

Final Technical Report for Award Number DE-SC0012407
Kinetic and Mechanistic Study of Vapor-Phase Free Radical Polymerization onto Liquid Surfaces

08/15/2014 - 12/31/2017

DE-USC-12407

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Abstract/Executive Summary

The primary objective of this proposal was to study vapor deposition of polymers onto liquid surfaces. Deposition onto liquid surfaces is a relatively new area of research because the past few decades have focused on deposition onto solid materials. We used initiated chemical vapor deposition to deposit polymers onto the liquid surfaces. The process is a one-step, solventless, free-radical polymerization process in which monomer and initiator molecules are flowed into a vacuum chamber. We found that the surface tension interaction between the polymer and the liquid determines whether a film or nanoparticles are formed. We also found that we could form gels by using soluble monomers. We found that we could tune the size of the nanoparticles by varying the viscosity of the liquid and the process parameters including pressure and time. These insights allow scalable synthesis of polymer materials for a variety of separation and catalysis applications.

Summary of Project Activities

We used our DOE funding (Award Number DE-SC0012407 entitled “Kinetic and Mechanistic Study of Vapor-Phase Free Radical Polymerization onto Liquid Surfaces,” 08/15/2014 - 12/31/2017) to study the nucleation and growth of polymers deposited onto liquid surfaces. The following four manuscripts have resulted from this funding and we highlight the key results below.

- 1) "Microstructured Films Formed on Liquid Substrates via Initiated Chemical Vapor Deposition of Cross-Linked Polymers," L. Bradley, M. Gupta, *Langmuir*, 2015, 31, 7999-8005.
- 2) "Two-Stage Growth of Polymer Nanoparticles at the Liquid–Vapor Interface by Vapor-Phase Polymerization," R. Frank-Finney, M. Gupta, *Langmuir*, 2016, 32, 11014-11020.
- 3) “Fabrication of ionic liquid gel beads via sequential deposition,” P. Karandikar, M. Gupta, *Thin Solid Films*, 2017, 635, 17-22.
- 4) “Synthesis of Functional Particles by Condensation and Polymerization of Monomer Droplets in Silicone Oils,” P. Karandikar, M. Gupta, *Langmuir*, 2017, 33, 7701-7707.

In our 2015 *Langmuir* paper,¹ we studied the deposition of poly(ethylene glycol diacrylate) (PEGDA) onto silicone oils and we found that chemical cross-linking resulted in the formation of films containing micron-sized coral-like features. Our experiments showed that the growth occurred by simultaneous aggregation of the polymer at the liquid surface and wetting of the liquid on the growing aggregates. The roughness of the films decreased with increasing liquid viscosity because of less aggregation on the liquid surface due to slower rates of polymer diffusion (**Figure 1**). This also led to less void space between the microstructures and therefore a decrease in the thickness of the microstructured films from 5.4 ± 0.3 to 2.7 ± 0.3 μm with increasing liquid viscosity from 5 to 500 cSt. Films formed instead of particles because the ethylene glycol diacrylate monomer is capable of forming chemical cross-links.

In our 2016 *Langmuir* paper,² we studied the growth of polymer nanoparticles at the vapor-liquid interface. **Figure 2** shows our results for polymer deposition onto silicone oils with viscosities of 100 cst, 500 cst, and 1000 cst. The radius increases as the viscosity decreases because polymer chains are able to diffuse faster at lower viscosities leading to a greater amount of aggregation. These results are in agreement with our work above that showed an increase in the roughness of the PEGDA films with decreasing viscosity.

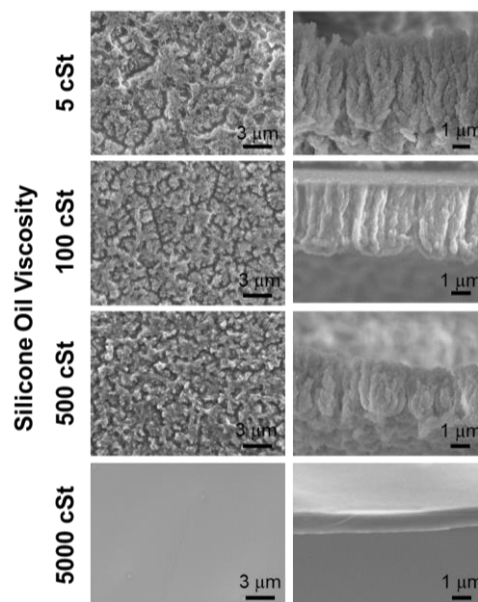


Figure 1. SEM images of bottom and cross-sections of PEGDA films deposited onto silicone oils of varying viscosities.

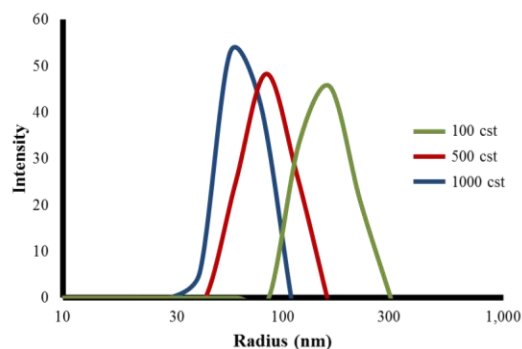


Figure 2. Overlaid histograms of the particle size distributions on 100 cst, 500 cst, and 1000 cst silicone oils.

In our 2017 *Thin Solid Films* paper,³ we demonstrated the fabrication of gel beads composed of ionic liquid (IL) and polymer. The IL droplets were kept spherical during the polymer deposition process by placement onto chromatography paper coated with fluoropolymer. We absorbed the monomer into the IL droplet and then introduced the initiator radicals. This sequential deposition process allowed polymerization to occur within the liquid droplet and therefore the beads were not attached to the underlying substrate and could be easily removed as shown in **Figure 3**.

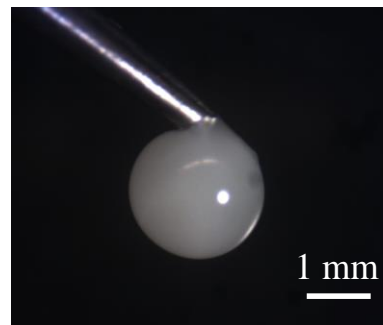


Figure 3. Gel bead held using a pair of tweezers.

In our submitted 2017 *Langmuir* paper,⁴ we studied the synthesis of polymer particles in silicone oil using a sequential vapor phase polymerization method in which monomer droplets were first condensed onto a layer of silicone oil and subsequently polymerized via a free radical mechanism. We found that at lower viscosities, a heterogeneous particle size distribution was produced where small particles were formed by engulfment of the monomer droplets at the liquid surface and large particles were formed by coalescence of the monomer droplets inside the liquid layer (**Figure 4**). Coalescence could be inhibited by increasing the viscosity of the silicone oil leading to a decreased average radius and a narrower size distribution of the polymer particles.

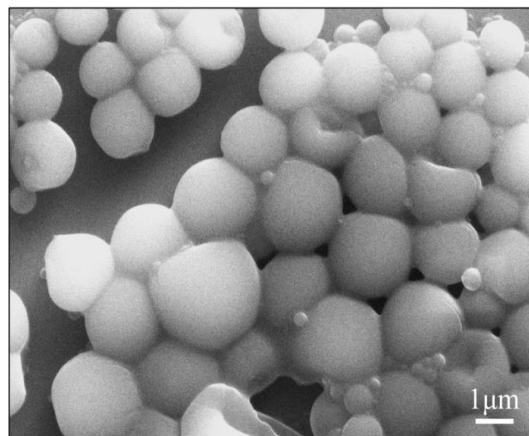


Figure 4. SEM images of polymer particles produced via monomer condensation and subsequent polymerization on 100 cst silicone oil.

Bibliography

1. "Microstructured Films Formed on Liquid Substrates via Initiated Chemical Vapor Deposition of Cross-Linked Polymers," L. Bradley, M. Gupta, *Langmuir*, 2015, 31, 7999-8005.
2. "Two-Stage Growth of Polymer Nanoparticles at the Liquid–Vapor Interface by Vapor-Phase Polymerization," R. Frank-Finney, M. Gupta, *Langmuir*, 2016, 32, 11014-11020.
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