A cationic fluorosurfactant for fabrication of high-performance fluoropolymer foams with controllable morphology

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A B S T R A C T

High internal phase emulsion (HIPE) technique has been of great interest for fabrication of polymer foams with controlled porous structures. However, for fluoropolymers, it has been a challenge to fabricate high-performance foams with controllable porous structures by HIPE due to the lack of suitable surfactant. Here, for the first time, a new type of cationic fluorosurfactant (CFS) is proposed to address this issue. The cationic fluorosurfactant is a diblock copolymer, Poly(2-dimethylamino)ethyl methacrylate-*b*-Poly(hexafluorobutyl acrylate) (PDMAEMA-*b*-PHFBA) synthesized by reversible addition–fragmentation chain transfer (RAFT) polymerization. For the prepared fluoro-diblock copolymer having similar fluorosegments to fluoro-monomer, this cationic fluorosurfactant can effectively stabilize high internal phase

emulsion (HIPE) system involving hexafluorobutyl acrylate monomer as oil phase, water as internal phase, DVB as cross linker and AIBN as an initiator. Polymerization of the HIPE system finally gave rise to novel flexible fluoropolymer foam, Poly(HFBA-DVB) with a porous morphology which can be tuned simply by the amount of the fluorosurfactant. As a high-performance porous material, the fluoropolymer foam demonstrated not only significant capacities and fast adsorption kinetic for separating various organic oils from water, but also has an excellent thermal stability up to 340 °C, indicating significant applications at extreme conditions.

Keywords: foams; oleophilic; high internal phase emulsion; macroporous; fluoropolymer; cationic fluorosurfactant

1. Introduction

Porous polymeric materials with well-defined specific surface properties and porosities are extremely important for their various applications such as scaffolds for tissue engineering[1], reaction supports for catalysts[2], separation membranes[3], controlled release matrices[4], oil adsorbents[5], heavy metal ion collectors[6], responsive materials and also templates for porous carbon and porous ceramics[7]. There are several ways to prepare interconnected porous materials, for example, gas blowing[8], by using super critical fluids[9], emulsion templating[7], sacrificial polymer templating[10], and self-assembled colloidal templating[11]. Among all, emulsion templating method is easily controllable and flexible to fabricate macroporous materials (pore size > 50 nm). This method also has an advantage of facile processability in preparing polymers of desired shapes, including monoliths, beads, membranes, often with well-

defined porosities and high specific surface areas (SSAs)[12]. Due to these reasons a great number of hydrophilic polymers, hydrophobic polymers, organic-inorganic composite materials, inorganic oxides porous materials, and porous metals have been reported using emulsion templating technique[13].

Emulsions having dispersed phase volume higher than 74.05% of the total emulsion volume, can reach to level of 99% [14, 15] are termed as high internal phase emulsions (HIPEs). It is the highest packing density of tightly packed mono-dispersed, non-deformable spheres [3, 16]. PolyHIPEs are porous emulsion-templated polymers synthesized by high internal phase emulsions (HIPEs). The morphology of these polyHIPE is quite original; however, as recently underlined, the terminology on that rather new and fast emerging field is not yet completely accomplished[17]. Oil-in-water (O/W)[18], water-in-oil (W/O)[19-22] and supercritical CO₂-in-water (C/W) [23, 24] emulsions are being used in preparation of homogenous polyHIPEs. Comparatively large cavities created by omission of internal droplets are known as “pores” interconnected by series of small interconnects, that is, “pore throats”.

Great efforts have been made to enhance the interconnectivity of polyHIPEs for different applications. Type and concentration of surfactant and cross linker [14, 21, 25, 26], energy input during HIPE preparation[16], locus of polymerization initiation[27, 28], nature and volume ratios of emulsion phases[29-31] are the most appealing factors in HIPE kinetic stability and morphology control such as pore size along with degree of interconnection. Among these factors, surfactants (amphiphiles) play a critical role in stabilizing the internal phase within the continuous phase, which is the key to achieve a polyHIPE with controllable morphology[32]. In addition to surfactants, solid particles, such as iron oxide, titania, silica, hydroxyapatite, polymer particles and carbon nanotubes, can also stabilize HIPEs which are often referred to as Pickering

HIPEs, but these type of HIPEs commonly have closed cell structures. In order to create interconnectivity or open porous structure, surfactants again come into play. A common strategy is to decrease droplet size and weaken the barrier of water-oil interface by adding surfactants to co-stabilize HIPEs[33]. It is also important to note that only a restricted number of surfactants are able to stabilize HIPEs. In order to stabilize the emulsion, usually a large amount of surfactant with concentration of 5-50 wt% with respect to the continuous phase is required[14, 34]. As these surfactant molecules are toxic in general [35, 36], it is necessary to remove them after polymerization, which generates undesirable extra production cost[37]. Researchers are trying to develop more “green” surfactants in order to enhance the properties of polyHIPEs. Traditional surfactants like Triton X-405[34], BRIJ35[38], and Span 80 have been used to emulsify W/O emulsions[7]. Amphiphilic block copolymers as surfactants, such as amphiphilic poly(ethylene oxide)-*b*-poly(styrene) (PEO-*b*-PS)[39], poly(4-vinylpyridine)-*b*-poly(ethylene glycol)-*b*-poly(4-vinylpyridine)[40] have recently been used for the stabilization of polyHIPEs. Therefore, there is still a great need for the development of effective and environmentally friendly surfactants for fabrication of high-performance polyHIPEs.

Controlled/living radical polymerization (CLRP) has revolutionized and revitalized the field of synthetic chemistry as it is now possible to synthesize a wide variety of previously inaccessible macromolecules under relatively mild conditions. By using CLRP the control over polymer molecular weight and less polydispersity has been achieved remarkably. CLRP includes atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization and reversible addition-fragmentation polymerization (RAFT)[41]. Among these methods RAFT polymerization has distinct advantages compared with others. It can be used to prepare polymers or copolymers with narrow molecular weight distribution. Molecular weight of the final product

can be anticipated from the ratio of monomer consumed to chain transfer agent (CTA). In addition RAFT polymerization has compatibility with a vast range of functional monomers, initiators and solvents. Also there is no undesired metal species introduced during RAFT polymerization process [42].

Most of polyHIPEs polymers are common materials polymerized by monomers based on hydrocarbons such like styrene, etc. With substitution of hydrogen atoms by fluorine ones, fluoropolymers possess physicochemical properties superior to conventional polymers in various aspects, such as chemical/oxidative stability, optical transparency, compatibility with solvents, and environmental stability[43]. For these significant advantages, there is an increasing interest in fluorine containing oils and fluorinated surfactants/block copolymers in the field of emulsion polymerization [44-47]. Therefore, polyHIPE represents an important strategy to diversify the properties and applications of fluoropolymers.

Because the conventional emulsifier cannot stabilize the fluorine-containing HIPEs systems, the development of effective fluorsurfactants for fluoropolymeric polyHIPEs is in critical needs, which have similar fluoro-parts compared with fluoromonomers. It is also difficult to prepare block copolymers having fluoropolymer segments with controlled block lengths, because of the hydrophobic as well as the lypophobic nature of the fluorinated segments. But, with the advent of RAFT polymerization such problems have been diminished by virtue of its superb compatibility with various fluoromonomers in solution and heterogeneous systems[48]. As a result, ionic[49-51] and non-ionic[52] fluorsurfactants have been studied in the literature. Among these reported studies, cationic fluorinated surfactants are much less investigated, mainly due to the difficulty in synthesis and purification [53]. It has been found that short chain fluorsurfactants containing 6 or 4 CF₂ units have very little bioaccumulation potential and

consequently better environmental safety attributes[53-56]. In this regard, cationic fluorosurfactants with limited CF_2 units represent an advanced surfactant with environmental friendliness because of their high surface activity and good water solubility[57]. Fluorinated emulsions are thus captivating but the availability of fluorosurfactants is circumscribed [58-60].

In this study, we report a new type of cationic fluorosurfactant (block copolymer), prepared by RAFT, as stabilizer for water-in-fluorinated oil (W/FO) HIPE i.e. fluoroemulsion. Based on this fluoro-HIPE, a highly porous fluoropolymer (PFP) foam with tunable morphology, which cannot be achieved by conventional cationic surfactants like CTAB, is successfully fabricated. Also the surfactants like Hypermer, Span 80 and Tween 80 fail to give regular polyHIPEs morphology. It is found that the cationic fluorosurfactants can not only stabilize the HIPE system, but also give rise to a highly porous and flexible material after polymerization. It is interesting to find that the porous morphology of the PFP foam can be simply and effectively tuned by the surfactant concentration. Finally, the significant properties of the porous fluoropolymer Poly(HFBA-DVB) are demonstrated by separating various types of oils from water surface, indicating a promising application in treatment of environmental pollution, such as oil spillages.

2. Experimental

2.1. Materials

Hexafluorobutyl acrylate (HFBA) was purchased from Fluorine Silicon Chemical Company and passed through basic alumina column to remove any inhibitors prior to use. 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99%) was supplied by Shanghai Macklin Biochemical Co. Ltd and passed through basic column as well to get rid of inhibitors.

Trifluoroethyl methacrylate, Divinyl benzene (DVB, 80%) and Dichloromethane were purchased from Aladdin. Dioxane, Tetrahydrofuran (THF), Tween 80, CTAB, Methylene Blue and Sudan III dyes were purchased from Sinopharm Chemical Reagent Co. Ltd. 2,2'-azobis-isobutyronitrile (AIBN) was ordered by Lingfeng Chemical Reagent Co. Ltd. n-Hexane (>97%) was supplied by Tianjin Fuyu Fine Chemical Company. Calcium carbonate dihydrated ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) was provided by Shanghai Zhanyun Chemical Co. Ltd. Deionized water was used throughout the experiments. Cumyl dithiobenzoate (CDB-RAFT agent) was synthesized and purified by the procedure given elsewhere[61].

2.2. Synthesis of Poly(2-dimethylamino)ethyl methacrylate Macro-Chain Transfer Agent.

The synthesis of PDMAEMA macro-chain transfer agent (macro-CTA) was conducted as follows. A 50 ml round bottom flask was charged with 2-(dimethylamino)ethyl methacrylate (DMAEMA; 5.2 g; 33 mmol), cumyl dithiobenzoate (CDB; 0.1838 g, 0.67 mmol), 2,2'-azobis-isobutyronitrile (AIBN; 0.0449 g, 0.27 mmol), CDB/AIBN molar ratio; 2.5, and 1,4-dioxane (12.9132 g). A magnetic stirrer was also placed in the flask. The sealed reaction vessel was purged with nitrogen gas and placed in a preheated water bath with agitation at 75 °C for 12 h. Then the product was quenched in ice water. The resulting PDMAEMA was purified by precipitation into excess cold n-hexane, and the product was dried at room temperature under vacuum for 24 h.

2.3. Synthesis of Cationic fluorosurfactant Poly(2-dimethylamino)ethyl methacrylate-b-Poly(hexafluorobutyl acrylate).

The already prepared macro-CTA (PDMAEMA; 3.1165 g; 0.49 mmol), hexafluorobutyl

Table 1

Formulation, morphology, specific surface area, porosity, HIPE stability ($\pm$ values represent standard deviation)

Sample ^a	CFS concentration (wt %) ^b	Conventional surfactant (wt %) ^b	DVB/HFBA mass ratio	Morphology ^c	Specific surface area (m ² /g) ^d	Porosity (%) ^e	HIPE stability (h)
1	1.2	0	0.1	closed	12.55 $\pm$ 1.2	73.86	< 0.5
2	2	0	0.1	closed ^j	13.60 $\pm$ 0.9	74.2	4.5
3	4	0	0.1	open	14.02 $\pm$ 1.3	78.32	24
4	9	0	0.1	open	14.61 $\pm$ 0.8	80.46	>72
5	11	0	0.1	open	14.92 $\pm$ 1.1	80.51	>72
6	13	0	0.1	irregular	--	--	48
7 ^f	0	9	0.1	irregular	--	--	>72
8 ^g	0	9	0.1	irregular	--	--	>72
9 ^h	0	9	0.1	--	--	--	< 0.5
10 ⁱ	0	9	0.1	--	--	--	NE ^k

^aThe internal phase volume of all HIPEs is 80.4 wt %. ^bWith respect to the continuous phase

^cSEM images ^dBET ^eliquid displacement test[62] ^fSpan 80 as conventional surfactant

^gHypermer as conventional surfactant ^hTween80 as conventional surfactant ⁱCTAB as

conventional surfactant ^j mostly closed ^k not emulsion. (2-column fitting)

acrylate (HFBA; 2.3 g; 9.7 mmol), 2,2'-azobis-isobutyronitrile (AIBN; 0.0278 g, 0.17 mmol), macro-CTA/AIBN molar ratio = 2.8, were dissolved in (1,4-dioxane; 12.7312 g). The reaction mixture was sealed in a 50 ml round bottom flask with a magnetic stirrer in it and purged with nitrogen gas to completely remove oxygen from the vessel. The deoxygenated solution was then placed in preheated water bath at 75 °C for 13 h with agitation. Then the product was quenched in ice water. The resulting di-block PDMAEMA-*b*-PHFBA was purified by precipitation into excess cold n-hexane, and the product was dried at room temperature under vacuum for 24 h. Finally, this di-block copolymer was used as cationic fluorosurfactant/stabilizer in preparation of HIPE.

2.4. Preparation and Polymerization of HIPEs.

Table 1 shows recipes with various concentrations of cationic fluorosurfactant and conventional surfactants to prepare HIPEs. A typical water-in-oil HIPE (sample; 4) with 80.4 wt % water internal phase was prepared as follows. Cationic fluorosurfactant (PDMAEMA-*b*-PHFBA; 0.3951 g) dissolved in hexafluorobutyl acrylate (HFBA; 3.5561 g). Then 2,2'-azobisisobutyronitrile (AIBN; 0.0395 g) and divinyl benzene (DVB; 0.3951 g) added into the oil and surfactant solution. Aqueous solution of 0.2M calciumchloride dihydrated ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; 18 g) was added drop wise with continuous mechanical stirring (450 RPM) of the solution. The mixture of HIPE was further allowed to stir for 20 min. After the full droplet phase entered into the continuous phase, the prepared emulsion was taken out from the centrifugal tube and put into the oven at 70 °C for 24 h to polymerize. After polymerization the sample was processed through soxhlet extraction to remove unreacted monomer and surfactant from polyHIPE. Finally the monolith obtained was dried at 70 °C for 24 h in an oven to obtain highly porous fluoropolymer foam. Similar systems of fluoro-HIPEs were prepared by replacing CFS with conventional surfactants Span 80 (Table 1; sample 7), Hypermer (Table 1; sample 8), Tween 80 (Table 1; sample 9) and CTAB (Table 1; sample 10) in order to check and compare the stability of HIPEs. Fluoro-HIPE with 9 wt% CFS concentration by using trifluoroethyl methacrylate (TFEMA) as raw material was prepared by the same procedure.

3. Characterization

3.1. Pore Structure, Pore and Pore Throat Dimensions.

The microstructure of porous fluoropolymer was studied by imaging fracture surfaces using scanning electron microscope (SEM) (S-2500, Hitachi Seiki Ltd., Japan). Prior to SEM

approximately 0.5 cm³ of each sample was fixed onto an aluminum stub with the help of carbon sticker and gold coated at 20mA for 60 s by using (Scan Coat Six SEM Sputter Coater, Edwards, Ltd., Crawley, United Kingdom) to ensure good electrical conductivity. Images of the fractured surfaces were taken from the top, middle and bottom sections to account for the variations in pore morphology because of droplet coalescence and sedimentation. Pore and pore throat dimensions were analyzed using Nano Measurer 1.2 software.

3.2. Specific Surface Area and Porosity.

Specific surface areas of porous fluoropolymers were determined by nitrogen adsorption isotherm using the Brunaur-Emmett-Teller (BET) model using surface area analyzer Micromeritics TriStar II 3020. Contaminants were removed via a “Degassing” step, prior to gas adsorption, where approximately 200 mg of each polyHIPE was heated to 120 °C in glass sample cells for 12 h. Porosities of the samples were calculated by the liquid displacement test[62].

3.3. Gel Permeation Chromatography.

Number average molecular weight and polydispersity index (PDI) of PDMAEMA and PDMAEMA-*b*-PHFBA was analyzed by gel permeation chromatography (GPC). The GPC measurements were performed at 25 °C by using “Waters 1500” that consists of HPLC pump and Refractive Index Detector. THF was used as a mobile phase at a flow rate of 1 ml/min. THF solution of PDMAEMA and PDMAEMA-*b*-PHFBA was injected at a concentration of 3ml/L after filtration through 0.45 µm pore size membrane.

3.4. ¹H NMR Spectroscopy.

¹H NMR spectra were recorded in DMSO using bruker Advance III 400 MHz nuclear magnetic resonance spectrometer at room temperature.

3.5. Optical Microscopy.

The size and the shape of HIPE droplets were observed by Nikon Eclipse LV100POL, Japan optical microscope after dropping the emulsions on glass slides. The optical micrographs were used to evaluate the droplet size distribution on counting at least 100 droplets per sample by Nano measurer software.

3.6. Hydrophobicity Measurement.

A contact angle instrument OCA drop shape analyzer (Data physics Co., Germany) was used to measure the hydrophobicity of porous fluoropolymer at room temperature.

3.7. Thermogravimetric Analysis (TGA).

Thermogravimetric analysis (TGA) was performed on Pyris Diamond TG/DTA (Perkin-Elmer Co.,USA) with heating rate of 10 °C/min and a scanning range of 30 to 550 °C in nitrogen atmosphere.

3.8. Oil Adsorbency Test.

0.15 g of Poly(HFBA-DVB) monolith foam in cylindrical shape (approximately 20 mm in diameter and 12 mm in height) was placed into the mixture of oil/water. After oil adsorption saturation Poly(HFBA-DVB) monolith was taken out from the oil/water mixture. The total mass of the monolith soaked with oil was weighed and oil intake capacity k was calculated as follows,

$$k = \frac{m_1 - m_o}{m_o} \quad (1)$$

Where m_o is mass of monolith before oil adsorption; m_1 is mass of monolith after oil adsorption. Three replicates were performed for each sample.

3.9. Degree of Openness Calculation.

Degree of openness of PFP was calculated by the relationship derived elsewhere[16]. The

Fig.1. Optical images of emulsion and droplet size distributions (The proportion of smaller pores increased with an increasing CFS concentration): (a) 4 wt% CFS concentration and (b) 11 wt% with respect to the continuous phase; (scale bar 20 μm). (2-column fitting)

typical equation used for calculation is given as follows,

$$O = \frac{N \cdot d^2}{4 \cdot D^2} \quad (2)$$

Where N is the number of pore throats, d is average pore throats diameter and D is average pore diameter.

4. RESULTS AND DISCUSSIONS

4.1. Structure and characterization of cationic fluorosurfactant (CFS).

RAFT solution polymerization was used to synthesize Poly(2-dimethylamino)ethyl methacrylate-*b*-Poly(hexafluorobutyl acrylate) (PDMEMA-*b*-PHFBA) by employing cumyl

dithiobenzoate (CDB) as RAFT agent. The composition and the structure were confirmed by ^1H NMR and GPC. The mean degree of polymerization (DP) of PDMAEMA macro-CTA was calculated to be 50 using ^1H NMR spectroscopy by comparing the integrated signals corresponding to the CDB aromatic protons at 7.1 – 8.1 ppm with those assigned to the 2 methylene protons of PDMAEMA at 3.9 – 4.18 ppm. The feature signals of PDMAEMA block $\delta = 2.29$ ((CH_3) $_2\text{NCH}_2\text{CH}_2$ –) (f H), $\delta = 2.56$ ((CH_3) $_2\text{NCH}_2\text{CH}_2$ –) (e H), $\delta = 4.05$ ((CH_3) $_2\text{NCH}_2\text{CH}_2$ –) (d H) and for PHFBA block $\delta = 5.99$ ($\text{CF}_3\text{CHF}_2\text{CF}_2\text{CH}_2$ –) (i H), $\delta = 4.55$ ($\text{CF}_3\text{CHF}_2\text{CF}_2\text{CH}_2$ –) (h H) appeared in the spectrum (Fig. 2a, c). The ^1H NMR DP of PHFBA came out to be 23.

Fig.2. ^1H NMR and GPC curves of: (a,b) PDMAEMA, and (c,d) PDMAEMA-*b*-PHFBA. (2-column fitting)

GPC was used to characterize molecular weight and its distribution. Only one single peak could be observed by the GPC chromatogram, which shows that amphiphilic block copolymer of (PDMAEMA-*b*-PHFBA) is composed instead of the mixture of homopolymers of both PDMAEMA and PHFBA. The representative GPC curves are shown in Fig. 2b,d. Good control and synthesis of the RAFT polymerization were proved by the narrow dispersity ($\bar{D}$; 1.12), molecular weight (M_n ; 6.3×10^3 g/mol) for the first block and ($\bar{D}$; 1.21) with increased molecular weight (M_n ; 8.3×10^3 g/mol) for diblock/Cationic fluorosurfactant.

4.2. Morphology and characterization of Poly(HFBA-DVB) stabilized by CFS.

While preparing HIPE, a significant amount of water was dispersed in the emulsion with assistance of cationic fluorosurfactant (PDMAEMA-*b*-PHFBA), leading to the stable water-in-oil emulsion. Then the organic continuous phase HFBA and DVB was polymerized, which resulted in solidification of polyHIPE. Water was then removed by drying dispersed phase to obtain highly porous fluoropolymer foam. The SEM images revealed that these polyHIPEs possessed an open porous interconnected and homogeneous structure, which was similar to the microstructures of typical polyHIPEs (Fig. 3c). PFPs obtained were highly flexible as shown in Video-1. From the video, it can be seen that on compressing these materials shrunk considerably and adopted original dimensions when pressure was released. These elasticity characteristics of PFPs are in sharp contrast to the brittleness of porous carbon materials.

This type of CFS stabilized fluoroemulsion showed excellent stability. Fig. 1 is depicting optical images and droplet size distribution graphs of the emulsion prepared by 4 wt% and 11 wt% CFS concentrations with respect to the continuous phase. The average droplet size of an emulsion decreased from 15.83 μm to 7.23 μm by increasing concentration of CFS. It is worth noticing here that even 4 wt% CFS concentration was able to give hierarchical open porous

structure along with good stability of HIPE. As the focus of many literature reports lies in minimizing surfactant concentration in emulsion stabilization[14, 34] such a small quantity is of the utmost important demand for an efficient surfactant nowadays, so in this way our designed system of CFS stabilized emulsion is very efficient. The same system of fluoroemulsion was prepared with conventional surfactants to check their ability and performance in the aspect of stabilization and polymerization to obtain porous structures. Span 80, Hypermer, Tween 80 and CTAB were used (Table 1, sample 7-10) and it was found that only after 30 minutes, a bilayer phase separation was observed in emulsions prepared by Tween 80 whereas CTAB failed to give fluoroemulsion, in contrast to the CFS stabilized fluoro-HIPE which demonstrated superb stabilization of more than 72 h without phase separation. Though HIPEs prepared from Span 80 and Hypermer showed obtrusive stability but both were unable to give porous materials after polymerization (Fig. 3a, b).

Fig.3. Effects of surfactant type on the morphology of the polyHIPEs samples (the loading of surfactant is 9 wt% with respect to the continuous phase) as studied by SEM images: (a) Tween 80, (b) Span 80, and (c) Cationic fluorosurfactant (main scale bar: 40 μm and inset scale bar: 5 μm). (2-column fitting)

Fig. S1 illustrates emulsion stability comparison of CFS against conventional surfactants. The first reason for the diversity in stability performance of conventional surfactants compared with the CFS stabilized fluoro-HIPE is the difference in viscosity between the two systems. As is well known, the stability of an emulsion system increases with increase in the viscosity [63]. Fluoroemulsion prepared by CFS showed high viscosity compared with the HIPEs prepared from Tween 80 and CTAB at the same concentration. Another reason for long stability and high porosity may be that CFS and oil used in HIPE both include fluorine part in them, hence fluoro-compatibility of both oil and surfactants led towards long emulsion stability and also obtained highly porous material after polymerization.

The effect of changing concentration of CFS on the morphology of porous fluoropolymer was investigated. When CFS concentration varied from 1.2 wt % to 13 wt % with respect to the total continuous phase, a dramatic change in morphology of the poly fluoro-HIPE was observed as shown in Fig. 4. When the concentration of CFS was low to 1.2 wt %, the closed pores morphology was dominant in the microstructure. However, when the cationic fluorosurfactant concentration was increased then the small pore throats began to develop and they led towards open cellular structure of the porous fluoropolymer. It shows that a certain critical amount of CFS is required to form the small droplets otherwise globules of the water result that give predominantly closed morphology (Fig. 4a, b). Although the phenomenon of pore throats formation is still under debate but it is believed that under this critical concentration all the water globules are completely surrounded by the oil, which prohibits pore throats formation. Slightly above 1.2 wt % CFS concentration the layer of the oil between the water droplets thins and starts to shrink back and the points where the internal phase droplets touch each other confer small openings (pore throats), which go bigger in number and size upon further addition of CFS (Fig.

4c-e). This phenomenon continued to increase until the level of CFS concentration comes when the thin oil layer disappeared after maximum shrinkage, at this stage struts rather than regular polyHIPEs formed[64]. As shown in Fig. 4f, at 13 % concentration of CFS, connectivity of the polymer lost and hence led towards catastrophic drop in bulk physical continuity along with the shrinkage of more than 40% to the undried PFP volume, which resulted in the irregular microstructure of polyHIPE. This is in agreement with previous works reported on how structural stability suffers when excess amount of the surfactant is used[65].

Fig.4. Adjusting the pore morphology by CFS concentration, SEM images of the polyHIPEs samples with: (a) 1.2 wt %, (b) 2 wt %, (c) 4 wt %, (d) 7 wt %, (e) 11 wt %, and (f) 13 wt % of CFS with respect to the continuous phase (main scale bar: 40 μm ; and inset scale bar: 5 μm) . (2-column fitting)

The specific surface area obtained was considerably higher as compared with the recent literature report on porous material[66] in which maximum of 6.9 m^2/g was achieved but here in

this case of PFP the specific surface area obtained was in the range of $12.55 \text{ m}^2/\text{g} - 14.92 \text{ m}^2/\text{g}$ (Table 1).

The influence of the cationic fluorosurfactant on the pore sizes and pore throat sizes of the porous fluoropolymer was investigated and the results are shown in Fig. 5. Pore throats got bigger and bigger in sizes by increasing fluorinated surfactant concentration. The average size of the pores decreased from $26.08 \mu\text{m}$ to $5.40 \mu\text{m}$ with increase in CFS concentration from 1.2 wt% to 11 wt% before losing typical polyHIPE morphology at 13 wt% CFS (Fig. 5a). The reason of decrease in diameter of pores is attributed to the increase of the droplet size which is due to the coalescence between many small droplets. It means that by increasing surfactant concentration to a certain level, coalescence decrease between emulsion droplets which hinder their size to grow gives smaller size pores[67].

Fig.5. Effect of CFS wt% on (a) Pore and pore throats diameter , (b) Openness of PFPs. (2-column fitting)

4.3. Openness and porosity.

Porosity of material has proved to be an important variable for specific surface area. Here in this case as shown in Table 1, BET surface area of PFP also showed strong dependency on the

number of pores per unit mass of the material. When porosity of the material was high the specific surface area of the material was high and when porosity decreased the specific surface area also declined upon decreasing surfactant concentration. Openness of the material is also an influential factor to analyze as it gives an idea about high interconnections between the pores. The surfactant concentration is believed to have profound effects on openness [67]. It is worth noting that openness of the interconnected porous material is directly proportional to the number and diameter of pore throats and inversely proportional to the pore size[16]. So in this case, an increase in openness of PFP by increasing concentration of CFS **was** observed which **was** also in agreement with previous literature studies[67, 68](Fig. 5b).

Fig.6. Water retention on the surface of PFP after heating the material at 200 °C for 3 h. (1-column fitting)

4.4. Contact angle, oil **adsorbency** and thermal stability.

The contact angle measurements are commonly used to specify the hydrophobicity of solid materials[69]. If the contact angle $\theta \geq 90^\circ$ the surface is said to be hydrophobic and if $\theta \leq 90^\circ$ then the surface will be hydrophilic[70]. Also fluoropolymers have been widely accepted to use

in applications where water penetration is not required. In this study, contact angle of the water was studied before and after heat treatment of the material and the same contact angles $140 \pm 1^\circ$ were found in both cases. Moreover hydrophobicity of such porous fluoropolymers retained even after heat treatment of the material at 200°C for 3 h (Fig. 6). Thermal stability of PHFBA-DVB was also analyzed with porous polymer prepared by the same concentration of CFS 9% by using TFEMA as monomer phase. Results of PFP prepared with HFBA showed remarkable stability performance at more than 340.69°C while porous polymer synthesized by TFEMA started to decompose even at 237.36°C . This higher stability of HFBA is due to greater number of fluorine atoms (F; 6), rather than in TFEMA which contains less fluorine atoms (F; 3). It means by increasing fluorine contents material will be more thermally stable. Also the thermal stability performance of PHFBA-DVB prepared in this study is considerably higher than that in the recent literature report which showed thermal stability of porous material at 310°C [66]. The representative TGA curves are shown in Fig. S2.

When a hydrophobic PFP was placed in oil-water mixture, it floated on the water surface and selectively adsorbed oil (Fig. 7a) thus exhibiting excellent selectivity. Oil was adsorbed very quickly in between pores of polyHIPEs while water wasn't adsorbed, therefore giving a constant straight line on 0 g/g adsorption for water in the rate curve as shown in Fig. 7b. Water retained on the surface of the polymer upon dribbling the drops of water (dyed with methylene blue), and on the same lines an organic oil (dichloromethane dyed with sudan II) dripped was instantaneously adsorbed by the PFP, which implies simultaneous hydrophobic and oleophilic character of the material (Fig. 7c). High hydrophobicity and oleophilcity is associated with the characteristic of fluorine and high porosity in poly(HFBA-DVB) microstructure, respectively.

Fig.7. Demonstration of the significant application of the polyHIPEs for oil/water separation. (a) Digital photos showing the oil adsorption process, (b) Rate curve for oil and water adsorption, (c) Hydrophobicity (water dyed with mehtylene blue) and oleophilicity (oil dyed with sudan II) demonstration. (2-column fitting)

Adsorption of different oils was analyzed by changing concentration of CFS in polyHIPEs. By increasing the concentration of cationic fluorosurfactant the oil adsorbency increases due to high porosity and after that, adsorption capacity of materials dropped because of the loss of regular HIPE porous morphology (Fig. 8).

Fig.8. Effect of CFS concentration on adsorption capabilities for different organic oils. (1-column fitting)

5. Conclusions

In summary, a new type of cationic fluorosurfactants (CFS), diblock (PDMAEMA-*b*-PHFBA), is developed as an advanced stabilizer for fluoro-HIPE system. Enabled by this new surfactant, a flexible fluoropolymer poly(HFBA-DVB) foam with controllable morphology and high performance is demonstrated. It is found that **conventional** surfactants **are** failed to stabilize/polymerize such fluoroemulsions to get porous structures. While the developed one, CFS, can effectively stabilize the fluoroemulsions and the resultant fluoropolymer foam shows very fast adsorption kinetics towards organic oils due to the well-controlled porous structures. Moreover, the fluoropolymer foam **shows high** thermal **stability** up to 340 °C. These significant properties of fluoropolymer foam will find promising applications in water/oil separation, porous templates for catalysts and so on.

Acknowledgements

The work was supported by the National Science Foundation of China [Grant No. 21304037]; and the Scientific Research project of Shandong Provincial Department of Education [Grant No. J11LB02].

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Graphical Abstract