Initiated CVD (iCVD) Polymerization in Liquid Crystal to Synthesize Polymer Particles

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Primary CNF Tools Used: Leica 300 CPD, Zeiss Supra SEM

Abstract:

Synthesis schemes targeting specific nanoscale polymer architectures have the potential to advance the efficacy of polymer materials for applications in biomaterials and beyond as tunable material solutions [1]. In our current work, we expand previous investigations of the synthesis pathway of divinylbenzene (DVB) via initiated chemical vapor deposition (iCVD) templated in nematic liquid crystals to begin to explore polymerization with alternative monomers and process conditions. Understanding the effect of tuning the precursor concentrations and substrate properties on the resultant polymer architectures will empower future efforts to produce shape-controlled polymer particles within this synthesis pathway.

Summary of the Research:

Many existing methods to control polymer microparticle architectures involve physical manipulations, which are difficult to scale [1]. Initiated chemical vapor deposition (iCVD) within a liquid crystal (LC) template provides a pathway to construct polymer nanoscale and micro-particles with specific architectures achievable based on the reaction conditions [2]. In iCVD, the polymer precursors–the monomer and initiator–are delivered continuously in vapor phase into a chamber alongside an inert carrier gas. A superheated filament radicalizes the initiator to allow the polymerization reaction to proceed. As the monomer and initiator molecules adsorb onto the substrate, free-radical polymerization occurs. iCVD eliminates the need for solvent-mediated reactions, which can result in impure polymer products, impacting the functionality and applicability of functionalized polymeric materials [3].

The innovation that inspired this project is the use of a liquid crystal (E7, a commodity liquid crystal containing a eutectic mixture of cyanobiphenyls and terphenyls) as a templating material rather than an isotropic (disordered) liquid. Liquid crystals are a phase of matter in between liquid and crystalline solids that acquire exciting and useful properties from heightened orientational and positional ordering of their constituent molecular subunits [5]. Researchers have taken advantage of the molecular level organization in these materials in iCVD systems to guide the polymerization process and control the particles' final conformation [2]. The identity of the substrate on which the film is prepared controls the properties and orientation of the mesogens within the LC thin-film. At the LC-air interface E7 adopts a perpendicular anchoring scheme while at the interface with untreated glass the mesogens will be anchored planarly in multi-domains. Chemical treatments octadecyltrichlorosilane (OTS) and Dimethyloctadecyl(3-(trimethoxysilyl) propyl)ammonium chloride (DMOAP) result in planar anchoring at the LC-substrate surface as well as inducing a single homeotropic domain across the LC film [1]. Representative illustrations of the different anchoring conditions are included in Figure 1. These treatment schemes offer the researcher an additional layer of control to the polymer template during the reaction. In addition to comparing polymer products on substrates with homolayers of OTS, and DMOAP treatments, gradient substrates prepared by the Genzer group at NC State–gradients of OTS to glass, DMOAP to glass,

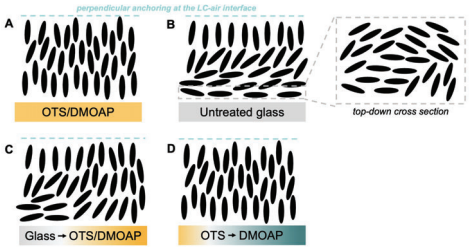

Figure 1: Illustration of anchoring effects on E7 for different substrate types.

and OTS to DMOAP counter gradients–were reacted to provide a comparison of both anchoring condition and the impact of anchoring strength and surface energy [5].

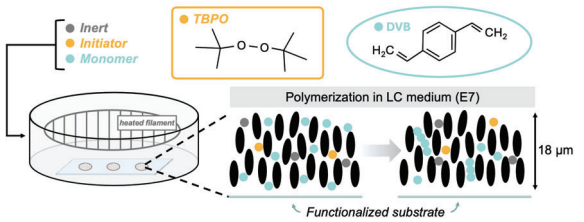

Figure 2: Schematic of in-lab set up for iCVD. Adapted from [1]: Jain, A. Science Advances 2024, 10 (45). https://doiorg/10.1126sciadv.adp5573.

Our experimental system, illustrated in Figure 2, reacts with controlled amounts of vaporized monomer and initiator tert-butyl peroxide (TBPO). The reaction takes place in a TEM grid containing nematic phase liquid crystal films (E7, TNI=60-63°C) mounted on a range of untreated and treated substrates. The chamber pressure is regulated to 150 mTorr and the sample stage is maintained at 20 °C. The reaction process is monitored in situ by a long focal length set up of a Keyence VHX 970F microscope and after reaction progress has been halted by SEM, confocal imaging, and microscopy on an Olympus BX41 microscope equipped with 4× and 20× objectives. Reactions were carried out at both high initiator to monomer ratios (~0.7 Monomer/Initiator) and low ratios (~0.15) at times ranging from 75 to 140 minutes. Critical point drying was employed to remove liquid crystal films while preserving the particles formed for imaging by SEM [1].

Conclusion and Future Steps:

Optical micrographs of films prepared on glass and homolayers of OTS and DMOAP showed that arrays of polymer nanospheres formed with greater regularity and covered a higher percentage of the available film area on DMOAP and glass than the OTS substrate (Figure 3). Analysis of particle sizes showed little significant variation in particle diameter between homolayer substrates: an observation confirmed with SEM imaging of representative polymer particles and particle clusters (Figure 4). Reactions performed on gradient films mirror this trend, with the sections of the film treated with DMOAP displaying a greater proportion of particle arrays than OTS. Analysis of reactions on the OTS to DMOAP gradient film further confirmed this trend, indicating that the anchoring orientation did not impact the formation of particle arrays. An implication of this finding is that the polymerization process occurs in the bulk LC or at the LC-air interface rather than on the LC-substrate interface. This hypothesis was supported by confocal microscopy which revealed that the nanosphere particles were positioned along a single focal plane within the LC bulk.

Determining the location of particle formation during the initiation and growth processes deepens knowledge of the dynamics of the polymerization reaction and,

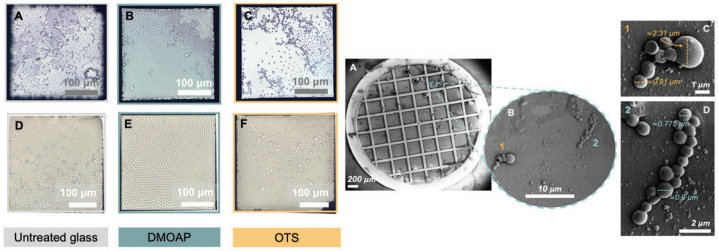

Figure 3 (Left) : White balanced optical micrographs showing the polymer products formed from high initiator to monomer ratio conditions (17.1 mTorr P(TBPO)/25.1 mTorr P(DVB)) (A-C) and low initiator to monomer ratio conditions (10.6 mTorr P(TBPO)/69 mTorr P(DVB)) (D-F). The DMOAP treated films (B,E) create more regular particle arrays than the untreated glass films (A,D) or the OTS treated films (C,F).
Figure 4 (Right): SEM images showing polymer nanoparticles. Low magnification (A) and high magnification are shown (B) alongside measurements of the range of particle diameters are also displayed (C, D).

in turn, will offer researchers greater insight into controlling the polymer architectures formed within the LC films. Future work will bring in more advanced imaging and characterization techniques, including AFM and advanced confocal microscopy, to detail this polymerization process and allow our understanding to empower iCVD studies of other monomer systems.

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