Production Polystyrene Micro-Emulsion as Template for Monolith Synthesis

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ABSTRACT Monolith have received much attention as high-performance chromatographic matrices due to its convective mass transfer and interconnected porous structure. Biodegradable polymers, free radicals and cross-linkers are among the templates used to form pore structure. However, poor heat dissipation and uneven pore size distribution across monolith remain as a key challenge in monolith fabrication. Therefore, this study aims to synthesize and characterize polystyrene micro-emulsion as template for monolith. The operating conditions for the synthesis of the polymeric micro-emulsion, that includes polymer concentration (14 - 35 wt %), surfactant concentration (1 - 9 wt %), temperature (30 - 70°C) and stirring rate (500 - 1000 rpm), were designed using Response Surface Methodology (RSM). The characterizations of resulting particles were observed using Scanning Electron Microscopy (SEM) and Inverted Microscope. The sizes of the particles were determined within range of 5.9 - 11.7 µm. Out of the 30 tested samples with different operating conditions, observation under the inverted microscope indicated homogenous particles of polystyrene microemulsion while some forming aggregations. Sample that was synthesized using 21 wt% polymer, 3 wt% surfactant, stirring rate at 875 rpm and heated at 40 °C resulted homogenous particles with particle diameter ranging from 7.92 µm to 8.80 µm. Good particle homogeneity was also obtained at a higher polymer concentration (35 wt %) using similar surfactant concentration and operating temperature at slower stirring rate (625 rpm). Samples aggregation were observed when using 35 wt % polymer, 7 wt % surfactant heated at 50°C at 750 rpm as well as sample under parameter of 25 wt% polymer wt % surfactant for 60°C stirring at 875 rpm. The findings of the study provide useful insights on the feasibility of polymeric micro-emulsion particles as a directing template for monolith fabrication with structured pores.

Keywords: Monolith; microemulsion particle; template;polystyrene;microspheres
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INTRODUCTION

Monolith is a porous material with interconnected pores that assist the transportation of analytes by flow rather than diffusion (Hong *et al.*, 2016). Owing to its ease of preparation, high column permeability and fast chromatographic separation speed monolithic capillary column has attracted a considerable attention in the field of micro-analysis and chromatography application. Furthermore, monolith serves good features such as lower bed pressure, better mass transfer performance, higher specific surface area as well as reliability to scale up (Gumba *et al*., 2016). In its application ,monolith has been widely applied in diverse applications include enzymatic bioreactor for bio-processing, protein purification , high performance liquid chromatography, filtration and separation or adsorption matrix in biomedical as well as environmental fields due to its porous interconnected pore structure (Acquah *et al*., 2016).In monolith preparation, commonly, organic polymer monolith consists of methacrylates, acrylamides or styrenes monomers. Pore structures in monolith created by the insertion of template and most used templates are biodegradable polymer or supramolecular aggregate, toxic additives like porogens, cross linkers and other compounds. There are various methods to fabricate monolith such as free radical processes, high internal phase emulsions, cryogels, living polymerizations (nitroxide mediated/organoterllerium initiators/atom transfer/ring opening metathesis), polycondensation and preparation of monoliths from soluble polymers (Svec, 2010). Among those methods available, most applied methods are thermal and photoinitiated radical polymerization.

However, existing methods has some drawbacks including poor heat dissipation, uneven pore distribution, "wall channel" effect and serves relatively low mechanical strength specifically during

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scale up (Gumba *et al.*,2016). Therefore, it is vital to search new techniques to overcome the drawbacks for the future of chromatographic function in monolith. Monteiro *et al.* (2016) stated that micro-particles ranging from 1μm to 1000 μm are micrometric system which have been extensively applied in the field of medical and pharmaceutical areas derived from micro-emulsion method is a potential template candidate in monolith since micro-emulsion method offers good control of pore size.

Micro-emulsion is a thermodynamically stable system and transparent system that can be prepared by few technique including solvent evaporation methods, spray drying, solution-enhanced dispersion method and hot melt technique. Among them techniques, the most applied method due to its ease of preparation is solvent evaporation method (Monteiro *et al.*, 2016). Monteiro *et al.* (2016) stated that micro-emulsion is best developed with polymer such as polycaprolactone and polystyrene. Polystyrene (PS) spheres has been extensively used as hard templates for various of hollow spherical materials (Zhang *et al.*, 2009) due to their good features such as low density, high surface area, excellent charge capacity, high permeability which made them highly potential in different fields such as storage and delivery of drugs , catalysis , separations , chromatography and immobilization system (Yoon *et al.*, 2006).

In this study we report on the synthesis and characterization of polystyrene micro-emulsion production as a based template in monolith. This study aims to produce polystyrene micro-emulsion by fine-tuning their variables such as synthesis temperature, polymer concentration, and surfactant concentration as well as stirring rate in order to produce good morphology of pores.

METHODOLOGY

Preparation of polystyrene microemulsion

The polystyrene microemulsion based template was synthesized by dissolving the polystyrene beads in dimethylformamide (DMF) at desired concentration. Surfactant Brij^{R} O10 was added into the solution to stabilize the microemulsion system. The solutions were continuously stirred for 1 hour until the polystyrene beads completely dissolved and evaporated under low pressure (Figure 1).

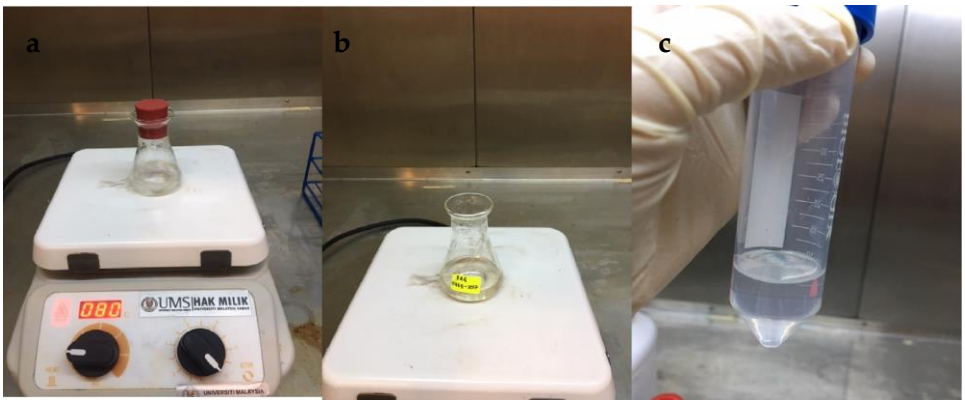

Figure 1. Processes involved in the preparation of polystyrene microemulsion. (a) Preparation of polystyrene microemulsion with (DMF) DimethylFormamide as solvent stirred continuously (b) evaporation of solvent under low pressure and continuously stirring. (c) Polystyrene microemulsion obtained in transparent in colour.

Experimental design for synthesis of polystyrene microemulsion

Experimental design for polystyrene microemulsion as monolith template was carried out by adopting a statistical analysis of Response Surface Methodology (RSM). The experimental design was designed by using Design-Expert Software adopting the Central Composite Design (CCD) of Response Surface Methodology. The independent variables identified in this experiment were (A) polymer concentration (%), (B) surfactant concentration (%), (C) temperature (°C) , (D) stirring rate and my response for this experiment was particle diameter (μm) as shown in Table 1.

Table 1. Experimental range and levels of variables used in central composite design.

Sampel	Parameter	unit	Low	High
A	Polymer concentration	%	21	35
B	Surfactant concentration	%	3	7
C	Temperature	°C	40	60
D	Stirring rate	rpm	625	1000

Characterization of polystyrene based microemulsion

The morphological study of polystyrene spheres was performed by Inverted microscope to observe the homogeneity as well as the particle diameter in micrometer (μm). Scanning Electron Microscopy (SEM) was used to observe the surface structure of the resulting microparticle.

RESULT AND DISCUSSION

Synthesis of polystyrene microsphere

Polystyrene microspheres were fabricated by using oil/water emulsification extraction/solvent evaporation technique. There were 30 samples carried out at different independent variables conditions as summarized in Table 1 by using Dimethylformamide (DMF) as an organic solvent and Brij^{R} O10 as a surfactant. Table 2 shows various independent variables produce different porosity and particle diameter size of the polystyrene microspheres. Based on the Table 2, sample conducted under run 13 showed a good homogeneity as it produced homogeneous pore distribution with standard deviation zero (0). Apart from that, sample under Run 4 and Run 15 as well obtained good homogeneity with standard deviation 0.21 and 0.41 respectively. Micro-emulsion is thermodynamically stable system that optically transparent formed when surfactant and co-surfactant mixed together as surfactant acts as stabilizer of this system.

Study by Margel (1991) shows diameter and size distribution of the microspheres are influenced by the monomer reaction , surfactant concentration solvent as well as the synthesis temperature (Gorsd *et al.*, 2012). Polymer concentration and stirring speed also play important role in particle size distribution (Kemala *et al.*, 2012). The plotted graph depicted a random distribution of particle diameter size since the reactant compositions were varied in order to study which parameter produced good particle size dsitribution. The particle size distribution for all samples produced average diameter ranging from 4 μm to 12 μm.

Table 2. Data from RSM for 30 Runs of polystyrene microemulsion.

Run	Independent variable				Dependent variable
	Polymer concentration (%)	Surfactant concentration (%)	Temperature (°C)	Stirring rate (rpm)	Particle size diameter (μm)
1	21	7	60	875	10.12±1.30
2	35	7	40	875	11.59±0.55
3	21	7	40	875	10.27±0.83
4	35	3	40	625	9.53±0.21
5	28	9	50	750	7.92±0.72
6	35	7	40	625	9.97±0.41
7	21	3	60	625	9.10±1.50
8	42	5	50	750	8.88±0.72
9	35	7	60	625	8.80±0.72
10	21	7	40	625	8.21±0.83
11	28	5	50	750	9.97±1.10
12	28	5	50	875	9.40±1.10
13	35	3	40	875	9.68±0.00
14	35	3	60	625	9.68±0.72
15	21	3	40	875	8.51±0.41
16	35	3	60	875	6.16±0.72
17	14	3	60	875	9.68±1.44
18	28	5	50	750	11.73±2.31
19	28	1	50	750	9.97±1.10
20	21	3	40	625	9.40±1.50
21	28	5	70	750	9.10±1.81
22	28	5	50	750	9.97±0.40
23	28	5	50	750	9.97±0.83
24	35	7	60	875	6.16±0.62
25	28	5	30	750	9.24±0.62
26	28	5	50	750	8.51±0.2
27	21	7	60	625	5.90±0.55
28	28	5	50	1000	7.77±2.55
29	28	5	50	500	4.99±0.83
30	21	3	60	875	8.22±2.73

Pore structure characteristics of polystyrene microspheres

These are few samples observed under the inverted microscope, It was observed in Figure (3a-b) that microparticles under parameter of Run 4 and Run 15 showed a good quality and favorable particle size without formation of aggregation whereas Figure (3c-d) microparticles influenced by Run 23 and Run 24 showed an aggregation formed between the microspheres. Previous study done by Kemala et al.,(2012) stated that aggregation able to formed due to the loading process of the microspheres dispersion also their sample storage.

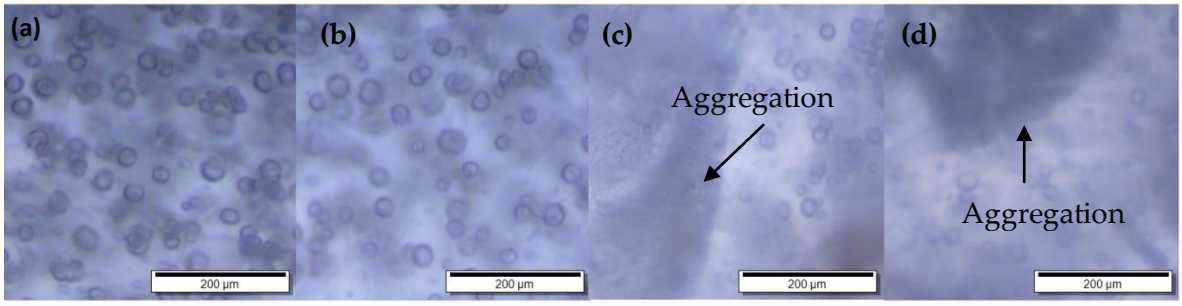

Figure 3. Inverted microscope image of polystyrene microemulsion by using brij^{R}O10 as a surfactant and Dimethylformamide as a solvent. (a) microemulsion was carried out at 35 wt% polymer concentration with 3% surfactant concentration, stirring rate 625 rpm for 40^{0} C (Run 4). (b) microemulsion was carried out at polymer concentration 21 wt% with surfactant 3% at stirring rate 875 rpm for 40^{0} C (Run 15). (c) microemulsion conducted at 28 wt% polymer concentration 7 wt% surfactant concentration at 750 rpm stirring rate for 50^{0} C (Run 23). (d) microemulsion at 35 wt% polymer concentration at 7 wt% surfactant stirring rate 875 rpm for 60^{0}C (Run 24).

SEM images of Run 4, Run 15, Run 23 and Run 24 shows a distribution and morphology of pore particle (Figure 4a-d). Run 4 shows a pore formation of the pores as well as Run 15, however, Run 23 produced some aggregation in between the pores while Run 24 shows a bad example of pore distribution as pore formation was failed to observe under SEM and aggregation was detected. Previous study conducted by Cho et al.,(2016) stated that aggregation occurred as the volatile solvent evaporated by heating them , inward capillary force tends to assemble the polymeric particles themselves which then lead to aggregation.

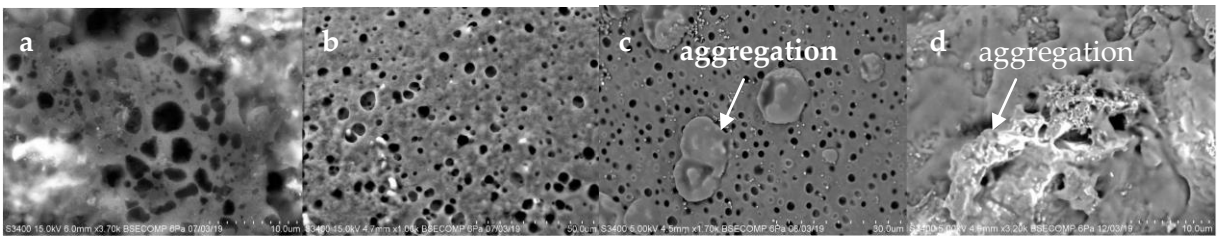

Figure 4. SEM images of pores distribution of polystyrene micro-emulsion of (a) Run 4 microemulsion was carried out at 35 wt% polymer concentration with 3% surfactant concentration, stirring rate 625 rpm for 40^{0} C. (b) Run 15 microemulsion was carried out at polymer concentration 21 wt% with surfactant 3% at stirring rate 875 rpm for 40^{0} C. (c) Run 23 microemulsion conducted at 28 wt% polymer concentration 7 wt% surfactant concentration at 750 rpm stirring rate for 50^{0} C and (d) Run 24 microemulsion at 35 wt% polymer concentration at 7 wt% surfactant stirring rate 875 rpm for 60^{0}C.

CONCLUSION

Polystyrene microemulsion was successfully synthesized by using water emulsification extraction/solvent evaporation technique. 30 Runs were completely synthesized and characterized and among them 30 Runs, best operating conditions are Run 4 and Run 15 while operating conditions of Run 23 and Run 24 produced bad quality of pore distribution with formation of agglomeration in between the pores. Microspheres/microparticles obtained ranging from 4 μm to 12 μm, random distribution of pores obtained since the operating conditions were varied. The findings of this study offers useful information of operating conditions for micro-emulsion as based template for monolith fabrication.

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