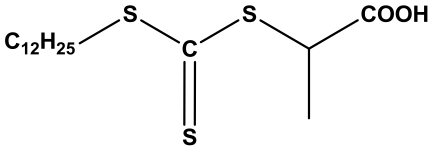
Supporting Information

Experimental

Materials

Styrene (St, Sinopharm Chemical Reagent Co., Ltd, SCRC for short) and divinylbenzene (DVB, Alfa Aesar) were used as the monomers to prepare PolyHIPEs. All the monomers were distilled under reduced pressure prior to the emulsion polymerization. Span80 or hypermer70 (A70, SCRC) were chosen as the emulsifiers. Oil-soluble initiator, azobisisobutyronitrile (AIBN, >99%) or water-soluble initiator, potassium persulfate (KPS, >99%), were employed in this work. $CaCl_2$ (SCRC) was added into the aqueous phase to suppress the Ostwald ripening. All the commercial reagents were used as received unless stated otherwise. The RAFT (reversible addition-fragmentation train transfer) agent, 2-{[(dodecylsulfanyl)-carbonothioyl] sulfanyl} propanoic acid, was synthesized and purified as reported.[1]



RAFT

Scheme 1. The structure of RAFT agent, 2-{[(dodecylsulfanyl)-carbonothioyl]sulfanyl}propanoic acid

Preparation

In a typical HIPE template polymerization the organic phase was prepared first by mixing 0.82 g DVB, 1.93 g St, 0.07 g RAFT agent and 0.91 g Span80 in a 3-neck round bottom flask with the mechanical stirring at 450 rpm. The aqueous phase was prepared by dissolving 0.05 g Kps and 0.25 g $CaCl_2$ into 18.25

g deionized water. The aqueous solution was then added slowly into the organic phase in the flask with stirring set at 450 rpm by a paddle rod connected to the overhead stirrer. After the addition of aqueous phase, the stirring was kept for another 30 minutes to achieve a viscous emulsion. The emulsion was then located into small tubes and sealed. The polymerization was started by putting the tubes into a thermostat with the temperature set at 65°C. After 24 hours the polymerization was stopped by taking the tubes out of the thermostat. The PolyHIPEs were then taken out of the tubes, exacted in a Soxhlet apparatus by methanol to remove the unreacted monomers, and finally dried in a vacuum oven at 100°C until constant weight was reached. Span80 was used in the preparation of Sample 1. Hypermer70 was used in the preparation of Sample 2~5 because it stabilized the emulsions with lower internal phase better in this work. In the preparation of PolyMIPE oil-soluble initiator, AIBN, was used instead of Kps because of the larger oil fraction in MIPE. No change was observed when different initiator was chosen.

In miniemulsion template polymerization method extra ultrasonication treatment was introduced during the preparation of emulsions. In the preparation of Sample 3, for example, the emulsion was first prepared following the same procedure employed for Sample 1. Then the emulsion was put into an ultrasonic cell disrupter and treated by ultrasound for around 8 minutes to reduce the water droplet size. After that the miniemulsion went through the same polymerization and extraction process to obtain the porous monoliths.

Characterization

The morphologies of monoliths were observed by scanning electron microscopy (SEM) method. Monoliths were first gold sputtered in Emitech 7620 (Sc7620, Quorum Ltd, UK) under the argon atmosphere to achieve necessary conductivity. The samples were then fixed to the sample holder and observed by SEM (ULTRA 55, Carl Zeiss Ltd, Germany). The size of void and throat was analyzed by the software of Image-Pro Plus©. At least 50 pores were measured from various parts of the sample.

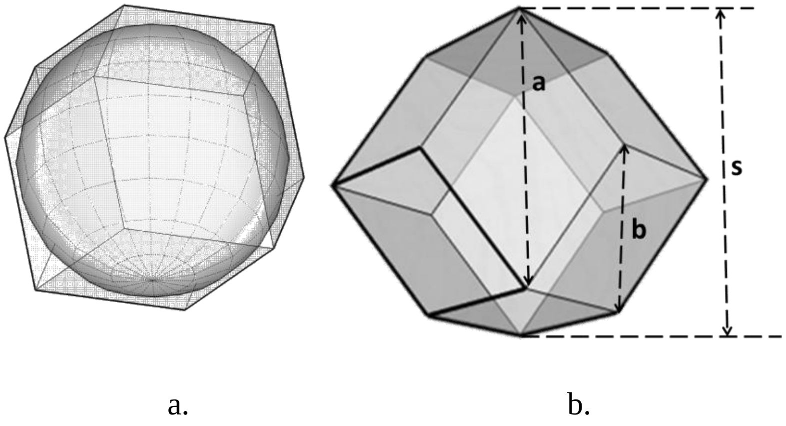
The mechanical properties of monoliths were characterized by a Universal Testing Machine (Zwick/Roell Z020, Zwick Ltd, Germany) equipped with a 25KN load cell. The samples with a diameter of 12 mm and height of about 20 mm were compressed at a rate of 2 mm/min until the deformation reached the set value. Compressive stress-strain curves were obtained and analyzed for their mechanical properties.

The monolith density, porosity and the size of throats were determined by an automated mercury porosimeter (AutoPore IV 9510, Micromeritics, America). The samples were weighted and placed into a sample cup. At low pressure the mercury filled up the free space inside the cup instead of entering the samples. The bulk volume of the monoliths can be obtained as a result. The monolith density was then calculated from the bulk volume and the weight. With the increase of pressure mercury was intruded into the sample’s pores beginning with the larger pores. The AutoPore could detect very slight changes in capacitance and gave the pore size distribution as a result.

The surface area of monoliths was obtained from nitrogen adsorption measurement. Around 0.2 g of sample was placed inside a glass sample cell and heated under vacuum (heating temperature of 100℃) overnight first to remove adsorbed impurities. Nitrogen adsorption measurement was then performed using a surface area analyzer. The nitrogen adsorption isotherms were analyzed by the Brunauer-Emmet-Teller (BET) model (Autosorb-1-C, Quantachrome Ltd, America) for the surface area.

Model development

To have a quantitative analysis of medium internal phase emulsion the water droplet is treated as a sphere embedded in a rhomboidal dodecahedron which has twelve identical faces as shown in Scheme 2a. Each face of rhomboidal dodecahedron is a rhombus. The dimension parameters including a, b and s are defined as in Scheme 2b. The major diagonal a and the minor diagonal b equal to $\sqrt{2}s/2$ and $s/2$, respectively. The volume of the rhomboidal dodecahedron unite is $s^3/4$. The diameter of the embedded sphere is defined as d.



a. b.

Scheme 2. The dimensional parameters of rhomboidal dodecahedron

When the sphere is inscribed in the rhomboidal dodecahedron, d equals to a. The sphere's volume fraction in the rhomboidal dodecahedron unit is 74%, which is viewed as the minimum internal phase fraction of HIPE. In MIPE, the spheres will be separated from each other. The shortest distance between the spheres is defined as h, which will reflect the thickness of the polymeric wall between the dispersing droplets.

$$h = a - d$$

The sphere's volume fraction in the rhomboidal dodecahedron unit is viewed as the internal phase fraction, *x*, for the whole emulsion

$$x = (\frac{\pi d^3}{6}) / (\frac{S^3}{4})$$

Simple derivation gives

$$x = \frac{\sqrt{2}\pi}{6} / \left(\frac{h}{d} + 1\right)^3$$

Please note this equation is only available for MIPE and LIPE, whose internal phase fraction is lower than 74%. Besides, in this model the droplets were treated as monodispersed, which is not the case in practical. A rough quantitative understanding about how the key dimensional parameters in MIPE vary can be obtained from this model, but accurate description of MIPE and LIPE requires a model taking the polydispersity of droplets into consideration.

Results

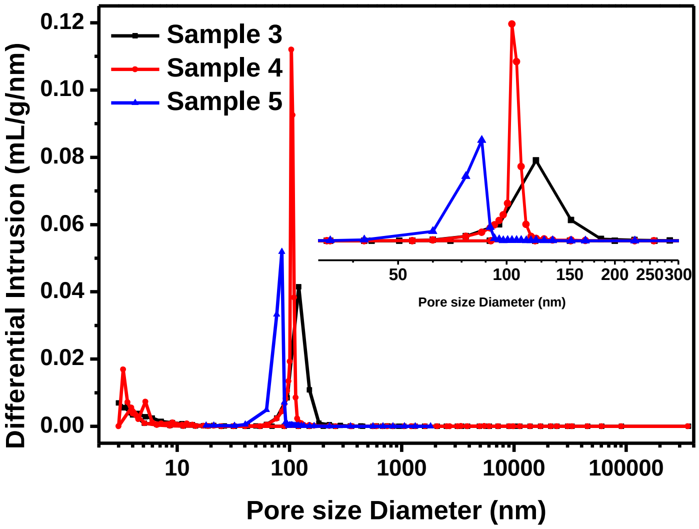


Fig. 1 The automated mercury porosimeter measurements of Sample 3~5

Table 1. Experimental results from literature and current work

No.	Porosity (%)		Void Size (um)	Calculated distance between voids (nm)	Pore structure[b]	Reference
	Theo[a]	Exp[a]				
1	70	70	3.6	67.5	O	Kovacic *et al.*[2]
2	60	59	4.0	314	O/C	
3	50	55	2.0	208	O/C	
4	60	73	5.8	26.6	O	Bismarck *et al.*[3]
5	60	73	3.1	14.2	O	
6	40	63	3.1	171	O	
7	34	61	4.3	286	O/C	
8	25	50	3.4	475	C	
9	67	69	0.343	8.11	O	Current work
10	54	55	0.318	35.2	O	
11	45	47	0.298	56.4	O	

[a] Exp and Theo stand for the experimental and theoretical values, respectively.

[b] O: open-cellular structure, O/C: open-cellular structure with closed-cells present, C: closed-cells structure

References

1. C. J. Ferguson, R. J. Hughes, D. Nguyen, B. T. T. Pham, R. G. Gilbert, A. K. Serelis, C. H. Such and B. S. Hawkett, *Macromolecules*, 2005, **38**, 2191.
2. S. Kovacic, K. Jerabek, P. Krajnc and C. Slugovc, *Polym. Chem.*, 2012, **3**, 325.
3. S. S. Manley, N. Graeber, Z. Grof, A. Menner, G. F. Hewitt, F. Stepanek and A. Bismarck, *Soft Matter*, 2009, **5**, 4780.