Effect of Temperature on Particle Morphology Polymerized via Initiated Chemical Vapor Deposition in Liquid Crystal

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Primary CNF Tool Used: Zeiss Supra Scanning Electron Microscope

Abstract:

The ability to create designed polymer particle shapes would greatly benefit many applications, including timed drug delivery and reconfigurable metamaterials because the polymer's intrinsic properties largely depend on the shape. Prior works from our research group have leveraged the use of an anisotropic medium, namely liquid crystals (LCs), as templates to direct the growth of polymer structures by initiated chemical vapor deposition (iCVD) [1]. In this work, we have successfully obtained a range of glycidyl methacrylate (GMA) and divinyl benzene (DVB) polymer morphologies in a one-step, one-pot polymerization process by iCVD in a nematic LC called E7 (a eutectic mixture of cyanobiphenyls). We established multiple substrate temperatures in a single polymerization run by leveraging a thermal gradient placed directly on a cooled reactor stage. A filament array above the stage radially heats the gradient, providing lower temperatures as the distance from the gradient to the filament increases. E7 has a nematic to isotropic phase transition temperature of ~ 60°C, above which the orientational order of the LC mesogens no longer exists. We have investigated the effect of temperature on the rate of evaporation and phase change of the LC by utilizing a brightfield and cross-polarized optical microscope placed directly over the reactor for in-situ monitoring. Using a set of controls and experiments, we have mapped a set of reactor conditions where temperature solely influences the progression of particle morphology, allowing us to study how the morphology varies with temperature. These conditions limit the amount of evaporation and prevent isotropic phase change of the LC. Structural characterization using the Cornell NanoScale Facility Zeiss scanning electron microscope reveals the formation of different particle morphologies as a function of the various temperatures achieved.

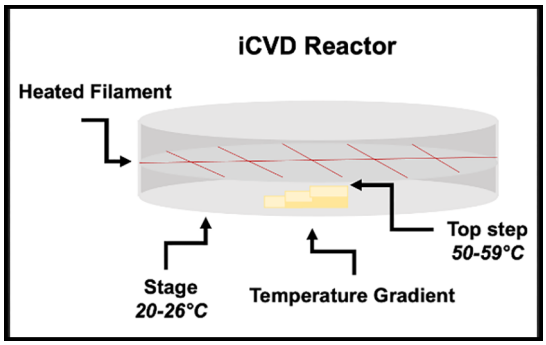

Figure 1: Schematic of the temperature gradient in the iCVD reactor.

Summary of Research:

Micro and nanoparticles are promising for future imaging, medical, and energy applications. The ability to synthesize and control the size and morphologies is crucial for utilizing these particles at an industrial scale. Initiated chemical vapor deposition (iCVD) is a promising technique for synthesizing nanoparticles since it allows for high control of continuous polymerization and provides multiple particle morphologies without external manipulation. We utilized liquid crystals (LCs) as an anisotropic medium to provide a template for the iCVD polymerization and to optically monitor the polymerization in-situ using a long-distance focal lens. Our work focused on determining the effect of temperature on the morphology of glycidyl methacrylate (GMA) and divinyl benzene (DVB) polymeric particles polymerized using the iCVD-in-LC system.

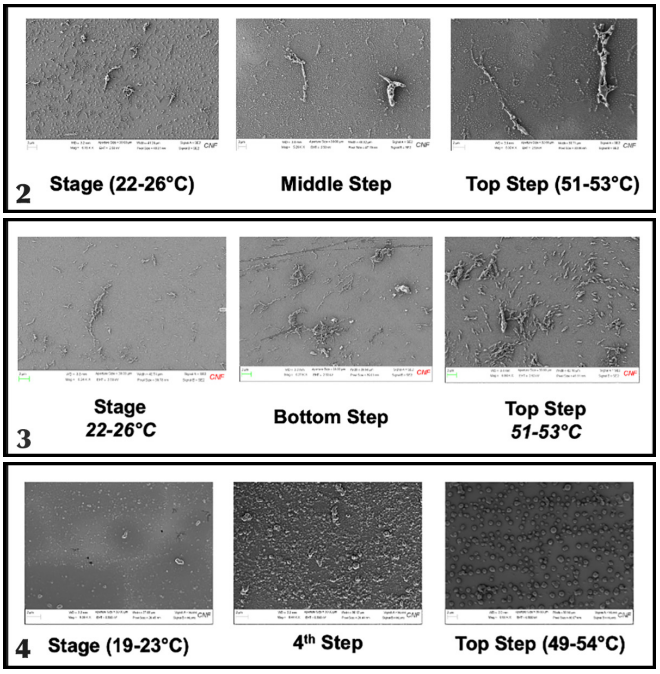

Figure 2: Morphologies of GMA particles polymerized on OTS. Figure 3: Morphologies of GMA particles polymerized on glass. Figure 4: Morphologies of DVB particles polymerized on OTS.

Utilizing a temperature gradient placed in the iCVD reactor, we achieved multiple temperatures within one polymerization run, as shown in Figure 1. The gradient was created by stacking glass slides in a staircase fashion. The reactor stage was cooled using a chiller set at 5°C, and a heated filament array was set above the reactor stage, reaching ~ 260°C. Our custom-built staircase sample holder experiences higher temperatures at the top step and lower temperatures at the bottom. We mapped the top step and reactor stage temperatures and consistently achieved a temperature difference of 20-25°C between the two extremes. We achieved multiple temperatures during each reactor run by placing samples on different steps of the staircase sample holder. This allowed us to compare the morphologies of the GMA particles polymerized in LC at different temperatures while minimizing the variables that could contribute to morphological differences. LCs are sensitive to temperature and change phase as temperature increases. The LC nematic phase provides mesogen orientational order and is the iCVD polymerization target phase. As temperature increases, the LC mesogens will transition to the isotropic phase; at this point, the LC loses its order and does not provide a templating effect. E7 LC was used for this project and has a nematic to the isotropic phase transition of ~ 60°C. To ensure the E7 remained in the nematic phase, we monitored multiple steps on the staircase and found no phase change of LC in the samples placed on any step during 30-minute and 60-minute polymerizations.

We also utilized two surfaces for the iCVD reactions: nochromix-treated glass and octadecyltrichlorosilane (OTS) substrates. Cross-polarized optical images of the LC samples were taken before and after the polymerization. We found negligible evaporation and no phase change of the LC during the 60-minute polymerizations for both glass and OTS samples using the optical images and the long-distance lens placed directly above the reactor. However, an anchoring change was observed at the mid-range temperatures for OTS from homeotropic to planar/tilted LC anchoring. We are currently investigating the cause of the anchoring change. After the polymerization, we characterized the morphologies of the GMA particles using a Zeiss Supra scanning electron microscope. We found that the particle morphology for GMA particles on OTS and glass does not drastically change their morphology but instead becomes larger and more elongated, as shown in Figures 2 and 3.

Utilizing the temperature gradient, we also polymerized DVB particles on OTS. We found that DVB particle morphologies differ more significantly than GMA polymerized at similar temperatures, as shown in Figure 4. The lower temperatures provide 300-400 nm diameter DVB nanoparticles. As temperature increases, DVB particles become larger and less symmetrical; at higher temperatures, they become symmetrical microspheres 1 μm in diameter. We hypothesize that DVB can achieve more morphologies because of crosslinking, while GMA is linear, achieving fewer morphologies.

Conclusion and Future Steps:

Using a temperature gradient, we achieved multiple temperatures during a single LC-templated iCVD reactor run, allowing the comparison of GMA morphologies at different temperatures. We found that the GMA morphologies do not differ significantly with increasing temperature but increase in size and elongation. DVB particles were also polymerized using the temperature gradient, and the obtained morphologies changed more significantly. Reproducible reactor runs must be done to ensure the GMA particles are fully characterized at the different polymerization temperatures. The temperature gradient created for this project can also be used in future polymerizations to achieve multiple temperatures within a single polymerization.

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References:

[1] Jain, A., Pal, S., Abbott, N. L., and Yang, R. (2023, March 10). Single-step synthesis of shape-controlled polymeric particles using initiated chemical vapor deposition in liquid crystals.