

MICROFLUIDIC SYNTHESIS OF POLYHEDRAL OLIGOMERIC SILSESQUOXANE (POSS) BASED ORGANIC-INORGANIC HYBRID MICROPARTICLES

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By
Umutcan Çalışkan
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Microfluidic synthesis of polyhedral oligomeric silsesquioxane (POSS)
based organic-inorganic hybrid microparticles

By Umutcan Çalışkan

September 2019

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.

Barbaros Çetin(Advisor)

Çağlar Elbüken

Hatice Duran Durmuş

Approved for the Graduate School of Engineering and Science:

Ezhan Karaşan
Director of the Graduate School

ABSTRACT

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Umutcan Çalışkan

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Advisor: Barbaros Çetin

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Utilizing microfluidic systems inevitably changes tools used in chemistry due to advantages such as handling differential volume, controlled reaction environment, enhanced mixing performance, less time required to complete reaction. Hence microfluidic reactors become more popular among microparticle synthesis tools. This research work presents synthesis of organosilica nano-cage structures, namely Polyhedral oligomeric silsesquioxane (POSS) particles, based on organic-inorganic hybrid microparticles by utilizing dispersion and emulsion polymerization methods. Firstly, poly(M-POSS) microparticles are synthesized via dispersion polymerization method by using continuous flow microreactors, one of which is operated on a hot plate and the other one has temperature controlled dual zone with embedded electrodes. Synthesized microparticles in microreactors are characterized in terms of morphology, thermal behavior and surface chemical structure. Effects of different parameters such as monomer, initiator and stabilizer amount are presented. Secondly, in a temperature controlled continuous flow microfluidic reactor with embedded thin film electrode, epoxy functional-POSS microparticles have been synthesized via emulsion polymerization method. Heater for the microfluidic reactor is designed by COMSOL Multiphysics and manufactured in cleanroom to achieve homogeneous temperature distribution. Effects of flow rate, temperature and concentration of monomers are presented. In addition, same microfluidic reactor without electrodes immersed in oil bath and polymerization is observed and results are compared with the electrode integrated reactor.

Keywords: microfluidics, organic-inorganic hybrid microparticles, microparticle synthesis, polyhedral oligomeric silsesquioxane (POSS).

ÖZET

MİKRO AKIŞKAN SİSTEM KULLANILARAK POLYHEDRAL OLIGOMERIC SILSESQUOXANE (POSS) TABANLI ORGANİK-INORGANİK PARÇACIK SENTEZİ

Umutcan Çalışkan

Makine Mühendisliği, Yüksek Lisans

Tez Danışmanı: Barbaros Çetin

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Mikroakışkan sistemlerin diferansiyel hacimde kullanımı, kontrollü reaksiyon ortamı, gelişmiş karışım performansı, daha az zamanda reaksiyon tamamlama gibi avantajları olduğundan, birçok alanda olduğu gibi kimya alanında da kullanılan araçları etkilemesi kaçınılmazdır. Bu doğrultudaki gelişmeler, mikroakışkan reaktörleri mikropartikül sentez araçları arasında daha popüler hale getirmiştir. Bu araştırma çalışması, dispersiyon ve emülsiyon polimerizasyon yöntemleri kullanılarak organik ve inorganik hibrit mikropartiküllere dayanan, organosilika nano kafes yapılarının yani çok yüzlü oligomerik silseskioksan (POSS) partiküllerinin sentezini sunmaktadır. İlk olarak, POSS mikropartikülleri, ısıtıcı üzerinde sürekli akış mikroreaktörü ve çift bölgeli sıcaklık kontrollü, gömülü ince film elektrota sahip sürekli akış mikroreaktörü kullanılarak dispersiyon polimerizasyonu yöntemi ile sentezlenmiştir. Mikro reaktörlerde sentezlenen mikropartiküller morfoloji, termal davranış ve yüzey kimyasal yapısı açısından incelenmiştir. Akış hızı, başlatıcı miktarı ve dengeleyici miktarı gibi farklı parametrelerin etkileri gömülü elektrotlu mikroakışkan reaktöründe çalışılmıştır. Ek olarak, geleneksel sentez teknikleri ile konvansiyonel reaktörler kullanılarak polimerizasyon gerçekleştirilmeye çalışılmış ancak mikropartikül oluşumu yerine, nano kümeler elde edilmiştir. İkinci olarak, gömülü ince film elektrotlu mikroakışkan reaktöründe, epoksi fonksiyonel-POSS mikropartikülleri emülsiyon polimerizasyonu yöntemi ile sentezlenmiştir. Mikroakışkan reaktöründeki ısıtıcı Comsol Multiphysics'te tasarlanmış ve homojen sıcaklık dağılımının sağlandığı görülmüştür. Akış hızı, sıcaklık ve monomerlerin konsantrasyonunun etkileri sunulmuştur. Ayrıca, yağ banyosuna batırılmış elektrotlar bulunmayan aynı mikroakışkan reaktörü kullanılarak polimerizasyon gerçekleştirilmiş ve elde edilen

parçacıkların karakterizasyonlarının sonuçları raporlanmıştır.



Anahtar sözcükler: Mikro akışkanlar, organik-inorganik mikroparçacı sentezi, Polyhedral Oligomeric Silsesquioxane (POSS).

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Chapter 1

Introduction

Fast developments in microfabrication techniques urge to use of microfluidic in which very small amount of sample fluid in the order of 10^{-9} to 10^{-18} liters is handled via $10\mu\text{m}$ to $1000\mu\text{m}$ channels in different areas such as point of care devices, lab-on-a-chip systems, chemistry as a synthesis and/or analysis of particles. The main motivations of microfluidics are based on molecular analysis, biodefence, molecular biology and microelectronics. In chemistry, improvements in microanalytical methods based on capillary have changed perspective of developers towards more compact methods than conventional methods. Moreover, microanalysis advancements have triggered the understanding of genomics, so microanalytical related molecular biology become hot topic in genomics. In addition, advances in bio-weapons forced governments think of early detection systems and detection in field via detectors for chemical and biological threats. To continue in this vein, high-throughput DNA sequencing, which requires high throughput, more sensitivity and more resolution compare to conventional methods, have been attracting attention, since genomics of the bio-weapons should be sequenced. Last but most important point is improvements in microelectronics. Developments in microfabrication techniques such as lithography techniques, silicon based fabrication techniques promote use of more compact systems. All these advancements and necessity to use more compact systems have been enforcing developments in microfluidics [1]. In the light of these developments, micro total analysis systems

(μ TAS) or lab on a chip was proposed by Manz *et al.* [2] as a concept of miniaturized total chemical analysis systems (TAS) in which chemical analysis could be done by microfluidic components with the help of advantages in phenomenon of microfluidics [3]. Hence, microfluidic platforms had been using in many different areas such as handling chemicals, manipulation and processing chemical reactions, detection, sequencing, analysis, separation, synthesis of particles [1, 3, 4].

As discussed by Elvira *et al.* [5], Haeberle *et al.* [3], Whitesides [1] and Wang *et al.* [6], microfluidic systems offers many advantages and advantages in chemistry is specifically discussed below.

- **require less amount of reagent to operate.** Low amount of sample provides more trial and less risk of hazard while working with chemicals. The effect of chance in parameters in reactions can be studied since sample is used lesser. In other words, it is easier to get information about reaction in microfluidics compare to conventional systems. Moreover, in synthesis, in which hazardous chemicals are used, it is safer to operate with less amount of reagent.
- **fast reaction.** Although, studies show that compare to conventional systems space-time yields is higher in microfluidics systems, it is faster to get results in microfluidic systems. Hence, fast reaction should be considered as getting result in microfluidic is faster. Since the amount of reagents and volume of reactors are less, reactions are completed faster. Products can be analyzed and if needed, trials can be performed multiple times in less amount of time. In conventional systems, getting optimized results takes more time.
- **safer reaction.** In hazardous operations, it is better to use less reagent. Explosion risks toxicity risks are reduced.
- **less thermal mass.** Volume of used reagents and operated systems are smaller compare to conventional batch systems. Less amount of heat is required to operate.

- **rapid heat transfer.** Especially in lab on a chip systems, since surface area to volume ratio in channels are high, heat transfer occurs rapidly.
- **enhanced portability and smaller footprints.** Chips used in microfluidic systems have less weight and smaller volume. Some examples such as insulin pumps or pregnancy tests can be carried in a pocket.

In microfluidic systems, glass, silicon and polymer based materials have been used. In the beginning, glass based materials were used in systems, because fabrication techniques of glass were well-known and conventional systems used glass based instruments. It is not easy to fabricate glass and since glass is not a good conductor compared to silicon, glass is not appropriate for microelectronic operations. Moreover, its thermal properties such as thermal conductivity is low compare to silicon. Hence, silicon started to used in microfluidic systems. Silicon is biocompatible, it is easier to fabricate and it offers enhanced thermal and electrical properties compared to glass. However, it is costly to fabricate silicon and glass. Furthermore, reactions can not be observed in silicon/glass based systems, because they are opaque. After the silicon/glass based systems, polymer, specifically polydimethylsiloxane (PDMS),based microfluidic systems became popular. They offer biocompatible, transparent, easier to fabricate and cheaper systems. Nowadays, silicon and polymers are preferred together based on the type of applications [1,3–6]. In chemistry, benefits of employing polymer based chips are easier observation of reaction (due to transparency), fast and cheaper fabrication and good thermal properties. On the other hand, polymer based chips are permeable which may not be preferred during reactions, absorb reagent in long period, but silicon based chips are not permeable and are chemically resistant. Hence, combined systems have been used in chemistry.

On the other hand, there are challenges needed to be solved in microfluidics. In chemistry applications, long operational time causes clogging in channels [1,4–6]. Porosity and chemical properties of material of chip, flow rate, reaction kinetics are important parameters in clogging, but it is reported that scale up the systems is not suitable for microfluidics systems [4]. Rather than scale up, numbering up, which means paralleled usage of multiple systems at the same time, is more

applicable. Moreover, the risk of contamination of channel walls are higher.

Organic-inorganic hybrid micro/nanoparticles are one of the most popular materials studied in the last decade because of their multifunctional properties. Due to their organic component, they are bio-compatible and have respecified wetting characteristics (hydrophobic/hydrophilic). In addition, their inorganic part gives them unique mechanical, electrical, and magnetic properties which consequently, makes them suitable for many different applications such as drug delivery, imaging, fuel cells, photo catalysts, cosmetics, packaging [7–12]. Among these hybrid particles, interest in polyhedral oligomeric silsesquioxanes (POSS) with cage structures has increased dramatically in the last few years. Unlike other hybrid materials, POSS has an inorganic core coated with organic substitutes. Having organic structures at the exterior of the material makes them compatible with other polymers which broaden their application areas [8]. The cage structure of polyhedral POSS—or poly(POSS)—and its derivatives have already been used for various applications. For instance, biocompatibility, thermal resistance, hardness, and composite structure of poly(POSS) was utilized for dental applications [13, 14] as well as an additive to enhance the thermal properties of materials [15]. Owing to mechanical and electrochemical properties, poly(POSS) was used as energy storage materials, proton exchange membranes, and supercapacitors [16]. Furthermore, cage structure and its functional groups allowed them to be used as a metal-free catalysis for the polymerization of polycaprolactone [17]. The modification of poly(POSS) with the addition of functional groups is also possible and through this, a variety of ionic properties can be obtained for applications in chromatographic separation in monolithic columns [18]. The synthesis of functional poly(POSS) can be performed by using photo initiation, thermal initiation, or click chemistry [18].

In the last few years, there have been several microfluidic reactors that are used for the synthesis of hybrid nanoparticles [19–21] and microparticles [22–28]. Among these, Hong *et al.* synthesized liposome-hydrogel hybrid nanoparticles by utilizing hydrodynamic flow focusing; Zhang *et al.* [19], Liu *et al.* [20] and Feng *et al.* [21] demonstrated the synthesis of core-shell nanoparticles composed of polymer core and lipid shell in multiphase liquid continuous flow reactors for

mainly drug delivery purposes [19–21]; Shiba *et al.* [23] presented the synthesis of nanoporous, monodispersed titanium dioxide-octadecylamine particles in a multiphase liquid continuous-flow microreactor. Prasad *et al.* [24] synthesized hybrid Janus microspheres in a droplet-based device with 3.5% of size variation. Lan *et al.* [22] and Zhao *et al.* [26–28] employed microreactors to synthesize hybrid microspheres composed of chitosan and silica. Lan *et al.* [25] performed an interface reaction to synthesize titania-silica core-shell microparticles in a droplet-based device. Table 1.1 summarizes the literature on hybrid particle synthesis for both batch methods and microfluidic approaches. All of these chemical synthesis techniques took place in conventional batch reactors, and until now poly(POSS) microparticles without any additional copolymer is not obtained successfully by a dispersion polymerization method in these systems. POSS synthesis was achieved using double zone temperature controlled microfluidic reactor and published by the author [29]. In addition to dispersion polymerization, emulsion polymerization method was used to synthesize POSS composite latexes which improve surface wettability and thermal stability of the composite surface [30]. Moreover, latex of P(GMA-POSS)-co-PMMA as a coating material is synthesized by employing emulsion polymerization and advancing in hydrophobicity, thermal and mechanical properties is achieved [31].

Table 1.1: Hybrid Particles in Literature

Reference	Year	Material	Reactor/Reaction Time	Application
M.Rizk <i>et al.</i> [13]	2017	Methacryl-functionalized POSS	Batch-wise synthesis	Dental applications
Y.Liu <i>et al.</i> [14]	2018	POSS nanocomposite resin	Batch-wise synthesis	Dental applications
R.Kunthom <i>et al.</i> [17]	2017	POSS-containing hyperbranched sulfonic acid groups	Batch-wise oxidation based synthesis	Not specified (NS)
L.Zhang <i>et al.</i> [19]	2015	Polymer core lipid shell nanoparticles	Multiphase Liquid Continuous flow microreactor	Drug delivery
Q.Feng <i>et al.</i> [20]	2015	Polymer core lipid shell nanoparticles	Multiphase liquid continuous flow reactor	Drug delivery
D.Liu <i>et al.</i> [21]	2017	Polymer core lipid shell nanoparticles	Multiphase liquid continuous flow reactor	Drug delivery
K. Shiba <i>et al.</i> [23]	2009	Monodispersed titanium dioxide-octadecylamine particles	Multiphase Liquid Continuous flow microreactor	NS
N.Prasad <i>et al.</i> [24]	2009	Hybrid Janus microspheres	Droplet-based microreactor	NS
W.Lan <i>et al.</i> [22]	2010	Hybrid chitosan and silica microspheres	Microreactor	NS
H.Zhao <i>et al.</i> [26]	2013	Hybrid chitosan and silica microspheres	Microreactor	NS
H.Zhao <i>et al.</i> [27]	2014	Hybrid chitosan and silica microspheres	Microreactor	NS
H.Zhao <i>et al.</i> [28]	2015	Hybrid chitosan and silica microspheres	Microreactor	NS
W.Lan <i>et al.</i> [28]	2011	Titania-silica core shell microparticles	Microfluidic interface reaction	NS
Y.Ma <i>et al.</i> [31]	2014	Latex of P(GMA-POSS)-co-PMMA nanoparticles	Batch-wise synthesis	Coating material

1.1 Dispersion Polymerization Method

Dispersion polymerization is used to produce micrometer ($1\text{-}10\mu\text{m}$) sized monodisperse polymeric particles. It arouses great interest with its high efficiency in preparing polymer particles with homogeneous size distribution and taking place in one stage [32, 33]. This method can be defined as a particular type of precipitation polymerization in which a monomer is polymerized within a reaction medium in the presence of a suitable stabilizer. The solvent is a good solvent for the polymerization monomer, stabilizer and initiator, but not for the polymer formed. The resulting polymer particles are stable in the reaction medium [34, 35]. Dispersion polymerization can be divided into two main stages. The first stage in which particles and nuclei are formed and aggregation prevails between them is the stage of particle formation. The next stage in which particle growth is predominant is particle growth stage [36]. In dispersion polymerization, all components are dissolved at the beginning of the reaction. When this homogeneous reaction mixture is heated, free radicals are formed by disruption of the initiator and continuous phase growth begins with monomer addition. Free radicals that reach a sufficiently high chain length subside and the stabilizer adsorbs to the surface of the formed particles to stabilize the particles. As soon as the particles are formed, monomer adsorption begins from the continuous phase. After formation of a sufficient number of particles which is capable of capturing free radicals in the continuous phase, the free radicals cannot grow to a high degree of polymerization. The polymerization essentially continues in the formation of monomer-swollen particles until all monomers are depleted [37]. Paine [38] determined that the in situ stabilizer formed by the chain transfer reaction of the radical and the stabilizer molecule plays an important role in the particle formation stage. According to Paine, the stabilized particles whose surface is coated with an in situ stabilizer do not cluster with each other. When the particles which capture the radicals in the continuous phase are sufficiently stabilized, no new nuclei or particles are formed. After particle formation, there are two manner where the polymerization will proceed; these are polymer particles and continuous phase. Most of the monomers and initiator are in continuous phase. Almost all initiation and growth reactions of oligomeric radicals occur in

continuous phase. When the number of stabilized particles holding the oligomer radicals in the continuous phase is sufficient, the growth and termination reactions of the polymer radicals occur within the particle [39].

The effect of various parameters on the production of monodisperse particles was investigated in many studies on dispersion polymerization. Molecular weight, size and size distribution of the particles synthesized by dispersion polymerization and monomer conversion depend many factors, namely, initiator type and concentration, stabilizer type and concentration, mixing speed and shape, polymerization temperature, composition and type of the dispensing medium, monomer/dispersion medium volumetric ratio [40, 41]. Numerous experiments have been conducted in the literature for various parameters related to dispersion polymerization. When polymerization experiments carried out at different temperatures in the range of 55-80°C with increasing polymerization temperature, it was observed that average particle size and size distribution was increased but the molecular weight of the polymer was reduced [42]. The type and composition of the dispersion medium is another factor affecting the average size and size distribution in dispersion polymerization. In dispersion polymerization, the desired dispersing media are those with high monomer solubility but low polymer solubility [40]. Systems with high monomer solubility and low polymer solubility are considered to be ideal [40]. To a certain level, the volumetric ratio of monomer/dispersion medium is directly proportional to the particle size formed. If this ratio increases too much, the size distribution also increases. In the experiments, it was observed that the size of polymeric particles decreased with increasing concentration of stabilizer [40]. In addition, it was observed that the raise in the amount of initiator dissolved in the monomer phase leads to a raise in the size distribution of the particles formed and a raise in the reaction rate [43, 44].

In the literature, water soluble polyacrylamide was prepared by dispersion polymerization. Researchers investigated the dispersion polymerization of acrylamide using poly (vinyl methyl ether) stabilizer with using 2,2 azobisisobutyronitrile (AIBN) [32, 45] and ammonium persulfate as initiators. Ye *et al.* [33] using AIBN and PVP in water/tert-butanol (TBA) synthesized polyacrylamide particles of 300-1000 nm size by dispersion polymerization. By this method, Cho *et*

al. [46] prepared polyacrylamide in ammonium sulfate using poly (acryloxyethyl trimethyl ammonium chloride) (PAOTAC) as stabilizer with using 2,2-azobiz (2-methylpropionamidine) dihydrochloride (AIBA) as the initiator.

Organic–inorganic hybrid microparticles are popular materials studied in the last decade because of their versatile properties. They are accepted biocompatible due to their organic component and have specified hydrophobic/hydrophilic characteristics. Besides that, the inorganic section facilitates them specific magnetic, mechanical and electrical features. Hereby, they have several application fields such as packaging, pharmacological distribution, photocatalysts, imaging and cosmetics. Within these hybrid particles, the attention on polyhedral oligomeric silsesquioxanes (POSS) raised significantly in the last few years. Recently, Kibar *et al.* [29] procured spherical monodisperse POSS microparticles. They carried out a simple one-pot synthesis procedure to acquire organic–inorganic hybrid microparticles in microfluidic reactors via dispersion polymerization. Furthermore, the synthesis of poly(POSS) in particle form inside a microfluidic system by dispersion polymerization was introduced first [29].

Nanoclusters were represented the group of nanoparticles, which is defined as particle in range of 1 nm to 100 nm in size, at least one dimension and size distribution in narrow range. When they gathered, the different types of bonding forces could be acting like ionic, metallic, covalent, wan-der walls or hydrogen bonds. The widely used and the best technique to determine the nanoclusters is transmission electron microscope (TEM) characterization [47].

A hydrogel is defined as connected hydrophilic polymer chains and chains create a network. In water as a dispersion medium, they can be observed as a colloidal gel. A three-dimensional solid results from the hydrophilic polymer chains being held together by cross-links. Because of the crosslinking hydrogel does not dissolved in water medium [48].

1.2 Emulsion Polymerization Method

Emulsion polymerization is a method of polymerizing a water-insoluble monomer by emulsifying in water with the aid of suitable emulsifiers. In emulsion polymerization, the medium contains water, monomer, micelle, and initiators [49]. Emulsion polymerization involves two immiscible phases. The dissolved monomer phase containing the initiator is dispersed in the water phase in emulsion form. The monomer phase is held in emulsion form in the dispersion phase with the aid of various emulsifiers. By emulsion polymerization, conjugated dienes such as butadiene and isopropene, vinyl acetate, vinyl chloride, various acrylates, polymerization of methacrylates and different copolymers of these monomers can be produced [50]. Emulsion polymerization is a unique example of chain radical polymerization. There are differences in reaction mechanism and characteristics such as dependence of molecular weight on polymer parameters and type of initiator used [51].

The emulsion polymerization can be divided into three groups according to the components present in the medium, such as conventional emulsion polymerization, reverse emulsion polymerization and emulsifier-free emulsion polymerization. In conventional emulsion polymerization, the emulsifier is dispersed with the monomer in a polar phase at the beginning of the reaction. As a difference in reverse emulsion polymerization, when the polarity of the monomer is very high, the polarity of the medium in which it is dispersed is much lower. In emulsifier-free emulsion polymerization, no emulsifying agent is added into the medium at the beginning of the reaction and emulsifiers are formed during the reaction [52].

Standard emulsion polymerization is polymerization of a monomer or mixture of monomers by free radical polymerization in an emulsifier aqueous solution. Water, monomer, emulsifier, initiator and chain transfer agents, buffer and sometimes a core latex are used to carry out this polymerization [53]. Buffers affect various impurities in emulsion polymerization, such as pH, hydroquinone between water and particulate phase. As a result, it affects the polymerization rate, molecular weight and particle size [54].

The emulsifier adsorbed on the surface of the monomer has a stabilizing effect and thus prevents the deterioration of the emulsion. When the polymerization starts, the monomers dispersed in the system proceed to the micelles and the monomer separates from the droplets and passes to the aqueous phase in order to maintain the monomer concentration in the aqueous phase. Micelles containing polymer and monomer adsorb emulsifier molecules in solution while growing. The monomer molecules which proceed to the aqueous phase by diffusion from the monomer droplets continuously feed the polymer particles and this process ensures that the monomer concentration remains constant. Over time, the monomer molecules decrease as the polymer particles grow, and the monomer molecules are depleted as the polymerization proceeds by 50-80%. Namely, all monomer molecules are interposed between the polymer particles. The polymerization ends with the termination of the chain reactions in the polymerization particles. In emulsion polymerization, 3 types of processes are applied: batch process, semi-batch process and continuous process. In the batch process, all substances are added to the reactor where the polymerization takes place. In the semi-batch process, the pre-emulsified monomers are added continuously or incrementally to the reactor where polymerization takes place. In the continuous process, all substances are completely added to a part of the reaction system and taken from another part of the latex reaction system partially or completely transformed [54].

Initiators: In emulsion polymerization, the initiators are selected according to their solubility in the monomer or solvent and the redox combination under the polymerization conditions. For these reasons, the type and concentration of the initiator affect the degree of polymerization [53]. As the concentration of the initiator increases, the degree of polymerization generally increases and the molecular weight decreases. Generally, 0.1-1% of monomer is used as initiator in polymerization processes. Water-soluble initiators such as potassium or ammonium persulfate, hydrogen peroxide and 2,2-azobis (2-amido-propane) dihydrochloride are used as initiators in emulsion polymerization. Iron ion persulfates are generally used in redox systems. In emulsion polymerization, water-soluble peroxides and persulfates are often preferred [54].

Emulsifiers: They are a class of chemical compounds known as amphiphiles and consist of two distinct regions, the first being polar (a dipole or charged group) and the other apolar (usually a hydrocarbon or halocarbon chain). Therefore, the molecules have limited solubility in any solvent and reduce the surface tension between the two phases. The best-known examples are generally the most used soaps, such as sodium or potassium salts of organic fatty acids such as oleic, palmitic or stearic acid. Besides, sodium dodecyl sulfate (SDS) is the most commonly used emulsifier in emulsion polymerization [52].

In emulsion polymerization, the choice of emulsifier is very important as it affects the polymerization rate. The emulsifier ensures a stable emulsion between the water and the monomer phase. The increased amount of dissolved monomer in the aqueous phase reduces the surface tension of the water/monomer phase [55]. Emulsifier usage facilitates that an organic compound which is insoluble in water can move into the micelle and dissolve in the emulsifier solution. The polymer beads formed during the reaction are coated with the emulsifier and remain without coagulation during and after the polymerization. Thus, the polymer particles are protected against collapse by using emulsifier [56].

Advantageously from other processes, the polymer molecular weight is directly proportional to the rate of polymerization in emulsion polymerization. Furthermore, the reaction temperature in emulsion polymerization is very low. Therefore, temperature control can be made easily. Since the viscosity of the medium is low, mixing and consequently heat transfer are easier. Therefore, the product transfer can be performed easily. Since water is generally used as a distribution medium, it is a low-cost and healthier method. In many applications, the product is synthetic latex and used directly. Examples include paint, surface coating, adhesives, latex foam, rubber. The disadvantage of emulsion polymerization compared to other processes is that more additives are used and additional processes such as separation, purification and drying are required to obtain the product from the emulsion medium if solid product is desired [51].

Dispersion polymerization has attracted great attention with high efficiency in preparing polymer particles with homogeneous size distribution and taking place

in one stage. Unlike emulsion polymerization, all components are dissolved at the beginning of the reaction in dispersion polymerization. In addition, the monomer phase dissolves in the dispersing phase, but the polymer formed at the end of the polymerization process does not dissolve in the dispersing phase [51]. According to research, it is stated that the stabilizer used in dispersion polymerization stabilizes the particles with the role of emulsifier as in emulsion polymerization. On the other hand, it is also noted that the stabilizer polymer molecules are inoculated into the resulting polymer and the formed co-stabilizer performs particle stabilization. However, it has been determined that both mechanisms play a role in stabilization [37].

Polymer nanoparticles (PNPs) have an important role in a wide spectrum of areas ranging from electronics, biotechnology, sensors, conducting materials, medicine and environmental technology [57]. Using emulsion polymerization method, several studies were conducted to produce polymer nanoparticules such as poly(methylmethacrylate) (PMMA), poly(ethylcyanoacrylate) (PECA), and poly(butylcyanoacrylate) by dispersion via surfactants into solvents as the organic phase [57]. In addition to these particles, emulsion polymerization is used for synthesis of Polyhedral Oligomeric Silsesquioxane (POSS)-based polymers which have advantages of inorganic ingredient (rigidity and thermal stability) with organic polymers (flexibility and ductility) [31]. For instance, Liao *et al.* [30] successfully synthesized new OvPOSS/FPSA composite latexes by pre-emulsification and emulsion polymerization. They provided a useful product which has improved thermal stability for industry.

1.3 Materials

Materials used throughout the thesis are introduced in this section.

Polyhedral Oligomeric Silsesquioxane $RSiO_{1.5}$ consists of radical group as hydrogen or any alkyl, alkylene, aryl, arylene. In addition to hydrogen, organofunctional derivative of alkyl, alkylene, aryl, or arylene groups can be

used [58]. Different structures namely random, ladder and cage structures can be seen in the silsesquioxanes. Advances in thermal behaviors, increased resistance to oxidation, improved surface hardening and mechanical properties, reduced viscosity in reaction, lower flammability are reported advantages of utilizing POSS in polymeric materials [58]. Moreover, it is organic-inorganic hybrid in which organic compound may coat the $(SiO_{1.5})_x$ that is inorganic framework. Hence, hydrocarbons may cover POSS hybrids.

Glycidyl Methacrylate (GMA) monomer contains both acrylic and epoxy groups with the versatility of design and performance required for the most demanding coating and resin applications. It is acquired from a methacrylic acid and a glycidol [59]. Its molecular formula is $C_7H_{10}O_3$. It allows copolymerization with various other vinyl monomers in aqueous and non-aqueous systems. The resulting polymers have a unique combination of epoxy functionality with an acrylic backbone. A wide selection of co-monomers allows easy control of physical and chemical properties such as solution viscosity. It provides cross-linking reactions with amines, carboxylic acids, anhydrides and hydroxyl-containing polymers. Glycidyl methacrylate is a liquid with a fruity odor and has no color. It floats on water. It is stable under recommended storage conditions ($+4^{\circ}C$). High temperatures may cause dangerous polymerization. The polymerization may be catalyzed by the presence of free radical initiators and peroxides, acids, UV light, bases or high temperature in the absence of air. Glycidyl methacrylate contains an inhibitor to minimize polymerization under recommended storage conditions. In case of use, inhibitor concentration and dissolved oxygen level should be maintained. Undesirable contacts with activated carbon or silica gel that may cause polymerization should be avoided. Besides, contact with oxidizing or reducing materials, strong acids or incompatible materials such as metals and metal oxides may cause undesirable results [59].

Sodium Dodecyl Sulfate ($CH_3(CH_2)_{11}SO_4Na$) is a synthetic organic compound and it is used as anionic surfactant in emulsion polymerization applications. Anionic head group and hydrocarbon tail make formation of miscelle in emulsion polymerization.

Azobisisobutyronitrile ($C_8H_{12}N_4$) is an oil-soluble thermal free radical initiator. Azo-group makes it highly reactive. It should be stored at 2–8°C and starts to decompose at 50°C. It was used in both dispersion and emulsion polymerization. In polymerization, decomposition of thermolabile compound (or initiator) enforces to formation of two free radicals which are 2-cyanoprop-2-yl-radicals in reaction medium [53,60]. It is soluble in EtOH which is dispersion medium and is not soluble in water which is emulsion medium. Since it is soluble in EtOH and decomposition temperature is below the boiling point of EtOH, it was chosen [53].

1.4 Objectives and Motivation

Microfluidics have been attracting attention green synthesis for almost 30 years due to need for advances in microanalytical techniques, microelectronics and molecular biology. Microfluidics offer many advantages in these fields, such as need for low amount of reagent, rapid reaction, increased thermal behaviors in terms of heat transfer and thermal mass, safer reaction and portability of the systems *et al.* [5], Haeberle *et al.* [3]. In chemistry, researchers have been applying these benefits into reactor systems to synthesize different size of particles. Enhanced heat transfer, reduced thermal mass and reagent amount provide more control on reaction. Monodispersity and control on size of particle can be achieved [6].

POSS become popular among researchers due to its unique properties such as advancements in thermal, mechanical and chemical behaviors in material that POSS is added. Moreover, it is organic-inorganic hybrid which can be coated and applied to wide range of area.

Main objectives of this thesis are presented below:

- **Conducting Green synthesis** represents low energy consumption, more health and environmentally friendly byproducts and simpler operation while increasing resultant product during the synthesis [61]. Green synthesis requires less amount of waste, lower toxicity and consumption of lower

amount of energy. Microfluidic systems have lower energy consumption and since low amount of reagent is enough, waste and risk of toxicity is reduced.

- **Producing poly(M-POSS) microparticle** is wide range of application areas such as chromatographic separation systems, energy applications, magnetic separation of DNA, RNA etc. Surface of the poly(POSS) can be covered by hydrocarbons and hybrid properties of POSS can be used. In literature, to the best of authors' knowledge, synthesis of poly(M-POSS) microparticle is not reported by using microfluidic platforms. Hence, poly(M-POSS) microparticle synthesis is the goal of thesis.
- **Synthesis of poly(M-POSS-co-GMA)** provides opportunity to use epoxy behavior in addition to advances of POSS. Stronger adhesives, thermal and mechanically advantageous coatings can be produced by use of epoxy.
- **Getting information about reaction** stresses effect of change in polymerization parameters on results. In microfluidic systems, low energy consumption, rapid reaction and low reagent consumption provide increased number of trials. Change in monomer amount, stabilizer amount, initiator amount and flow rate is investigated.

1.5 Outline of the thesis

This research work consists of four major sections as follow:

Chapter 1 consists of introduction to microfluidic systems, organic inorganic hybrids, synthesis of microparticles and polymerization types. Advantages of microfluidic systems, fields of use of organic inorganic hybrids and previous works for hybrid synthesis are presented.

Chapter 2 demonstrates synthesis of poly(M-POSS) microparticles via dispersion polymerization. Batch and microfluidic systems, which comprise chip on hot plate and heater embedded chip, have been introduced and their comparisons

are presented. Design and fabrication of microfluidics chips are elaborated and experimental works for synthesizing poly(M-POSS) microparticles are presented. How change in monomer amount, stabilizer amount and initiator amount affects results are investigated.

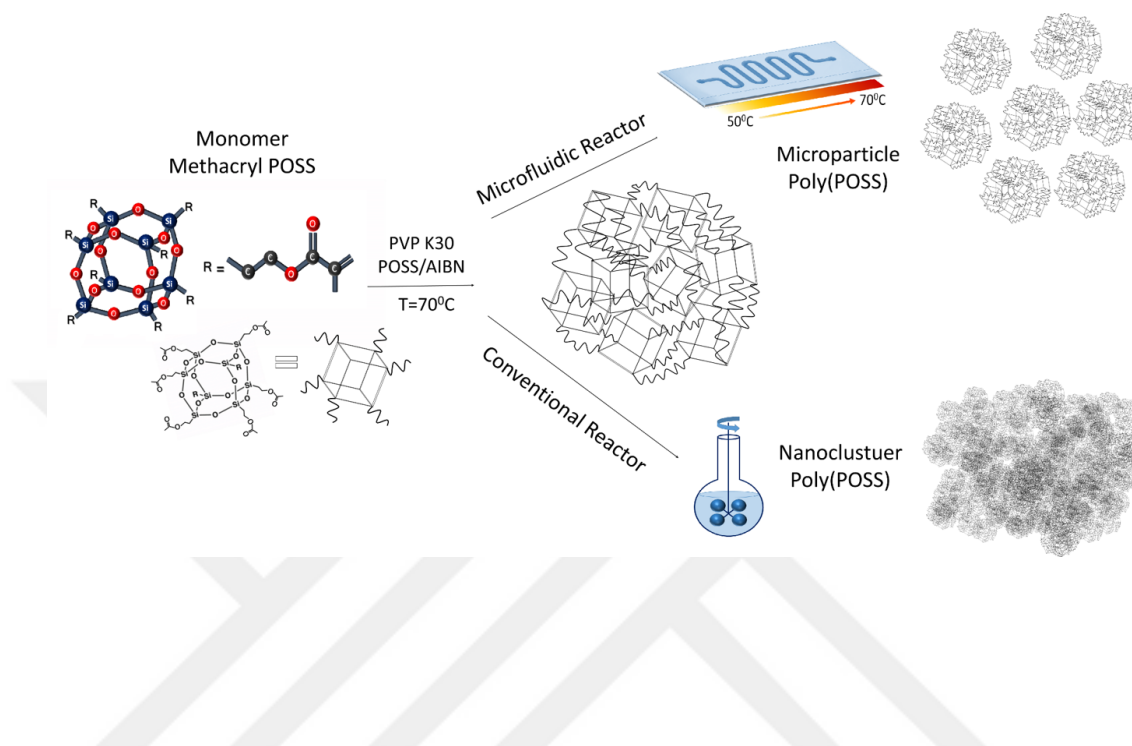
Chapter 3 introduces poly(M-POSS-co-GMA) organic-inorganic hybrid synthesis by using emulsion polymerization in microfluidic chip in oil bath and microfluidic chip with embedded electrode. How to design the electrode by utilizing COMSOL software and how to fabricate designed chip is presented. Experimental work for synthesis and characterization of synthesized particles and their comparisons are presented.

Chapter 4 presents indications and their implications. Future research directions to improve the performance of microfluidic system is presented.

Chapter 2

Synthesis of Poly(M-POSS) Microparticle

In this chapter, the demonstration of synthesis of poly(M-POSS) microparticle via dispersion polymerization is presented. Three different configurations, namely batch reactor, microfluidic reactor on hot plate and microfluidic reactor with emdedded electrode, are proposed and details of configurations are given. Materials used in synthesis and methods used in characterization are introduced. Fabrication steps of microfluidic reactors are reported. Experimental procedure and recipe used in dispersion polymerization is presented. Dispersion polymerization results are shown and the effect of change in initiator amount, monomer amount and stabilizer amount is demonstrated. Graphical abstract of this chapter is below.



2.1 Materials and Methods

2.1.1 Materials

Azobisisobutyronitrile (AIBN), polyvinylpyrrolidone (PVP) K-30 and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich (Schnelldorf, Germany). AIBN was washed with methanol and recrystallized before used. Monomer Methacryl polyhedral oligomeric silsesquioxanes (M-POSS) cage mixture (MA 0735) was supplied from Hybrid Plastics Inc (Hattiesburg, MS, USA). Absolute ethanol (Abs EtOH), methanol, 2-propanol and acetone was purchased from Merck (Kenilworth, NJ, USA). Sylgard 184 Polydimethylsiloxane (PDMS) and curing agent from Dow Corning (Midland, MI, USA). Distilled deionized (DDI) water was obtained from Millipore/Direct Q-3UV water purification system in Bilkent University Institute of Materials Science and Nanotechnology National Nanotechnology Research Center (UNAM).

2.1.2 Characterization

Morphological characterization of the results were performed by using Environmental Scanning Electron Microscope (ESEM, Quanta 450 SEM, Akishima, Tokyo, Japan) in UNAM. By using SEM, surface characteristics and size distribution of resultant particles were investigated. Elemental analysis of surface was carried out by using energy dispersive X-ray (EDX) in ESEM. All particles were coated with Au-Pd via precision coating. ESEM was operated under high vacuum mode. While using EDX, 15 kV as an acceleration voltage and 3.0 as a spot size were chosen. Different magnifications like 5,000x (20 μm), 10,000x (10 μm), 20,000x (5 μm), 30,000x (3 μm), 50,000x (2 μm), 100,000 (1 μm) and 200,000x (500 nm) and different acceleration voltage values such as 5 kV, 10 kV and 15 kV were set for acquiring the images. The structure was analyzed by Fourier Transform Infrared Spectroscopy (FT-IR, Nicolet 6700-Thermo Scientific, Waltham, MA, USA). Analysis was completed in 400 to 4000 cm^{-1} range with 4 cm^{-1} resolution. Thermal behaviors of synthesized materials were determined by thermogravimetric analysis (TGA, PerkinElmer Diamond, Akron, OH, USA) with 10°C/min working under airflow in the temperature range of 50-700°C.

2.1.3 Reactor Types

Three types of reactors were employed to synthesize particles. As a starter, conventional batch reactor with in-house developed container/laboratory infrastructures was used. Organic phase was dissolved in dispersion medium in ultrasonic bath for 5 minutes. The dispersion mixture was put into an oil bath heated by hot plate for polymerization at 70°C for 6 hours and the medium was magnetically stirred at 250 rpm.

In addition to conventional batch reactor, two different configurations were utilized using microfluidic chips. Firstly, microfluidic chip in which dispersion medium was pumped continuously through channels using syringe pump (New Era type NE300, Farmingdale, NY, USA) was heated on hot plate as seen in

Figure 2.3. During polymerization, the temperature distribution on microfluidic chips was controlled by using a DAQ controller (IOTECH Daqbook/2000, Norton, MA, USA) and a thermal camera (FLIR A325sc, Sweden). Secondly, continuous flow microfluidic reactor with embedded electrodes was utilized to synthesize particles. Instead of a hot plate, thin film heaters which provided control on temperature via voltage tuning was sputtered on opposite side of channels of microfluidic chip as shown in Figure 2.4. Flow control and temperature measurements were performed using the same equipment used in the hot plate configuration.

2.2 Design and Fabrication of Microfluidic Reactor

AIBN as a thermal initiator requires 55°C to be activated. Dispersion solution has to be held at 70°C to complete the polymerization. Hence, two different temperature zones are needed in microfluidic reactors. In addition, because of the fact that dispersion polymerization had two stages, two zones were created. Length of the particle growth stage which was second zone, designed three times of nuclei formation stage which was first zone. Based on the given requirements, the mold of microfluidic reactor was designed by Computer Aided Software SolidWorks. Technical drawing details of the mold are given in the Appendix. Total length of the channels is 1177 mm which consist of 272 mm first zone and 905 mm second zone. Micromachining was utilized to fabricate master mold in microfluidic systems. Aluminum mold was manufactured by a 3-axis micromachining center (PROINO Z3X Micro Maker, Mikro Protez Ltd.Sti., Ankara, Turkey). The fabricated mold is shown in Figure 2.2-A. The chip was fabricated using PDMS molding. After the fabrication, simple chemical cleaning, which is explained in Appendix, is used to clean aluminum mold. PDMS (Sylgard 184 Polydimethylsiloxane, Dow Corning Midland, MI, USA) and curing agent was mixed in 10:1 by mass ratio and degassed under vacuum at room temperature. Following degassing, PDMS mixture was poured into the mold and degassed for 15 minutes. Then, the mixture was baked at 80°C for 90 minutes. The cross linked PDMS

was gently peeled off with a knife from the mold. Two holes as an inlet and an outlet of the chip were punched out. As a substrate, microscope slide (Marienfeld Company) with a dimension of 76 mm×52 mm× 1 mm was used. Simple Chemical Cleaning was employed. PDMS channels and glass substrate were bonded by using Nanoplas asher. Both surfaces are treated at 30°C with an Oxygen flux of 25 sccm and Nitrogen flux of 5 sccm and RF power of 150 W for 1 minute. After the treatment, PDMS channels and glass substrate were bonded and kept in the oven at 80°C for 10 minutes. PVC tubing which had 1.5 mm by 2.1 mm diameter was attached to inlet and outlet, and sealed by using PDMS (mixed in 5:1 by mass ratio). The structure seen in Figure 2.2-B shows the microfluidic chip. This chip was used in two different configurations for microparticle production. In the production on the hot plate, the chip was placed directly on the hot plate and no modifications was applied. However, as demonstrated in Figure 2.1, extra steps were required for the electrode embedded microfluidic chip to generate double zone configuration.

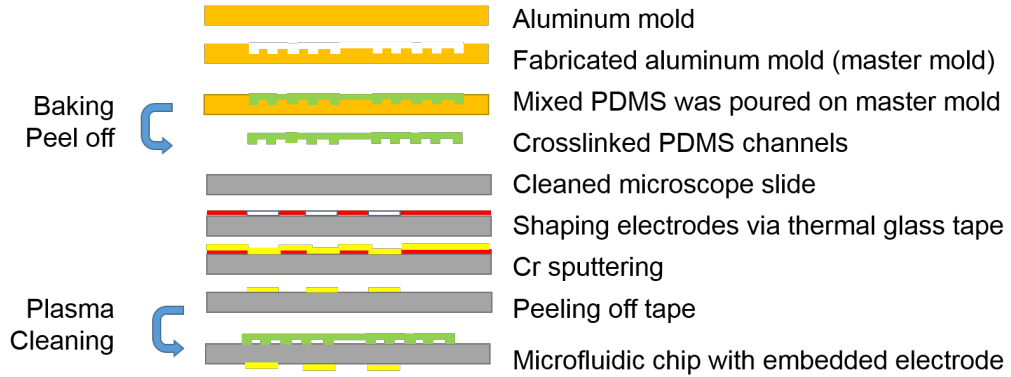


Figure 2.1: Demonstration of fabrication steps of microfluidic chip with embedded electrode

For electrode embedded reactor, before the asher step, the glass was cleaned using the simple chemical cleaning method. The thermal glass tape was adhered to the cleaned glass and the electrode was shaped. In Advance Research Laboratory, glass was coated with chromium using sputtering device (LH Leybold AG, L-560, Cologne, Germany). The electrodes were adjusted so that excessive

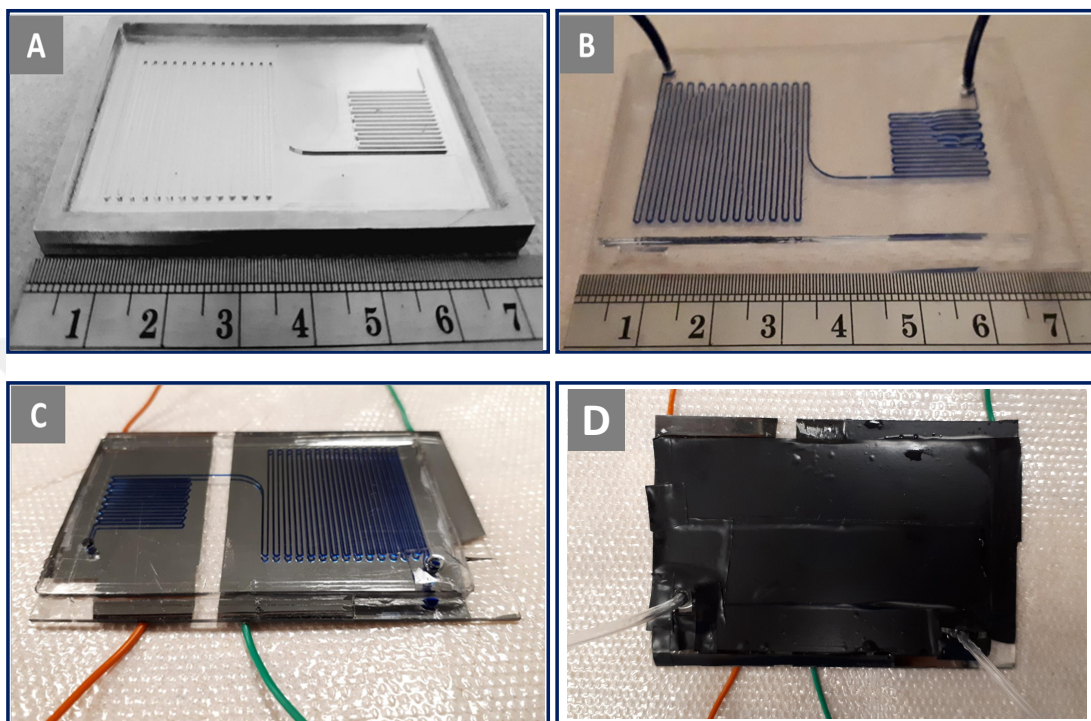


Figure 2.2: A) Fabricated aluminum mold, B) Microfluidic reactor for hot plate configuration, C) Fabricated microfluidic reactor with embedded electrode D) Microfluidic reactor covered with tape to increase thermal camera's reading performance

heating at the connection points does not affect the channels. Cr-coated glass was bonded with PDMS channels via asher. PVC tubing was connected to the inlet and outlet of the chip and sealed. Then, the electrode wires were connected by Elecolit 325 (Panacol) conductive epoxy. The chip was baked at 50°C for 2 hours to cure the epoxy. Then, using voltmeter, connections were verified and resistance values were checked. Final chip is presented in Figure 2.2-C.

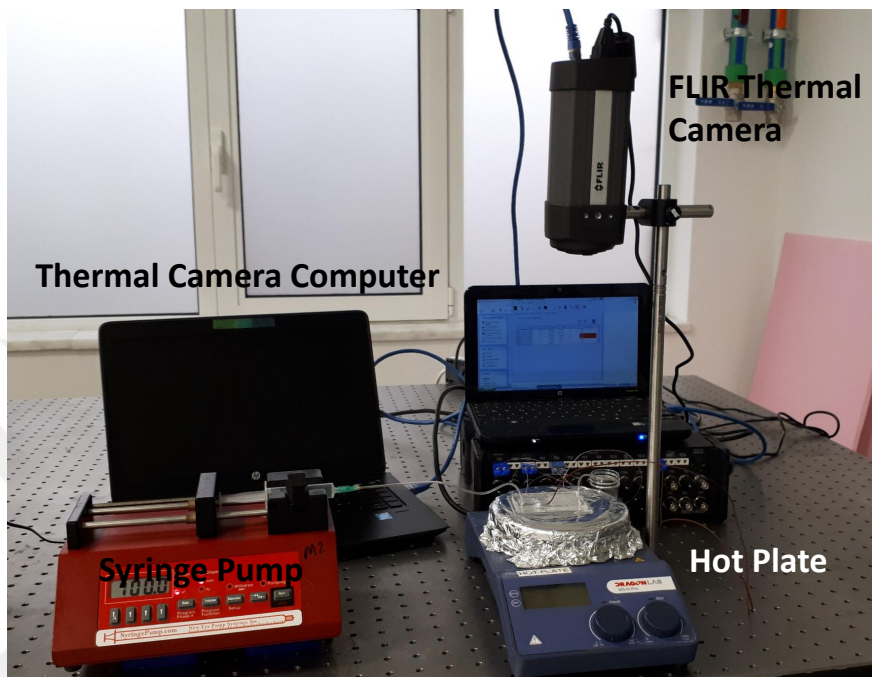


Figure 2.3: Experimental setup of microfluidic reactor on hot plate

2.3 Experiments

The dispersion mixture was consist of AIBN as an initiator, M-POSS as a monomer and PVP K-30 as a linear non-ionic stabilizer and SDS as a non-ionic surfactant in absolute ethanol as a dispersion medium. As proposed similar methacrylate studies such as in Bahar *et al.* [44], in beginning of the optimization, monomer concentration was determined as 5% of reaction medium then changed based on results. Syringe pumps were used to deliver the liquids at desired rates into the microfluidic devices. For microfluidic reactors, thermocouples and thermal camera were employed to monitor the temperature. For microfluidic reactor on the hot plate, the reaction temperature was set to 70°C and microfluidic reactor was placed near the edges since it was observed that hot plate surface did not have homogeneous temperature distribution. It was observed that the temperature varies 4°C from center to edge. Experimental setup and components are shown in Figure 2.3.

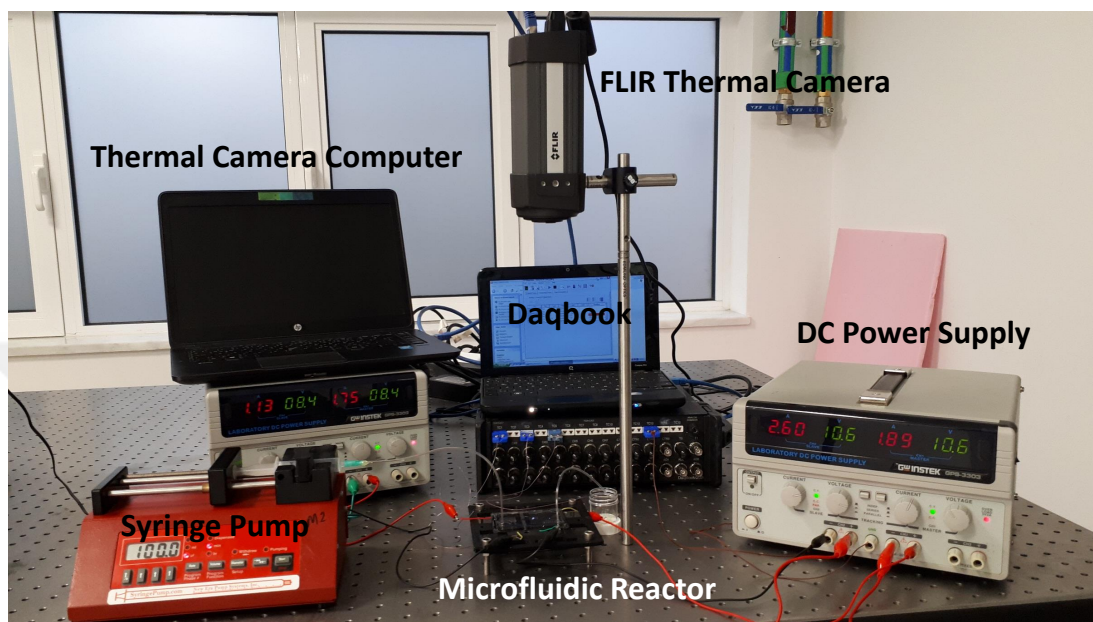


Figure 2.4: Experimental setup of microfluidic reactor with integrated thin film electrode

As seen in the Figure 2.4, for microfluidic reactor with embedded electrode, temperature was gradually controlled from 50°C to 70°C. Voltage values were adjusted while feedback were collected via thermocouples and thermal camera. Then, the reacted liquids were collected into a 2 ml Eppendorf at the outlet of the microfluidic reactors.

The temperature controlled hotplate with a magnetic stirrer was used for conventional batch system polymerization. Five milliliters of dispersion mixture was put in flat bottom glass bottle with a magnetic stirring bar; and it was sealed and placed in an oil bath. The reaction took place on the hot plate for which the temperature was set to 70°C. During the synthesis, magnetic stirring at 250 rpm for 6 h was employed. At the end of the synthesis in all three reactors, poly(M-POSS) was collected by centrifuge for 5 min at 10000 rpm. Resultant white-colored hybrid structures were washed with ethanol and DI water several times to remove unreacted medium and monomer. Finally, the particles were dispersed in 1% SDS containing DI water. Since in dispersion polymerization, all

agents have to be solvable in dispersion medium, EtOH was chosen as a solvent for POSS monomers. However, after the polymerization, poly(POSS) particles were not solvable in EtOH medium. Hence, after the washing process which includes EtOH dilution, the resultant chemicals are concluded to be poly(POSS).

2.4 Synthesis in Batch Reactor

First, the conventional batch technique was employed to obtain poly(M-POSS) microparticles. Generally, dispersion polymerization is useful to obtain uniform microparticles [44]. However, it was observed that the monomer methacryl POSS was not suitable to produce microparticles by dispersion polymerization in conventional batch reactor. The results obtained by this method are shown in Figure 2.5. The synthesis in the conventional reactor was carried out in three different monomer ratios where the other parameters were kept constant. The constant parameters of reaction medium were 15 ml of absolute ethanol, 0.012 g PVP-K30 (0.1% w/w reaction medium), and 0.06 g AIBN (0.5% w/w reaction medium). The monomer amount was varied as 0.06 g (0.5% w/w reaction medium), 0.12 g (1.0% w/w reaction medium), and 0.24 g (2.0% w/w reaction medium) in Figure 2.5. The prepared dispersion medium was magnetically stirred at 250 rpm at 70°C for 6 h to complete polymerization. The nanocluster was obtained as shown in Figure 2.5-(A,B). Since the main aim of the study was achieving microparticles, nanoclusters were not characterized in detail. It was observed that in Figure 2.5-(A,B), the size and shape of results were not microparticle. Although, in Figure 2.8-(C), surface chemical structural characteristics were similar to microfluidic reactor's results, in Figure 2.9-(C), degradation profile were altered and in first step of degradation, temperature was higher than the results of microfluidic systems. These results suggested that in second stage of the dispersion polymerization there was a problem, most likely due to type of the stabilizer. Additional bonds were formed, so resultant structure was not particle. Hence, the resultant structure was interpreted as nanocluster.

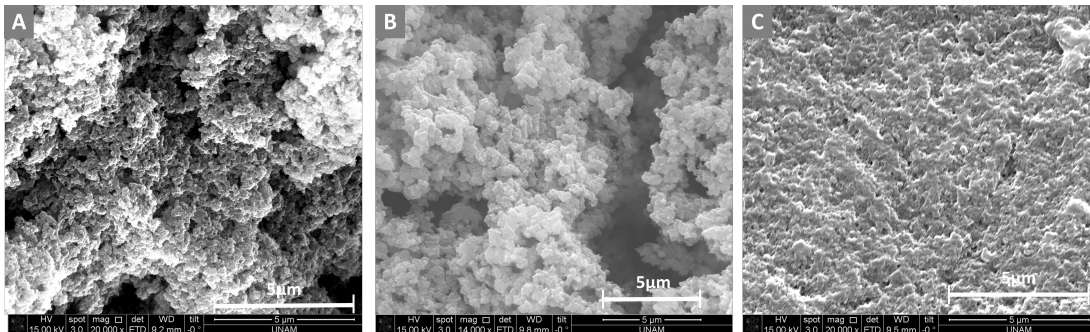


Figure 2.5: SEM image and morphological character of poly(M-POSS) obtained by dispersion polymerization with different monomer amounts: (A) 0.06 g POSS, (B) 0.12 g POSS, and (C) 0.24 g POSS in conventional batch reactor. (Reaction conditions: magnetically stirred at 70°C for 6 h)

2.5 Synthesis in Microfluidic Reactors

The heating required to activate the initiator and complete the polymerization was provided in two different ways as shown in Figure 2.6. First, the microfluidic reactor was heated with embedded electrodes Figure 2.6-(A). As an alternative, the microfluidic reactor was placed on the hot plate that is at 70°C Figure 2.6-(B). In the microfluidic reactor with embedded electrodes, two temperature zones were tuned by using thermocouple and thermal camera (FLIR, 325a). 50°C and 70°C heating zones are illustrated in Figure 2.6-(A). In the microfluidic reactor placed on the hot plate, two temperature zones were achieved, but in the first zone temperature was above the 60°C. Desired distribution could not be achieved as seen in Figure 2.6-(B). Temperature distribution could not be controlled precisely due to restriction of the hot plate. If temperature was increased, in the second zone temperature would get higher and might cause droplet formation.

As seen in Figure 2.6-B, temperature of the right edge of the chip was slightly more than 70 °C since it was placed on the center of hot plate which is set to 70 °C. Difference between the right edge and left edge was controlled by the nature

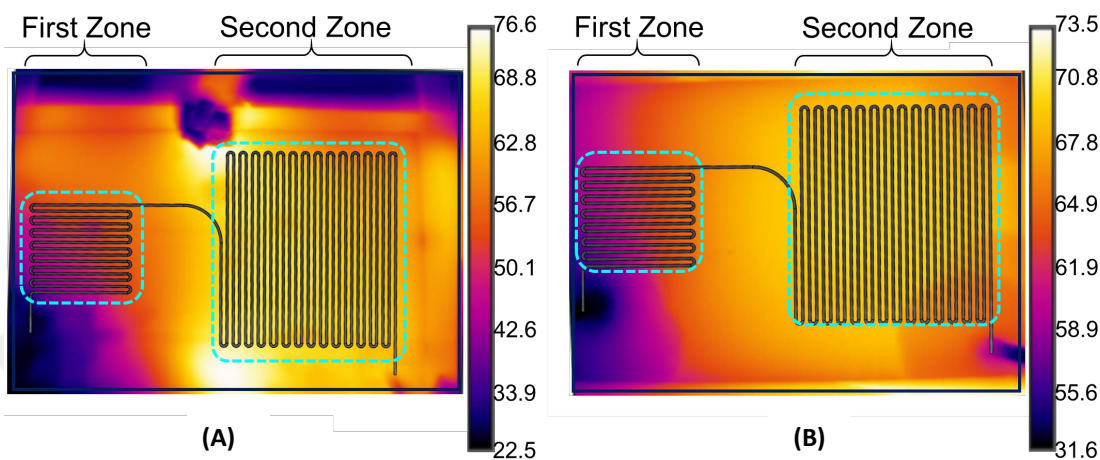


Figure 2.6: Thermal camera images of (A) electrode embedded microfluidic reactor and (B) microfluidic reactor placed on hot plate

of the hot plate. It was observed that at the center, the temperature of hot plate was over 70°C . From the center to the edge, the temperature was decreasing slightly and almost 4°C observed via thermal camera. Hence, the temperature distribution in the chip was homogeneous whereas the chip was on the hot plate could not be controlled precisely. As discussed before, almost 20°C was needed from the right edge to the left edge of the chip. So, the first zone of reactor was placed after the hot plate which enables the control via voltage supplied to the embedded electrodes, hence two temperature zones could be created on the chip. However, on electrical connection parts, increase in temperature was observed since heater was not designed properly. In Figure 2.6-A, it can be seen that the first zone on the chip was at desired temperature.

The center and corner of the hot plate was at different temperature ranges and the variation was around 4°C . To obtain two different thermal regions in the microfluidic chip, the first zone of the reactor was placed at the corner of the hot plate and waited for steady-state to be reached for desired temperature in the second zone. Temperature of the second zone was more critical than the first one, since the reaction and dispersion fluid has restrictions like boiling point. This placement of the microfluidic reactor on the hot plate reduced the repeatability of

the experimental procedure. On the other hand, electrode embedded microfluidic reactors provided an opportunity to precisely control the temperature during the reactions repeatedly. The temperature of both zones could be controlled by changing voltage values. Each section was attached to the different DC power supplies sections as seen in Figure 2.4. The morphological character of poly(M-POSS) particles synthesized by using three different reactor types is given in Figure 2.7.

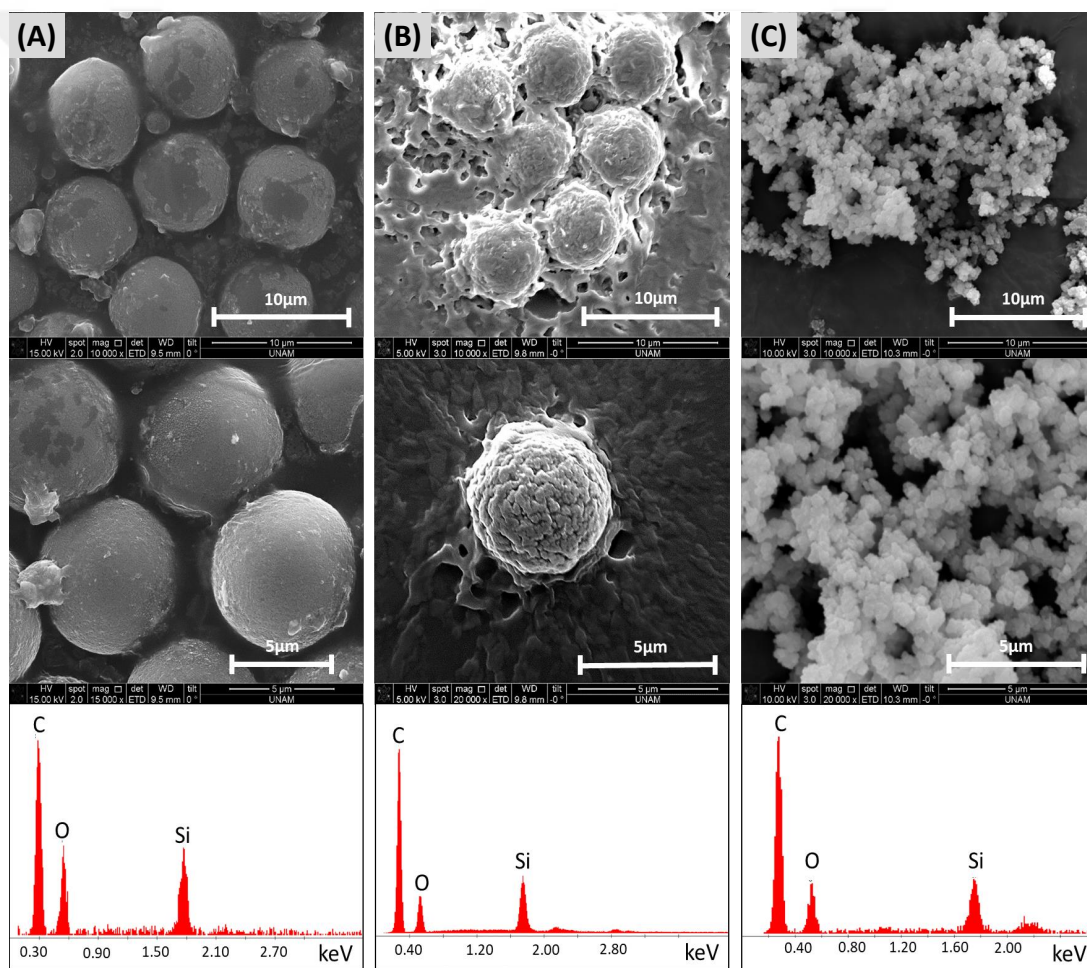


Figure 2.7: SEM images and EDX spectra of poly(M-POSS) synthesized in (A) microfluidic reactor placed on hot plate, (B) electrode embedded microfluidic reactor, and (C) conventional reactor

It can be clearly seen that round shaped poly(M-POSS) microparticles were

obtained using both of the microfluidic reactors. On the other hand, the conventional synthesis technique was not resulted in poly(M-POSS) microparticles. Although, magnetic stirring was sufficient for mixing the dispersion medium in the conventional reactor, it could not provide the required reaction control of the microreactor as opposed to the controlled mixing and heating in the microfluidic systems. The structure of the synthesized poly(M-POSS) particles is characterized by FTIR and EDX. As seen in Figure 2.7, all synthesized forms of poly(M-POSS) have organic (carbon and oxygen content) and inorganic (silicon) part on their surface. The chemical bonds of hybrid structure are defined and specified by FTIR as seen in Figure 2.8 and Table 2.1. It can be clearly seen that the pattern of FTIR peaks is the same for all synthesized structures. The cage (Si–O–Si) structure of silica peak is in the range of 1200–1050 cm^{-1} and strong stretching in 1100 cm^{-1} . The peak at 1730 cm^{-1} indicates C–O bonds, which comes from the methacrylate backbone of POSS on the poly(M-POSS) structure. The weak stretching vibration of C–H bonds is associated with the peaks at 2960–2890 cm^{-1} [62].

Table 2.1: FTIR peaks of synthesized Poly(M-POSS) structures

Functional Group	Wavenumber (cm^{-1})	Vibration Type
CH ₃	2960	Stretching vibration
CH ₂	2890	Stretching vibration
—C=O	1730	Stretching
—C—H	1470	Scissoring
—C—H	1390	Bending
—Si—C	1260	Asymmetric vibration
Si—O—Si	1100	Stretching vibration
C—O	981	Bending
CH ₂	913	Out-of-plane bending
CH ₂	851	Out-of-plane bending
C—H	754	Bending
Si—C	697	Stretching vibration

The comparative thermal degradation behaviors of synthesized poly(M-POSS) structures are given in Figure 2.9. The thermal degradation profiles of the microparticles synthesized by both of the microfluidic reactors are similar. The degradation process of poly(M-POSS) had three steps for all resultant products

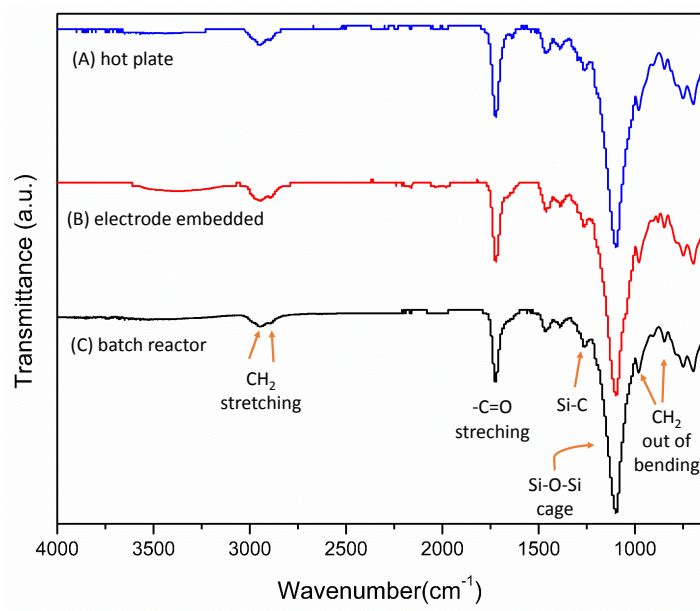


Figure 2.8: Surface chemical structural characteristics of synthesized poly(M-POSS) in (A) microfluidic reactor placed on hotplate, (B) electrode embedded microfluidic reactor, and (C) batch reactor.

in any synthesis technique. Compared to poly(M-POSS) microparticles, the nanocluster form of poly(M-POSS) synthesized with the conventional batch system has higher degradation temperature for the first step of degradation. The agglomeration on nanocluster structures altered the initial degradation profile. This difference could be explained by having more inter molecular bonding in the nanocluster structure. All synthesized poly(M-POSS) have very sharp decreasing peaks at the second inflection point in Figure 2.9 at DTG curves. All forms of poly(M-POSS) begin to decompose and significantly lose more than 35% of their organic part between 350 and 450°C. The specific point of degradation in which the weight loss reaches its maximum is nearly at 415°C for the poly(M-POSS) structures synthesized by using the batch system and electrode embedded microfluidic reactor. The poly(M-POSS) microparticles synthesized by using the microfluidic reactor placed on the hot plate have a degradation temperature of 419°C. This degradation profiles are similar to those of POSS composites, which were studied in the literature.

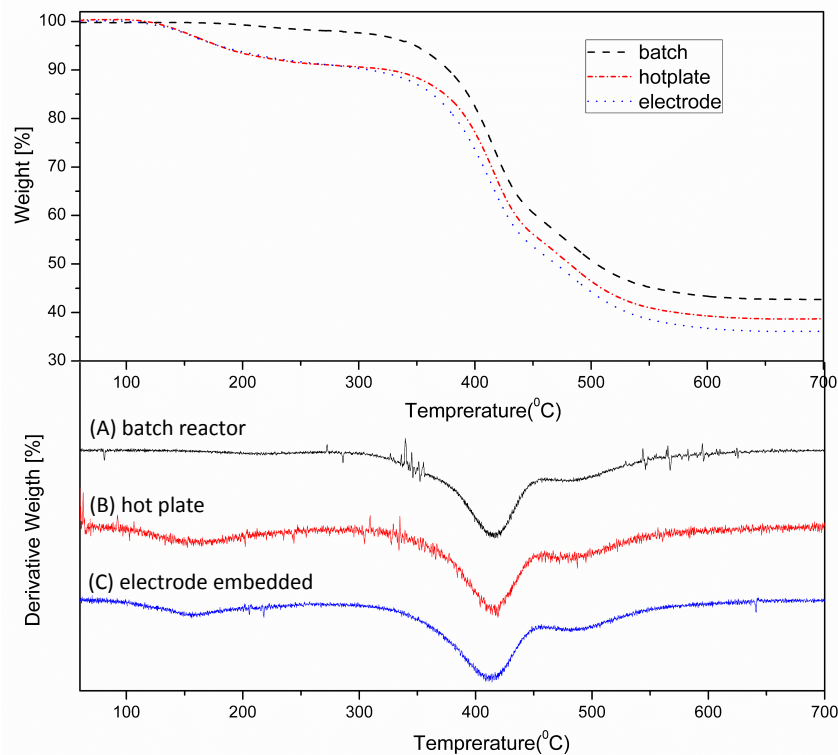


Figure 2.9: TGA and DTG curves weight % loss of poly(M-POSS) structures synthesized in (A) batch reactor, (B) microfluidic reactor placed on hotplate, and (C) electrode embedded microfluidic reactor.

The effect of initiator amount on the polymerization was analyzed by changing the mass ratio of AIBN while the other parameters were held constant as 0.125g POSS, 0.0125g PVP-K30 in 15ml dispersion medium. The initiator amount was changed as 0.03g, 0.06g, and 0.12g and was added to the prepared dispersion medium. The polymerization of each dispersion medium was performed within (i) the microfluidic reactor placed on the hotplate with a flow rate of $15\mu\text{l}/\text{min}$: (ii) the microfluidic reactor with embedded electrodes with a flow rate of $90\mu\text{l}/\text{min}$ flow. After the polymerization, since the particles were insoluble in ethanol, the resultant medium was washed with ethanol to remove the unreacted reaction medium. Then the remaining product was washed with water and dispersed in 1% SDS containing DDI-water.

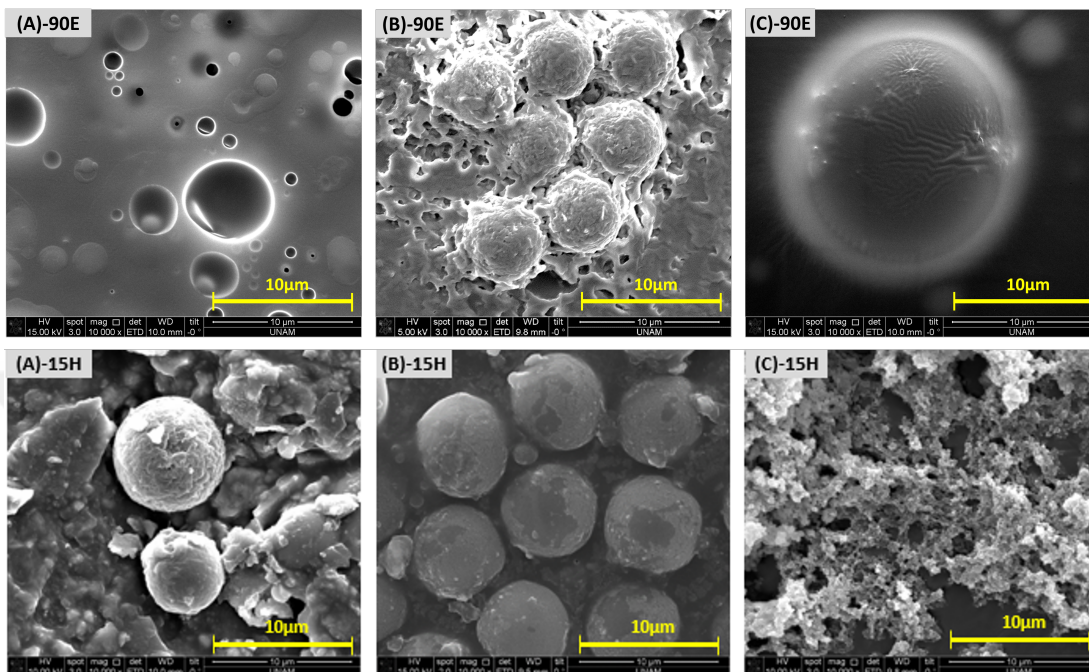


Figure 2.10: The morphological character of poly(M-POSS) microparticles while sweeping the initiator ratio(AIBN amount with respect to POSS amount by weight)(A) 25% (w/w), (B) 50% (w/w), (C) approximately equal amount to monomer. The microfluidic reactor placed on the hot plate (flow rate of $15\mu\text{l}/\text{min}$) is represented as -15H and the microfluidic reactor with embedded electrode (flow rate of $90\mu\text{l}/\text{min}$) is represented as -90E

As seen in Figure 2.10, the particle formation and size distribution change with the initiator amount. The spherical particle form begin to change towards nanoparticle form when the amount of initiator is increased in the microfluidic reactor placed on the hot plate. The reason of this change could be explained by the nature of the free radical polymerization mechanisms, and flow rate. Basically, initiator attacked to the double bond ($\text{C}=\text{C}$) vinyl group of methacrylate part of POSS structure and created free radicals in the dispersion medium. During the polymerization, these free radicals made bonds with each other in the microchannel. The increasing amount of the initiator creates more free radicals, which could increase the possibility of making bonds in the channel at reduced flow rates. The nanocluster form was obtained by increasing the amount of

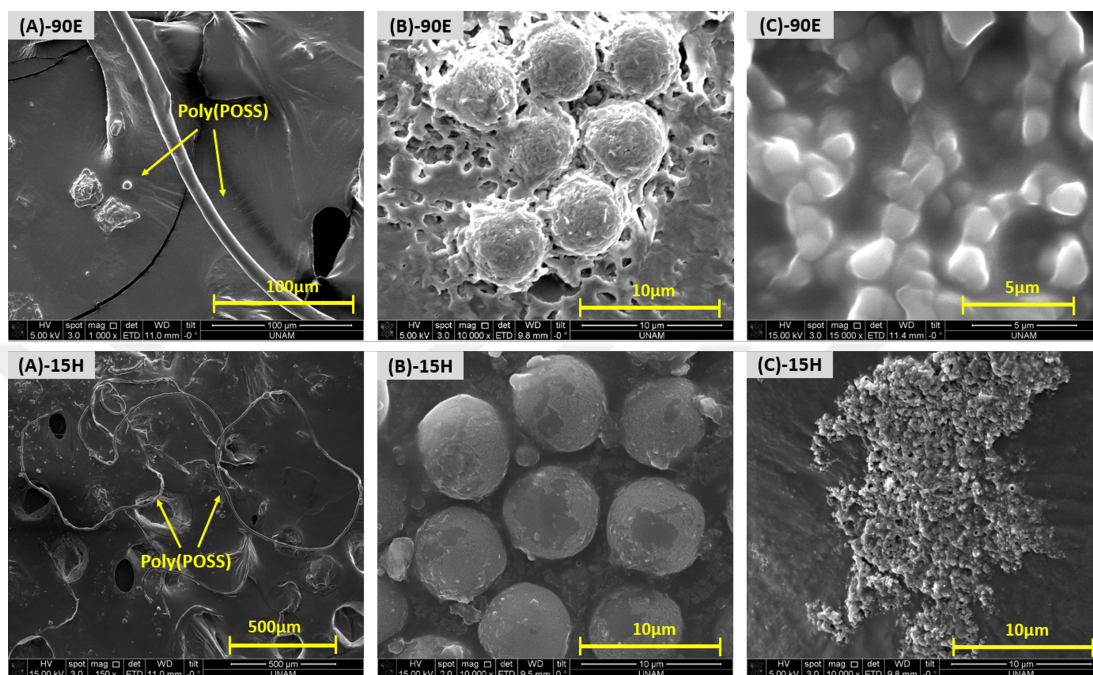


Figure 2.11: The morphological character of poly(POSS) polymerization within the microfluidic reactor with embedded electrodes by changing the stabilizer ratio to dispersion (PVP K-30 amount with respect to dispersion medium by weight /volume): (A) 0.04% (w/v), (B) 0.075% (w/v), (C) 0.14% (w/v) while the other parameters held constant. The microfluidic reactor placed on the hot plate (flow rate of $15\mu\text{l}/\text{min}$) is represented as -15H and the microfluidic reactor with embedded electrode (flow rate of $90\mu\text{l}/\text{min}$) is represented as -90E

initiator at slow flow rates in microfluidic system placed on the hot plate. In addition, few minutes later after the initiation of polymerization, the channels got clogged by the formed poly(M-POSS) nanoclusters due to the slow fluid flow (i.e. low drag force on the clusters) and hydrophobic interaction between PDMS and poly(M-POSS) in nanocluster form.

The effect of the stabilizer amount on the polymerization was analyzed by changing the mass ratio of PVP K-30 while the other parameters held constant. The constant parameters were prepared as 0.06g AIBN, 0.125g POSS in 15ml of dispersion medium. The initiator amount was changed as 0.006g, 0.0112g, and 0.022g and added to the prepared dispersion medium.

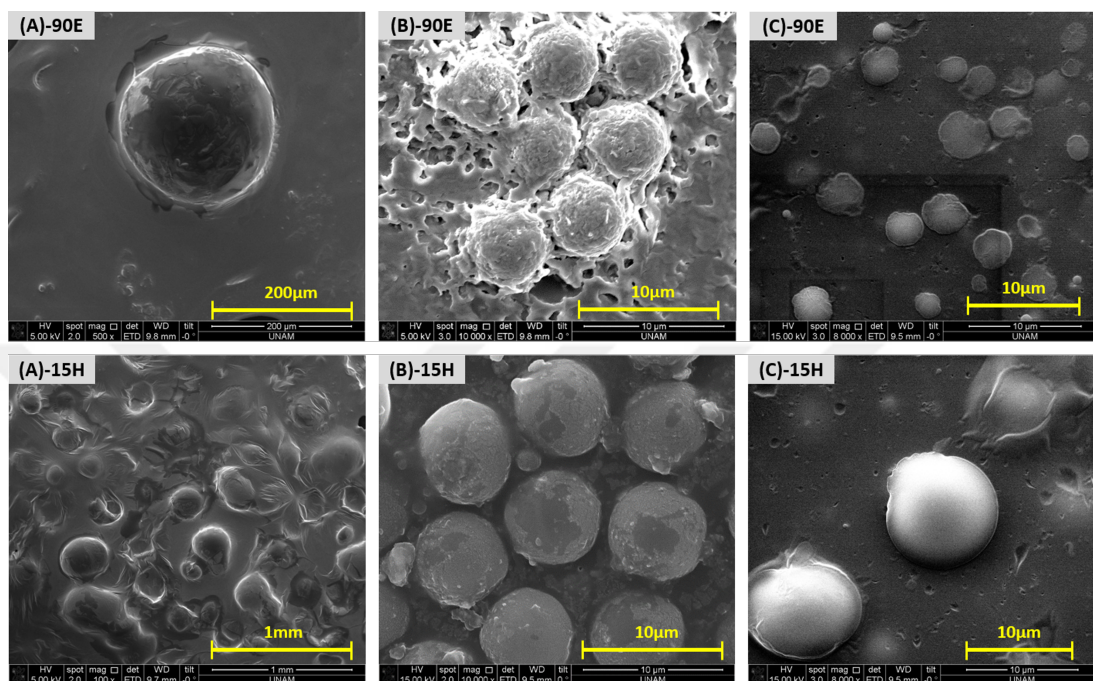


Figure 2.12: The morphological character of poly(M-POSS) microparticles while sweeping monomer ratio to dispersion (POSS amount with respect to dispersion medium by weight /volume):(A) 0.4% (w/v); (B) 0.8% (w/v), (C) 1.6% (w/v) while the other parameters held constant. The microfluidic reactor placed on the hot plate (flow rate of $15\mu\text{l}/\text{min}$) is represented as -15H and the microfluidic reactor with embedded electrode (flow rate of $90\mu\text{l}/\text{min}$) is represented as -90E

The particle form of poly(M-POSS) cannot be obtained by decreasing amount of stabilizer (PVP K30) as seen in Figure 2.11-A-15H and Figure 2.11-A-90E. Mostly, the characteristic of poly(M-POSS) structure was obtained in the form of nanowires because the free radicals created sticky ends and randomly bonded in the dispersion medium. Increasing of stabilizer provided a dispersion medium, which was suitable to generate particle shape poly(M-POSS) structure as seen in Figure 2.11-B-15H and Figure 2.11-B-90E. It was observed that the particle size got smaller and eventually form nanoclusters in the presence of high amount stabilizer as seen in Figure 2.11-C-15H and Figure 2.11-C-90E.

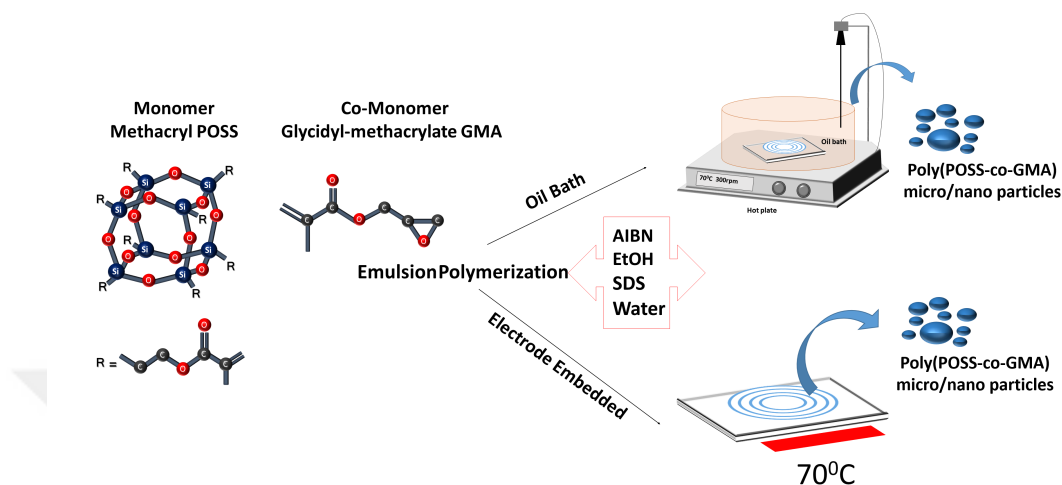
The effect of monomer amount on the polymerization was analyzed by changing the mass ratio of POSS while the other parameters held constant. The constant

parameters were prepared as 0.06g AIBN, 0.0112g PVP-K30 in 15 ml of dispersion medium. The monomer amount was changed as 0.06g, 0.125g, and 0.250g and added to the prepared dispersion medium. The morphological characteristics of poly(M-POSS) polymerization within the microfluidic reactor placed on the hotplate and microfluidic reactor with embedded electrodes by varying monomer ratio are given in Figure 2.12-15H and Figure 2.12-90E, respectively. As seen in Figures 2.12-15H, the reduction in monomer amount adversely affected the formation of regular shape particle in the microfluidic reactor. Increasing monomer amount in the dispersion medium increased the size of the resultant product. On the contrary, the particle diameter decreased with an increase in monomer ratio in the dispersion medium in electrode embedded microfluidic reactor as seen in Figure 2.12-90E. In addition, the amount of resultant product was increased by an increase in monomer with polydisperse size distribution range as seen in Figure 2.12-(C)-90E. The differences of these two behaviors could be explained by efficient heating mechanisms with appropriate flow rate for the initiation step of the free radical polymerization in dispersion medium. When the initiator activated by heat and attacked to create free radical groups of POSS, there must be sufficient amount of monomer in continuous flow medium for the polymerization. As seen from the Figure 2.12, the flow rate of microfluidic reactor placed on hot plate was provided appropriate medium to obtain particle shape poly(M-POSS) at low monomer amounts Figure 2.12-(A)-15H. The electrode embedded microfluidic system was more suitable with higher flow rate; even at low monomer amount ratios, the giant microparticles (approximately $200\mu\text{m}$ which is half of the channel width) was still produces by using it with low amount of resultant product Figure 2.12-(A)-90E.

Chapter 3

Synthesis of Poly(M-POSS-co-GMA) Microparticles

Chapter 3 introduces poly(M-POSS-co-GMA) organic-inorganic hybrid synthesis via emulsion polymerization. Two different configurations namely, microfluidic chip in oil bath and microfluidic chip with embedded electrode, are utilized to synthesis of microparticles. Materials used in synthesis and methods used in characterization are introduced. How to design the electrode by utilizing COMSOL software and how to fabricate designed chip is presented. Change in polymerization parameters have been investigated and presented. Characterization of synthesized particles synthesized under different polymerization conditions are studied. Graphical abstract of this chapter is below.



3.1 Materials and Methods

3.1.1 Materials

Main hybrid monomer, Methacryl Polyhedral Oligomeric Silsesquioxane (POSS) cage mixture (MA-0735) was purchased from Hybrid Plastics Inc (Hattiesburg, MS, USA)). Co-monomer glycidyl methacrylate (GMA), an emulsifying agent sodium dodecyl sulfate (SDS) and thermal initiator 2,2 -Azobisisobutyronitrile (AIBN), which was recrystallized from methanol before use, were obtained from Sigma-Aldrich (Schnelldorf, Germany). The Millipore/Direct Q-3UV water purification system was used to supply distilled deionized (DDI) water. Absolute ethanol (Abs EtOH), methanol, 2-propanol and acetone was purchased from Merck (Kenilworth, NJ, USA)). Sylgard 184 Polydimethylsiloxane (PDMS) and curing agent was purchased from Dow Corning (Midland, MI, USA).

3.1.2 Reactor Types

Two types of microfluidic reactor were utilized to synthesize poly(M-POSS-co-GMA) microparticles via emulsion polymerization method. First microfluidic reactor was immersed into oil bath which is on hot plate. Hot plate was adjusted temperature using thermocouple as seen in Figure 3.5. Second one was microfluidic reactor with embedded electrodes which was designed by using Comsol Multiphysics. The solution is composed of distilled deionized (DDI) water as an emulsion medium, a thermal initiator, POSS and Glisidil Metakrilat (GMA) monomers and stabilizers. Due to the nature of the reaction, homogeneous 70°C temperature distribution is enough in microfluidic reactor.

3.2 Design of Embedded Electrode Microfluidic Reactor

Simulations in COMSOL provide information about how the temperature is distributed in chip when it reaches steady state and how electrodes should be designed. Since the temperature in channels can not be measured precisely, simulations provide insight about temperature distribution in channels. Throughout the experiments, it is observed that temperature distribution on PDMS surface is match with the results in simulation. Hence, temperature in channels can be guessed according to simulation. Spiral channels geometry was fabricated because of the fact that compare to the straight channels, spiral channels had a smaller footprint. Smaller footprint made temperature control easier for this application since there was no need to control multiple temperature zones. Designed channels had a dimension of 200 μ m by 200 μ m. The distance between the channels was 400 μ m in order to machine the brass easily and total length of the channels was 1150 mm with 20 turns as seen in Figure 3.4-(a). Since the thermal conductivity of silicon (130[W/(mK)]) is higher than that of glass (1.38[W/(mK)]), as a substrate silicon wafer was preferred to achieve better homogeneity in temperature. Moreover, silicon wafer have better surface quality compare to glass types. Hence,

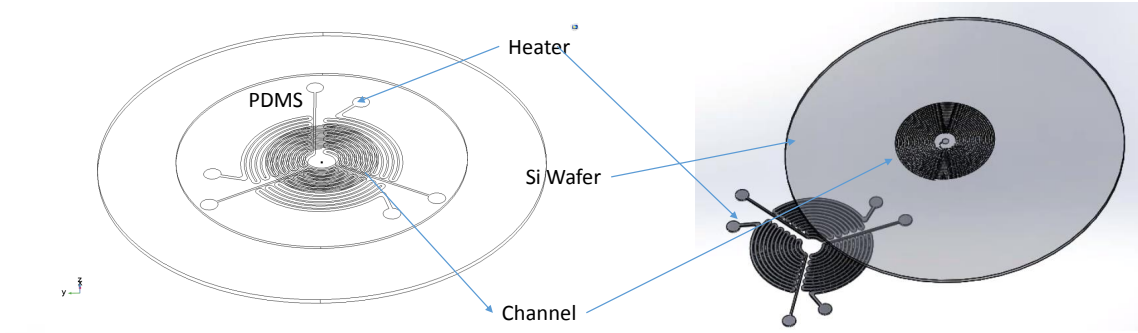


Figure 3.1: Depiction of microfluidic reactor

thermal evaporation and sputtering operations are more successful in Si wafer. As an input for the simulation, convective heat transfer occurs on chip surfaces. Joule Heating was applied at the back of the wafer using thin film electrode. Inside the channels, convective heating occurs. Utilizing these input data shown in Figure 3.2, flow and heat transfer coupled Comsol Multiphysics model was constructed. In heat transfer module, boundary heat source was defined on electrodes to simulate Joule heating. In addition, heat flux was defined on the chip surface. In order to simulate the convective heat transfer and to define the flow properties, non-isothermal pipe flow was implemented. Center of the spiral as inlet and outer edge of the spiral as outlet was defined. Wall heat transfer was added to the module to ensure the convective heat transfer. Newtonian fluid model with quadratic discretionary for all variables was employed. Non-isothermal pipe flow provides 1D approach to CFD simulation. Instead of 3D computation, 2D computation is enough using this module. Thanks to non-isothermal pipe flow module, number of degrees of freedom is decreased.

Since the thin film is deposited on surface, Electric Currents Shell module was employed in order to simulate the thin film behavior. Using this module film behavior can be captured without 3D simulations. Ground and electrical connections were defined on designed heater which is drawn in SolidWorks. As seen in Figure 3.2, homogeneous temperature distribution is achieved in microfluidic chip.

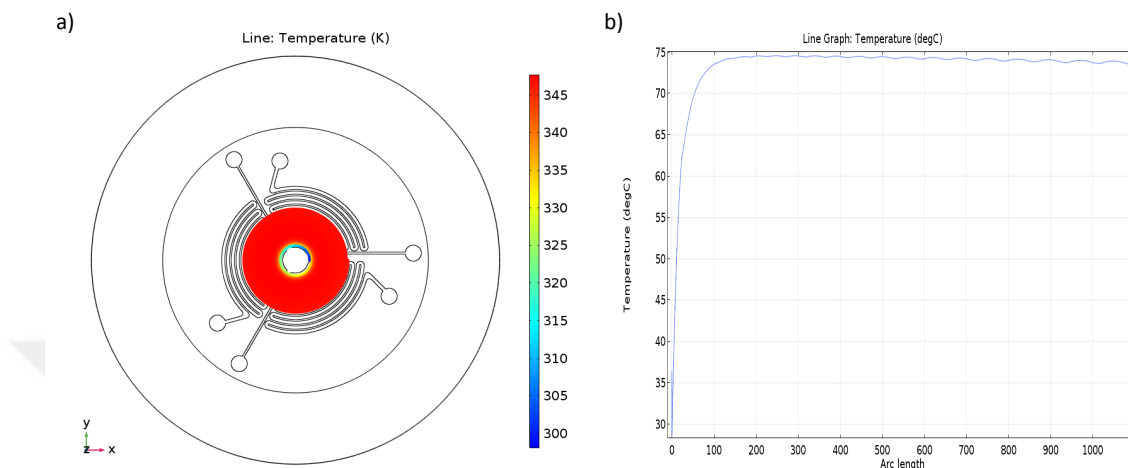


Figure 3.2: Temperature distribution in microfluidic reactor

3.3 Fabrication of Microfluidic Reactors

Microfluidic chip was prepared to be used in a heated oil bath. Brass mold was processed on micromachining center in order to obtain the mold in Figure 3.4-(A). Simple chemical cleaning procedure was employed to clean the mold. The PDMS mixture, which was stirred at a ratio of 1:10 by mass and degassed, was poured into the mold, then degassed again. After the process, it is baked at 80°C for 90 minutes. The crosslinked PDMS mold formed the channels and PDMS was removed from the master mold as seen in Figure 3.4-(B). The inlets and outlets were punched out. Microscope slide was subjected to simple chemical cleaning and clean glass and PDMS channels was adhered via asher. PVC tubing was connected and sealed with PDMS mixture in which PDMS base and a curing agent mixed in a 5:1 mass ratio.

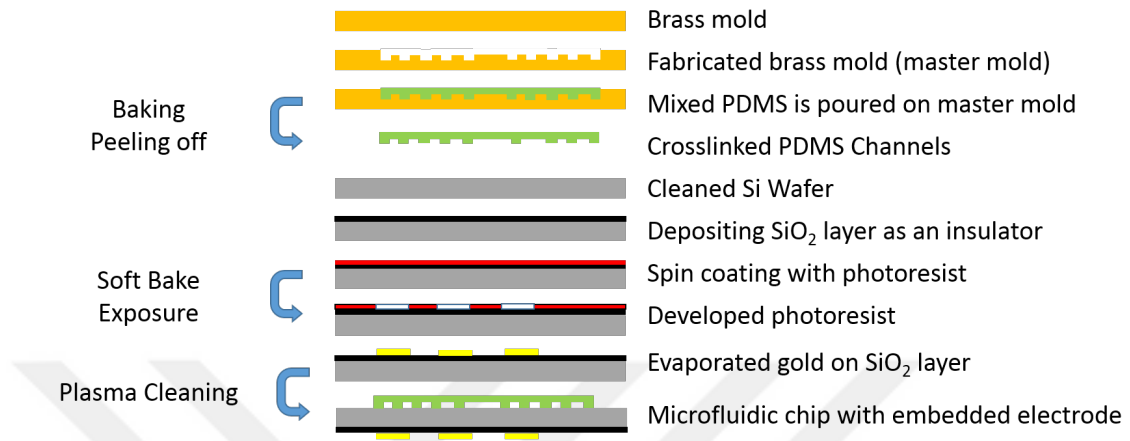


Figure 3.3: Demonstration of fabrication steps of microfluidic reactor with embedded electrode

Microfluidic reactor with an embedded electrode was fabricated as a second configuration. PDMS bonding and thin film electrode bonding qualities were affected by quality of surface. Hence, double side polished SI prime wafer (UniversityWafer, Inc, USA) with $500\mu\text{m}$ thickness was chosen in order to get smoother surface. After PDMS channels were prepared as seen in Figure 3.4-(A,B). The steps for fabrication is given below and demonstration of fabrication steps are presented in 3.3.

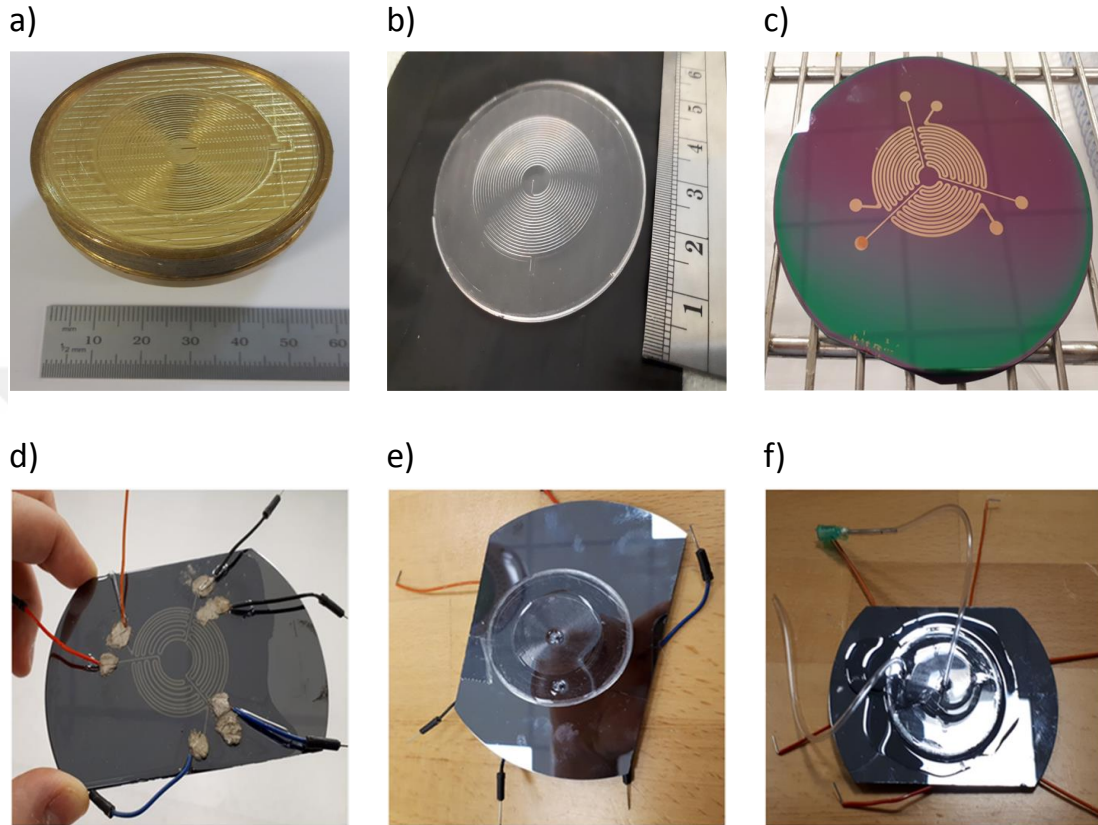


Figure 3.4: Fabrication steps of microfluidic reactor with embedded electrode: A) fabricated brass mold, B) Crosslinked PDMS channels, C) after growing SiO_2 on the back side, thin film heater is deposited on surface, D) electrical connections on the heater, E) Si wafer bonded with PDMS channels, F) final version of chip

1. Simple Chemical Cleaning Procedure was followed to clean Si wafer.
2. Since Si wafer was highly electrically conductive, in UNAM cleanroom Plasma-enhanced chemical vapor deposition(PECVD) (Plasma-Therm, LLC) was used to grow silicon dioxide as a insulation layer on a back side of wafer.
3. Wafer Priming with hexamethyldisilazane(HMDS) to produce a polar surface on back side of the wafer before photoresist coating. This step ensured the adhesion of photoresist.

- (a) HMDS should be around 20°C.
- (b) Spin coating of HMDS
 - i. Parameters: 30 Sec, 4000 rpm and 1000*rpm/s*
- 4. Spin coating of photoresist (positive photoresist AZ 5214E)
 - (a) Photoresist should be around 20°C.
 - (b) Parameters: 30 sec, 4000 rpm and 1000*rpm/s*
 - (c) This parameters caused edge bead configuration which was preferable among waveform or corona configurations for this application.
- 5. Soft bake in hot plate to increasing photoresist density by evaporating the solvent in PR
 - (a) Parameters: 110°C for 60-75 sec
 - (b) Keep the wafer at room temperature for 5 min
- 6. Exposure step to transfer the futures
 - (a) Since the feature of the heater was more than the resolution of the printer, instead of Cr photomask, acetate paper was preferred. It was cheaper and easier to print compare to the Cr mask.
 - (b) Parameters:
 - i. Process: Manual Top Slide
 - ii. Process Mode: Transparent
 - iii. Exposure Mode: Constant Dose
 - iv. Contact Mode: Soft Contact
 - v. Separation: 200 nm
 - vi. Thickness of the mask: 2.3 mm
 - vii. Thickness of Substrate: 0.5 mm
 - viii. Thickness of Resist: 1.5 μm
 - ix. Dose: 400*mJ/cm*⁻²

7. Development by using mixture of AZ 400K with DI-Water.
 - (a) Mix AZ 400K with DI-Water, 5:40 by mass ratio
 - (b) Put the wafer into mixture for 5 minutes
 - (c) Inspection of the features under the microscope every 2 minutes.
8. Hard bake in hot plate to harden the photoresist
 - (a) Parameters: 100°C for 8-12 min
 - (b) Keep the wafer at room temperature for 10 min
9. Thermal Evaporation using thermal evaporator (MiDAS PVD 3T, VAKSIS, Inc, Turkey)
 - (a) Chromium as a mid layer and Gold as a main layer are deposited on the surface and 3.4-(C) is obtained.
 - (b) Parameters:
 - i. For Cr Density:7.2 and Impedance: 28.95
 - ii. For Gold Density:19.3 and Impedance: 23.18
10. Plasma cleaning using Asher in UNAM Cleanroom to bond the embedded electrode wafer with PDMS channels and 3.4-(E) is achieved.
11. Electrode connections are attached employing silver conductive epoxy (Elecolit 325, Panacol,Inc) as seen in 3.4-(D).
 - (a) Parameters: base A and base B of the elecolit is mixed 1:1 by mass ratio
 - (b) Baked at 50°C for 2 hours.
12. PVC tubing connections at the inlet and outlet was sealed by applying PDMS (mixed 5:1 by mass ratio) and baked at 80°C for 90 min as seen in 3.4-(F).

3.4 Experimentation

In order to synthesize the poly(M-POSS-co-GMA) microparticles, emulsion polymerization was used in microreactor environment. Since in dispersion polymerization the number of particles was low, polymerization technique was changed. Miscelles in emulsion provided controlled reaction environments and each one were acted as reactors. Moreover, co-polymerization was ensured by using miscelles. If dispersion was used, poly(GMA) and poly(M-POSS) might be observed. Polymerization medium was prepared as follows: POSS as a main hybrid monomer, GMA as co-monomer and AIBN as a thermal initiator was dissolved in EtOH by using ultrasonication for 5 min. SDS as an emulsifying agent was added in DDI water. The emulsion medium was sonicated for 5 min. The transparent monomer and initiator containing solution was immediately added into SDS dissolved DDI water. The solution color spontaneously turned into white and emulsion medium was again sonicated 5 min. The final emulsion was polymerized in microfluidic chips in two types of heating system. The emulsions prepared in two different monomer ratios are given in Table 3.1.

Table 3.1: Amount of mixture components in experiments

POSS	0.1g	0.1g
GMA	0.05ml	0.1ml
AIBN	0.02g	0.02g
ETOH	0.3ml	0.3ml
WATER	5ml	5ml
SDS	0.0125g	0.0125g

The first configuration was microfluidic reactor immersed in an oil bath which was heated up using a hot plate. As seen in Figure 3.5, the hot plate was adjusted temperature via thermocouple. By using magnetic stirrer at the center of the bath, homogeneous temperature distribution was tried to achieve in the oil bath.

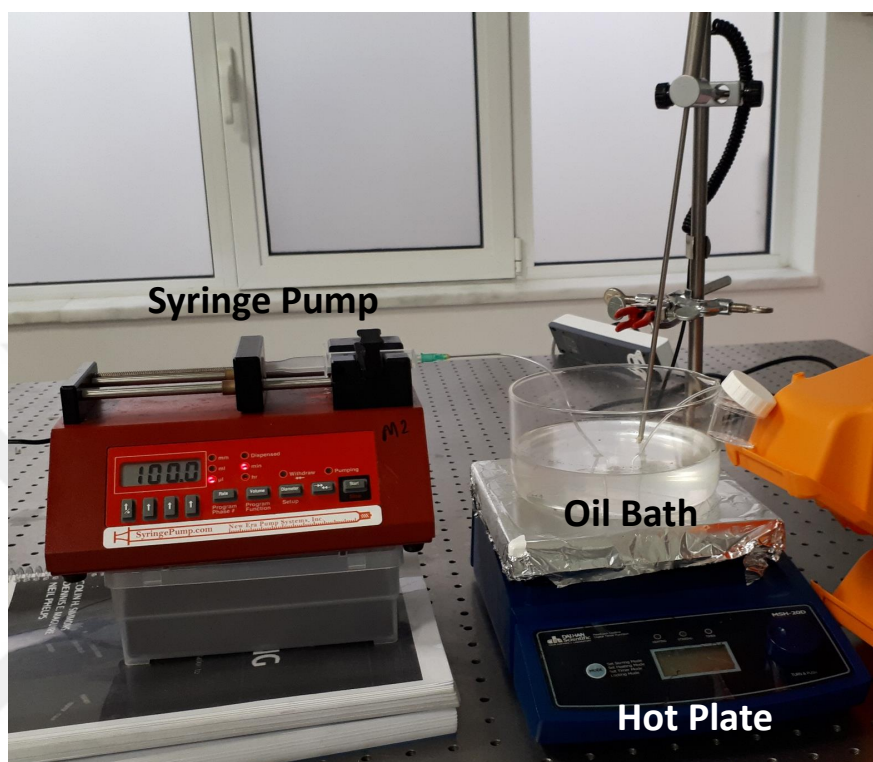


Figure 3.5: Experimental set up of microfluidic reactor in oil bath

However, the center was always at higher temperature compare to the edge. Microfluidic chip in oil bath system was heated by hot plate and as discussed in Section 2, hot plate had disadvantages while temperature on chip was important. In addition to drawbacks of hot plate, oil bath had a huge volume compare to channels in microfluidic chip. In oil bath, since the thermal mass was higher than the embedded electrode, it was harder to control temperature. More precise control on temperature in chip was provided via embedded electrode which is designed based on simulation in COMSOL Multiphysics.

As seen in the schematic in Figure 3.6, the magnetic stirrer was at 300 rpm and bath was at 70°C. After the steady-state was achieved in oil bath, emulsion medium was pumped into the reactor. It is important to wait till the steady-state, otherwise repeatability of the experiment becomes questionable. In addition, the reactor and thermocouple needed to be aligned and in each experiment, the

reactor should be located at the same point. Hence, it was not easy to construct same configuration for each experiment.

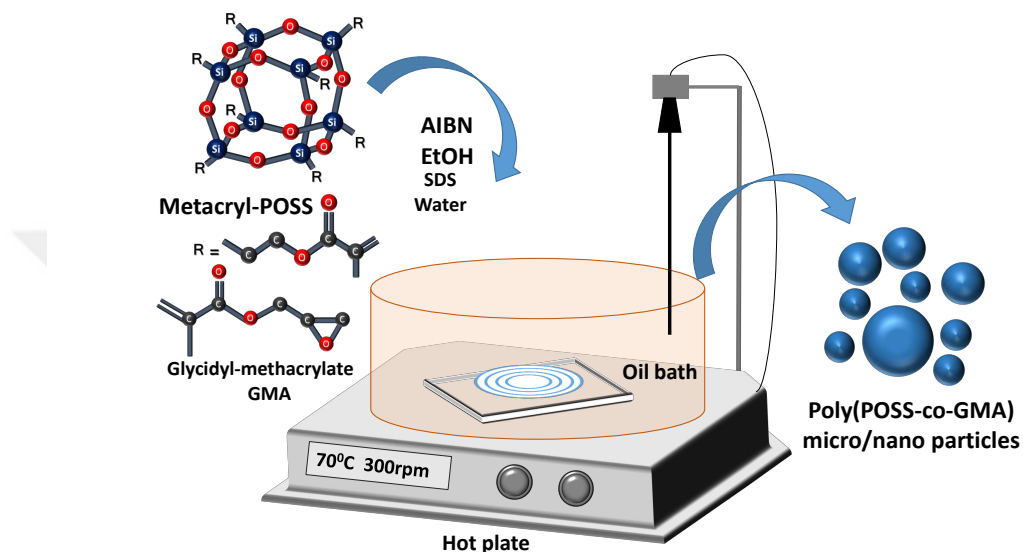


Figure 3.6: Synthesis schematic of POSS GMA in immersed microfluidic reactor

The polymerization medium was prepared as 100% (wt/wt) main monomer. For this, 0.1 g POSS monomer in 300 μ l EtOH by 5min ultrasonication. Then, the thermal initiator 0.02 AIBN was added into solution and dissolved in ultrasonic batch. The 0.0125 g SDS was added in 5 ml DDI water. The emulsion medium was sonicated another 5 min. The transparent monomer and initiator containing solution was immediately added in SDS dissolved DDI water. The solution color spontaneously turned into white and this emulsion medium was sonicated 5 min more. Prepared emulsion medium was pumped into microfluidic reactor in different flow rate 90 μ l/min, 40 μ l/min and 20 μ l/min. Obtained material was centrifuged at 10000 rpm for 3 min and white precipitation is washed by EtOH and DDI water by several time to remove unreacted reaction medium. The morphological character of washed product was analyzed by SEM-EDAX.

The effect of flow rate onto morphological character to final product investigated by SEM. Compared to three different flow rate products, the best result was

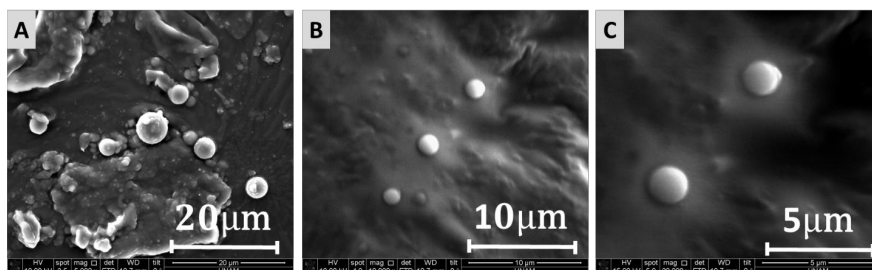


Figure 3.7: The morphological character of poly(POSS) particles obtained by 90 $\mu\text{l}/\text{min}$ flow rate in different magnification bar A)5000X, B) 10000X, C) 20000X

obtained with 40 $\mu\text{l}/\text{min}$ in more monodisperse form in Figure 3.8. The high flow rate regime 90 $\mu\text{l}/\text{min}$ was not enough to convert the poss monomer to polymeric microparticle form as seen in Figure 3.7. The low flow rate regime 20 $\mu\text{l}/\text{min}$ was provided sufficient heat to active the thermal initiator AIBN for the polymerization in Figure 3.9. However; the microparticles begin to loose their spherical form and monodispersity and more likely gelation tendency was observed.

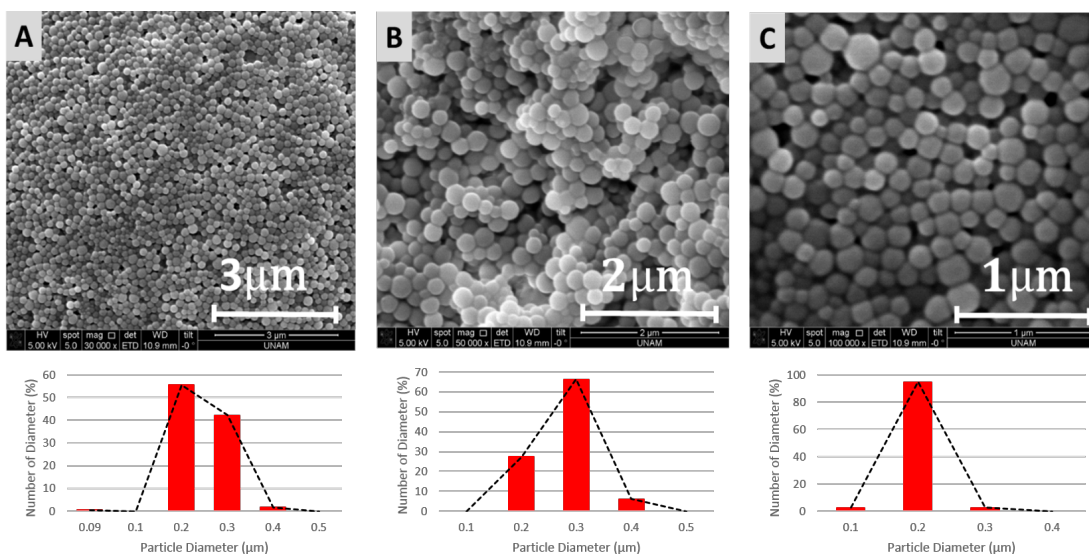


Figure 3.8: The morphological character and size distribution of poly(POSS) particles obtained by 40 $\mu\text{l}/\text{min}$ flow rate in different magnification A)30,000X, B) 50,000X, C) 100,000X

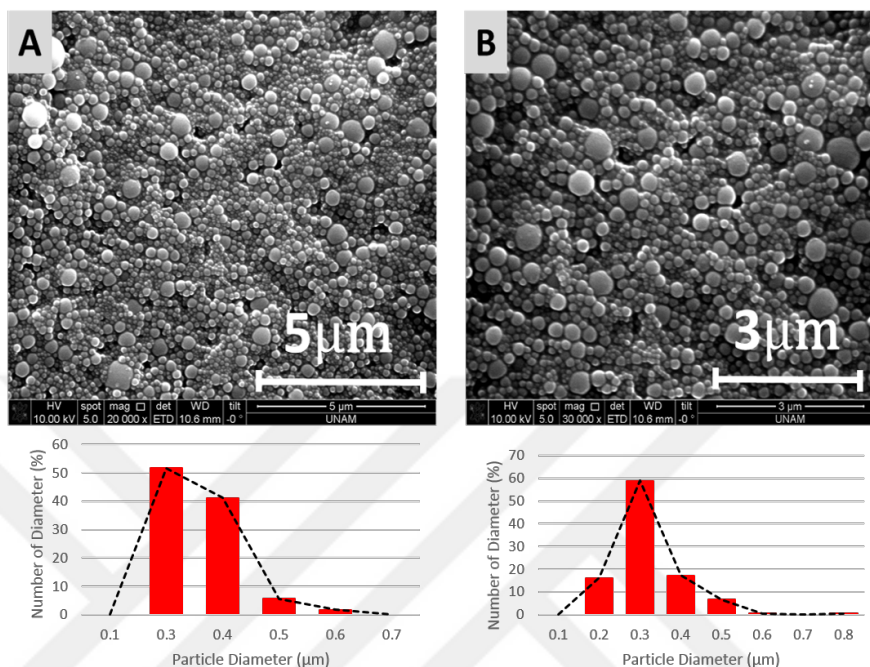


Figure 3.9: The morphological character and size distribution of poly(POSS) particles obtained by 20 $\mu\text{l}/\text{min}$ flow rate in different magnification A) 20,000X, B) 30,000X

The second configuration was microfluidic reactor with embedded thin film heater. As seen in 3.10, three different DC power supplies were employed to supply enough amount of voltage. Syringe pump was used to adjust the flow rate and FLIR thermal camera and thermocouples were aligned to get right feedback in order to adjust temperature in reactor. The polymerization medium was prepared as 50% (wt/wt) main monomer with parameters given in Table 3.1. For this, POSS monomer and GMA as co-monomer dissolved in EtOH by 5min ultrasonication. Then AIBN was added into solution and dissolved in ultrasonic batch. The SDS is added in DDI water. The emulsion medium was sonicated another 5 min. The transparent monomer and initiator containing solution was immediately added in SDS dissolved DDI water. The solution color spontaneously turns into white and this emulsion medium was sonicated 5 min more. The final emulsion was polymerized in microfluidic chips in electrode embedded.

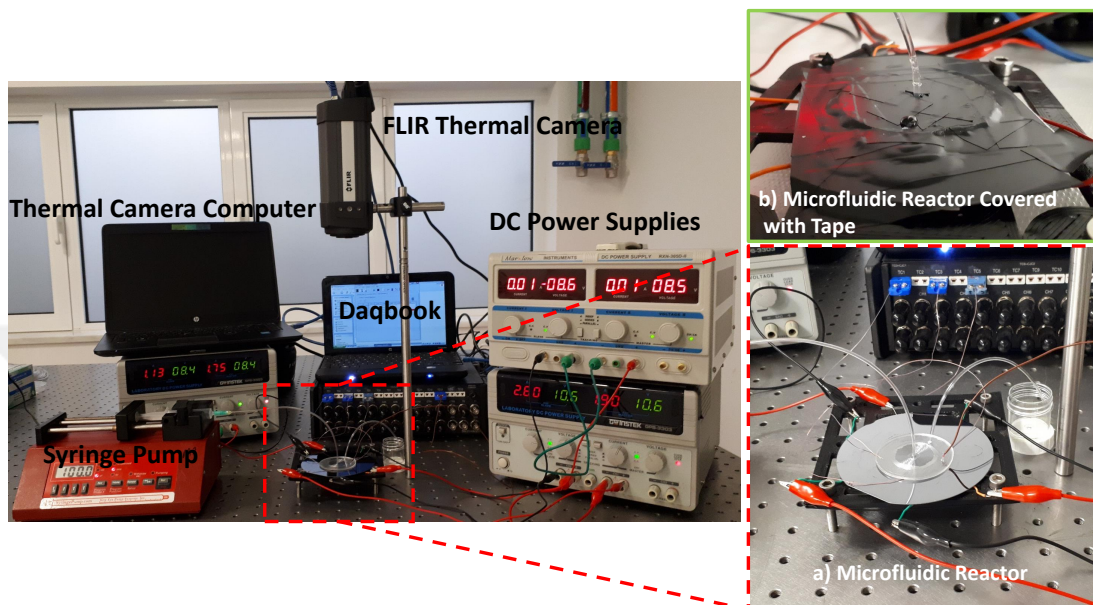


Figure 3.10: Experimental set up of heater integrated microfluidic reactor

Morphological character of poly(M-POSS-co-GMA) particles is shown in Figure 3.11. The spherical particles were obtained in polydisperse form with $50 \mu\text{l}/\text{min}$ flow rate. Addition of co-monomer epoxy functional GMA effected the final product morphology. Particles are agglomerated because the during the polymerization the sticky ends of monomers (the double bonds) are opened by thermal initiator and made new bonds uncontrollably. The percentage of co-monomer GMA is decreased as 5% by weight in total monomer amount with parameters given in Table 3.1 to observe the effects on final product. Same procedure was followed. Decreasing co-monomer amount was effected the general morphology of the particles. The gelation was decreased. The spherical form of the particles is apparently observed in Figures 3.12 and 3.13. Additionally, compared to oil bath heating system, the higher flow rate for the synthesis results in higher throughput per unit time.

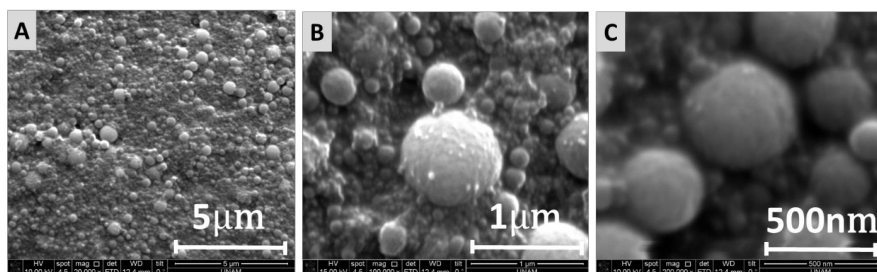


Figure 3.11: The morphological character of poly(M-POSS-co-GMA) particles obtained by 5ul/min flow rate in different magnification bar A)20000X, B) 100000X, C) 200000X

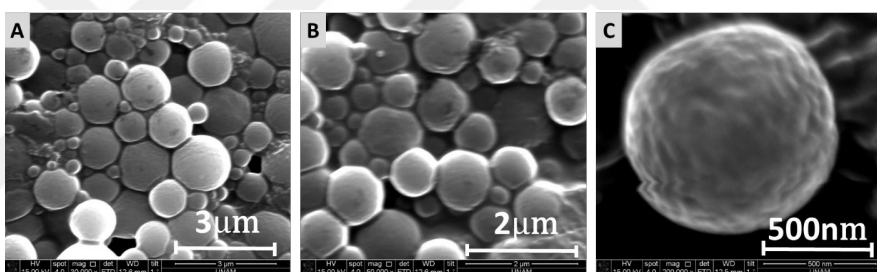


Figure 3.12: The morphological character of poly(POSS-co-GMA) particles containing 5% GMA as co-monomer in weight obtained by 50ul/min flow rate in different magnification bar A)20000X, B) 30000X, C) 50000X

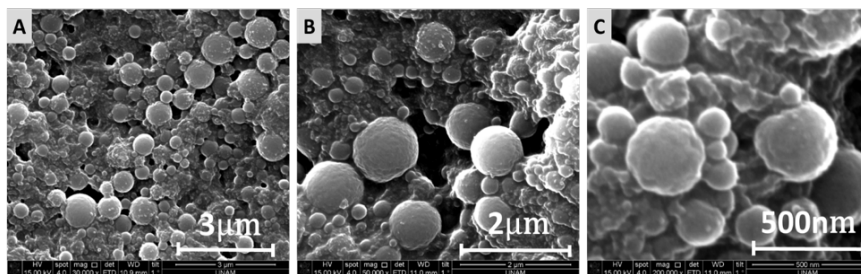


Figure 3.13: The morphological character of poly(POSS-co-GMA) particles containing 5% GMA as co-monomer in weight obtained by 100ul/min flow rate in different magnification bar A)20000X, B) 30000X, C) 50000X

It can be clearly seen that round shaped poly(M-POSS-co-GMA) microparticles were obtained using both of the microfluidic reactors. The structure of the synthesized poly(M-POSS) particles is characterized by FTIR and EDX. As seen in Figure 3.15, poly(M-POSS-co-GMA) and poly(M-POSS) have organic (carbon and oxygen content) and inorganic (silicon) part on their surface. The chemical bonds of hybrid structure are defined and specified by FTIR as seen in Figure 3.14. It can be clearly seen that the pattern of FTIR peaks is the same for all synthesized structures. The cage (Si–O–Si) structure of silica peak is in the range of $1200\text{--}1050\text{ cm}^{-1}$ and strong stretching in 1100 cm^{-1} . The peak at 1730 cm^{-1} indicates --C=O bonds, which comes from the methacrylate backbone of POSS on structures. The weak stretching vibration of C–H bonds is associated with the peaks at $2960\text{--}2890\text{ cm}^{-1}$ [62]. The peaks at 1260 cm^{-1} , 850 cm^{-1} and 755 cm^{-1} are attributed to the Si–C bonds.

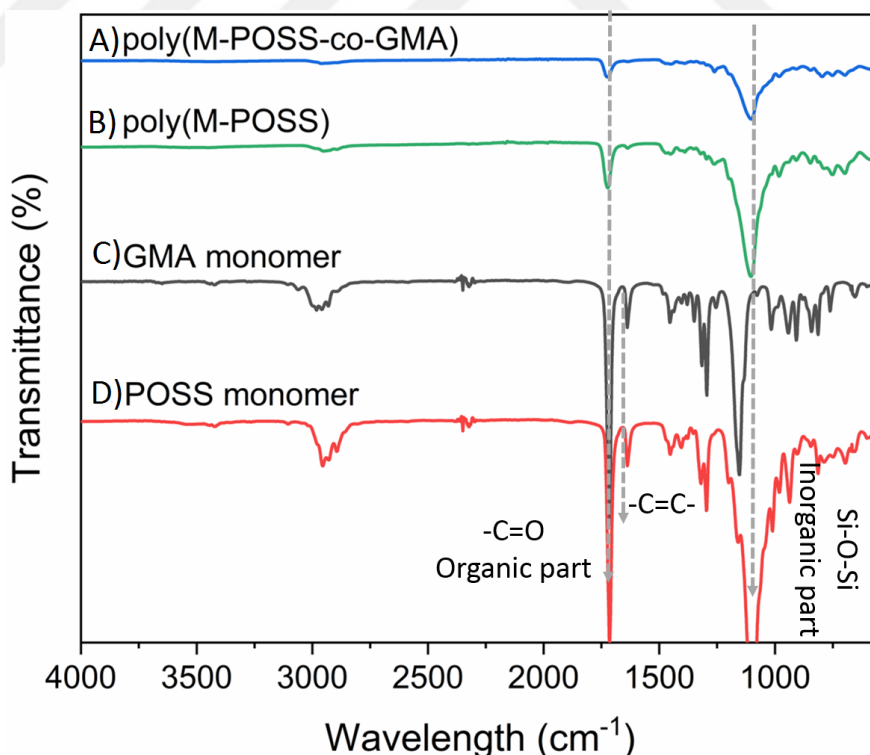


Figure 3.14: FTIR comparison of POSS monomer, GMA co-monomer, poly(M-POSS) and poly(M-POSS-co-GMA)

As seen in Figure 3.14, monomers have -C=C- vinyl groups which appear at 1640cm^{-1} , but in poly(M-POSS) and poly(M-POSS-co-GMA) the peak disappears which indicates double bond stretching was removed by polymerization. Monomers are converted to polymer. Comparison of the poly(POSS) and poly(M-POSS-co-GMA) are presented in Figure 3.15. In figure Figure 3.15, the fingerprint region of FTIR spectrum was clearly exhibited the functional group of GMA co-monomer. The strong peak at 1100cm^{-1} belonged to Si-O-Si cage structure of POSS as an inorganic part of the hybrid structure. The organic part was obtained from metacryl back bone of monomers and it can be seen as -C=O bond at 1730cm^{-1} .

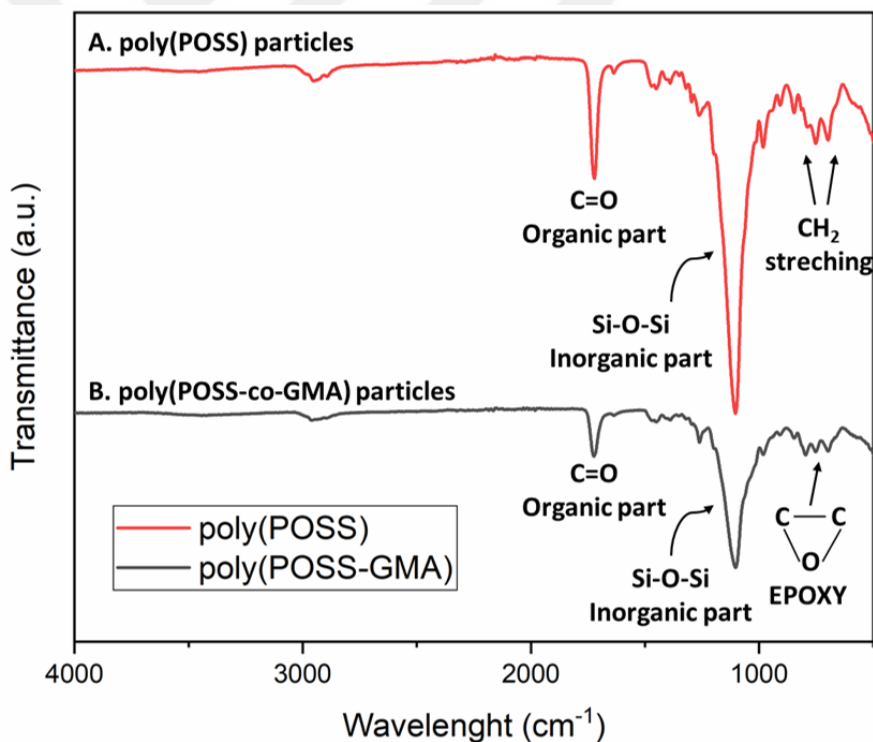


Figure 3.15: FTIR comparison of poly(M-POSS) and poly(M-POSS-co-GMA)

Chapter 4

Summary and Future Research Directions

Microfluidic systems offers great premises in many different areas such as point of care, lab-on-a-chip systems, chemical systems, genome technologies etc. Their unique characteristics such as less amount of time to complete a reaction, handling differential volume, cheap manufacturing, high throughput, controlled reaction environment and portability [1, 3, 4]. Thanks to these advances, chemist is get familiar to microfluidic systems since the beginning of the 1990s [1]. In laboratories, instead of huge flask or glass based tools, microfluidic reactors have been used, due to specific advances like temperature as reaction parameter is easily controlled in differential volume. Moreover, handling less amount of volume provide faster results and reaction times. The effect of the change in mix components can be observed immediately. Hence, researchers can try different mixtures in lesser time [4].

This thesis presented use of microfluidic reactors in synthesis of microparticles under different conditions. Two different polymerization types namely dispersion and emulsion was utilized and different microfluidic reactor configurations were employed to synthesize microparticles via dispersion and emulsion polymerization. Dispersion polymerization ended up microparticle formation in microfluidic

reactors. First configuration was microfluidic chip on hot plate. Trials in chip ended up with poly(M-POSS) microparticles. To get more control on temperature distribution thin film electrode was deposited under the microfluidic chip and by changing voltage values temperature in zones was controlled. Microparticle formation was observed also in microfluidic chip with embedded electrode. Since microfluidics reactors require less amount of reagent and the reaction is completed faster compare to conventional reactors, effect of monomer amount, stabilizer amount and initiator amount was studied. On the other hand, it was observed that by using same recipe for dispersion medium, in conventional batch system nanocluster formation was observed instead of microparticle. EDX image showed that C, O and S existed in result and FTIR image confirmed that chemical structure was same as resultant particles in microfluidic systems. However, in SEM images, it was observed that size of the results were smaller than micron. Moreover, in TGA, temperature of first step of degradation was higher and initial degradation profile was altered. Hence, it was concluded that extra bonds in cluster enforced these changes and the result was nanocluster. Problems in second stage of dispersion, in which bond formation is completed, can be responsible for this cluster formation. As a future direction, different type of stabilizer might be used to ensure micro/nano particle formation. Furthermore, X-ray photoelectron spectroscopy (XPS) can be used to get deeper insight information about surface chemistry. Moreover, due to their carbon-silica composite structure, the nature of poly(M-POSS) is a revolutionary next generation hybrid material. The poly(M-POSS) structures in the form of microparticles or nanoclusters have strong potential in many application areas. Depending on their high thermal resistance, biocompatible behavior of the silica part and easy modification of carbon content of poly(M-POSS) make them suitable for dental materials, energy saving materials, and/or fillers. The micrometer size of hybrid particles could be suitable in stationary phase of chromatographic separation systems. Poly(M-POSS)microparticles could be further derivatized in the magnetic form or decorated with noble metals for uses such as SERS detection, catalysis, magnetic separation of DNA, RNA or hyperthermia studies on cancer research.

As a second part of the thesis, poly(M-POSS-co-GMA) microparticles were

synthesized via emulsion polymerization in microfluidic reactors. In both reactors, poly(M-POSS-co-GMA) was produced. Design and fabrication steps of microfluidic reactors was given. Effect of different flow rates were investigated and optimum flow rates were shown. For further studies, droplet based microfluidic reactors can be utilized with embedded electrode. In continuous flow reactors, clogging is common due to the fact that reaction takes place in the medium. However, in droplet based systems, reaction is completed in droplet. The reagent ratios can be controlled and manipulated by changing the flow rate [4–6]. In addition to droplet based microfluidic reactor, liquid–liquid multiphase flow can be employed with embedded electrode. Since there is no contact with micro channels walls, clogging will not be observed. Narrower particle size distribution is expected [6].

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Appendix A

Simple Chemical Cleaning

Simple Chemical Cleaning procedure is used in different operations such as cleaning of mold, microscope slides, Si wafer. Since it is common procedure, it is presented in Appendix. "...” represents the product that is cleaned

1. Immerse the into acetone bath with ultrasonic agitation (Kudos SK1200H) for 5 min,
2. Immerse the into 2-propanol bath with ultrasonic agitation for 5 min
3. Immerse the into De-Ionized Water(DI-Water) bath with ultrasonic agitation for 5 min
4. Rinse ... under the free flowing DI-Water for 15 sec
5. Dry by blowing air/nitrogen
6. Put ... into convection oven at 80 °C for 5 min

Appendix B

Technical Drawings

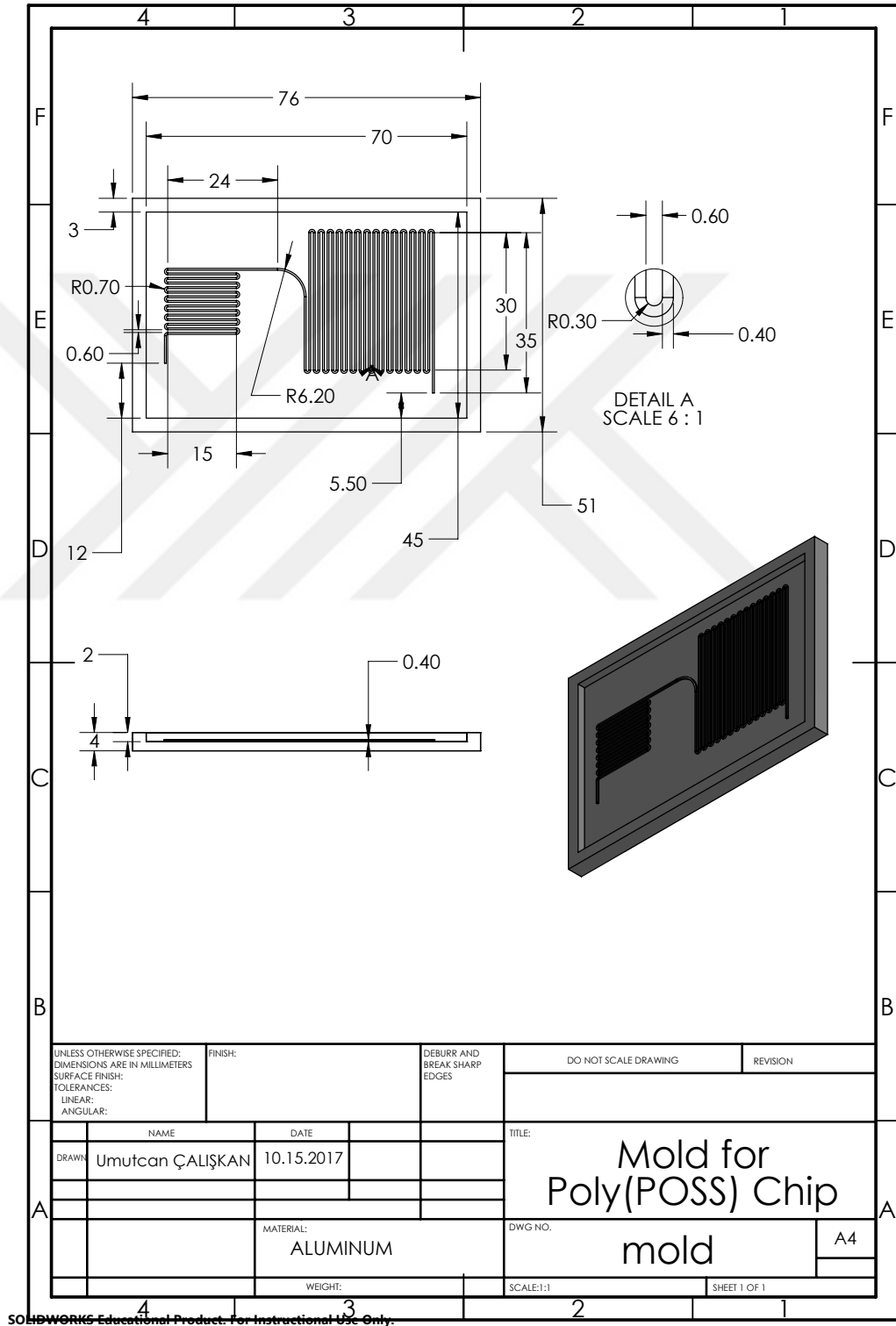


Figure B.1: Technical Drawing of the POSS microfluidic chip