplet polymerization to address these challenges. In a chemical vapor deposition reactor, vaporized monomers condense onto a cold substrate, forming droplets that polymerize upon introduction of an initiator. Using a photoresist template with circular holes, we achieved monodisperse, hexagonally arranged polymer droplets. Removing the photoresist revealed concave-shaped polymers with potential nanoscale lens or drug delivery applications. This method offers precise control over particle size and morphology, paving the way for large-scale production and diverse biomedical applications.

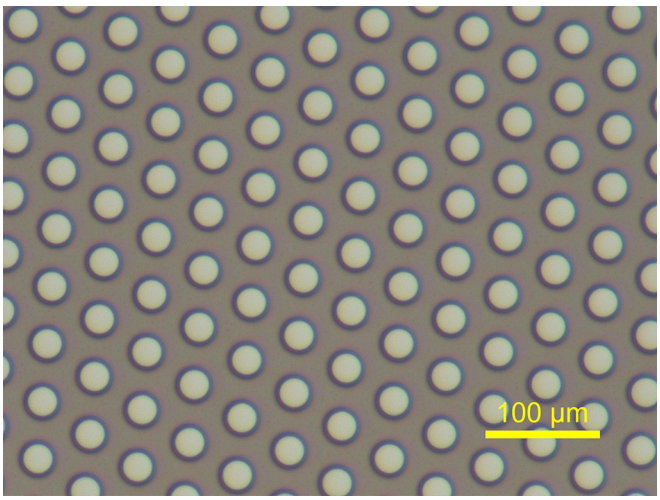

Figure 1: Optical microscopy image of SPR220-4.5 photoresist with a hexagonal array of circular holes with 30 µm diameter.

Summary of Research:

Non-spherical polymer particles have shown great potential as drug delivery vehicles, exhibiting unique flow dynamics in blood vessels that enhance permeation through the vessel walls. However, the synthesis of non-spherical particles has been challenging due to complicated, time-consuming, and inefficient multi-step processes. Recently, our group demonstrated a facile and scalable synthetic strategy in the vapor phase, called condensed droplet polymerization [1].

In brief, within a conventional chemical vapor deposition vacuum reactor, vaporized monomer is introduced and subsequently condensed dropwise onto a cold substrate. These monomer droplets grow through continuous condensation and coalescence.

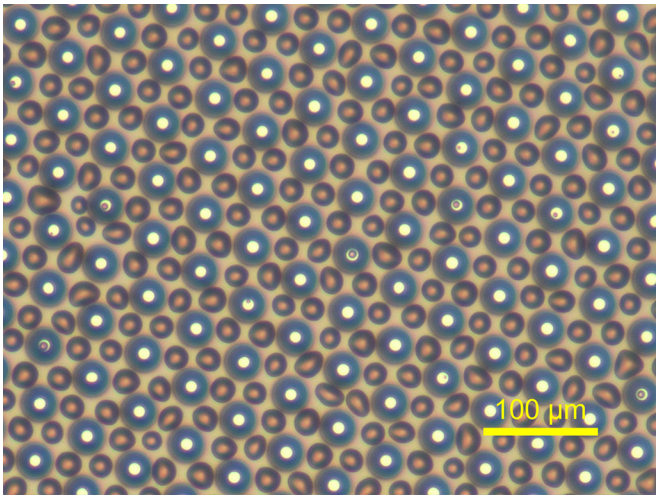

Figure 2: Optical microscopy image of benzyl methacrylate monomer droplets condensed on the photoresist template shown in Figure 1.

Once the droplet reaches the desired size, an initiator is introduced and decomposed into reactive radicals by heated filament arrays, initiating polymerization of the droplets. After a few minutes of polymerization (typically less than 2 minutes), the reaction is terminated by turning off the filament array and evacuating the reactor, resulting in polymer dome arrays. This CDP process has demonstrated that polymer particle size and morphology can be controlled and is suitable for large-scale production due to its rapid vacuum process. However, the random nature of condensation leads to a broad distribution of polymer particle sizes, which needs to be addressed. For drug delivery applications, the production of monodisperse polymer particles is critical to ensuring predictable and controlled drug release.

To address this issue, we created a template with an array of circular holes in the photoresist (Figure 1) and conducted the experiment using this template. The condensed droplet polymerization experiments confirmed that monomer droplets condensed simultaneously inside the holes and on the surface of the photoresist, regardless of the thickness of the photoresist (1 to 10 μm). As shown in Figure 2, when a densely packed hole array was used, we observed that monodisperse monomer droplets arranged themselves in a hexagonal pattern. This was an important result, demonstrating the potential to produce polymer domes of uniform size.

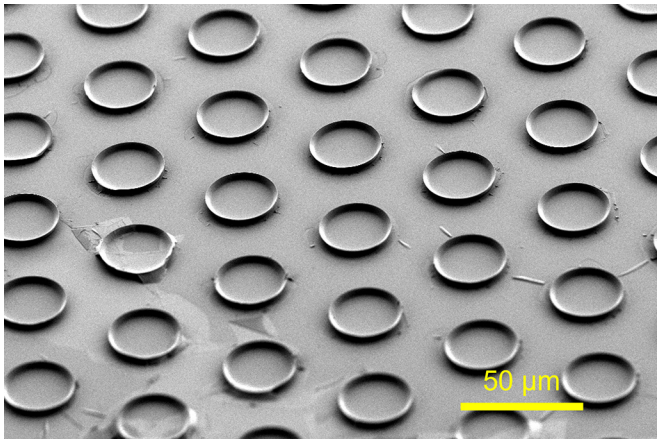

Figure 3: Scanning electron microscopy image of poly(benzyl methacrylate) patterns on Si substrate.

Interestingly, after completely removing the photoresist, the polymer formed inside the holes initially exhibited a concave shape due to the meniscus of the monomers (Figure 3). These polymer particles with such shapes are being closely monitored because they may exhibit nanoscale lens properties or unique drug delivery characteristics.

Conclusions and Future Steps:

In conclusion, our study demonstrated the effectiveness of the condensed droplet polymerization method in producing non-spherical polymer particles with controlled size and morphology. By utilizing a photoresist template with an array of circular holes, we achieved monodisperse monomer droplet condensation and observed hexagonal arrangement patterns. These results highlight the potential of the process for large-scale production of uniform polymer domes, which are critical for drug delivery applications due to their unique flow dynamics and enhanced permeation properties. To build these findings, we are currently looking at further refinement of the patterned substrate design to enhance the uniformity of monomer droplet condensation, aiming for even more precise control over particle size, shape, and distribution.

References:

[1] Franklin, Trevor, Danielle L. Streever, and Rong Yang. "Versatile and rapid synthesis of polymer nanodomes via template-and solvent-free condensed droplet polymerization." Chemistry of Materials 34.13 (2022): 5960-5970.