One-Pot Synthesis of Organic–Inorganic Hybrid Polyhedral Oligomeric Silsesquioxane Microparticles in a Double-Zone Temperature Controlled Microfluidic Reactor

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ABSTRACT: Polyhedral oligomeric silsesquioxane (POSS) particles are one of the smallest organosilica nano-cage structures with high multifunctionality that show both organic and inorganic properties. Until now poly(POSS) structures have been synthesized from beginning with a methacryl-POSS monomer in free-radical mechanism with batch-wise methods that use sacrificial templates or additional multisteps. This study introduces a novel one-pot synthesis inside a continuous flow, double temperature zone microfluidic reactor where the methodology is based on dispersion polymerization. As a result, spherical

monodisperse POSS microparticles were obtained and characterized to determine their morphology, surface chemical structure, and thermal behavior by SEM, FTIR, and TGA, respectively. These results were also compared and reported with the outcomes of batch-wise synthesis. © 2019 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2019**, 57, 1396–1403

KEYWORDS: dispersion polymerization; hybrid microparticles; microfluidic reactor; microparticle synthesis; microreactor; nanocluster; organosilica; POSS; thermal control

INTRODUCTION 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 biocompatible and have prespecified wetting characteristics (hydrophobic/hydrophilic); in addition to these, their inorganic part gives them unique mechanical, electrical, and magnetic properties.^{1–5} Consequently, they have several potential application areas such as drug delivery, imaging, fuel cells, photocatalysts, cosmetics, packaging.^{3,6} 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 substituents. Having organic structures at the exterior of the material makes them compatible with other polymers that broaden their application field.²

The cage structure of polyhedral POSS—or poly(POSS)—and its derivatives have already been used for various applications. For instance, the biocompatibility, thermal resistance, hardness, and composite structure of poly(POSS) was utilized for dental applications.^{7,8} Poly(POSS) was also used as an additive to enhance the thermal properties of materials.⁹ The mechanical and electrochemical properties of poly(POSS) also enabled

them to be used as energy storage materials, proton exchange membranes, and supercapacitors.¹⁰ The cage structure and its functional groups allowed them to be used as a metal-free catalysis for the polymerization of polycaprolactone.¹¹ 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.¹²

The synthesis of functional poly(POSS) was done by using photo initiation, thermal initiation, or click chemistry.¹² Additionally, methacryl-POSS monomer was used as copolymer to obtain microparticles by RAFT precipitation polymerization and used as a drug carrier.¹³ All of these chemical synthesis techniques took place in conventional batch reactors, and until now poly(POSS) microparticles without any additional copolymer was not successful to obtain by a dispersion polymerization method in these systems. In this article, we introduce the synthesis of poly(POSS) in particle form with dispersion polymerization inside a microfluidic system for the first time.

Microfluidic reactors are one of the most promising tools in materials research for the synthesis of micro and nanoparticles. Their ability of providing precise control over reaction conditions such as residence time in second, concentration of reagents

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in nanoliters to microliters, mixing ratios and temperature, compared to conventional batch-wise techniques, lead to monodisperse particle sizes and shapes.^{14,15} Until today, microfluidic reactors, or microreactors, were utilized to synthesize several different types of particles such as metals,^{16,17} metal oxides,^{18,19} polymers,^{20,21} metal-organic frameworks,²² quantum dots^{23,24} as well as hybrid particles.^{25,26} These studies were successful in synthesizing micro/nanoparticles with improved properties compared to the conventional batch techniques. These reactors were designed based on the requirements of the reaction to be carried inside. Flow in microreactors can be droplet based or continuous, and they can have a controlled heating for processes that require high temperatures. Overall, these studies were able to achieve better results compared to the batch techniques in terms of size and shape distribution as well as morphology.

In the last few years, there were several microfluidic reactors that were used for the synthesis of hybrid nanoparticles^{27–30} and microparticles.^{26,31–36} Among these, Hong et al., synthesized liposome-hydrogel hybrid nanoparticles by utilizing hydrodynamic flow focusing; Zhang et al., Liu et al. and Feng et al. demonstrated the synthesis of core-shell nanoparticles composed of polymer core and lipid shell in continuous flow reactors for mainly drug delivery purposes^{28–30}; Shiba et al. demonstrated the synthesis of nanoporous, monodispersed titanium dioxide-octadecylamine particles in a continuous-flow microreactor³¹; Prasad et al. synthesized hybrid Janus microspheres in a droplet-based device with 3.5% of size variation³²; Lan et al. and Zhao et al. employed microreactors to synthesize hybrid microspheres composed of chitosan and silica^{26,34–36}; and Lan et al. performed an interface reaction to synthesize titania-silica core-shell microparticles in a droplet-based device.³³ Table 1 summarizes the literature on hybrid particle synthesis for both batch methods and microfluidic approaches.

To the best of authors' knowledge this is the first study in the literature to obtain poly(POSS) microparticles by using a temperature-controlled microfluidic reactor. The synthesis method was developed by utilizing three different reactors which were (a) conventional batch reactor, (b) microfluidic reactor placed on hotplate, and (c) electrode embedded

microfluidic reactor. The batch system was not suitable to produce microparticle form of poly(POSS) by dispersion polymerization whereas due to the controlled mixing in small scales, it was possible to apply this method in microfluidic systems.

In microfluidic reactors, the polymerization parameters such as flow rate and concentration were optimized in preliminary studies. First, the flow rates were varied from 15 to 90 $\mu\text{L}/\text{min}$, and then the optimum flow rates for the microfluidic reactor and initiator, monomer and stabilizer concentrations in the dispersion medium were varied to determine the effects on polymerization. In all steps, the morphological changes were evaluated by SEM. The surface chemical structure of poly(POSS) were characterized by FTIR, and the thermal degradation behaviors of synthesized poly(POSS) in three different reactors were analyzed by TGA. As a result, simple one-pot synthesis procedure was developed to obtain novel organic-inorganic hybrid microparticles by dispersion polymerization in microfluidic reactors.

EXPERIMENTAL

Materials and Methods

Main monomer methacryl POSS cage mixture (MA-0735) was purchased from Hybrid Plastics Inc (Hattiesburg, MS, USA). The linear nonionic stabilizer Polyvinylpyrrolidone (PVP) K-30, sodium dodecyl sulfate SDS were obtained from Sigma-Aldrich (Schnelldorf, Germany). The thermal initiator AIBN (Azobisisobutyronitrile) was washed with methanol and recrystallized before it was used and also bought from Sigma-Aldrich (Schnelldorf, Germany). Reaction and flow medium absolute ethanol and other solvents acetone, 2-propanol were purchased from Merck (Kenilworth, NJ, USA). Distilled deionized (DDI) water was supplied from Millipore/Direct Q-3UV water purification system. Aluminum block (10 cm $\times$ 10 cm) was used for the mold preparation. Sylgard 184 Polydimethylsiloxane (PDMS) and curing agent was purchased from Dow Corning (Midland, MI, USA).

Fabrication of the Microfluidic System

Channel geometry is designed in computer-aided software SolidWorks. The mold was fabricated by a 3-axis micro-machining center (PROINO Z3X Micro Maker, Mikro Protez Ltd.

TABLE 1 Hybrid Particles in Literature

Material	Reactor/Reaction Type	Application	Ref
Methacryl-functionalized POSS	Batch-wise synthesis	Dental applications	7
POSS nanocomposite resin	Batch-wise synthesis	Dental applications	8
POSS-containing hyperbranched sulfonic acid groups	Batch-wise oxidation based synthesis	Not specified (NS)	11
Molecularly imprinted polymer (MIP) microparticles containing methacryl POSS	RAFT precipitation polymerization	Anti-cancer drug	13
Liposome-hydrogel hybrid nanoparticles	Microreactor/flow focusing device	Targeted drug delivery	27
Polymer core-lipid shell nanoparticles	Continuous flow microreactor	Drug delivery	28–30
Monodispersed titanium dioxide-octadecylamine particles	Continuous flow microreactor	NS	31
Hybrid Janus microspheres	Droplet-based microreactor	NS	32
Hybrid chitosan and silica microspheres	Microreactor	NS	26,34–36
Titania-silica core shell microparticles	Microfluidic interface reaction	NS	33

Şti, Ankara, Turkey). Fabricated mold was used as master for PDMS chip as shown in Figure 1(A). After the fabrication, mold was soaked in 2-propanol with ultrasonic agitation to deburr the fabricated mold. To clean the surface of the mold, it was soaked into acetone, 2-propanol, and DDI water with ultrasonic agitation, finally it was heated in oven at 100 °C.

Afterward, PDMS mixture consisting of prepolymer and a curing agent was mixed in 10:1 by mass ratio and degassed under vacuum at room temperature. Degassed PDMS blend was poured into the aluminum mold and heated at 80 °C for 90 min. The cross-linked PDMS replica was gently removed from master mold without damaging the microchannels. The inlet and outlet ports were opened by hole punching.

A glass slide to seal the channels was cleaned by soaking in acetone, 2-propanol, and DI water in ultrasonic bath for 5 min in each steps. The slide was dried with air blow and heated in oven. The punched PDMS replica and cleaned glass slide were treated in tabletop atmospheric plasma cleaner (Harrick Plasma Cleaner, Ithaca, NY, USA) for 40 s. After plasma treatment, the replica and glass were contacted for bonding. The prepared microfluidic channels had final dimensions of 400 µm × 400 µm (width × height) with 1177 mm length. Finally PVC serum tubing was connected to the inlets and outlets of the device for the delivery of the reagents as shown in Figure 1(B).

The newly designed microfluidic chip had two streamed sides for temperature control as shown in Figure 1(C). Chrome electrode structures were obtained on a glass surface via sputtering technique by using LH Leybold AG, L-560 (Cologne, Germany) in Bilkent University Advanced Research Laboratories.

Synthesis of Poly(POSS) Polymeric Cage Silica Microparticles

Organic–inorganic hybrid poly(POSS) microparticles were synthesized by dispersion polymerization technique. Absolute ethanol, AIBN, and PVP-K30 were used as solvents for the reaction. The reaction medium was prepared by dissolving 0.125 g POSS in 15 ml of ethanol. The stabilizer 0.0112 g PVP-K30 (0.1% w/w reaction medium) and thermal initiator 0.06 g AIBN were added into this mixture and put into ultrasonic bath for 2 min.

Syringe pumps (New Era type NE300, Farmingdale, NY, USA) were used to deliver liquids at desired rates to the microfluidic

devices. The reaction temperature was set to 70 °C on hotplate and gradually controlled in electrode embedded one from 50 to 70 °C. The reacted liquids were collected into a 2-ml Eppendorf at the outlet of the microfluidic reactor. 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 oil bath. The reaction took place on a hot plate for which the temperature was set to 70 °C. During the synthesis, magnetic stirring at 200 rpm for 12 h was used. At the end of the synthesis in all three reactors, poly(POSS) was collected by centrifugation for 5 min at 10000 rpm. Resultant white hybrid structures were washed with ethanol and DI water several times to remove unreacted medium and monomer. Finally, particles were dispersed in 1% SDS containing DI water.

Characterization

The morphological characteristics of hybrid structures were determined by SEM (Quanta 450 SEM; Akishima, Tokyo, Japan) using acceleration voltages of 5, 10, and 15 kV with 5 and 10 µm magnification bars. Energy dispersive X-ray spectroscopy was used to analyze the surface chemistry. The structure was analyzed by FT-IR (Nicolet 6700-Thermo Scientific, Waltham, MA, USA). The thermal behaviors of synthesized materials were determined by thermogravimetric analysis (TGA-PerkinElmer Diamond, Akron, OH, USA) with 10 °C/min working under air-flow in the temperature range of 50–700 °C. During polymerization, the temperature distribution on microfluidic chips was controlled using a DAQ controller (Iotech Daqbook/2000, Norton, MA, USA) and a thermal camera (FLIR A325sc, Sweden).

RESULTS AND DISCUSSION

The dispersion polymerization method was utilized in both microfluidic reactors and conventional batch system. Figure 2 shows the synthesis procedure of organic–inorganic hybrid structures with this method. As a result, with the conventional batch system, it was not possible to produce microparticles; instead nanoclusters were obtained. On the other hand, the microparticle form of poly(POSS) was successfully obtained by using microfluidic reactors. This could be explained with the advantage of preventing coagulation in microfluidic systems as opposed to large-scale systems in which active groups are sticking to each other due to nonuniform mixing rates.

FIGURE 1 Steps of microfluidic reactor fabrication: (A) Microfluidic mold, (B) PDMS microfluidic chip, and (C) Electrode embedded microfluidic chip. [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 2 Schematic representation of poly(POSS) synthesis by dispersion polymerization method. [Color figure can be viewed at wileyonlinelibrary.com]

The reaction took place at 70 °C for all production systems. First, the conventional batch technique was employed to obtain poly(POSS) microparticles. Generally, dispersion polymerization is useful to obtain uniform microparticles.³⁷ However, we showed that the monomer methacryl-POSS is not suitable to produce microparticles by dispersion polymerization in conventional batch reactor. The results obtained by this method are shown in Figure 3.

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 3. The

prepared dispersion medium was magnetically stirred at 250 rpm at 70 °C for 6 h to complete polymerization. The nanocluster structure of poly(POSS) were obtained as shown in Figure 3(A,B). The nanocluster forms have transformed into a bulk polymer form by increasing the amount of monomer as depicted in Figure 3(C). None of these cases resulted in microparticles.

In the development of the microfluidic synthesis of poly(POSS), the composition of the initiator dispersion mixture, monomer, and stabilizer ratios were determined by the preliminary studies (please see the Supporting Information). The designed microfluidic reactor has two different temperature zones. The first zone is for preheating, and the second one is for polymerization. The preheating zone is necessary to reach the initiator activation temperature, which is approximately 55 °C for AIBN. The second zone is set to 70 °C,

FIGURE 3 SEM image and morphological character of poly(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) [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 4 Thermal camera images of (A) microfluidic reactor placed on hot plate and (B) electrode embedded microfluidic reactor [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 5 SEM images and EDX spectra of poly(POSS) synthesized in (A) microfluidic reactor placed on hot plate, (B) electrode embedded microfluidic reactor, and (C) conventional reactor [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 6 Surface chemical structural characteristics of synthesized poly(POSS) in (A) microfluidic reactor placed on hotplate, (B) electrode embedded microfluidic reactor, and (C) batch reactor. [Color figure can be viewed at wileyonlinelibrary.com]

which is below the boiling temperature of the dispersion medium.

The heating required to activate the initiator and complete the polymerization was provided in two different ways as shown in Figure 4. First, the microfluidic reactor was placed on the hot plate that was at 70 °C [Fig. 4(A)]. As an alternative, the microfluidic reactor was heated with embedded electrodes [Fig. 4(B)]. In the second reactor, the temperature was precisely determined and checked for two different zones by using DAQ controller, while a thermal camera was used to monitor the temperature gradient on two different heating zones as illustrated in Figure 4.

As seen in Figure 4, the temperature gradient profiles show that both systems have two different heating zones by using the reaction medium absolute ethanol as mobile phase in microfluidic reactors. However, the microfluidic reactor placed on the hot plate could not be controlled precisely. The center and corner of the hot plate were at different temperature ranges. 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 gradient. This placement of microfluidic reactor on hot plate reduced repeatability of the experimental procedure. On the other hand, electrode embedded microfluidic reactor gave an opportunity to precisely control the temperature during the reaction.

The morphological character of poly(POSS) particles synthesized by using three different reactor types is given in Figure 5. It can be clearly seen that round-shaped (poly)POSS microparticles were obtained using both of the microfluidic reactors. On the other hand, the conventional synthesis technique did not result in poly(POSS) microparticles. Although, magnetic stirring was sufficient for mixing the dispersion medium in the conventional reactor, it could not provide required reaction

control of the microreactor as opposed to the controlled mixing and heating in microfluidic systems.

The structure of the synthesized poly(POSS) particles was characterized by FTIR and EDX. As seen in Figure 5, all synthesized forms of poly(POSS) have organic (carbon and oxygen content) and inorganic (silicon) part on their surface. The chemical bonds of hybrid structure were defined and specified by FTIR (Fig. 6 and Table 2). 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(POSS) structure. The weak stretching vibration of C—H bonds is associated with the peaks at 2960–2890 cm^{-1} .³⁸

The comparative thermal degradation behaviors of synthesized poly(POSS) structures are given in Figure 7. The thermal degradation profiles of microparticles synthesized by both of the microfluidic reactors were similar. The degradation process of poly(POSS) had three steps for all resultant products in any synthesis technique. The inflection points and degradation percentages (ΔY) are given in Table 3. The first step of degradations was around 158 and 156 °C for microparticles synthesized in both of the microfluidic reactors with a weight loss of approximately 9% at the first step. Compared to poly(POSS) microparticles, the nanocluster form of poly(POSS) synthesized with the conventional batch system has higher degradation temperature for the first step of degradation and the percentage of their weight loss is around 2.5% as reported in Table 3. Furthermore, the degradation peak was slightly visible, as shown in Figure 7 (A). The agglomeration on nanocluster structure altered the initial degradation profile. This difference could be explained by having more intermolecular bonding in the nanocluster structure.

All synthesized poly(POSS) had very sharp decreasing peaks at the second inflection point in Figure 7 at DTG curves. All forms of poly(POSS) began to decompose and significantly lose more than 35% of their organic part between 350 and 450 °C. The specific point of degradation in which

TABLE 2 FTIR Peaks of Synthesis Poly(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

FIGURE 7 TGA and DTG curves weight% loss of poly(POSS) structures synthesized in (A) batch reactor, (B) microfluidic reactor placed on hotplate, and (C) electrode embedded microfluidic reactor. [Color figure can be viewed at wileyonlinelibrary.com]

the weight loss reaches its maximum was nearly at 415 °C for the poly(POSS) structures synthesized by using the batch system and electrode-embedded microfluidic reactor. The poly(POSS) microparticles synthesized by using the microfluidic reactor placed on the hot plate had a degradation temperature of 419 °C. This degradation profiles were similar to those of POSS composites, which were studied in the literature.³⁹

The final step of degradation exhibited slow and weak characteristics, as shown in Figure 7. The thermal decomposition temperature of the batch synthesized poly(POSS) nanocluster structure was slightly higher than that of the microparticles synthesized by using microfluidic reactors, as given in Table 3. The nanocluster form of poly(POSS) could have the cross-

linking bonds between silica and carbon content of their structure. That is why their degradation profile is more stable than the microparticle form of poly(POSS).³⁹ It can be clearly seen that after the final degradation point of 480 °C, less than 40% of the ceramic part of the all poly(POSS) structures remained as residual in crucible (Table 3).

CONCLUSIONS

This study shows that it is possible to synthesize organic and inorganic hybrid poly(POSS) structures in the form of micrometer-sized particles by a single-step dispersion polymerization by utilizing microfluidic reactors. Moreover, it also presents a detailed analysis on how different reactor types affect the morphology of poly(POSS) structures. As a result of this study, it was found that poly(POSS) could be obtained in microparticle form by applying dispersion polymerization inside microfluidic reactors with double-temperature zones, while the same method produces poly(POSS) nanoclusters when applied in the conventional batch reactors. Compared to the conventional batch reactors, microfluidic reactors have an advantage to obtain fast optimization results with little amount of resultant product. The importance of one-step production technology is to eliminate the drawbacks such as very long reaction time and excess use of materials in all steps of production.

TABLE 3 Weight Loss of Poly(POSS)

Sample Name	Inflection Points					
	Step I	$\Delta Y\%$	Step II	$\Delta Y\%$	Step III	$\Delta Y\%$
Batch	229 °C	2.5	415 °C	40.5	490 °C	19.0
Hotplate	158 °C	9.4	419 °C	36.5	487 °C	15.9
Electrode embedded	156 °C	8.8	414 °C	36.7	482 °C	15.2

ΔY : percentage of decomposition.

Due to their carbon-silica composite structure, the nature of poly(POSS) is a revolutionary next generation hybrid material. The poly(POSS) structures in the form of micro particles 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(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. The novel poly(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 summary, we have focused on synthesizing poly(POSS) microparticles in temperature-controlled continuous microfluidic reactors and compared our results with the results obtained from a conventional batch reactor. As an emerging technology, microfluidics has been continuing to provide us new horizons to obtain novel materials with more control. We believe that the information gained from the present study will be an inspiration for developing further techniques to synthesize unique hybrid materials.

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