

DESIGN OF A DROPLET-BASED MICROFLUIDIC SYSTEM FOR HYBRID POLYMER NANOPARTICLE SYNTHESIS

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By
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We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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Droplet microfluidics is advantageous in synthesizing microparticles for both confining their size to the physical dimensions of the droplet and providing a monodisperse result due to rapid mixing inside the droplets. Thusly named microreactors became the focus of the microfluidics community in the recent decade due to their superior ability to control the reaction environment. In this study, for the application of microreactors, a hybrid organic-inorganic material that became prominent in last years named polyhedral oligomeric silsesquioxane (POSS) is chosen. POSS is a polymer that, beside its hybrid nature, shows heat resistance property which made its use in protective painting applications and high radical group affinity that can be utilized to further configure its material properties. This study proposes two microreaction systems for monomer POSS with thermal and photopolymerization methods that aim to increase monodispersity and solve the clogging problem encountered in previous studies by introducing the oil phase in the system. Feasibility of systems was investigated numerically using COMSOL Multiphysics and analyses showed adequate heating of and mixing in microreactors. A robust post-processing procedure is proposed to remove excess oil from the sample. Measurements showed microdroplet and sub-micron particle generation where the size distribution of these particles are quantified using MATLAB. Though the use of oil in the system proved to be another challenge, hexane based substitute materials are proposed for future work.

Keywords: Microfluidics, Droplet-Based Flow, Microparticles, POSS Particles, Microreactors.

ÖZET

HİBRİT POLİMER NANOPARÇACIK SENTEZİ İÇİN DAMLACIK TEMELLİ MİKROAKIŞKAN SİSTEM TASARIMI

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Damlacıklı mikroakışkanlar, parçacık boyutlarını damlacığın fiziksel boyutu ile sınırlandırıp damlacık içerisinde etkin karışımla eş dağılımlı parçacıklar meydana getirdiğinden mikroparçacık sentezinde avantajlı konumdadır. Bu sebeple tasarlanan mikoreaktörler de reaksiyon ortamının kontrolündeki üstün özellikleri nedeniyle son dönemde mikroakışkan topluluğunun odağı hâline gelmiştir. Bu çalışmada, mikoreaktör uygulaması için geçmiş yıllarda öne çıkan organik-inorganik hibrit yapılı polihedral oligomerik silseskuioksan (POSS) malzemesi seçilmiştir. POSS, hibrit yapısına ilaveten koruyucu boya uygulamalarında yer almasını sağlayan ısı direnç özelliği gösteren ve malzeme özelliklerinin daha da özelleştirilebilmesini sağlayan yüksek radikal gruplara bağlanma yatkınlığı bulunan bir polimerdir. Bu çalışma, monomer POSS kullanarak eş dağılımlılığı artırmak adına ısı ve ışıl polimerleşme yöntemleri ile önceki çalışmalarda karşılaşılan tıkanma sorununu çözmek amacıyla sisteme yağ fazı ilavesi bulunduran mikoreaksiyon sistemi önermektedir. Sistemlerin uygulanabilirliği COMSOL Multiphysics kullanılarak incelenmiş ve analizler sonucunda mikoreaktörlerin yeterince ısınabildiği ile karışıma elverdiği görülmüştür. Örneklerdeki yağın ortamdan uzaklaştırılması için ise bir son işlem prosedürü geliştirilmiştir. Ölçümler sonucunda mikrodamlacık ve mikronaltı parçacık oluşumu görülmüş ve bu parçacıkların boyut dağılımı MATLAB ile belirlenmiştir. Sistemde yağ kullanılması bir başka zorluğa sebebiyet verse de gelecek çalışma olarak heksan temelli malzeme ikamesi önerilmiştir.

Anahtar sözcükler: Mikroakışkanlar, Damlacık Temelli Akış, Mikroparçacıklar, POSS Parçacıklar, Mikoreaktörler.

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In short, though I have no idea about the equation itself, I acknowledge all the current states and initial conditions of the universe(s?) which have led to this outcome.

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Chapter 1

Introduction

Microfluidics study fluid flow in scales with less than 1 mm characteristic length. Fluid flow can be within microchannels or on surfaces; in both cases, viscous forces are dominating inertial forces, leading to low Reynolds (Re) numbers. Flow in small scale provides several advantages, such as the requirement for less sample; precise control of temperature, concentration, and residence time [1]. Therefore, microfluidic systems are used in biological detection and sensing, separation, cell lysis nanomaterial sorting and micro/nanomaterial synthesis.

This thesis focuses on synthesizing polyhedral oligomeric silsesquioxane (POSS) hybrid particles by using microfluidic systems. In the synthesis of particles, monodispersity of size and shape distribution is essential for the success of the process. In order to achieve uniform particles, reaction conditions should be controlled precisely so that each sample experiences the same temperature, residence time or concentration. Therefore, microreactors are superior to conventional batch techniques for such processes.

This chapter discusses the microfluidic systems in the literature that were developed for microparticle synthesis and explains the motivation for designing such a system for POSS particle synthesis. In the end, an overview of the thesis is provided.

1.1 Microfluidic Systems for Microparticle Synthesis

Micro and nanoparticles have broad applications in fields such as optical detection [2, 3], sensing [4, 5], drug delivery [6, 7], and imaging [8]. For all these applications, uniform property of these particles is required so that the same output can be obtained from each particle. Even though particles are conventionally mass-produced in batch reactors, synthesizing sub-micron particles having uniform properties is challenging. In batch-wise synthesis, large scale systems are used where it is not easy to control reaction temperature or concentration uniformly. For instance, the parts of the beaker closer to the heater have higher temperatures than the parts further away from the heat source. This type of nonuniform heat distribution results in polydisperse particle formation.

Microfluidic systems have various advantages such as working with small sample amounts, easy manufacturing, precise control and portable size [1, 9, 10, 11, 12, 13, 14]. Due to these advantages, microfluidic systems are desired in micro-nano particle synthesis and devices designed for this purpose are named microreactors.

Flow in microreactors can be droplet-based or continuous. In droplet-based microreactors, fluids containing reagents are carried as separate segments, or droplets, using an immiscible carrier fluid. In continuous flow reactors, flow is not segmented, and mostly, a single type of fluid that contains reagents passes through the channel.

1.1.1 Continuous Flow Microreactors

Continuous flow microfluidic reactors are made out of microchannels that contain a single fluid or multiple miscible fluids that do not interrupt the steady flow. Designing and operating devices that utilize continuous flow is straightforward and low-cost, making them preferable for research purposes. In continuous flow,

having Reynolds number Re smaller than one leads to a laminar flow which does not favour mixing. Therefore, complicated active or passive mixing methods must be used to obtain a uniformly mixed reaction medium [15, 16]. Furthermore, the fully developed flow inside the channel has a parabolic velocity profile. Therefore, the particle velocity near the walls is close to zero, and slower speed increases the probability of contamination. In such scenarios, preventing clogging requires pre-treatment of the walls or covering them with a lubricant before the experiment begins [17].

One of the first reported microfluidic reactors is a continuous flow system that synthesizes quantum dots [18]. In this work, *Chan et al.* used glass substrate to fabricate a microfluidic reactor and heated these channels to achieve synthesis at elevated temperatures. Continuous microfluidic systems were later utilized in polymer particle synthesis [16]. However, due to difficulty in mixing, channel contamination and control of residence time due to parabolic flow profile, continuous microfluidic systems are not as popular as droplet-based systems for particle synthesis.

1.1.2 Droplet-Based Microreactors

Droplet-based or segmented flow diverges from the continuous flow by allowing one fluid, called continuous phase, to shear-off and encapsulate the other, called the droplet or dispersed phase, in a droplet shape. For chemical reaction purposes, when the reagents are encapsulated within a droplet, the reaction itself is physically confined to a specific volume, limiting the size of the end product [19, 20]. Since the droplets have a small volume, the reaction time constant is also reduced due to faster heating and cooling of samples [21, 22, 1]. On the other hand, mixing within droplets is very rapid due to the circular flow profile. Mixing can be further accelerated by adding sinusoidal shaped channels that decrease the diffusion length in droplets [23, 24] which is critical in laminar flow conditions. These properties of droplet microfluidics make it a desirable method for performing controlled chemical reactions and polymerization [10, 25, 26].

In the past few years, droplet-based systems became popular for especially polymer and hybrid particle synthesis. Recently *Yang et al.* used a droplet-based reactor to synthesize hollow polymeric particles [27]. In this work, latex within a sodium chloride, an aqueous solution, is used as the droplet phase whose volume controls the microparticle size. In another study, *Wahab et al.* synthesized particles composed of chitosan and iron oxide using a multi-step reactor in which droplets of chitosan and iron oxide precursors are formed separately and later merged for particle precipitation and curing [9]. Janus microparticles are also synthesized by microfluidic systems and mostly within droplets. *Zhang et al.* recently synthesized monodispersed microgel particles compartmentalized by utilizing coflowing streams that form droplets in the channel [28]. Another work on Janus particle synthesis was recently shown by utilizing a droplet-based system where the particles were composed of two polymer parts with individual drug release abilities [29].

1.1.2.1 Droplet Generation Methods

In this thesis, a microfluidic system that is capable of droplet generation will be utilized for particle synthesis; therefore, a short review of droplet generation methods is provided in this subsection.

The primary mechanism of droplet generation is due to the shear force applied by a continuous fluid on the droplet phase [30]. The generation dynamics depend on the geometry and flow rate ratio of two fluids [31, 32]. Different active and passive droplet generation schemes using this principle are proposed in the literature [26, 33]. The examples include the single T-junction, an experimental version shown in Figure 1.1, and a double T-junction that enables flow focusing and better wetting the walls by continuous fluid [34, 35]. Other developments include using tapered channels and separating flow coming from opposite faces that opens a way to produce alternating droplets consisting of different materials [36, 37]. Also, it is possible to increase the pressure difference between leading-trailing edges [38] and increase the cutting pressure by adding a necking as in Figure 1.2 [39].

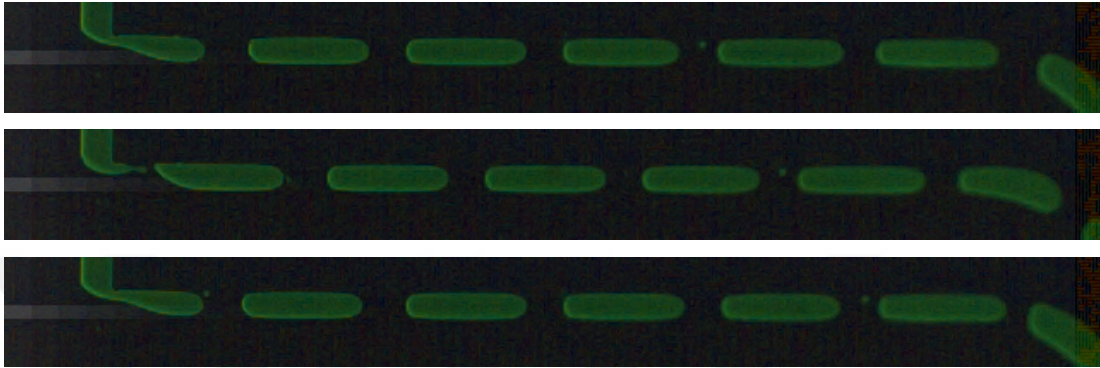


Figure 1.1: High-speed camera images of fluorescent droplets with 0.5 s intervals in a single T-junction.

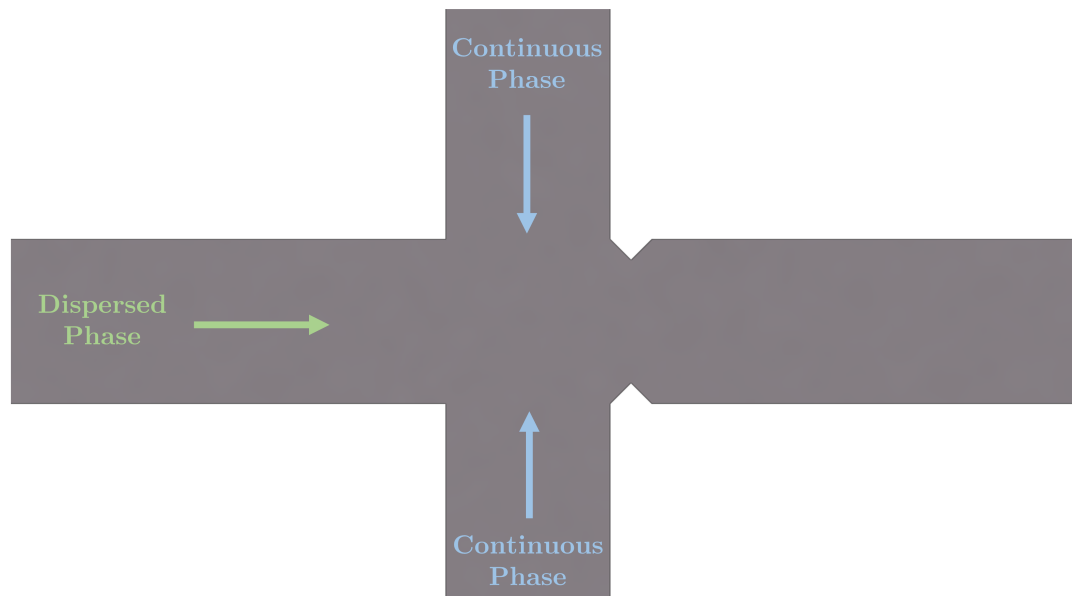


Figure 1.2: Necking region helps droplet generation by providing a stable break-up point.

1.2 POSS Hybrid Particles and their Synthesis

Polyhedral oligomeric silsesquioxane (POSS) is a unique hybrid structure with a silica-cage core with pendant organic groups [40]. The inner three-dimensional inorganic cage structure formed by silsesquioxane unit that consists of silicon atoms ($n=8$) linked with oxygen atoms ($n=12$), and the outer organic groups ($n=8$) merged to create this hybrid structure. The hybrid molecule has the formula as $(RSiO_{1.5})_n$, where n is the number of atoms ($n=6,8,12$) which affects the size of the hybrid molecule [41]. Due to the inorganic-cage structure shape, POSS is the smallest possible silica particle with a nanoscopic size of around 1.5 nm [42]. The organic (R) groups provide an unlimited source of functionality to this hybrid molecule that enables integration of many properties. The solubility [43], conductivity [44], porosity [45], reactivity [46], inert [47], catalytic [48], optical [49], thermal [50], mechanical [51], or physical [52] properties of the material could be changed depending on the difference in the R groups of POSS.

The hybrid structure became attractive and offered many possibilities with functional arms such as epoxy, amine or vinyl-end organic compounds. As the radical groups are open to modification or chemical reactions, countless molecule designs and applications arose into the field [53]. Due to high thermal resistance, POSS nanoparticles were used as fire-retardant composite material [54]. The separation efficiency and antifouling performance of POSS nanoparticles have made them a preferred filling material in membrane technologies [55]. As an additive, POSS nanoparticles provide high mechanical strength to conventional polymers [56]. The biocompatibility of POSS nanoparticles allows many biological applications such as drug delivery and tissue engineering [57], dental applications [58] and biological separation technologies [59].

The hybrid POSS and POSS-containing particles could be prepared using various synthesis techniques through R functional group. The organic R groups provide reactive compounds such as metachryl-, glycidyl-, aminopropylisobutyl- on silica-cage to create new polymer chains, co-polymerization, graft or attach other polymers via different polymerizations [60]. The POSS nanoparticles are

obtained mainly by conventional polymerization methods: emulsion, suspension, precipitation, and dispersion polymerization. In emulsion polymerization, surfactant formed micelle in either water or oil reaction medium. Every micelle droplet (from 100 nm to 10 μ m) contains a monomer for the polymerization by adding an initiator. The common types of emulsion polymerization are oil-in-water (O/W), water-in-oil (W/O), and multiple-emulsion type (W/O/W) [61, 62]. The critical parameters in emulsion polymerization are heat transfer, surfactant type, amount, and composition in the reaction medium. In suspension polymerization, the initiator is soluble in the monomer phase, and the monomer is insoluble in water. Monomer and initiator mixture formed droplets (size range from 100 nm to 5 mm) in suspension medium and stabilized against coalescence, using stabilizers, surfactants, protective colloids, and stirring. Each monomer droplet is an independent reaction locus where the polymer chain propagates. Therefore, the monomer droplet size is almost equal to the resultant polymer size [63]. The resultant product could be spherical particles or irregular shapes depending on the polymer's solubility in its monomer [64]. In precipitation polymerization, monomer and initiator are soluble in the reaction medium, generally water. The polymer is obtained by efficient agitation and insoluble form in the reaction medium [65]. Dispersion polymerization is a type of precipitation polymerization, which differs by the addition of a stabilizer in the reaction medium [66]. Many studies have been reported in the literature with these conventional techniques and summarized in Table 1.1.

Table 1.1: POSS particle studies in the literature.

POSS Related Particles	Method/Mechanism	Outcome	Ref
Batch-wise Synthesis			
A star-shape POSS containing copolymer	Click Chemistry-Copolymerization	Increasing conformation stability of polymer	[67]
POSS-poly(glycerol methacrylate)	Atom transfer radical polymerization (ATRP)-Precipitation polymerization	Self-assembled tadpole-shaped nanoaggregates	[68]
(M-POSS) containing microparticles	RARF-Precipitation polymerization	POSS-based molecular imprinted polymer for drug delivery	[69]
∞ Star-shape POSS nanoparticles	RAFT-Chain Transfer Agent (CTA) polymerization	Enhance mechanical performance and thermal stability	[70]
Monodisperse POSS based microparticles	Thiol-Michael dispersion polymerization	POSS content enhances UV resistance	[71]
POSS latex particles	Emulsion polymerization	Spherical-shape micro/nanoparticles	[72]
P(GMA-POSS)-co-PMMA	Epoxide ring-opening emulsion polymerization	Improve adhesive property and thermal properties	[62]
Continuous Microfluidic Synthesis			
Monodisperse POSS microparticles	Dispersion polymerization	High thermal resistance and composite structure	[73]

Batch systems have been the conventional particle synthesis method for many decades. Being the most straightforward method and yielding a large amount of material, it is still the most popular method when a more volumetric production, rather than accuracy, is desired [74]. Polymerization of POSS has also been studied by using in batch systems through thermally activated techniques that may require hours to complete [75]. Microreactors, on the other, hand is an emerging technology and very suitable to satisfy the shortcoming of the batch systems by providing a controllable environment. The droplet generating geometries are mainly employed due to superior volume control in the microchannel. Recently, *Kibar et al.* showed the synthesis of POSS microparticles by utilizing a continuous flow microfluidic reactor that can apply dispersion polymerization [73]. This study was the first effort to utilize a microreactor in POSS synthesis.

In this thesis, a microfluidic reactor is designed to perform addition polymerization to synthesize monodispersed POSS particles for the first time. The polymerization mechanism varies as addition polymerization and condensation polymerization. In the addition polymerization mechanism, the double or triple bond of an organic molecule (monomer) breaks and adds new monomer units to the growing polymer chain. In condensation polymerization, monomers or oligomers react with each other to form a polymer chain by releasing side molecules, such as water or methanol, from the chemical structure [76]. While the conventional silica nanoparticles produced by Stöber process is based on a series reaction of tetraethyl orthosilicate (TEOS) hydrolysis and polycondensation mechanism, Methacryl-POSS (M-POSS) polymerization is carried out through double bonds with additional polymerization mechanism. During polymerization, the thermal or UV initiator creates a free radical by attacking double bonds of M-POSS monomer. The polymer chain grows in droplets during the propagation step. Polymerization continues until it turns into a non-reactive polymer.

1.3 Thesis Overview

The motivation for this study is to improve the size uniformity of the POSS particles by utilizing droplet-based microreactors to produce particles in the order of 100 μm with high uniformity. By utilizing addition polymerization and in-situ emulsion polymerization, it is aimed to obtain even smaller particle sizes and try to have even superior size distribution by mixing reagents in channel for the first time in literature. This method is also promising to solve the clogging problem in previous POSS polymerization studies [77] by introducing the oil phase as the continuous fluid. The thesis is organized as follows:

Chapter 2 describes the one-step POSS based hybrid particle synthesis in a droplet-based microfluidic reactor by photopolymerization. The main goal is to design and fabricate a microreactor to synthesize hybrid particles in one step. In this chapter, novel designs are developed to obtain microreactors and photolithography steps to fabricate the microreactors are explained. Moreover, the droplet formation is clarified and mathematically supported by numerical studies for these designs. Photopolymerization parameters of POSS are experimentally optimized, and results are comprehensively discussed.

Chapter 3 focuses on the methods and results of emulsion polymerization experiments. The experiments are divided into two subsections where thermal polymerization and UV photopolymerization techniques are discussed. Both experiments are conducted under the same conditions to evaluate and compare the results better. The main difference of this section to previous studies is the making emulsion in-situ for continuous mixing. Results in this section include the Scanning Electron Microscopy (SEM) and Fourier-Transform Infrared Spectroscopy (FTIR) analyses.

Chapter 4 concludes the thesis by summarising the previous chapters, discussing the advantages and disadvantages of the methods, providing suggestions on improvements and possible future work.

Chapter 2

Droplet-Based Microfluidic Reactor Design for Poly(M-POSS) Microparticles

2.1 Design of the Droplet Generation Unit

There are many methods and geometries to generate droplets in a microfluidic device. In this study, flow focusing geometry with a necking was chosen for two main reasons: better wetting the walls by continuous phase from both directions and having a consistent break-up location. Before fabricating the necked microchannels, a benchmark test for polymerization speed was conducted to determine the microfluidic channel length. According to these calculations and flow speed, two different microchannels were designed and shown in Figure 2.1. Both have the same channel width (200 μm), height (200 μm) and length (600 mm); the only difference is the shape where one is spiral and other is straight with sharper curves. This was intended to observe the effect of channel geometry on mixing performance. In these designs, the left-most part is the droplet phase inlet, top and bottom are the oil inlets and the outlet is at the right.

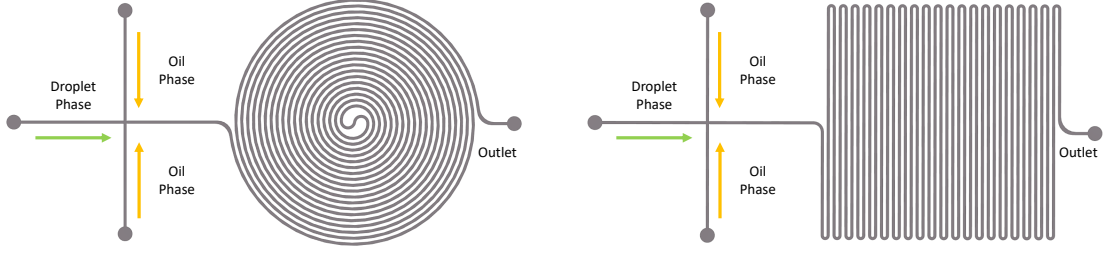


Figure 2.1: Two different droplet-based microreactors designed for POSS particle synthesis.

2.2 Numerical Analysis

Droplet generation simulations are fundamentally multiphase simulations in which different fluids or different phases of the same fluid exist simultaneously. In these situations, there may exist several disconnected closed curve interfaces. COMSOL Multiphysics can model the dynamics of the fluid flow using Equations 2.1 and 2.2 to formulate Navier-Stokes and continuity, and uses the Level-Set Method formulation in Equation 2.3 applied to fluid flow by [78, 79].

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u} + \mathbf{F} \quad (2.1)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (2.2)$$

$$\frac{\partial \Phi}{\partial t} + \mathbf{u} \cdot \nabla \Phi = \gamma \nabla \cdot \left(\varepsilon \nabla \Phi - \Phi(1 - \Phi) \frac{\nabla \Phi}{|\nabla \Phi|} \right) \quad (2.3)$$

The left-hand side of the Level-Set equation governs the motion of the interface and the right-hand side provides the numerical stability adjustments introduced mainly by COMSOL. Here; Φ denotes the level set variable representing the fluids with discrete values of 0 and 1, $\mathbf{u}$ represents the velocity field, γ is the stabilization parameter and ε can be interpreted as the interface thickness where the transition occurs. Since the γ value is purely numerical, an approximately correct value is

determined by consulting the documentation and studying the provided example cases. Value of ε can be physically approximated by taking recommended values as benchmark. For the surface tension σ and contact angle θ_w values, standard documented values were used. The Level-Set Method uses Equations 2.4 and 2.5 to solve the density and the viscosity of the multiphase medium.

$$\rho = \rho_1(1 - \Phi) + \rho_2\Phi \quad (2.4)$$

$$\mu = \mu_1(1 - \Phi) + \mu_2\Phi \quad (2.5)$$

A three dimensional simulation is constructed to model the droplet generation unit and the following serpentine channels. Serpentine channels were kept short due to computational limitations but eventually a similar behaviour was observed in the experiments meaning the simulation of the entire channel is not necessary. Consulting the mesh convergence analysis of similar applications that are studied in [80], the corners in the geometry and the relatively complex physics of the fluid at the junction and the necking region called for a more detailed meshing so the mesh seen in Figure 2.2 was constructed. Looking at the physics of the problem, utilizing symmetry and applying a symmetric boundary condition to reduce the number of elements and gain computational advantage was found favourable. Volumetric flow rate condition is used for inlets, and atmospheric pressure condition is used for outlet.

The values on the Table 2.1 are selected according to respective oil - water elements where the continuous phase is silicone oil and the droplet phase is water. In reality, the chemicals used in the experiments are much more complex. However, the solver module here is limited to two-phase flows and this analysis is performed to give an insight and an approximation. According to this analysis, a still image shown in Figure 2.3, the designed geometry generates stable droplets and the break-up always occurs at the necking region. Simulations also showed that the pressure values inside the microchannel are in the order of hundreds of Pascals which will prevent the bonding failure in the device. Simulations also showed that two critical non-dimensional parameters were identified as the flow

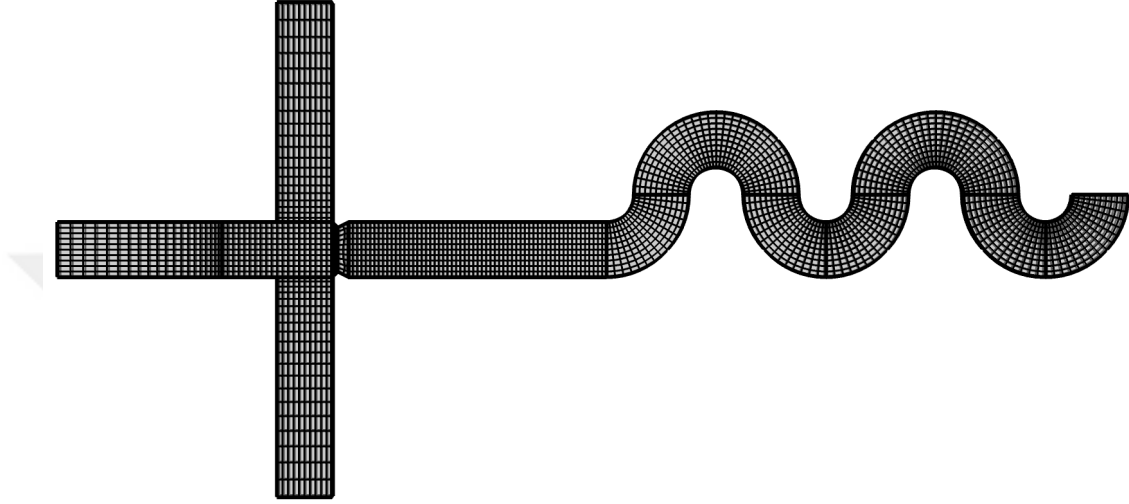


Figure 2.2: The mesh of the droplet generation unit that is refined at necking region to better resolve the physics.

Table 2.1: Parameters used in the COMSOL Multiphysics simulation.

Simulation Parameters			
Continuous Phase Flow Rate	$V_{continuous}$	5	$\mu\text{L min}^{-1}$
Continuous Phase Density	$\rho_{continuous}$	950	kg m^{-3}
Continuous Phase Viscosity	$\mu_{continuous}$	10	mPa s
Droplet Phase Flow Rate	$V_{droplet}$	5	$\mu\text{L min}^{-1}$
Droplet Phase Density	$\rho_{droplet}$	1000	kg m^{-3}
Droplet Phase Viscosity	$\mu_{droplet}$	1	mPa s
Surface Tension	σ	5e-3	N m^{-1}
Interface Thickness	ε	5	μm
Reinitialization Parameter	γ	5e-2	m s^{-1}
Contact Angle	θ_w	135	$^\circ$
Slip Depth	β	5	μm

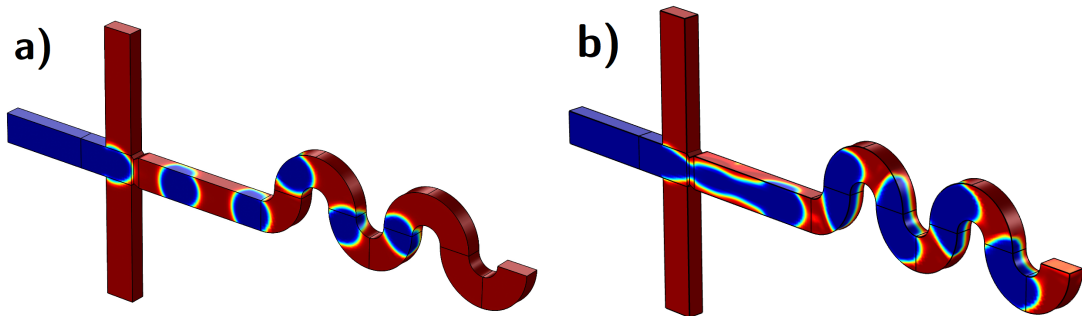


Figure 2.3: COMSOL Multiphysics simulations of the droplet generation with necking geometry. a) Flow-rate ratio of continuous phase to droplet phase is 1:1. b) Flow-rate ratio of continuous phase to droplet phase is 1:2.

rate and viscosity ratios of continuous to droplet phase. It is observed that a viscosity ratio of 100:1 and flow ratio less than 1:1 is required to generate stable droplets.

2.3 Fabrication of the Microreactor

Finalizing geometry, a simple two-step soft-lithography procedure seen in Figure 2.4 and detailed in Appendix A.2 was followed to create a master-mold. A 4-inch silicon wafer cleaned with acetone, IPA and water is first spin-coated with SU-8 2005 (Microresist) negative photoresist to create a thin adhesion layer for structures to be built on. This base layer is heated, flooded with UV light and heated again to solidify. For the main structure layer, wafer is spin coated with much thicker SU-8 2050 (Microresist) that can reach required structure height. The same heating and exposing steps are followed with the addition of chromium mask to the UV exposition. Resulting SU-8 covered silicon wafer is drowned in developer to remove unsolidified parts and washed with IPA as the last step of mold fabrication. This mold is then covered with a 10:1 PDMS : curing agent (Sylgard 184) mixture and left to cross-link in 80 °C for 2 hours. The solid PDMS is peeled off from the mold, the inlet and outlet holes are punched, and then bonded to a clear glass slide with the help of a plasma cleaner. Finally, 1.5 mm × 2.1 mm PVC tubings cut in the same length to standardize the hydraulic resistance were

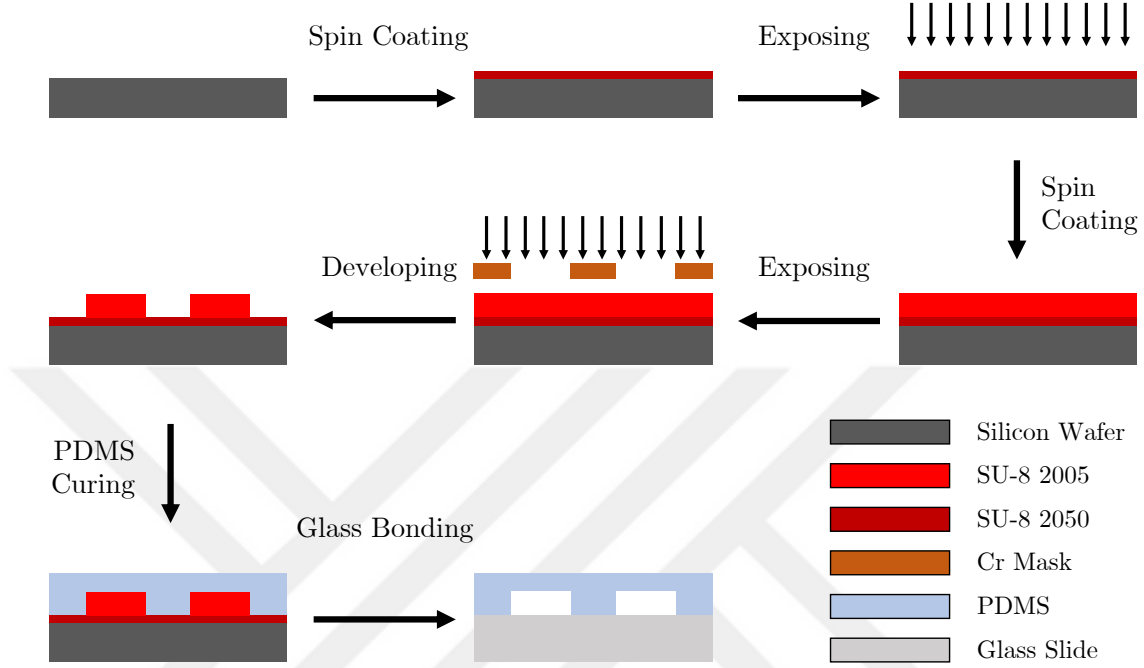


Figure 2.4: Fabrication steps showing two-step soft lithography and glass bonding.

connected to inlet and outlets.

2.4 Experimental Set-up and Materials

The experimental set-up consists of two syringe pumps are connected to capillary tubings and their flow rates are set to values given in Table 2.1. First, the silicone oil (378364, Sigma-Aldrich) is injected to system to wet all the channel walls. When the channels are filled with oil, the monomer is pumped and the flow is observed until it comes to a steady-state droplet producing condition. During this time, a high-speed camera is placed on top of the system with a focusing gap of 10 cm to monitor the channels. After the flow reaches to steady-state and the droplets are observed, the ultraviolet (UV) light source is placed directly on the microchannel to start the polymerization.

Table 2.3 provides a list of all materials used in droplet solution. The methacryl

Table 2.2: Different materials used to capture the optimum droplet formation mixture.

Experiment	Monomer		UV Initiator	Solvent		Surfactant			Result
	EGDMA ul	POSS mg	Darucor ul	EtOH ul	H2O ul	SDS mg	P123 mg	SPAN-80 mg	
Benchmark				3000	3000				Benchmark test for droplet generation
#1		250	100	3000	3000				Droplets are generated, monomer crystallized, no polymerization
#2		250	100	1000	1000				Decreased water to prevent crystallization to no avail
#3		250	100	5000				2%	Removed water and added surfactant to oil phase, no droplets
#4		250	100	5000			25		Changed surfactant to adjust surface tension no droplets
#5		250	250	5000		25			Changed surfactant to adjust surface tension no droplets
#6	250	250	100						Removed ethanol completely, used co-monomer instead, almost working
#7	500	250	50						Droplets generated with polymerization

POSS (m(POSS)) (MA0735, Hybrid Plastics) is used as the base monomer that will eventually lead to polymeric POSS particles. Ethylene glycol dimethacrylate (EGDMA) (335681, Sigma-Aldrich) is used to dilute the viscous m(POSS) and act as a co-monomer at the same time. Darocur 1173 (405655, Sigma-Aldrich) is the photoinitiator in the system. First, m(POSS) is transferred to a sample container by a metal spoon. Then, EGDMA is added to the same container using a micropipette. The initiator is added to the system last to prevent accidental activation. With the addition of an initiator, reaction starts only when light with a specific wavelength is provided to activate initiator, in this case it corresponds to the UV range. Photopolymerization is especially useful on sensitive systems as it does not directly heat the system and can be focused on intended region, therefore its highly preferred in microreactor systems [15, 81, 82]. For example, in the systems where this external activation energy is provided by heat, in due time the temperature is evenly distributed across the chip due to the intrinsic material properties of glass and partially PDMS. One downside of using UV light with PDMS-glass bonded chips is that both PDMS and glass completely reflect or absorb the low-UV spectrum. Therefore, a particular 10 W UV source with 385 nm wavelength that is closer to the visible spectrum was used in the experiments.

Table 2.3: Material table for droplet based polymerization

Type	Material	Amount	Unit
Monomer	m(POSS)	250	mg
Co-Monomer	EGDMA	500	μL
Initiator	Darocur	50	μL

The viscosity of the materials used in the system are very diverse, for example viscosity of m(POSS) is orders of magnitude higher than water, therefore when preparing the droplet phase the correct concentration of m(POSS) was found by conducting some experiments. Table 2.2 shows the main combinations of concentrations used to achieve optimal droplet generation conditions. The full table can be seen in Appendix B.1.

Stable droplet generation is crucial for the success of these experiments; therefore, the monomer solution was diluted with water and ethanol to reduce its viscosity. In addition, surfactants were introduced to both water/ethanol mixture such as SDS, P-127 and F-123 and to oil phase such as SPAN-80 to create a stable interface between the fluids to promote droplet formation. Different concentrations of different surfactants were tried to balance to form a stable droplet.

As a result of these experiments, a sure mixture containing another monomer called EGDMA was found. When the co-monomer EGDMA was mixed with m(POSS), stable droplet generation was observed at the necking cross-section in Figure 2.5. When droplets are observed, the UV source is turned on and polymerized droplet samples are collected from outlet.

2.5 Experimental Results

Figure 2.5 shows the droplets formed at the junction of the flow-focusing device and moving along the channel without contacting the walls. The generation was stable and droplets were uniformly sized during the observation period. After a while, the inlet tubings were detached from the device due to high pressure.

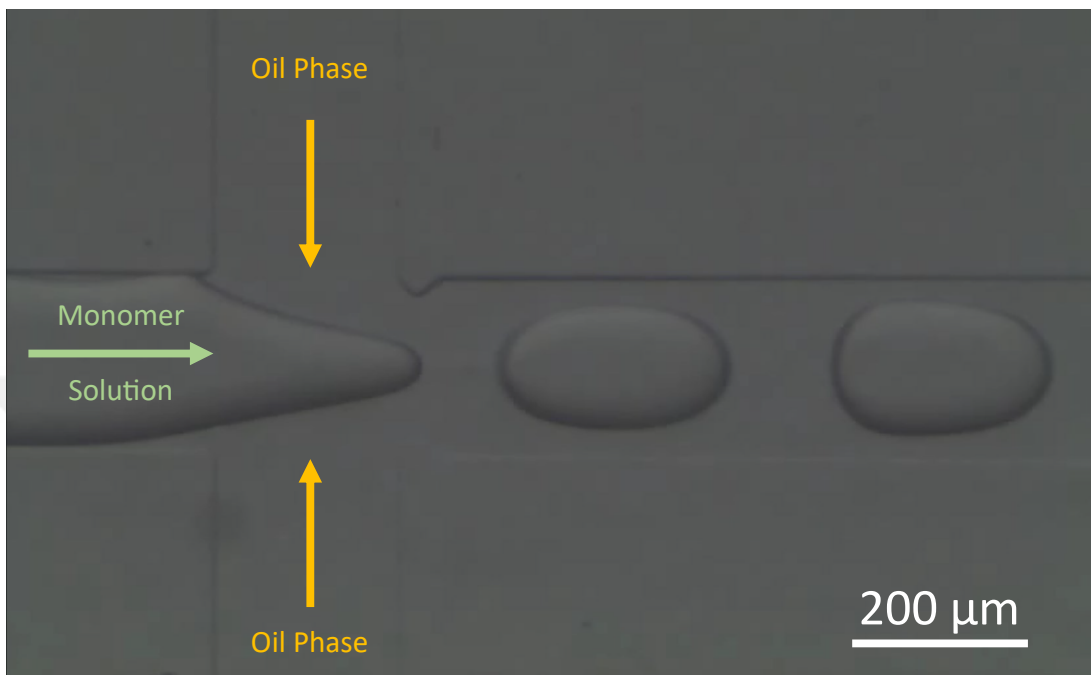


Figure 2.5: Droplets are successfully produced in the system.

This increase in pressure can be attributed to both droplets sticking to the channel wall due to inadequate oil flow or droplets merging to grow in size and eventually clogging the channel. Figure 2.6 shows the case where droplets are stuck to the channel wall.

Figure 2.7 shows an example of an almost complete channel clogging. Complete channel clogging also prevents oil from flowing and causes pressure to develop around inlets which eventually causes PDMS bond to fail or tubings to detach.

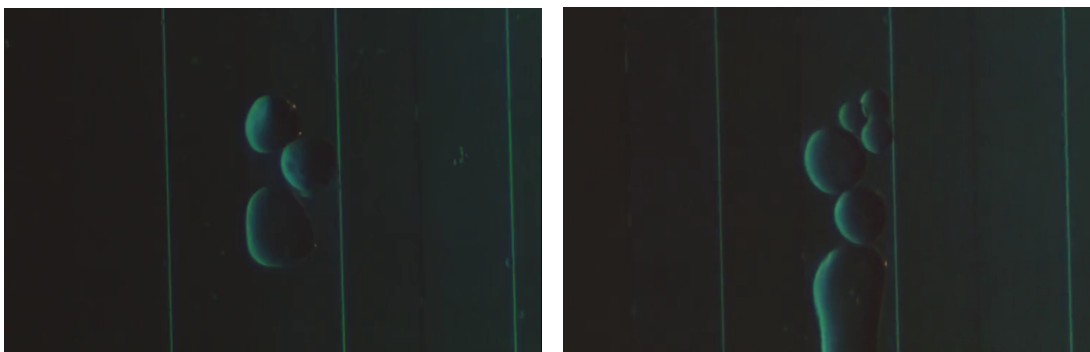


Figure 2.6: Droplets are stuck both to the wall and themselves.

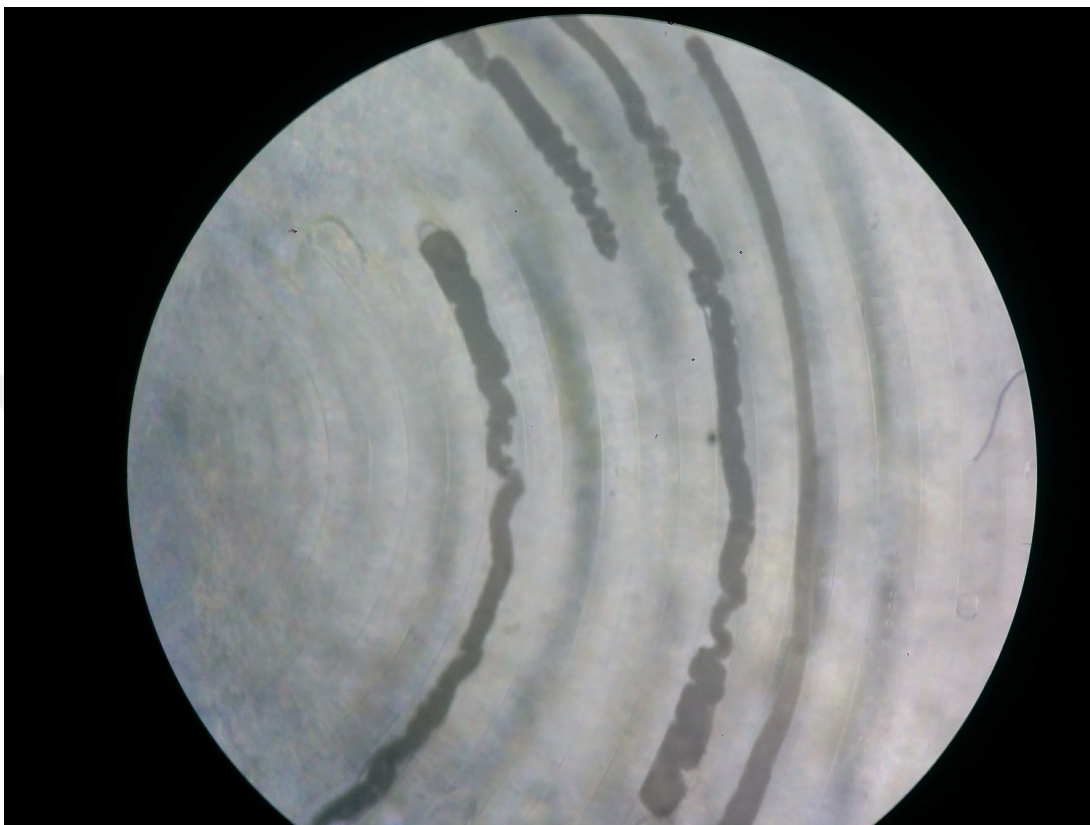


Figure 2.7: Polymerization inside microchannel causing clogging.

This failure mode is mainly observed in spiral channels, suggesting the possibility of varying friction along the channel which can be explained with changing curvature. U-turns of the straight channels also occasionally caused two close droplets to merge and eventually come to a halt to clog the channel.

The problem was solved by increasing the oil flow rate and reducing the UV light's power for these failure modes. Trying both options, the image in Figure 2.8 displays the droplets going through the outlet with nearly spherical shapes. To assess the polymerization, the collected samples were washed and later morphologically analyzed by the SEM (Quanta 450 ESEM). It is found that the same chip can be used up to three times to achieve the same result if adequately washed with IPA, EtOH and water after each use.

After enough sample is collected from the outlet of microreactor, a robust washing procedure detailed in Appendix C is followed to remove all the excess

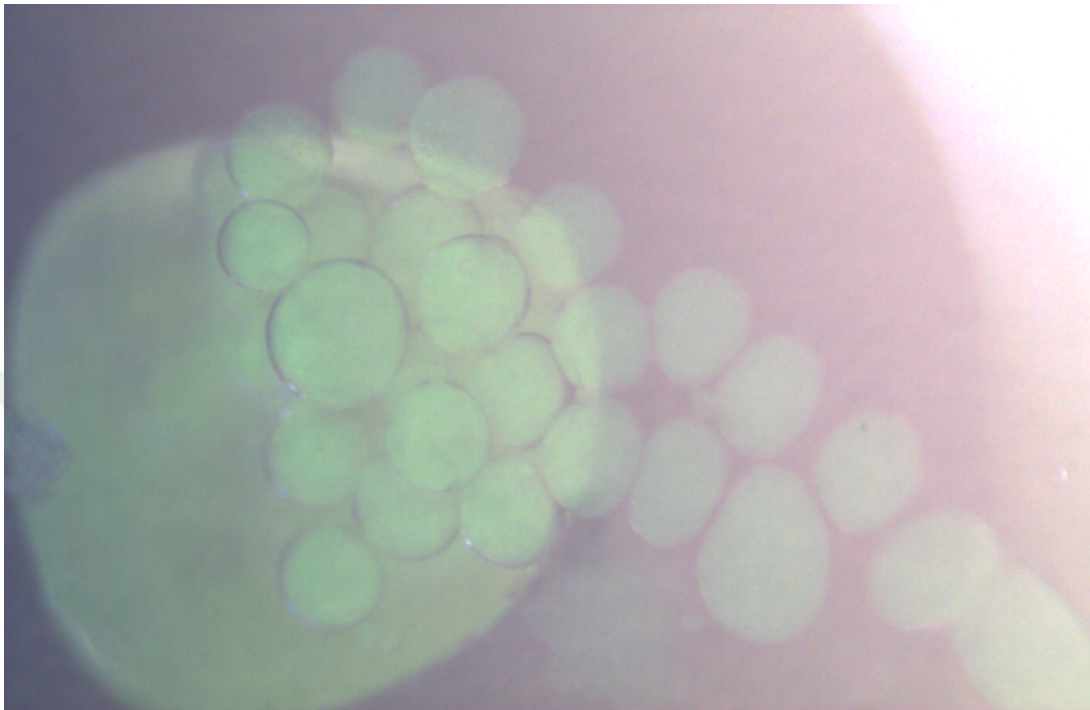


Figure 2.8: Stable droplets at the outlet of the microchannel but deformation implies they are not polymerized.

oil and surfactant. There are methods trying to remove the manual labour from collecting and washing by introducing two more channels that run washing fluid and guides to direct particles [83]. However, they require significantly more material, complex channel geometries and before-hand knowledge on particle sizes or drag characteristics. Hence here the aforementioned procedure is used utilizing the laboratory's existing equipment. After the washing and drying, SEM images in Figure 2.9 clearly shows solid, somewhat circular shapes with $200\text{ }\mu\text{m}$ diameter that matches the width of the used microchannel.

Film-like smooth layer surrounding all shapes is the residual oil left from the washing procedure. Oil, silicone oil especially, is tough to remove from the actual material. Even with standard solvents like ethanol and isopropanol, removing all the oil is challenging. Therefore, although the ethanol washing at the last step can be repeated as many times as required, with the increased flow rate there seems to be too much oil and decreasing it causes clogging in the system. Also, since the washing procedure is manual and has many steps, unfortunately, it is

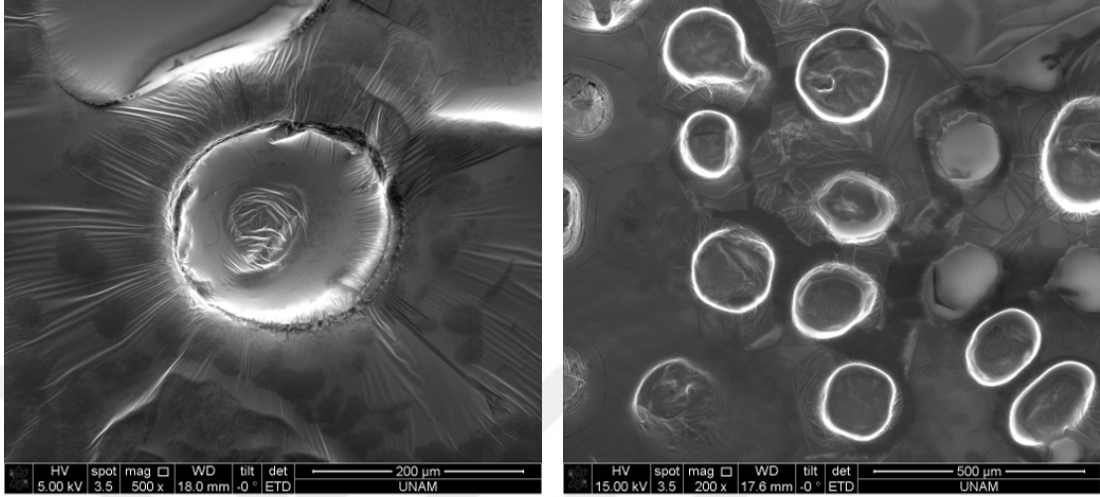


Figure 2.9: SEM images of the collected droplet samples.

possible to lose some valuable sample.

Droplet generation and transportation in microfluidics are rapid processes that needs to be investigated in at least real-time and ideally with high-speed measurement devices such as high-speed cameras [32], analogue sensors [84] or MEMS devices [85]. For this study, consecutive high-speed camera images were used to determine the particular and distributional velocities of the droplets, droplet generation frequency, droplet volumes and the uniformity by image processing using MATLAB.

In this image processing algorithm, after choosing an appropriate observation window manually on screen, images are segmented as droplet and background and every calculation is then based on droplet parts. First, leading edge of a droplet is found and followed frame by frame to average its leading-edge velocity. Averaging is applied to reduce noises coming from low resolution of the camera and the pulsating syringe pumps. Then, mean and standard deviation of these droplets are calculated and the outliers are omitted from the dataset, and a distribution profile is plotted according to this dataset.

Histogram in Figure 2.11 shows normal distribution with thin peaks for our experiment, which is ideal since this is a physical system and error sources like syringe pump pulsation, fluid uniformity and elasticity of the tubing and PDMS

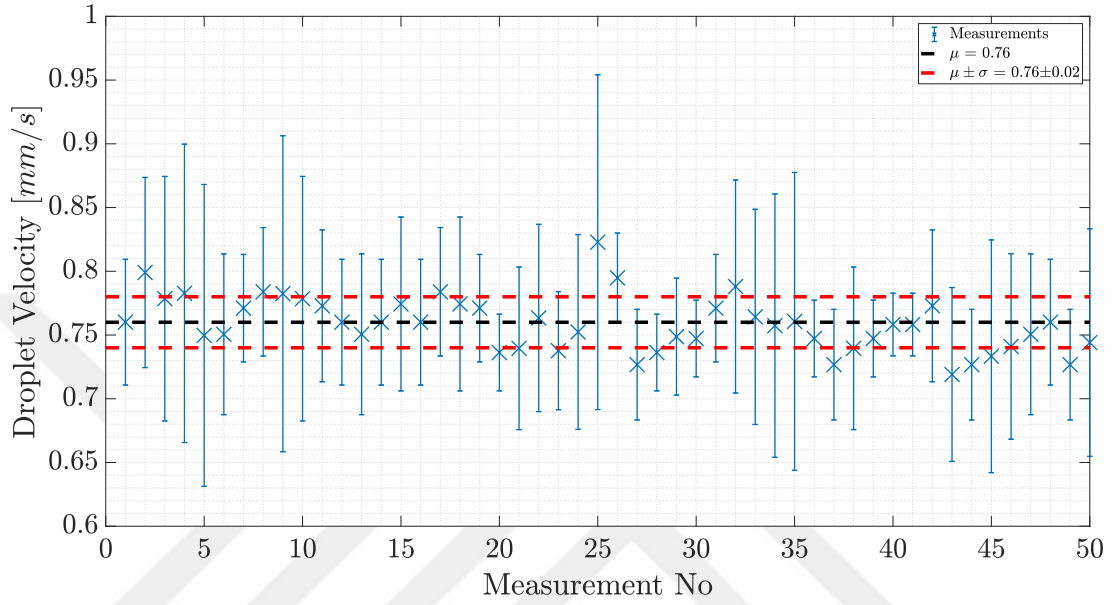


Figure 2.10: Droplet velocity measurements for each sample.

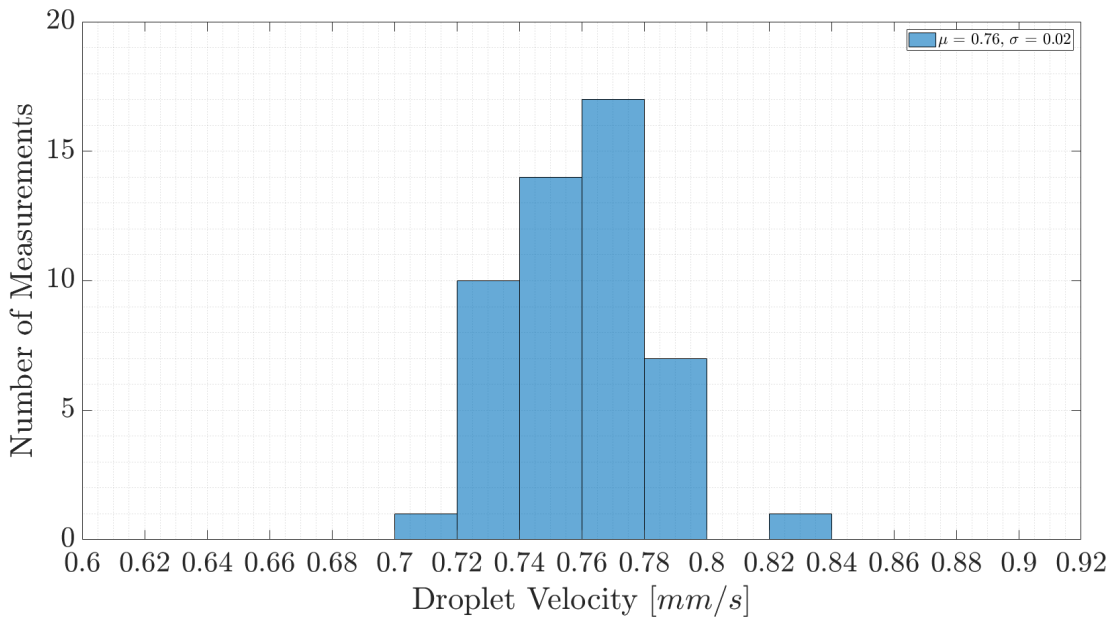


Figure 2.11: Overall droplet velocity distribution.

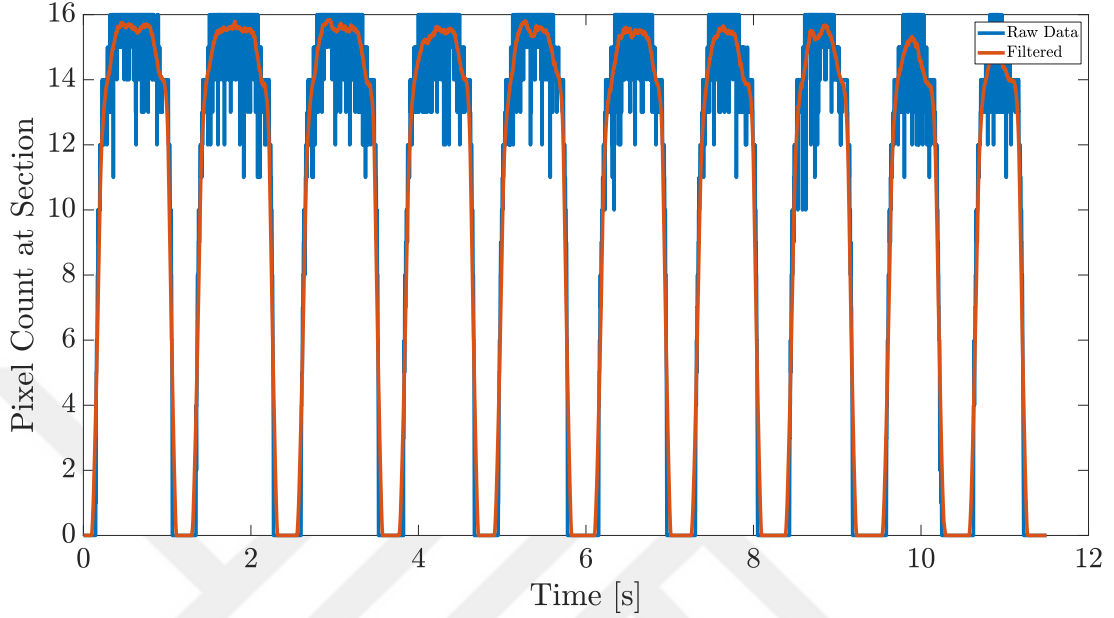


Figure 2.12: Number of pixels registered as droplet at a cross-section.

itself can be counted as contributing factors.

In the second phase, a cross-section is chosen from the previously selected observation window and the number of droplets representing pixels going through this cross-section is calculated. Again, due to the resolution of the high-speed camera there are high frequency noises in the measurements so a rolling average filter is used. As the last step, Fourier Transform is applied to the signal to get a frequency spectrum where the most prominent peak, aside from the peak at zero, gives us the droplet generation frequency of the system. The most obvious reasons for having harmonics and distributed frequencies, such as in Figure 2.13, are the system's nonlinearities and uncertainties, but the principle frequency is evident.

From the same set of data, one can also calculate the volume of each droplet by simply integrating the pixels from one end to the other. Figure 2.14 shows the effective radius for the droplets generated in a $200\text{ }\mu\text{m}$ wide microchannel with camera. It reports the monodispersity of the droplets, calculated as the ratio of standard deviation to the mean and called coefficient of variation (CV). Effective radius is also calculated by treating all droplets to have perfect spherical shape

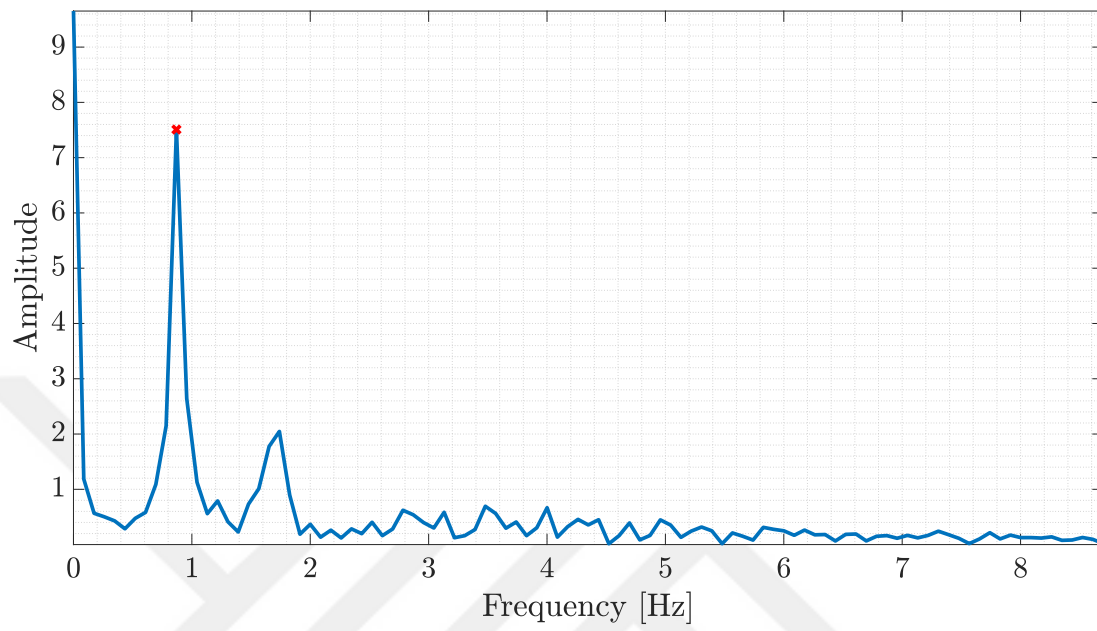


Figure 2.13: Overall droplet generation frequency distribution.

and applying volumetric formula.

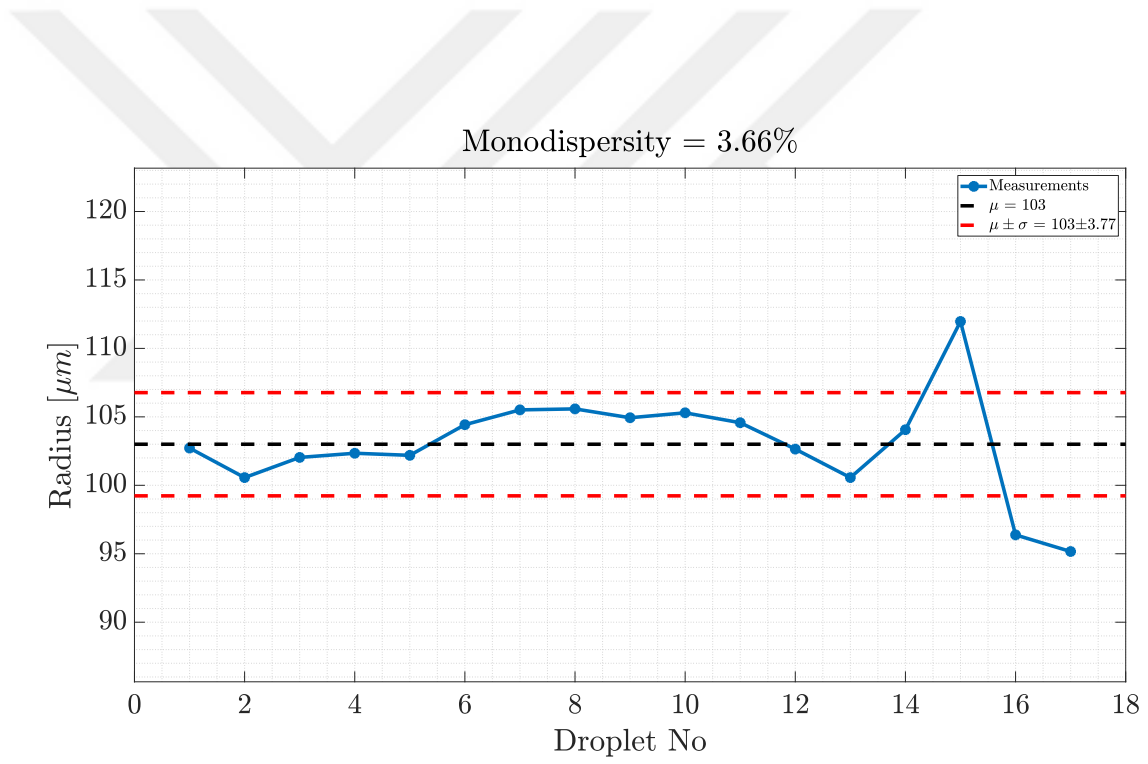


Figure 2.14: Radius of every generated droplet during the camera capture period.

Chapter 3

Poly(M-POSS) Microparticle Synthesis with Emulsion Polymerization

This chapter focuses on emulsion polymerization, intending to produce even smaller and uniform particles. It is divided into two parts as thermal polymerization, and UV photopolymerization, the same set of experiments are conducted for both and the results are compared.

3.1 Thermal Polymerization Method

Thermal polymerization differs from UV polymerization on one minor but essential aspect: the initiator. Here the initiator is changed from Darocur to Azobisisobutyronitrile (AIBN) that is activated with thermal energy instead of light. It activates at 50 °C, which is helpful since most laboratory applications are conducted at either room temperature or below. Using a thermal initiator brings one more small change to system in terms of monomer solvent. Ethanol's boiling

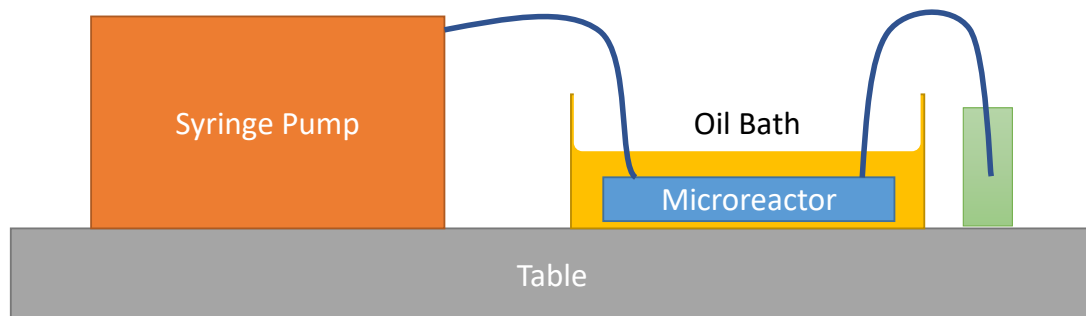


Figure 3.1: Thermal polymerization setup.

Table 3.1: Material table for thermal polymerization

Type	Material	Amount	Unit
Monomer	m(POSS)	200	mg
Initiator	AIBN	20	mg
Solvent	DMSO	2	ml
Surfactant	SDS	300	mg
Solvent	H ₂ O	5	ml

temperature is around 75 °C at room pressure and goes slightly above AIBN’s activation temperature to ensure full activation causes ethanol to evaporate rapidly. This evaporation causes hectic movements in the microchannels since both the pressure changes and flow includes compressible fluids. Also, the evaporation of a considerable part of the carrying fluid causes particles to stick to walls easier, which is a problem we must avoid. This problem can be solved by replacing ethanol with dimethyl sulfoxide (DMSO). DMSO is a polar solvent, not precisely like ethanol but behaves similarly; its boiling point is around 200 °C so the system can be heated up significantly more, actually the water will start to evaporate before DMSO.

In these experiments sodium dodecyl sulfate (SDS) is used as surfactant. The surfactant amount required for critical micelle concentration is determined through the literature, [73]. Materials in Table 3.1 are mixed in two separate containers. First, the monomer is weighed and mixed in ultrasonic shaker with solvent added on top; then, initiator is added to the mixture and everything is mixed one more time with ultrasonic shaker. In the second container, water is

Table 3.2: Properties of silicone oil.

Silicone Oil Properties			
Density	ρ	950	kg m^{-3}
Kinematic Viscosity	ν	1000	cSt
Dynamic Viscosity	μ	1000	mPa s
Specific Heat	c_p	100	$\text{J kg}^{-1} \text{K}^{-1}$
Thermal Conduction Coefficient	k	0.6	$\text{W m}^{-1} \text{K}^{-1}$
Volumetric Thermal Expansion Coefficient	β	1×10^{-3}	K^{-1}

poured then the powdered SDS is added to water and mixed with an ultrasonicator.

3.1.1 Feasibility Analysis

Before starting the experiments, some preliminary analyses were conducted to see if enough heat could be supplied to system. A 3D COMSOL Multiphysics simulation was created to model the chip with its materials and the heated oil medium in which the microfluidic system is inserted to provide uniform heat flux. Working fluid inside the microchannel was chosen as water, glass slide as quartz and PDMS was already available in built-in materials. Material properties of Silicone oil in the laboratory is manually entered.

A time-dependent study that uses domains depicted as crosssectional view in Figure 3.2 seemed appropriate for such an application as it could yield results on how fast the system reaches to the steady state. All oil interacting surfaces were selected as natural convection surfaces except the first 10 mm of the microchannel to see the conduction effects and have an idea if partial dipping was required for the experiment. Symmetry of the system was utilized to decrease the computational cost. Fluid inside the channel is selected as water and convection boundary condition is applied to the channel surfaces. The flow velocity of the fluid is chosen as 1 mm s^{-1} as it is predicted in the experiments. According to results, after the first 60 mm, the temperature almost perfectly reaches the ambient temperature in around 60 s, which means the system can be considered to be

at the steady-state at all times for all practical purposes.

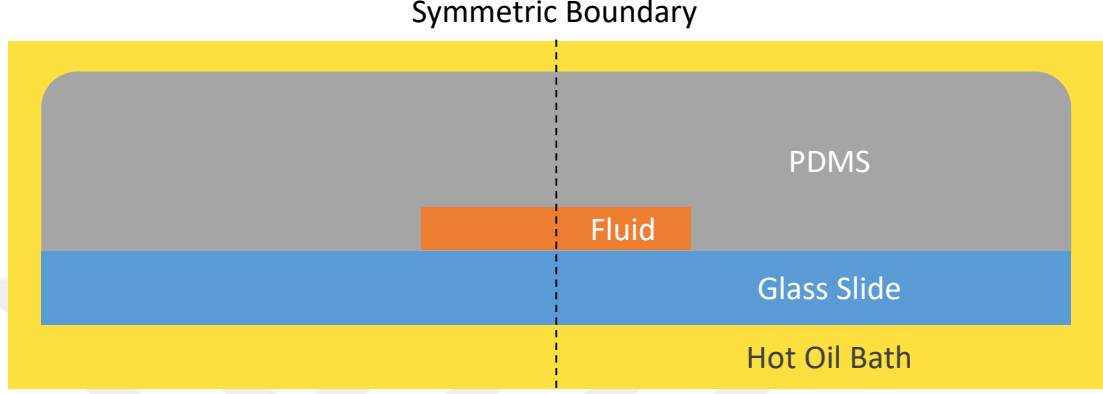


Figure 3.2: Materials and geometry used in the COMSOL Multiphysics simulation.

We could confirm the numerical analysis by looking at the convection coefficient of the oil around glass slide. Equation 3.1 utilizes the Nusselt number given for flow over horizontal plate to infer the convection coefficient h assuming the face looks down. Analytical result obtained here agrees with the coefficient obtained from COMSOL, which is found $275 \text{ W m}^{-2} \text{ K}$, on average for bottom and top facing surfaces.

$$Nu = \frac{hL}{k} = 0.54Ra^{1/4} \implies h \approx 220 \text{ W m}^{-2} \text{ K} \quad (3.1)$$

$$T_E = (T_I - T_W) \exp\left(-\frac{hA}{\dot{m}c_p}\right) + T_W \quad (3.2)$$

Then, Equation 3.2 can be used to calculate the exit temperature of the fluid in a channel. Two assumptions should be noted to use this equation. One, the fluid inside the channel is water and two, the wall temperature is constant at whole channel at all times. First assumption was already made for the sake of approximation and the second can be justified with the high convection rate of the oil around device.

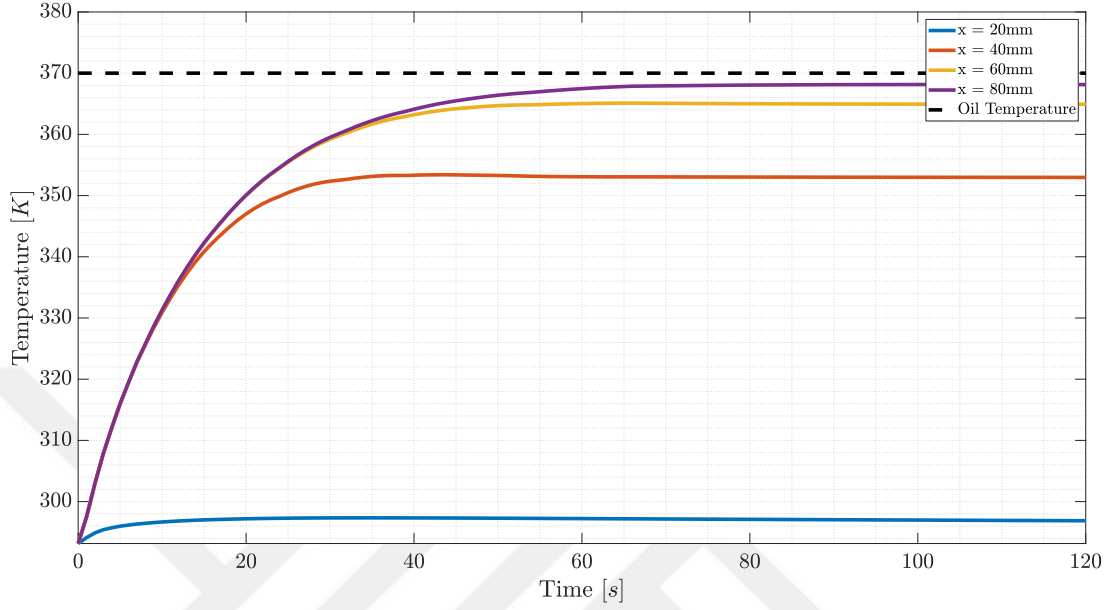


Figure 3.3: The temperature at different cross-sections of the channel with respect to time.

$$Re = \frac{\rho u L}{\mu} = \frac{1000 \text{ kg m}^{-3} \times 1 \text{ mm s}^{-1} \times 270 \text{ mm}}{1 \text{ mPa s}} = 0.27 < 1 \quad (3.3)$$

Since the emulsion polymerization lacks the mechanisms that help droplets with the mixing due to highly laminar flow (Equation 3.3), conditions should be checked to see if this set-up can provide sufficient mixing. Another simulation was created in COMSOL to understand the mixing of monomer and surfactant solutions. Fluids with different concentrations of the identical particles (one with 0, the other 10 mol m^{-3}) are released from inlets of the geometry and encounter in a slightly wider mixing chamber, then go together through the same outlet channel. As seen in Figure 3.4, even with the laminar mixing, meaning the turbulent effects were not considered in the simulation, the fluids almost perfectly mix in 20 mm length.

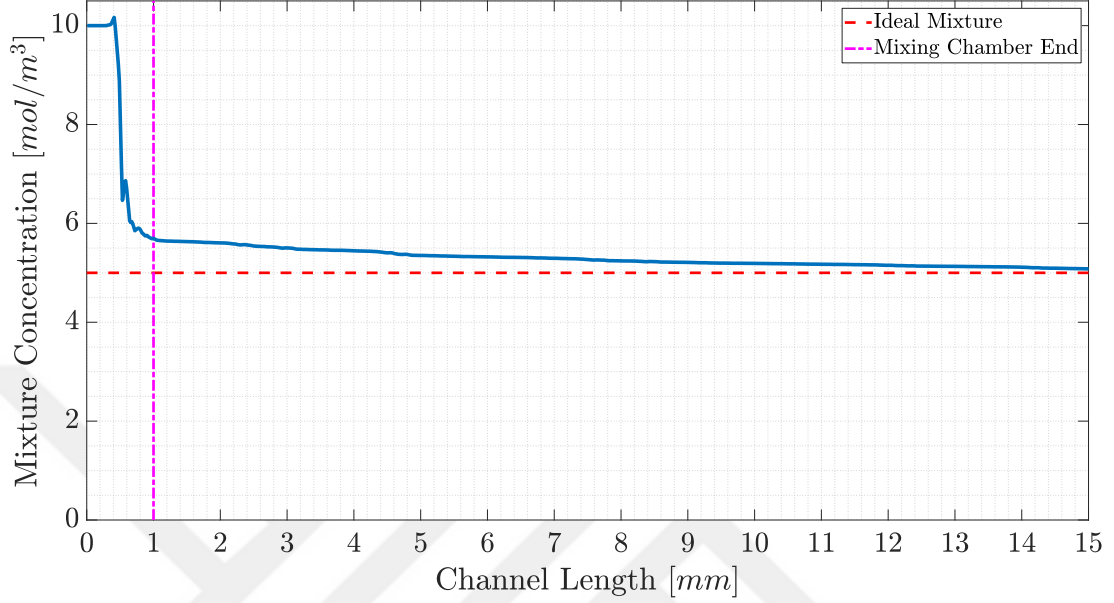


Figure 3.4: Mixing of two fluids with 0 and 10 mol m^{-3} .

Table 3.3: Experimental conditions for the thermal polymerization.

Experimental conditions		
Medium temperature	70	$^{\circ}\text{C}$
Microchannel width	400	μm
Monomer flow rate	4	$\mu\text{L min}^{-1}$
Surfactant flow rate	2	$\mu\text{L min}^{-1}$
Oil flow rate	2	$\mu\text{L min}^{-1}$

3.1.2 Experimental Set-up

Figure 3.5 shows the entire system starting with mixing of monomer and surfactant solutions in mixing chamber. Then, before the heating begins, the mixture is focused with oil from two sides to wet the walls to prevent clogging. Clogging of the channels was a significant complication in previous studies.

The same fabrication steps in Section 2.3 are used and the complete technical drawing of the microchannel can be seen in Figure A.1. After the PDMS - glass bonding and connecting the tubings to inlets and outlets, flow rates of the syringe pumps are set according to Table 3.3.

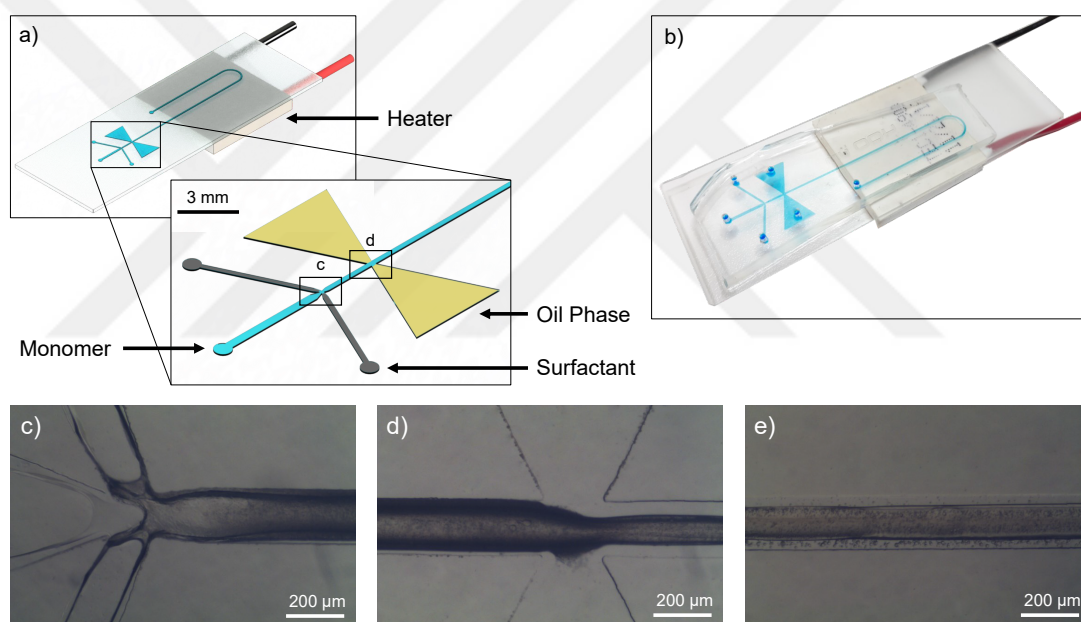


Figure 3.5: Thermal emulsion polymerization setup.(a) The chip in its entirety with a custom Peltier heating unit. (b) Actual image of the produced microchannel and attached unit. (c) Mixing of monomer and surfactant solutions. (d) Focusing mixture with oil to prevent clogging. (e) Particles polymerizing along the channel.

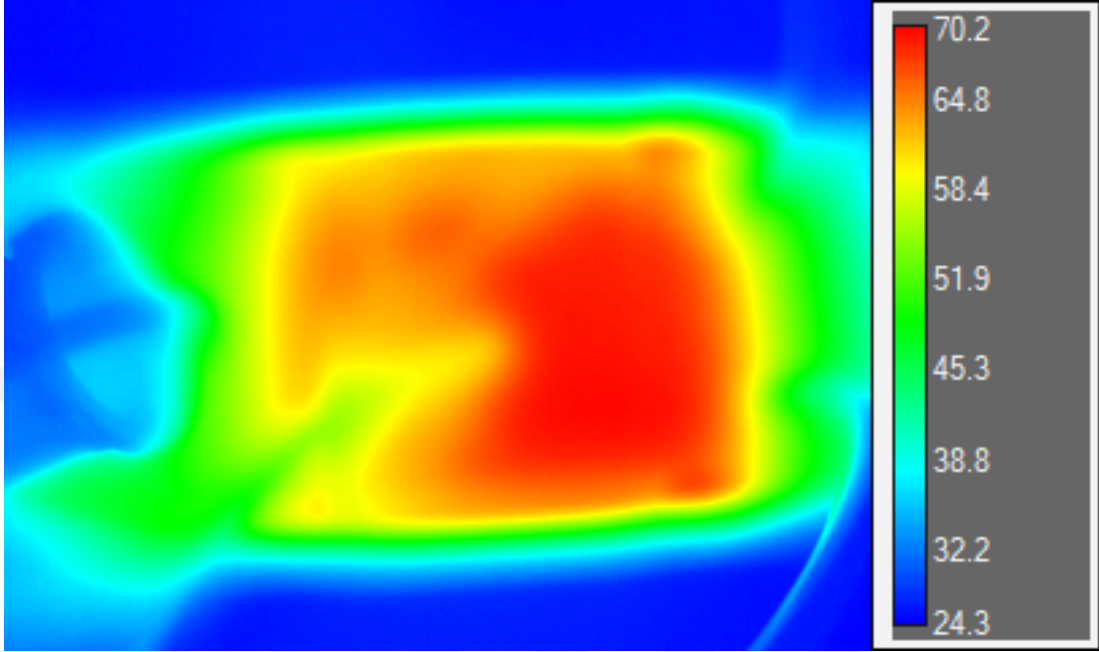


Figure 3.6: Thermal camera reading of the temperature distribution in hot oil bath.

Waiting a couple of minutes for heated units to reach steady-state, a hand-held thermal camera was used to observe the temperature distribution on the microchannel. Figure 3.6 shows the thermal measurement once the steady-state is reached. The small protrusion in bottom left corner is the inlet tubing and to the right channel continues where it is seen form red representation that reached 70°C. Conduction along glass and PDMS material seems to have heated even the unintended parts as discussed in UV polymerization. However, since the temperature only rises to 50 °C on those regions, it does not pose a major threat. Experiments were also conducted by using a simple TEC1-4905 Peltier unit with 17 W heating power that is directly attached below the microchannel using simple isolation tape. Heating from a single side has the disadvantage of causing a temperature gradient between top of the PDMS chip and the bottom surface of the glass and this gradient is measured to be 10 °C at the extreme conditions. Therefore, even with a simple Peltier unit, the experiment could be conducted by taking measurements from the easily reachable top surface of the chip and calculating the temperature at the bottom by adding this constant deviation, with safety margin if needed.

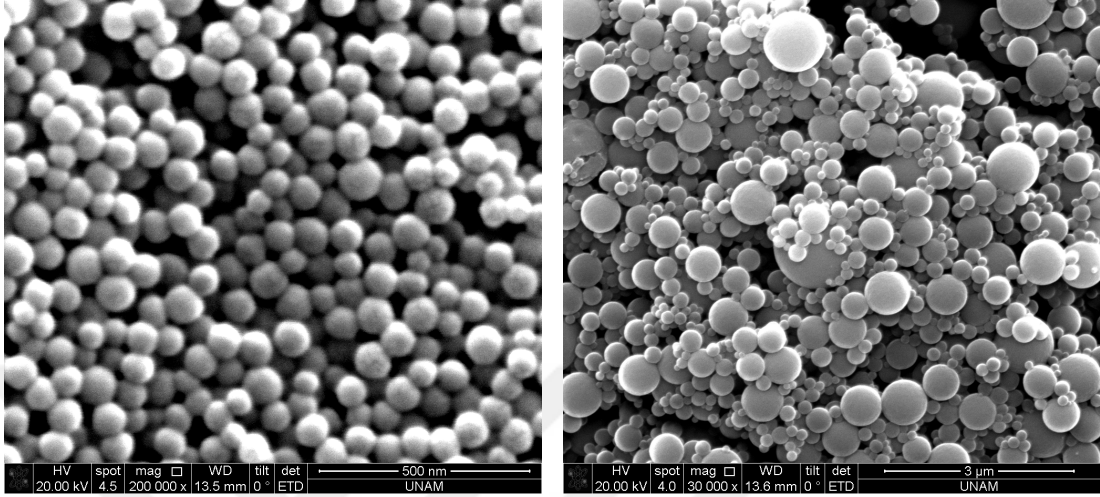


Figure 3.7: SEM images of particles produced with (left) lower surfactant concentration (0.15 g SDS/5 mL H₂O) and (right) higher surfactant concentration (0.30 g SDS/5 mL H₂O)

3.1.3 Experimental Results

Obtained results with two different surfactant concentrations are shown in Figure 3.7. Here, at first glance, two pieces of information can be inferred: the experiment with lower surfactant concentration yielded both smaller and more uniformly sized particles. Both SEM images show consistently sub-micron sized and properly distributed clean particles. The maximum resolution of the image was 500 μm and that shows particles with 50–60 μm diameter. On the other hand, high concentration image was taken with a 3 μm scale to make the size range more visible. Here we see particle diameters ranging between 50–500 μm which is an unwanted polydispersed case.

Putting these images through an algorithm to find a size distribution was necessary. For that, the `IMFINDCIRCLE` function of the MATLAB software was used. This function finds the circles with diameter in a given range using Hough Transform and outputs the centres and radii of found circles. Two distributions were obtained and are shown in Figure 3.8 and Figure 3.9. Figure 3.8 shows a more normal distribution with average particle radius of 31.1 nm whereas average radius in Figure 3.9 is found to be 132.8 nm. Two distributions differ on the range as

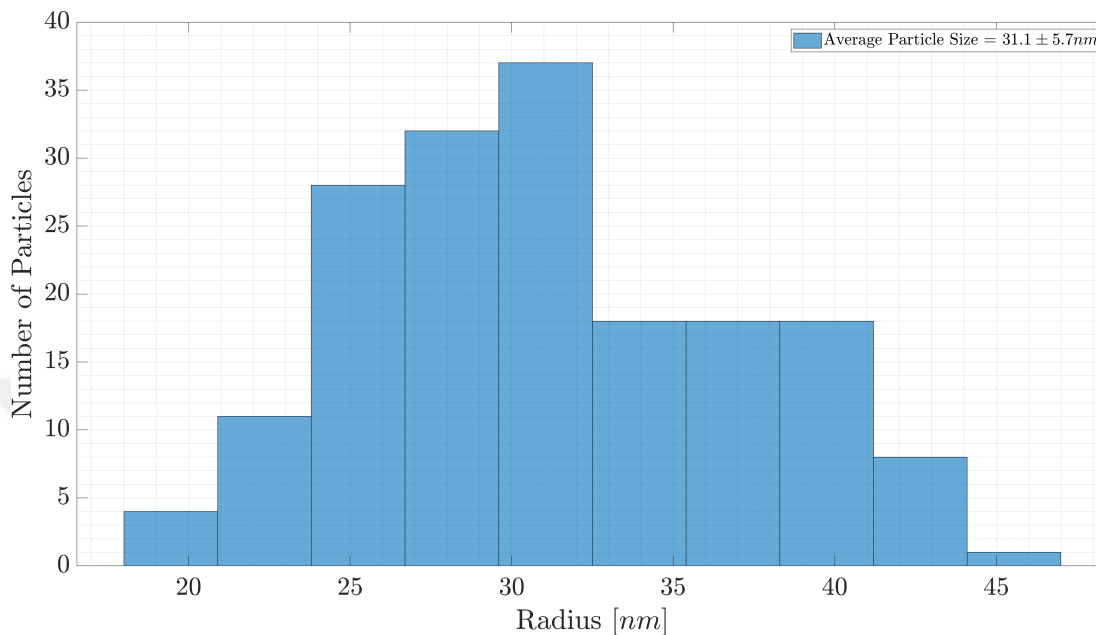


Figure 3.8: Size distribution of particles produced with lower surfactant concentration (0.15 g SDS/5ml H₂O)

well where the first one shows 5.7 nm, the second 70.5 μm standard deviation. Divided to average radii, these correspond to 18% and 53% deviation from mean.

Aside from the size information, chemical structure and elemental analysis information should be obtained to see if these particles have organic-inorganic components of poly(POSS), regardless of their morphology. So, two different methods of measurement were used: FTIR and Energy-Dispersive X-ray Spectroscopy (EDX). In Figure 3.10, FTIR image shows prominent peaks around 3400–3000 cm^{-1} which are the O-H bonds coming from the liquid ethanol medium the particles are dissolved in and this is expected. The fingerprint region to the right gives more information about the specific bonds. Another peak at 1700 cm^{-1} corresponds to the organic C=O part of poly(POSS) and the most significant peak at 1000 cm^{-1} is the cage shaped Si-O-Si structure. FTIR gives information about molecular bonds, whereas EDX provides the direct elemental content of the focused particle. Along with the SEM images, EDX spectrum shows high carbon and silicon content with a relatively lower amount of oxygen. Though in some other cases high carbon could have been attributed to carbon tape behind the material, here with the high silicon it proves the material is a POSS polymer.

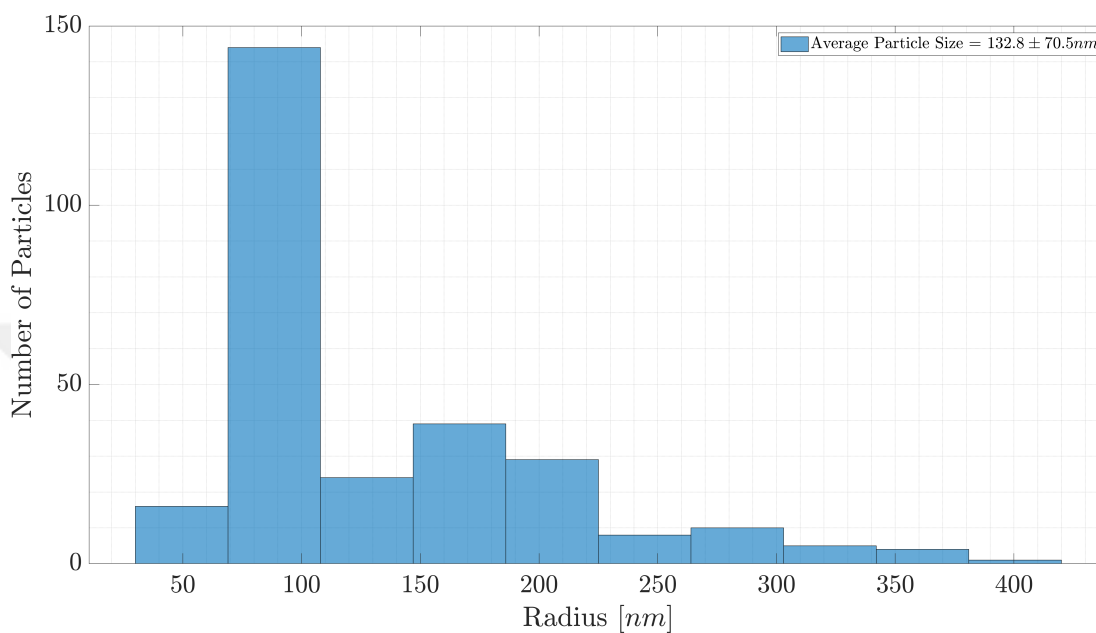


Figure 3.9: Size distribution of particles produced with lower surfactant concentration (0.30 g SDS/5ml H₂O)

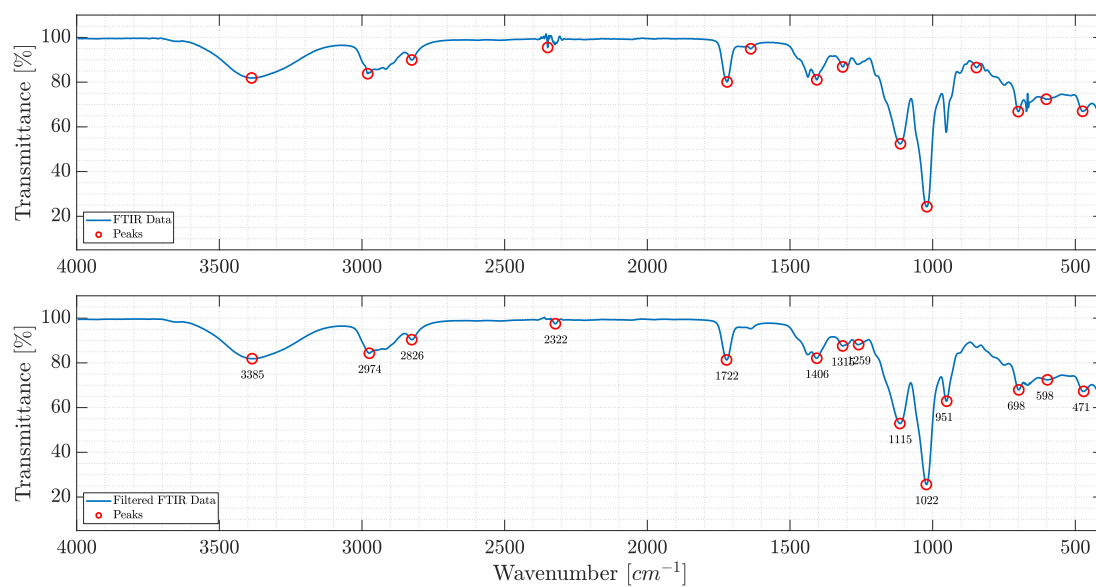


Figure 3.10: (Top) Raw, (bottom) filtered FTIR spectrum of the thermally polymerized poly(POSS) particles denoting prominent peaks.

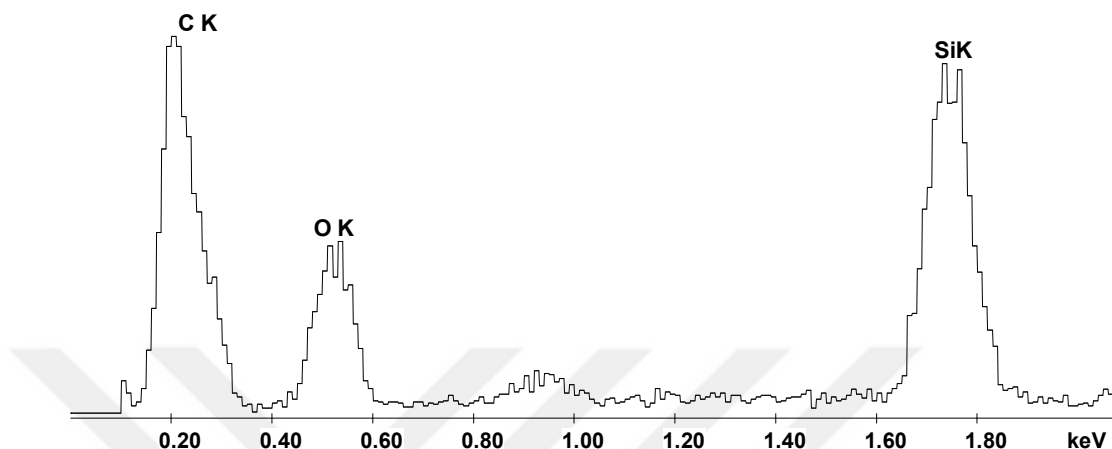


Figure 3.11: EDX analysis of the particles showing high carbon and silicon concentration.

On the earlier experiments, to be consistent with the previous studies [77], glycidyl methacrylate (GMA) was also used as a co-monomer. On top of the standard materials in Table 3.1, 0.1 mL GMA was added and the experiments were repeated. When the same polymerization, washing and measurement steps were applied to the sample following SEM images were obtained. Comparing with Figure 3.7, Figure 3.12 shows an increase in the aggregation of particles with filler in between. Looking at the clear regions in other areas, one can conclude that this filler is not oil; else it would be seen in the entirety of the image. Instead, this is the effect of the only single parameter changed in the experiment, addition of GMA. Simply having more materials to polymerize and most possibly increased concentration enabled more polymerization, resulting in this aggregation.

Although the materials in and conditions of each experiment are held constant as much as possible, due to fluctuations in various equipment, the experiment may give way to unpolymerized or not completely polymerized particles. One example of this case can be seen in Figure 3.13. So much as the particles are washed clean and there is no sign of oil residue, several particles are in non-circular shapes, suggesting the polymerization was not completed when these particles exited from the outlet. Another conclusion such as they are not polymerized could be reached had particles not retained their integrity through rigorous washing and

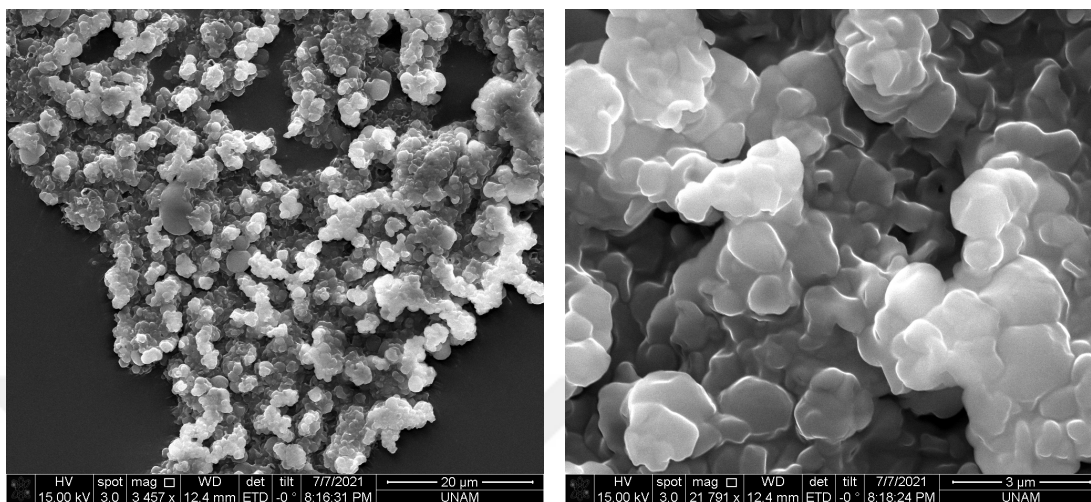


Figure 3.12: Particles that have filler material in between, most possibly GMA.

centrifuging processes.

3.2 UV Photopolymerization Method

Photopolymerization was also utilized to initiate the polymerization in the microreactor. In these experiments, instead of thermal initiator AIBN, the photoinitiator Darocur 1173 (2-hydroxy-2-methylpropiophenone) is used; all used materials can be seen in Table 3.4. This initiator is not activated by visible light but it needs UV light. Also, to supply the demand for UV, an LED light source with 365 nm wavelength and 10 W lighting power is acquired. Since the UV light sources produce excessive heat, a centrifugal fan and a copper finned heatsink were added to the system; else it stops operating in 5 minutes due to overheating.

3.2.1 Experimental Set-up

To conduct the photopolymerization experiments, first a simple set-up as in Figure 3.14 was built. In the preliminary experiments, it was observed that even

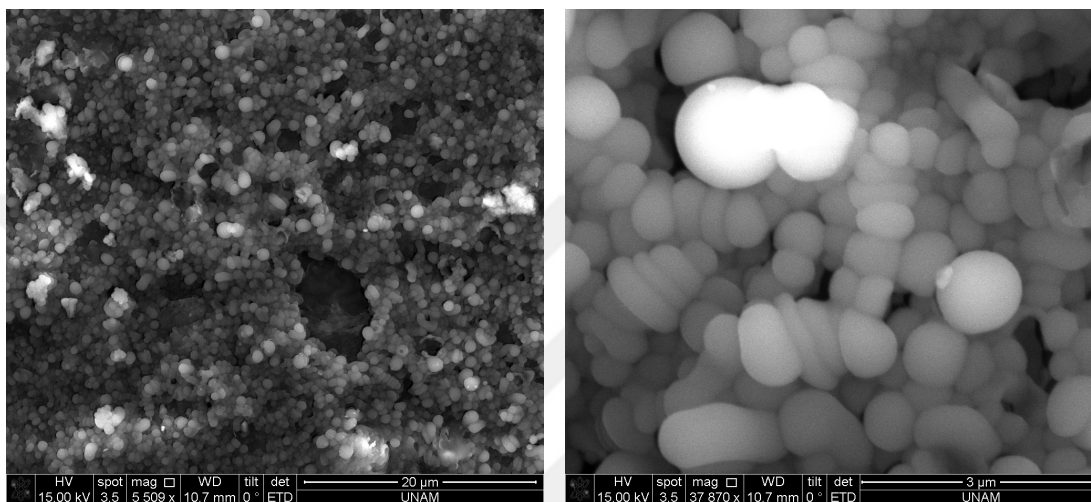


Figure 3.13: Unpolymerized particles in thermal polymerization experiments.

Table 3.4: Material table for UV polymerization

Type	Material	Amount	Unit
Monomer	m(POSS)	200	mg
Initiator	Darocur	25	ml
Solvent	EtOH	2	ml
Surfactant	SDS	300	mg
Solvent	H ₂ O	5	ml

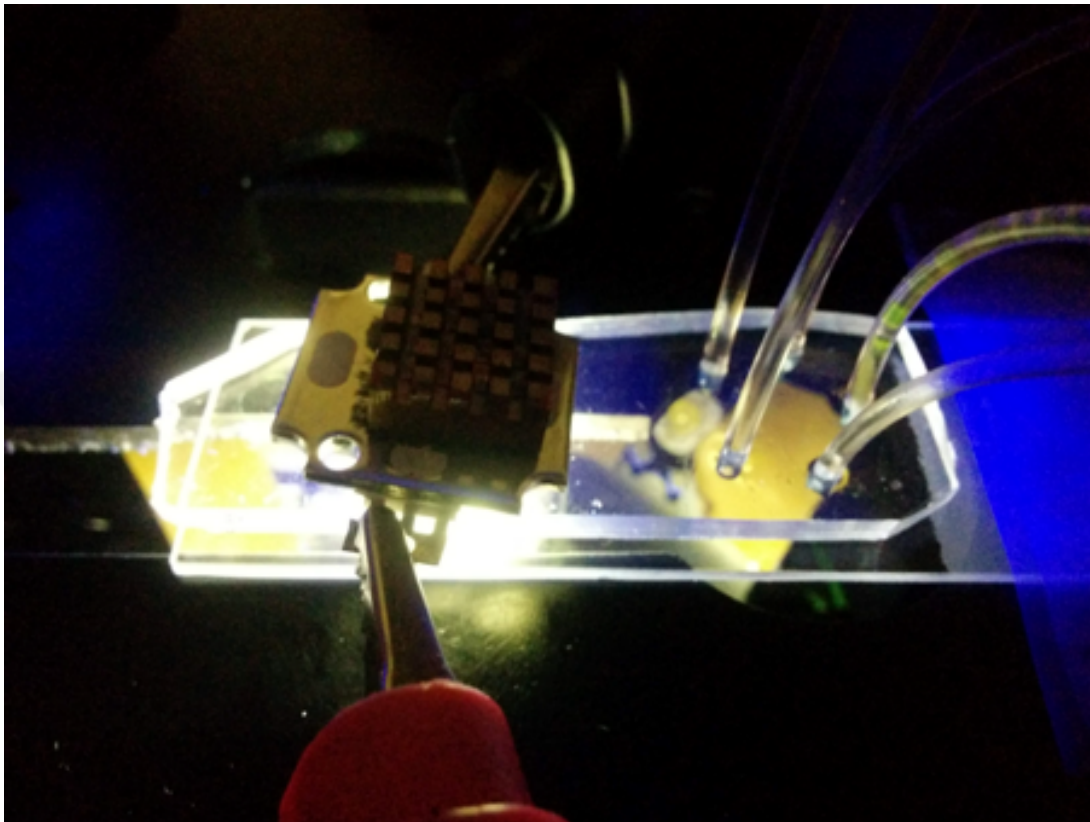


Figure 3.14: UV polymerization set-up with UV lamp showing purple shifted UV light around inlet in dark.

when the UV light is specifically turned away from the inlet tubings, PDMS chip and glass slide reflected the light and caused the inlet to be exposed as seen in figure. This initiates the polymerization within the monomer inlet tubing (specifically unfocused pure monomer solution), eventually clogging the inlet. Clogging here is caused by the incident angle of light produced by the source that is between $120\text{--}140^\circ$. Due to this reason, another UV light source was sought in National Nanotechnology Research Center (UNAM). A microscope with a laser UV light source was found but the power was not specified. So, after doing some experiments, it was found that although laser is much better focused than the LED light, due to either having not enough power or very limited exposure time, it could not polymerize the particles inside the moving fluid. One reason could be the transmittance of PDMS and glass to varying UV wavelengths, as there is a sharp decrease below 385 nm [86, 87].

Table 3.5: Experimental conditions for the UV polymerization.

Experimental Conditions		
UV lamp voltage	10	V
Microchannel width	400	μm
Monomer flow rate	4	$\mu\text{L min}^{-1}$
Surfactant flow rate	2	$\mu\text{L min}^{-1}$
Oil flow rate	2	$\mu\text{L min}^{-1}$

A mechanical aperture is placed in front of the LED lights to physically limit the spread. Lamp voltage was set to 10 V which was found to be enough power to start polymerization and use the lamp for hours with the help of a blower fan. Without the use of fan, the maximum stable point that could be reached is around 9–9.5 V after that as the lamp heats up its resistance goes down and draws more power to heat itself even more. Rest of the conditions are the same with the thermal experiments and can be seen in Table 3.5.

3.2.2 Experimental Results

Figure 3.15 shows the SEM image results of the UV polymerization experiment after the washing step. The particles are clear of any oil layer, meaning the image can be analyzed to get a size distribution using the standard algorithm.

When analyzed, size distribution of around 500 particle in the image is shown as a histogram in Figure 3.16. Distribution is comparable with the thermal experiments Figure 3.9, with 161.7 nm mean radius and 63.3 nm standard deviation corresponding to 39% monodispersity. This result indicates that the monomers can be polymerized and polymerized particles almost one to one match the ones obtained from the thermal method without drawbacks such as evaporation and thermal conduction.

When the washing procedure fails to clean the whole oil residue, cases seen in Figure 3.17 can be encountered. This is the worst possible outcome for the measurement since no particles can be seen from the obscuring oil layer. Even the

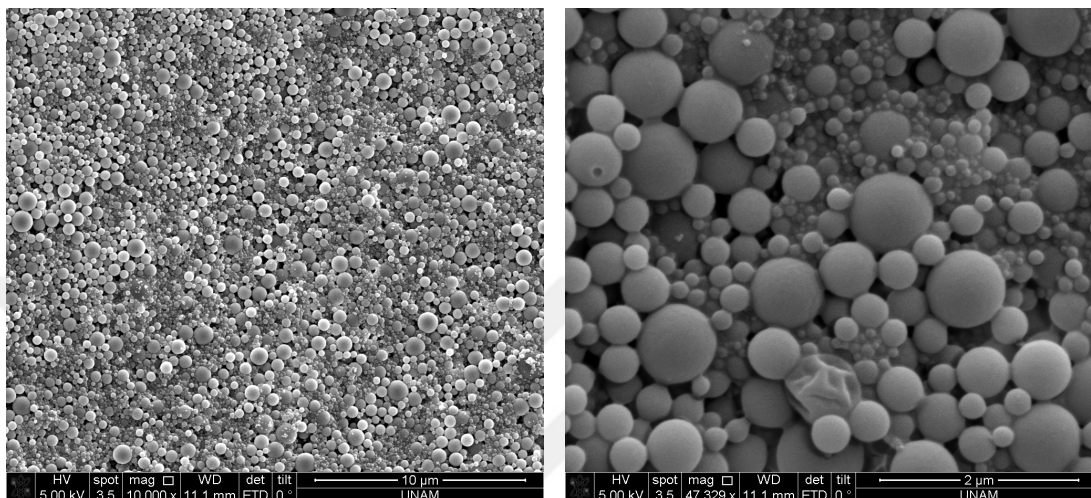


Figure 3.15: UV polymerization resulted in non-uniform sub-micron particles.

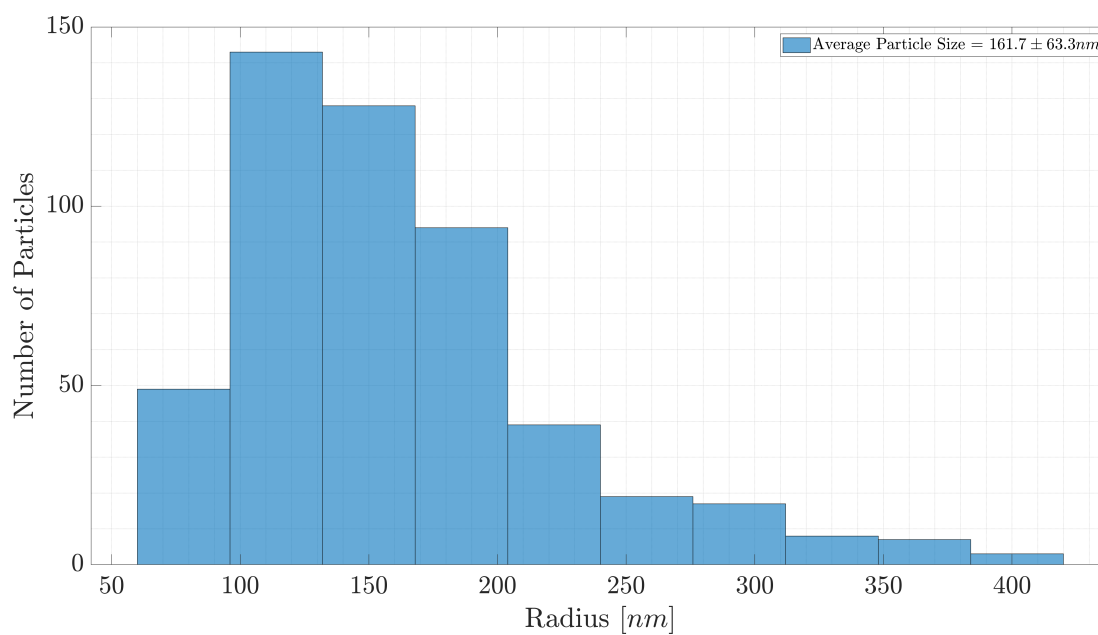


Figure 3.16: Size distribution of particles produced with UV photopolymerization.

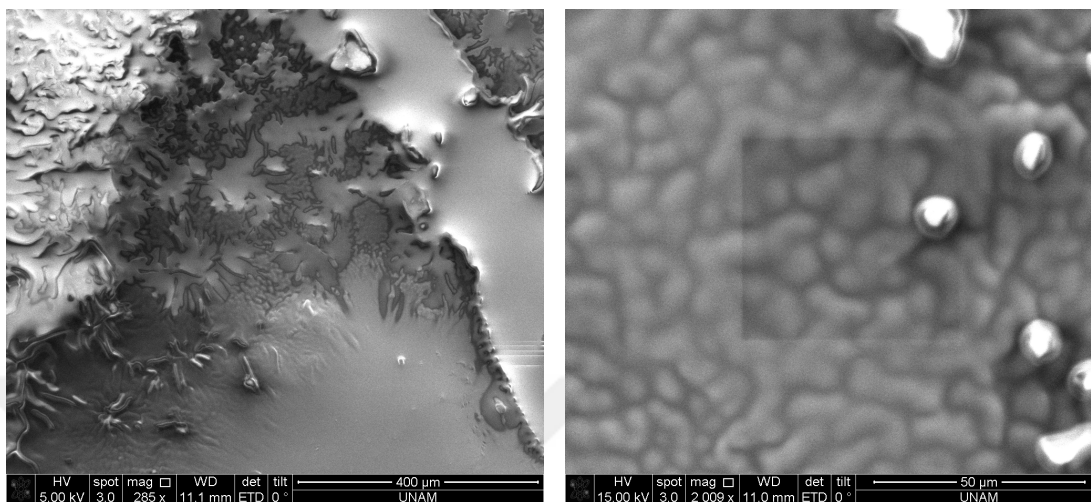


Figure 3.17: Unwashed oil layer on the particles entirely preventing imaging.

gold/palladium material coated by sputtering seems to shift as the positioner of SEM move around, disrupting the imaging even further so much so that focusing under $50\text{ }\mu\text{m}$ becomes impossible.

In some experiments, washing partially fails and the particles can be seen with bare eyes. In these cases, as in Figure 3.18, particles can be seen as if they are spread thin but this is again due to residual oil. It covers the particles at the bottom, showing only the ones at the top.

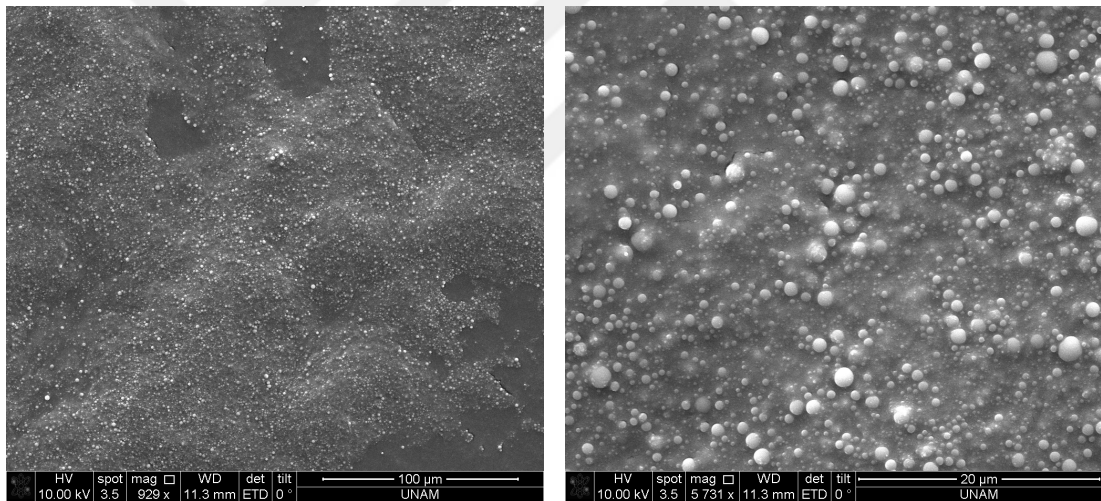


Figure 3.18: Oil layer partially blocking the background and showing as if the particles are spread thin.

Chapter 4

Conclusion and Future Work

In this study; POSS material was investigated in two categories as droplet-based bulk polymerization and emulsion polymerization where the emulsion polymerization technique was repeated with both thermal and photo-initiators. Clogging problem was observed in droplet-based bulk polymerization experiments. Subsequently, the oil flow rate was increased to prevent clogging but this resulted in excessive oil in the SEM images that covered the whole surface and lead to unpolymerized droplets in general.

In both thermal and UV initiated emulsion experiments, significant improvements were observed in produced particles. Both experiments produced promising results and the new designs made for thermal emulsion setup enabled hours of experimentation time compared to previous studies that clogged under an hour leading to more material efficiency. Particles with sizes around 30–150 μm were successfully obtained and imaged. These images, when measured, yielded uniformly sized particles depending on the surfactant concentration which was understood to be a crucial parameter on size distribution. Decreasing the surfactant concentration resulted in decreased diameter and deviation in size up to 18%, so a future study could investigate the relation and obtain even better distributions since these values are comparable with studies that range in 5% to 15%.

The main problem observed with the systems is the fine tuning of oil amount and polymerization speed. Though wetting the walls by introducing oil to the system prevents accumulation and later clogging, the end product collected from the outlet contains oil covered samples. Washing surfactant and other possible dirt or chemicals are easy compared to oil. In order to remove the oil, to have clear SEM images, the particles should be washed with ethanol or other oil solvents. Since this is done manually, it is possible to lose some part of the already small number of particles.

To solve this problem, hexane and hexadecane can be proposed as lubricants though their use will be limited to photopolymerization due to their volatility. After the collection, since they are relatively more volatile, the solution can be heated or left to evaporate to remove the continuous phase hexanes. One side effect of these materials is their reactivity with standard plastics used in the experiments. For example, even when first filled in a syringe, hexadecane slightly damages the sealing of the plastic pistons and makes it harder to move. Glass syringes could be used to circumvent this issue. Similarly, lubricants with lower viscosity than silicone oil could be used in emulsion polymerization techniques; materials with low viscosity would be easier to remove. In droplet generating systems, lowering continuous phase viscosity may unsettle the stable droplet formation; therefore, a gradual decrease is advised.

The ultraviolet light sources are another problem that must be carefully studied as well. Apart from the low transmittance of PDMS on low wavelengths, standard LED ultraviolet lights in the market emit the light as a 120–140° cone, not as a straight line. When the it is emitted in such a way, since the angle is considerably large, light scatters inside PDMS and between PDMS - glass and illuminates almost every area of the microchannel. This is a highly undesirable situation as this way, the monomer solution at the inlet will be polymerized as well, clogging the whole inlet. Preventing this problem requires either putting an optical apparatus in front of the source to focus the light or have a laser source that comes with an already focused beam. First method is a crude one since it would be highly dependent on the source and if that were changed would be useless. Second is a better but relatively expensive option. Powerful LED lights

are more accessible than the laser ones and though the laser being focused is a good thing, it shines a smaller area, lowering the exposure time of particles inside fluid.



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Appendix A

Fabrication

A.1 Technical Mask Drawing

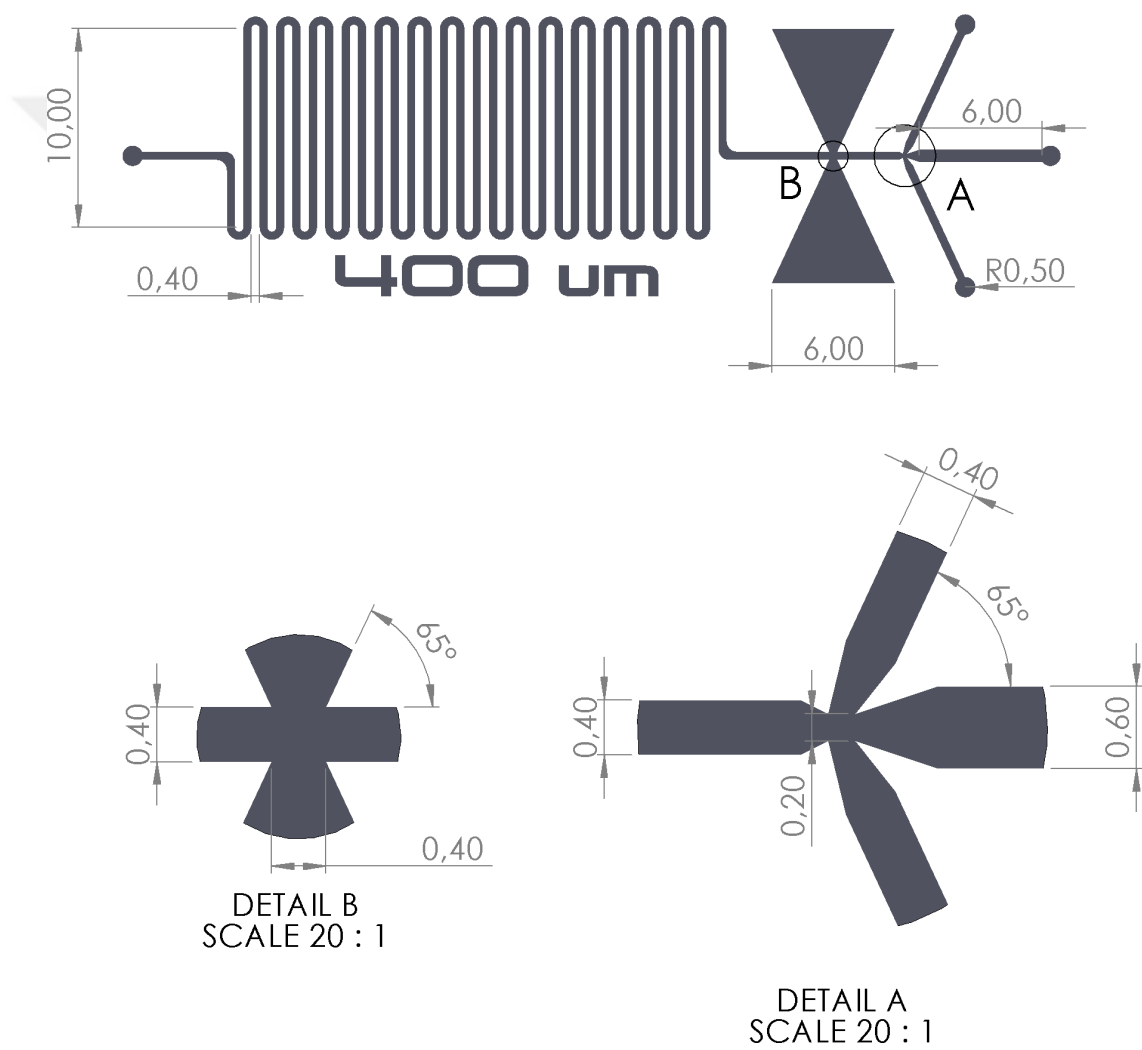


Figure A.1: Technical drawing for the emulsion creating the microfluidic channel.

A.2 Fabrication Recipe

This recipe allows the user to create 100 μm thick SU-8 structures on an SI wafer. To change the structure height, simply change the coating speed at the main layer coating phase according to SU-8 datasheet and adjust the resist thickness parameter.

1. Cleaning

- (a) Rinse the SI wafer with acetone, IPA and DI water,
- (b) Remove the remaining droplets by blowing N_2 ,
- (c) Remove the residual liquid by leaving the wafer at 120 °C, oven for 5 minutes

2. Base Layer Coating

- (a) Using 4 mL SU-8 2005, spin coat at:
 - i. 500 rpm, with 100 rpm/s acceleration for 25 s
 - ii. 2500 rpm, with 200 rpm/s acceleration for 40 s
- (b) Remove the edge beads using an acetone-soaked napkin
- (c) Pre-bake on aluminium foil on a hot plate for:
 - i. 2 minutes at 65 °C,
 - ii. 4 minutes at 95 °C,
 - iii. 1 minute at 65 °C,
- (d) Flood the wafer with UV light using the following settings:
 - Manual top side
 - Soft contact
 - Separation : 100 μm
 - Mask Thickness : 2.3 mm
 - Sample Thickness : 0.5 mm
 - Resist Thickness : 2 μm
 - Intensity : 120 mJ cm^{-2}

(e) Post-exposure-bake on aluminium foil on a hot plate for:

- i. 1 minute at 65 °C,
- ii. 3 minutes at 95 °C,
- iii. 1 minute at 65 °C,

3. Main Layer Coating

(a) Using 4 mL SU-8 2050, spin coat at:

- i. 500 rpm, with 50 rpm/s acceleration for 40 s
- ii. 2200 rpm, with 300 rpm/s acceleration for 35 s

(b) Remove the edge beads using acetone soaked napkin

(c) Pre-bake on aluminium foil on a hot plate for:

- i. 3 minutes at 65 °C,
- ii. 8 minutes at 95 °C,
- iii. 2 minutes at 65 °C,

(d) Expose the wafer to UV light, under the appropriate mask, with following settings:

Manual top side

Soft contact

Separation : 200 μm

Mask Thickness : 2.3 mm

Sample Thickness : 0.5 mm

Resist Thickness : 100 μm

Intensity : 230 mJ cm^{-2}

(e) Post-exposure-bake on aluminium foil on a hot plate for:

- i. 3 minutes at 65 °C,
- ii. 8 minutes at 95 °C,
- iii. 2 minutes at 65 °C,

4. Development

(a) Drown the SI wafer in SU-8 developer

(b) Agitate slowly for 9 minutes

- (c) Rinse with IPA and DI water
- (d) Check the wafer; if needed, agitate 1 more minute
- (e) Remove the developer by blowing N_2



Appendix B

Experiment Details

B.1 Experimentation Table

Table B.1: Different materials used to capture the optimum droplet formation mixture. The middle row shows the droplet generation experiments that were conducted without using any monomer to understand the effect of surfactants in droplet formation.

Monomer		UV Initiator	Solvent		Surfactant				
EGDMA μL	POSS mg	Darocur μL	EtOH μL	H ₂ O μL	SDS mg	F-127 mg	P-123 mg	SPAN-80 mg	PVA mg
	250	250	3000	3000	37.5				
	500	500	300	3000	37.5				
	250	250	5000			25			
	250	125	5000			25			
	250	100	5000					2,0%	
	250	100	5000					0,5%	
	250	100	5000					1%	
	250	100	5000				25		
		100	2500				5		
		100	2500				7,5		
		100	2500				10		
		100	2500				15		
		100	2500				17,5		
		100	2500				20		
		100	2500				22,5		
		100	2500				25		
			3000	3000					
	250	100	3000	3000					
	250	100	1000	1000					
	1000	50							
	250	100	500	500			50		
	250	100	500	500			15		
	500	200	500	500					
	250	200	1000	1000					
	800	200	200						8%
250	250	100							8%
250	250								
250	250	100							
250	250	50							
500	250	50							

Appendix C

Post Processing Protocol

The washing procedure is as follows;

1. Collect sample from chip outlet,
2. Centrifuge for 3 min at 15 000 rpm until sedimented,
3. Wash with water, water/EtOH mixture and EtOH with the following steps;
 - (a) Remove floating liquid and add 1ml washing solution,
 - (b) Dissolve the particles using an ultrasonic shaker,
 - (c) Centrifuge for 3 min at 15 000 rpm until sedimented
4. Repeat last EtOH washing three times,
5. Remove the remaining EtOH leaving around 100 μ L,
6. Dissolve the particles using an ultrasonic shaker,
7. Draw the dissolved solution using a micropipette,
8. Put the solution on SEM stub and leave it to dry at room temperature.



Figure C.1: Washing procedure to remove oil from samples and prepare them for SEM imaging.