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Poly(HIPEs), Applications and Modifications

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Abstract: **This review paper summarizes the current knowledge about high internal phase emulsion polymerization (PolyHIPEs), route of polymerization, where an emulsion is formed. The polymerization of the external phase occurs around emulsion droplets of the internal phase, thus creating an open, highly interconnected porous network, after the removal of the internal phase. This review further describes the characteristic features of these monolithic materials, and their application in several areas in material science, such as solid supported organic chemistry, sensoring, cell culturing and tissue engineering. The paper additionally describes how each of these characteristics can be tailored in order to meet the requirements for the desired applications.**

Keyword: **high internal phase emulsion polymerization, PolyHIPEs, review, porous, applications.**

I. INTRODUCTION

The aim of this review paper is to provide the reader with a broad overview about PolyHIPEs, and it is intended to answer the following three questions:
1. What are PolyHIPEs?
2. What are PolyHIPEs used for?
3. How to functionalize PolyHIPEs?

II. LITERATURE REVIEW

1. What are PolyHIPEs?

PolyHIPEs are porous emulsion-templated polymers, synthesized within high internal phase emulsions (HIPEs). Now known for many years [1], the generic term PolyHIPE was coined by Unilever researchers to describe these polymeric foams [2], originally developed as carriers and absorbents for liquids [3], followed by a number of Unilever patents [4], including patents on polyHIPEs as substrates and as templates for porous carbon [5].

High internal phase emulsions are highly viscous, paste-like emulsions[5], which make up a very concentrated dispersed systems [6] in which the dispersed phase occupies more than 74.05% of the whole volume fraction [7]. The major, dispersed phase is usually referred to as internal phase, the minor, continuous phase as external phase [4 - 8].

The characteristic PolyHIPE monoliths are the result of the polymerization of the external phase around the droplets of the internal phase, followed by solidification of the external phase, the emulsion droplets are embedded in the resulting material [9]. Due to high concentration of the internal phase, droplet size distribution is usually polydisperse, and deformation into non-spherical shapes occurs, leaving only a thin film of external phase between adjacent droplets [5]. Subsequent removal of the internal phase gives rise to a porous replica of the emulsion [10]. Since this is a simple molding process, in which the liquid precursor emulsion is placed in some polymerization vessel or mold, a wide range of sample shapes and sizes is available [9].

The ensuing porous matrix is characterized by a trabecular morphology [11] consisting of micrometer sized, almost spherical voids, interconnected via a plurality of much smaller pores, here referred to as windows [12], and the much smaller pores present within the walls of certain PolyHIPEs are called pores [9], as illustrated in fig. 1.

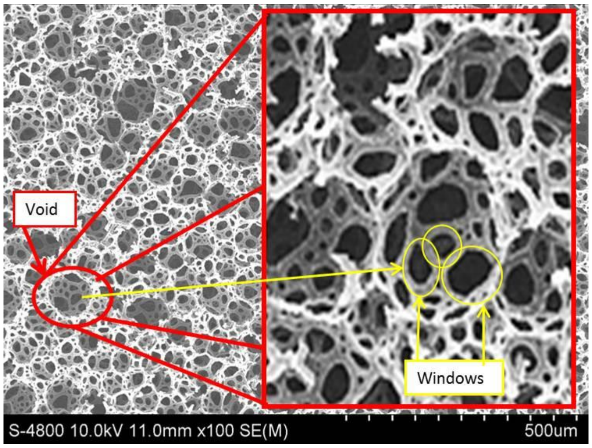

Fig.1. SEM micrograph of a PolyHIPE monolith, showing its characteristic structure consisting of almost spherical voids, interconnected via a plurality of much smaller pores, referred to as windows.

The open-cell polymers are characterized by an extremely low dry bulk density, typically less than 0.1 g cm-3 [13], and possibly as low as 0.01 g cm-3 [14], due to complete interconnection between all neighboring voids. The average void diameter in a PolyHIPE material can be varied over a range from around 1 mm to greater than 100 mm [9], and pore size ranges from 5 to 100 μm [5]. The total pore volume can be up to 10 cm^3g^{-1} [5]. Although the morphology of the material is highly porous and interconnected, the relatively large void size results in a low to moderate surface area of around 3–20 m2 g-1 [15], however, values of up to 700 m^2 g^{-1} can be achieved [9]. The mechanical properties of PolyHIPEs are similar to conventional gas-blown polystyrene foams, although the smaller void sizes (in most cases) and higher degree of cellular spherical symmetry of the emulsion-derived foams produces higher compressive strengths [13].

The process of preparing PolyHIPEs is extremely simple [9]. Monomer(s) plus, usually, a cross-linking agent, and a suitable surfactant are mixed together as external phase. The internal phase liquid, usually water, a water soluble initiator, and a stabilizer [16], is added slowly and drop wise, to the external phase, while it is stirred constantly during the addition to break up larger droplets[9], and to obtain a uniform emulsion [5]. Mixing is followed by polymerization of the external phase, which depends upon the initiation system used [5]; thermal, redox, catalytic, UV, or microwave induced initiation. Due to slight shrinkage of the polymer film during the polymerization because of monolith volume contraction [17], small interconnecting ruptures are formed in the adjacent walls separating the individual internal phase droplets from each other, creating a bi-continuous structure, consisting of highly interconnected open-cell porosity within a continuous polymer scaffold [4]. Once all of the internal phase liquid has been added, the emulsion is cured. The obtained monolith is then often treated by soxhlet extraction, for complete removal of the internal phase, which has now become continuous. Yielding voids in place of the internal phase droplets and results in a highly interconnected, open-cell, emulsion-templated porous structure [4].

The by far most widely investigated PolyHIPE base material is styrene/divinylbenzene[9]. While acrylates and methacrylates have also been investigated in details, there is still a long list of monomers that can be used to produce polyHIPEs with unique properties [13].

2. What are PolyHIPEs used for?

As a result of the unique characteristics, and highly interconnected nature of the porous monoliths, PolyHIPEs are finding applications in various fields of material science [18]. The open cellular morphology makes them good candidates as damping materials [19] for thermal and acoustic insulation within engine compartments and other enclosures. The highly interconnected macro-porous structures can be advantageous for achieving high transport rates to micro-porous walls for molecular storage applications [4].

One area in which PolyHIPEs have been exploited extensively is as supports for solid phase synthesis [9]. Sherrington and Small describe the use of crosslinked polystyrene PolyHIPE in granular form as a support for a polyacrylamide gel used in solid phase peptide synthesis [20]. Further, PolyHIPEs have been found to be beneficial as matrices from which to prepare electrochemical sensors [9]. It was proposed that the porous nature of the PolyHIPE material would enable the integration of separation with sensing, allowing the sensors to be used in the presence of contaminants found in ‘real’ liquid media [9] (soil particles, blood cells, proteins, etc.). PolyHIPE materials have alsobeen used in biological and biomedical applications. For example, as potential substrates for tissue engineering have been described [9]. PolyHIPE materials containing biodegradable polyesters such as poly(3-caprolactone)[21] or polylactide [22] were prepared, and their abilities to support the growth of different cell and tissue types was investigated. PolyHIPEs are further finding applications in areas such as solid supported organic chemistry, sensors, cell culturing and tissue engineering.

Due to the wide range of potential applications, this chapter has been divided into 3 sections:
a. PolyHIPEs as separation media
b. PolyHIPEs for tissue engineering
c. PolyHIPEs for specialty applications
Table 1 summarizes relevant publications for the respective fields.

TABLE 1: RELEVANT PUBLICATIONS IN RESPECTIVE FIELD OF APPLICATION

Principal Author	Published	Title
PolyHIPEs as separation media		
Moine L.	2003	Preparation of high loading PolyHIPE monoliths as scavengers for organic chemistry
Pulko I.	2007	Atrazine removal by covalent bonding to piperazine functionalized PolyHIPEs
Lucchesi C.	2008	New functionalized polyHIPE materials used as amine scavengers in batch and flow-through processes
Tunc Y.	2010	Acrylic-based high internal phase emulsion polymeric monolith for capillary electrochromatography
Klemm E.	2011	Hybrid integrated plant concept with 2nd Process Intensification field for Ammonia Production from Biomass
PolyHIPEs for tissue engineering		
Laurencin CT.	1996	Tissue engineered bone-regeneration using degradable polymers: the formation of mineralized matrices
Akay G.	2002	Microcellular polymer materials as cell growth media and novel polymers
Akay G.	2004	Microcellular polyHIPE polymer supports osteoblast growth and bone formation in vitro
Robert S.	2011	Injectable PolyHIPEs as High-Porosity Bone Grafts
PolyHIPEs for specialty applications		
Kataky R.	2003	PolyHIPE materials for Advancing the Capabilities of Electrochemical Sensors: A Feasibility Study
Burke D.R	2010	Development of Novel Polymeric Materials for Agroprocess Intensification

a. PolyHIPEs as separation media

The permanent, well-organized structure with large voids, highly interconnected via several smaller windows, exhibits excellent flow properties [23]. Several studies [24 - 26] have shown that PolyHIPEs can be used under flow-through conditions. Their main advantage over other materials is that their fully open structure is combined within a monolithic format. The combination of these characteristics offers opportunities for flow-through applications such as rapid separation media [27]. Furthermore, it has also been shown that PolyHIPEs promote good diffusion of fluids towards immobilized functional groups [28]. Hence, PolyHIPEs have proven to be effective amine scavengers in batch flow processes [29].

PolyHIPEs bearing tertiary bromoester groups were first prepared by polymerization of a concentrated inverse emulsion, fulfilling all the requirements of scavengers, such as: high loading, good accessibility given by the mobility of the grafted chains and a structure which allows the rapid diffusion of fluids. Moreover, the monolith format permits easy and rapid manipulation [27].

Firstly in 2007, Lucchesi C. and her team were able to produce scavenger polyHIPEs bearing an electrophilic group by copolymerization of a functional monomer with divinylbenzene. The team had previously shown that azlactone was a very promising electrophilic ring to scavenge nucleophiles like primary amines and that an efficient immobilization of amines could be achieved using well-defined azlactone- functionalized ‘‘Rasta” beads synthesized by atom-transfer radical polymerization [30]. They had also shown that sericin, a natural protein could be immobilized onto polypropylene films functionalized with grafted macromolecular chains containing azlactone groups [31]. Such applications have been implemented in batch flow processes. Solid-supported scavengers are of particular interest in organic synthesis as they can selectively remove excess reagents and by-products from the reaction mixture leaving a purified product in solution [32], [33].

Since PolyHIPE polymer supports have already proved their versatility in the usage as scavengers in batch and flow through applications, Pulkoet. al[34] examined the removal of atrazine, a controversial chlorotriazine herbicide, banned in the European Union for more than a decade, but still widely used in the U.S., from aqueous solutions by PolyHIPEs. Their unique pattern of large voids connected via windows and the porosity of the continuous phase makes them more versatile than usual macroreticular resins in terms of solvent compatibility.

The PolyHIPE material was based on 4-nitrophenylacrylate and styrene, and further functionalized with piperazine. The average diameter of the voids was around 32 μm and the average diameter of the windows approximately 1.5 μm. Prior to testing, the monolithic polymers were powdered by grinding. This work showed that PolyHIPE supported piperazine removal is effective also in the case of lower excess of reactive groups in relation to atrazine which suggests good accessibility of reactive sites. It is believed that the reactive ester approach and PolyHIPE architecture are very suitable for the preparation of functional polymers for atrazine removal. Furthermore, the nature of the reaction between the supported piperazine and the pesticide molecule makes this approach attractive also for the removal of other triazine type pesticides.

Syngas cleaning techniques, which offers the simultaneous removal of tars, moisture and heavy metal ions during ammonia production from biomass, has developed a system to include PolyHIPEs as microreactors or catalyst support into their systems. Again, the hierarchic pore structure prevents diffusional restrictions and allows selective adsorption of surface active species in which the thermodynamic driving force is based the ‘confinement phenomenon’[35].

PolyHIPEs have also proven to be good alternatives to conventional capillary columns in capillaryelectrochromatography (CEC). Conventional columns are difficult to produce, since the interparticular voids in the packed columns cause slower mass transfer because of diffusion [36] between these voids and the pores within the particles. Hence, inhomogeneous packing or bubble formation could be reduced by monoliths [37]. Furthermore, the monoliths allow high flow velocities and superior mass transport at low back pressure due to their large pores and more open pore structure in comparison to packed columns [38] [39], resulting in high permeability and fast separation [40]. The selectivity of the separation is controlled by the polarity of the monolith and the retention can be adjusted by the polarity of mobile phase and monolith surface [41].

Tunc at al. [40] produced 90% porous PolyHIPE monolithic columns, according to the procedure described previously [42], from isodecylacrylate crosslinked with divinylbenzene in the continuous phase. The average diameter of the voids was 8.9±2.7 μm, and the average diameter of the windows was 2.0±0.9 μm. The pore size distribution was in the range of 2-5 μm, and the surface area was 5.44m^2/g.

These columns, indicated a strong electro-osmotic flow (EOF) without any additional EOF generating monomer probably due to the presence of ionizable sulfate groups coming from the water-soluble initiator, and were successfully used for the separation of alkylbenzenes. A column efficiency of up to 200,000 plates/m could be achieved. Overall, the PolyHIPE monolith showed successful chromatographic performance in the separation of alkylbenzenes without the use of EOF generating monomer.

b. PolyHIPEs for tissue engineering

PolyHIPEs are a relatively new approach for the production of high-porosity scaffolds. An ideal scaffold material would serve and support the growth of new tissue and encourage migration of cells to border areas of a defect site, and provide a source of inductive factors to support cell differentiation [43]. The tunable architecture of polyHIPE foams makes them attractive candidates for tissue engineered bone grafts. Most research on the development of polyHIPE bone grafts [44-49] has focused on styrene-based or unsaturated polyester-based macromers. These styrene-based systems had excellent pore morphology; however, they were non-biodegradable which limited their use as a scaffold for tissue engineering purposes [50 - 53].

Akay et al. [54] prepared polyHIPEs based on styrene and divinylbenzene in the external phase, according to the procedure previously described [55] by the team. The surface of the obtained polyHIPEs was modified with hydroxyapatit to increase penetration and proliferation rates of osteoblasts [54]. PolyHIPEs of various pore sizes were used and the results demonstrated in vitro cell–polymer compatibility, with osteoblasts forming multicellular layers on the polymer surface and also migrating to a maximum depth of 1.4mm inside the scaffold after 35 days in culture [54]. The material was further able to support the differentiation of osteoblasts and the production of a bone-like matrix.

The ability to synthesize a fully biodegradable polyHIPE without a toxic diluent that could also cure at physiological temperatures was demonstrated by Moglia R.S. et al. [56] and provided an important adaptation of emulsion templating. A unique feature of this polyHIPE system is that the HIPE retains a viscosity that is suitable for injection prior to cure, making the application as an injectable, tissue engineered bone graft possible. A process which offers distinctive advantages over current alternatives in terms of deployment and tissue integration.

Propylene fumaratedimethacrylate was synthesized to be used as a biodegradable macromer with appropriate viscosity and hydrophobicity for emulsification. Incubation of the HIPE at 37 °C was used to initiate radical cross-linking of the unsaturated double bond of the methacrylate groups to polymerize the continuous phase and lock in the emulsion geometry. The resulting polyHIPEs exhibited ~75% porosity, pore sizes ranging from 4 to 29 μm, and an average compressive modulus and strength of 33 and 5 MPa, respectively [56]. These findings highlight the great potential of these scaffolds as injectable, tissue engineered bone grafts.

c. PolyHIPEs for specialty applications

Beside the afore mentioned common applications for PolyHIPEs, new possibilities are frequently being reported.

Kataky R. et al. [57] studied the feasibility to use PolyHIPE based materials for electrochemical sensing, with the goal of working towards a cholesterol sensor via PolyHIPE amperometric sensors and biosensors.

Homogeneous PolyHIPE thin films (thickness ca. 200 μm) with controlled porosity using molding techniques were successfully synthesized. The membranes could further be functionalized by physical and/or chemical means, introducing electroactive functional species such as ionophores, electron mediators, enzymes and other proteins, and were then incorporated into the following materials: ligands capable of sensing cations; enzymes (e.g. pepsin); graphite particles or carbon fibers.

Burke D.R. et al. [58] developed novel polymeric material for agroprocess intensification. The basic PolyHIPE material was crosslinked styrene–divinylbenzene polymer with 90 vol. % porosity. The transformation of hydrophobic styrene–divinylbenzene PolyHIPE to hydrophilic form was conducted by microwave sulfonation. The obtain hydrophilic polymers had water adsorption capacities of 10-fold and 18-fold with nominal void sizes of 20 and 150 μm, respectively. When these polymers were used as a soil additive at 0.5 wt % with increasing water stress (normal, semiarid, and arid conditions), the dry biomass yield increased by about 30, 140, and 300%, respectively, after 21 days of cultivation [58].

3. How to functionalize PolyHIPEs?

In order to make use of the unique structure and characteristics of PolyHIPEs, modification and functionalization of the structure is imperative. Modification allows alteration of the monolithic properties with respect to mechanical properties, surface area, pore morphology as well as surface chemistry and thus can overcome some of the limitations of organic polyHIPEs [59]. Due to the immense width of field, in the following a description of several selected examples of the modification and functionalization of major characteristic PolyHIPE features.

Since surface area and void size are strongly affected by the concentration of crosslinking co-monomer [60], [61], type and amount of surfactant [62] and type of inert diluent solvent [63 - 66], it can be modified by a change in type and concentration of one or more of these factors. For example, the generally rather low surface area of PolyHIPEs could be increased by either a higher degree of crosslinking [65] or by post polymerization functionalization inducing additional crosslinking [67]. Furthermore, soxhlet extraction can be used not only to remove left over parts of the solvent, but also to remove other residual materials, resulting in an increased surface area [16], [68].

The void size is strongly affected by the physiochemistry of the oil phase [69]. The phase percentage dictates the amount of oil that will surround a water droplet. Of course, the higher the percentage of the aqueous phase, the bigger and more interconnected the voids. However, if the emulsion viscosity is very high, the shear stress might not be sufficient to break up larger droplets, leading to a less interconnected structure [70]. The lowering of the cloud point by stabilizing salts effects increases the void size by controlling the packing density of surfactant molecules in the interfacial film [70]. The salt level of the emulsion was found to have a tremendous effect on the pore size. Thus a 10-fold reduction in cell size can be obtained by changing the conditions from no salt to 10 g of K_2S0_4/100 mL water, where most of the change occurs when the salt level has reached 0.005 g/100 mL [71]. The addition of a porogenic solvent dilutes the interfacial layers and leads to an increased void diameter [70]. The mean size of voids and windows could be decreased by nanocomposite elastomeric copolymer foams. These foams have been prepared from PolyHIPEs containing 2- ethylhexylacrylate, styrene, divinylbenzene, and organo-modified montmorillonite [72]. The incorporation of modified clay further led to lower emulsion torque, approximately to a characteristic value of the emulsion viscosity.

By tuning the preparation conditions and monomer content, polyHIPE materials with both, high surface area and open interconnecting structure with larger pores could be obtained, giving the material functional properties like low density, high permeability, appropriate surface area, etc. This was demonstrated by Sevšek U. et al. [73], when they successfully incorporated methacrylic acid into a polyHIPE matrix. The authors further stated that acid groups could be easily functionalized into very reactive acid chloride functionalities and further with nucleophiles. This would open opportunities for a wide variety of applications.

Krajnc P. [74] et al. showed successfully that PolyHIPE supports with various loadings of –OH groups could be prepared. Materials possessing the Wang linker, used frequently in solid phase synthesis, were prepared by a two-step procedure by attachment of 4- hydroxybenzaldehyde and subsequent reduction. The resulting materials were esterified efficiently with 4-iodobenzoic acid, a component of Suzuki cross coupling reactions. Subsequently, it was shown that tris(hydroxymethyl)aminomethane functionalized PolyHIPE could serve as a linker for attachment via esterification.

The growth and differentiation of osteoblast within a polyHIPE based matrix could be greatly improved by the incorporation of the biologically inspired self-assembling peptide hydrogel (RAD16-I, also called PuraMatrix^{TM}), as a biomaterial [75].

III. CONCLUSION

PolyHIPEs result from the polymerization of the continuous phase of an emulsion. These monolithic materials are finding applications in several areas of materials science, such as separation media, templates for tissue engineering, and specialty applications. According to the need for the desired application it is possible to control physical, mechanical, and morphological features such as void size, degree of interconnection and total surface area. It is expected that further research and development will extend the range of potential applications of PolyHIPEs.

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