

Macroporous Polymer Mixers

A Dissertation presented by

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The work described in this thesis was carried out in the Department of Chemical Engineering at Imperial College London between October 2011 and March 2015. Except where specific reference is made, the material contained in this thesis is the result of my own work. This thesis has not been previously submitted in whole or in part for the reward of a degree at this or any other university.

Michael Tebboth

2015

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Publications Relating to this Thesis

Tebboth M, Menner A, Kogelbauer A, Bismarck A. *Polymerised high internal phase emulsions for fluid separation applications*. 2014 [1]

Tebboth M, Kogelbauer A, Bismarck A. *Micromixing in Emulsion Templated Macroporous Polymers characterised by the Bourne reaction*. 2015 [2]

Tebboth M, Kogelbauer A, Bismarck A. *Liquid-Liquid Extraction within Emulsion Templated Macroporous Polymers*. [3]

Tebboth M, Kogelbauer A, Bismarck A. *Highly Permeable Macroporous Polymers via Controlled Agitation of Emulsion Template*. [4]

Tebboth M, Kogelbauer A, Bismarck A. *Heterogeneous Nitroreduction in a Palladium/PolyHIPE Reactor*. In preparation

Abstract

Macroporous polymers produced by polymerising the continuous phase of high (or medium) internal phase emulsions (H/MIPes), commonly known as poly(merised)HIPes (or polyMIPes), have been intensively researched over the past two decades. They have been investigated for use in many diverse applications including chromatography, membranes, sorption, electrodes, bioengineering and filters amongst others. However this work investigates the use of their intricate internal pore structure for the mixing of fluids passing through polyHIPes.

When producing polyHIPes (also polyMIPes) by polymerisation of HIPE and MIPE templates it was found that the pore size could be controlled effectively by varying the energy used to agitate the emulsion template. The gas permeability of polyM/HIPes increased linearly with increasing mean pore throat diameter for a given porosity. Through both residence time distribution experiments and examination of homogenous micromixing it was shown that the mixing in single-phase liquids increased when passed through a polyHIPE as the mean pore throat diameter decreases. There was no difference in mixing performance observed between polyHIPes produced from Pickering emulsions compared to those produced from surfactant stabilised emulsions. By performing the liquid-liquid extraction of caffeine from aqueous solution with ethyl acetate within a polyHIPE flow cell it was shown that the overall mass transfer coefficient decreased with smaller mean pore throat diameters suggesting more effective mixing. The porosity of the polyHIPE monolith was not found to affect the overall mass transfer coefficient. It was possible to produce interfacial areas, up to $17,600 \text{ m}^2\text{m}^{-3}$, between the two immiscible liquid phases within polyHIPes, comparable to industrial extraction methods such as mixer settlers. Impregnating the polyHIPE flow cells with palladium allowed examining whether it is possible to use them as three phase catalytic reactor for nitroreduction. The gas-liquid mixing within the reactor was found to be insufficient to prevent the reduction being mass transfer limited even in the reactors containing the smallest mean pore throat diameters. Less than 0.2% of the palladium catalyst within the reactor was lost from the polyHIPE pore structure during the nitroreductions reactions for all the polyHIPE reactors tested.

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Motivation and Scope

This thesis investigates the potential of macroporous polymers produced by polymerisation of the continuous phase of emulsion templates to mix various fluids. It was postulated that their intricate internal pore structure could provide for effective mixing of fluids passed through them as the individual fluid elements are continuously reoriented, in a manner similar to a conventional static mixer but at significantly lower flow rates. Moreover, the pore wall surfaces could also provide potentially sufficient solid-fluid interface for heterogeneous catalysis. Since poly(merised)HIPEs have the inverse pore structure of packed bed reactors, i.e. the void space in one is filled by beads in the other, they could potentially fulfil the function of trickle beds with the advantage of higher porosities. PolyHIPEs are usually prepared in the form of monoliths, which avoids problems of fluid bypassing. PolyHIPE fluid mixing elements could potentially find applications in the fine chemical and pharmaceutical industries where manufacturing is increasingly moving to low flowrate continuous processes away from batch operations [5].

A significant amount of research has been carried out into polymerised high internal phase emulsions (polyHIPEs) in the past two decades with the number of patents and publications relating to them increasing rapidly year on year [6] since commercialisation was first attempted by von Bonin et.al. in the 1960s [7] and Unilever in the 1980s [8]. Chapter 1 reviews published work that this research builds upon, looking into the synthesis of polyHIPEs, from emulsion formation, stabilisation and polymerisation to the many potential applications that these structures have been explored for. Chapter 2 deals with general experimental techniques used throughout the research; i.e. it describes how flow cells were produced for the fluid mixing experiments. The production of the emulsion templated, macroporous cross-linked polystyrene (poly(styrene-co-DVB)) used in this thesis is discussed in Chapter 3. This chapter describes in detail how the energy input used to agitate the emulsion used as a template for the resultant porous polymers can be used to control their final internal pore structure and gas permeability.

The remaining chapters describe how the tailored pore structure of polyHIPEs affects fluids that are forced through their internal highly porous structure. The potential of polymerized high and medium internal phase emulsions to act as homogenous mixers for aqueous solutions is discussed in Chapters 4 and 5; specifically in Chapter 4 the residence time distribution of a pulse input through a polyHIPE flow cell is related to its pore structure while in Chapter 5 the rate of mixing is characterised by performing two competitive homogenous reactions (4th Bourne reaction) in a polyHIPE flow cell.

Chapters 6 and 7 describe the mixing of two immiscible fluids using polyHIPEs; namely of a liquid-liquid and gas-liquid mixture. The extraction of caffeine from water to ethyl acetate is examined in Chapter 6, with the extent of two phase mixing quantified by the calculated overall mass transfer coefficient. From this the interfacial area formed between the two fluids as they passed co-currently through the polyHIPE pore structure could be determined. Finally in chapter 7 the potential use of polyHIPEs as mixers and catalyst support for the nitroreduction of organic compounds was examined by producing polyHIPE flow cells containing a palladium catalyst. Through the flow cell was passed a mixture of gaseous hydrogen and liquid ethyl acetate, containing a reducible organic compound to observe if the sufficient gas-liquid mixing occurred to allow the reduction reaction to take place and how the extent of reaction was effect by variations polyHIPE structure.

Chapter 1: Introduction to Macroporous Emulsion Templated Polymers

1. High Internal Phase Emulsions (HIPEs)

Emulsions are biphasic mixtures of immiscible liquids, where one of the liquids, called the dispersed phase is present as droplets, while the other is called the continuous phase. Most commonly the two liquids are an oil (organic) phase and an aqueous phase; however, immiscible organic phases [9] can also be used as can fluids like supercritical carbon dioxide [10]. Emulsions can be either oil-in-water (O/W) or water-in-oil (W/O) depending on factors such as relative volumes of the two phases, the ratio of viscosity between the two phases, the type of emulsifier, the concentration of emulsifier, pH and the temperature. High internal phase emulsions (HIPEs) are defined as emulsions which have an internal volume greater than 74.05% [11, 12] or over 70%, which was the original definition given by Lissant [13]. Similarly other emulsions can be classified as medium internal phase emulsions (MIPEs) and low internal phase emulsions (LIPEs) with internal phase volumes of 74-30% and less than 30%, respectively.

An internal volume of 74.05% represents the maximum internal phase volume possible in an emulsion containing monodispersed spherical droplets [14]. However, HIPEs of up to 98% [15-17] internal phase volume have been successfully produced, due to the ability of the internal phase droplets to deform from spherical droplets into polyhedra. At an internal phase volume fraction between 74% and 94%, the droplets pack as a rhombohehral decaherals (RHD) and above 94% tetrakaidecahedron (TKDH) (truncated octahedron) packing is preferred [13, 18]. These both allow tessellation in three dimensions.

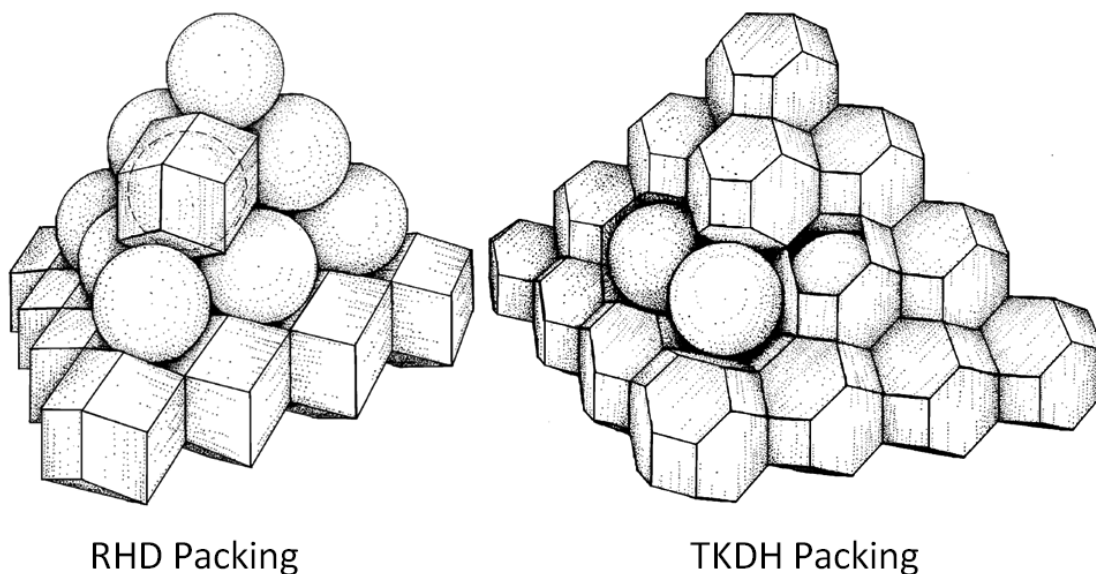


Figure 1. Dispersed phase droplets in a HIPE take up different confirmation depending on the internal phase volume fraction. Rhombohehral decaheral (RDH) packing (left) is favoured between 74% and 94% while tetrakaidecahedron (TKDH) packing occurs at internal volume fractions above this [19].

However in reality, droplets in a HIPE are inevitably polydispersed to some degree, meaning they do not deform to the extent that would be required if it was a monodispersed system. This is because smaller droplets can pack into spaces between larger droplets, increasing the internal phase fraction without necessarily deforming any of the droplets

The deformation of the droplets leads to a structure analogous to that of gas-liquid foams. Where droplets are forced together and deformed into polyhedra, lamellae are formed where only two interfaces are in contact. In these, the films are separated only by an extremely thin layer of continuous phase which is extremely important for the production of pore throats in polyHIPEs. Where the films of three droplets are forced together a plateau border is produced while at the junction of four films, a vertex will be formed. Vertexes and plateau borders contain the vast majority of the dispersed phase.

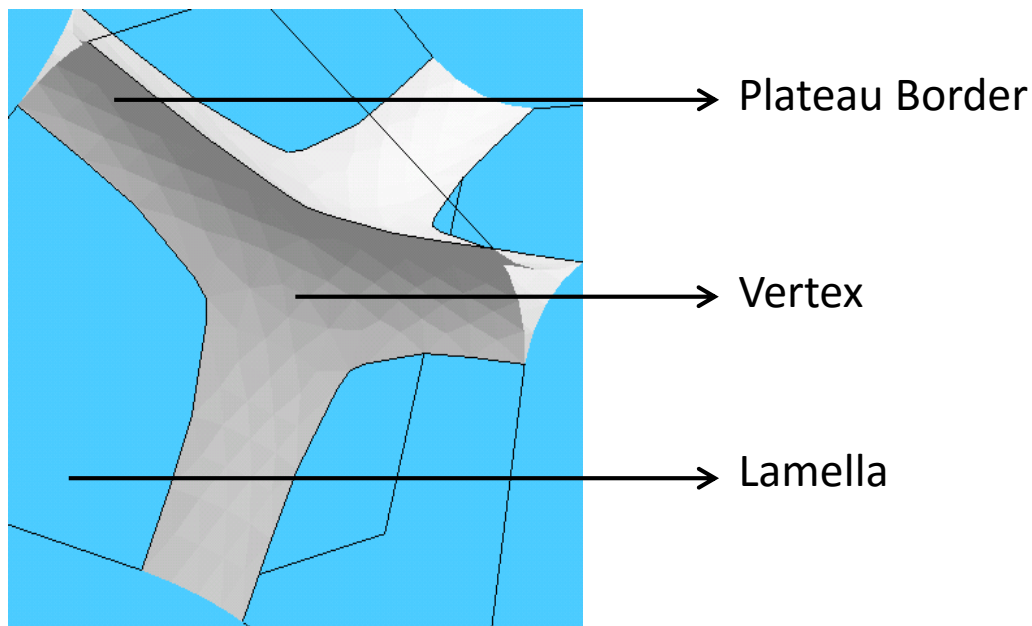


Figure 2. Diagram demonstrating the relationships between a vertex, plateau borders and lamella. These structures form as the internal phase volume of an emulsion is increased forcing the droplets to deform upon contact with each other.

Typical droplet sizes in HIPEs can range from $0.5\mu\text{m}$ upwards [20] meaning that HIPEs are opaque; unless they contain coloured additives such as particles or dyes they are usually white due to the scattering of light by the emulsion droplets.

1.1. Surfactant Stabilised Emulsions

The most common method for stabilising emulsions makes use of the unique properties of molecules called surfactants (SURFace ACTIVE AgeNTS). These have the property of being absorbed strongly (but not irreversibly) at the interfaces between immiscible phases [21]. Surfactants act at these surfaces as they are amphiphilic, containing both polar and non-polar groups. Therefore, to reduce unfavourable interactions, molecules will align themselves across the interface with the polar end in the more polar phase and the non-polar end in the more non-polar phase. The basic structure of a surfactant is a polar head group connected to one or more long hydrocarbon tails that act as the hydrophobic end of the molecule.

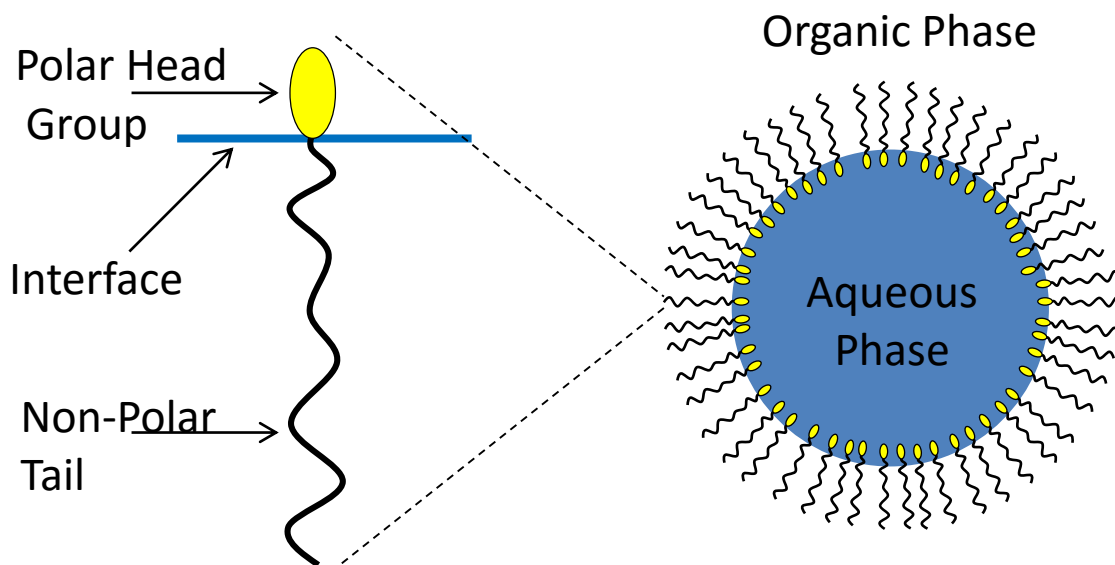


Figure 3. Surfactant molecules orientate themselves at the interface between phases.

The polar head group of the molecule can have many different forms dependent on the application that the surfactant is required for. It can be non-ionic using polar functional groups, such as alcohol, to give the head group polarity or it can be ionic (cationic, anionic and zwitterionic). These head groups are important as they often dictate the behaviour of the surfactants, and hence the emulsions they stabilise, under changes in pH, temperature and other conditions [22]. In solution surfactants will begin to self-aggregate, producing micelles [23, 24], if the surfactant concentration exceeds a limit known as the critical micelle concentration.

Surfactants are the most commonly used method for stabilising emulsions. As the concentration of surfactant increases at the interface a monolayer is formed between the two phases reducing the interfacial tension and increasing the viscosity resulting in a lower driving force towards coalescence [25]. Further stabilisation of the emulsion occurs due to the Gibbs-Marangoni effect [26], which is caused by gradients in the interfacial tension caused by differing local concentrations of surfactant along the interface. As fluid flows from areas of low interfacial tension (high surfactant concentration) to areas of high interfacial tension (low surfactant concentration) the Gibbs-Marangoni effect will act to increase surfactant concentration in areas where it is low causing fluid to flow into the film between two approaching droplets forcing them apart; however this will occur only if the surfactant is present in high concentration in the continuous phase.

The relative size and shape of the hydrophobic tail and head groups of the surfactant determine the surfactant packing parameter [27]. This determines whether the interface will be more stable as a convex or concave surface and so is an important factor in determining which phase is likely to be the dispersed phase. For example, a bulky hydrophobic tail will promote a W/O emulsion, as in order

to accommodate a surfactant monolayer the interface will have to curve making the aqueous side of the interface concave. The reverse is also true, meaning a large head group relative to the tail will promote O/W emulsions. If the head and tail groups are of similar size, then the curvature of the emulsion will be zero and structures such as bicontinuous microemulsions and lamellar phases [28] may be formed.

The suitability of a surfactant to stabilise a given system is indicated by its hydrophilic-lipophilic balance (HLB), which is a measurement of how hydrophilic or lipophilic a surfactant is. The HLB can be calculated by several methods [29, 30] but one of the most common is Davis's method [31] shown in **Equation 1**, in which x and y are the number of hydrophilic and lipophilic groups respectively and H and L are values assigned to those groups based on experimental data.

$$HLB = xH - yL + 7$$

Equation 1

Therefore a low HLB means that the surfactant is lipophilic, while a higher HLB means it is more hydrophilic. It has been found that the phase in which the surfactant is more soluble is generally the continuous phase in an emulsion [32]. Therefore in order to stabilise W/O emulsions the HLB value should be between 2-6 with an optimum around 4.3 [14], while an O/W emulsion requires a higher HLB, between 12-18. However, the HLB concept is limited [33] as other factors such as temperature and pH can affect a surfactant's HLB [34]. Some common surfactants used to stabilise W/O emulsions are Span 80 [35, 36] and various Hypermers [37].

1.2. Particle (Pickering) Stabilised Emulsions

The alternative to using surfactants to stabilise emulsions is to use nano-sized particles alone or in conjunction with surfactants [11, 38-41]. Although known since 1903 [42] particles emulsions have attracted increasing interest in recent decades as they are often much cheaper than surfactants, less sensitive to droplet coalescence caused by raised temperatures and are in general less harmful to the environment [43, 44]. They also allow for the production of multiple emulsions which have applications such as liquid membranes [45] and drug delivery [46].

Particles act to stabilise emulsions principally by forming a dense layer at the interface between phases [47] which acts as a mechanical barrier to prevent the coalescence of dispersed phase droplets [48]. Alternately if particles repel each other so will individual droplets coated in such particles preventing droplet contact. This mechanical barrier is especially important in HIPEs as their droplets are in such close contact with each other. Stabilisation of the emulsion can also be enhanced if there is a significant concentration of particles in the continuous phase such that a

network of particles can form surrounding the particle preventing them approaching each other. However it has been demonstrated that particles that strongly repel each other, hence forming a well ordered but dilute covering on the droplets surface, can also effectively stabilise an emulsion [49]. This is achieved by the particle bridging mechanism whereby as two droplets come into contact a particle is absorbed simultaneously in the interfaces of both droplets. If a particle in this situation is absorbed such that the majority of the particle is in the continuous phase then this will lead to droplet flocculation but the interfaces will be kept apart preventing coalescence.

However some coalescence may occur before a stable droplet size is reached in particle stabilised emulsions [15]. The decrease in surface area of the droplets leads to the concentration of particles at the interface to increase over time meaning a point can be reached where the particle concentration is high enough to prevent further coalescence under those conditions.

Unlike surfactants which are constantly in equilibrium with their surroundings, adsorbing and desorbing from the interface continually, particles adsorb irreversibly at an interface [50]. This is due to the particle removing an area of high energy surface where the two immiscible phases contact each other when it absorbs than a surfactant molecule. The ability of a particle to stabilise and emulsion therefore is dependent on the energy of the interface, i.e. the interfacial tension (γ), and the area of interface removed by an adsorbing particle, which depends on the size and wettability of the particle. The wettability of the particle is measured by its contact angle in a given two phase system. The contact angle of a particle is analogous to the HLB [51] of a surfactant molecule as it demonstrates to what extent a particle is hydrophobic or hydrophilic. A particle which sits evenly across an interface has a contact angle of $\theta = 90^\circ$ (measured into the denser phase, here through water) therefore a hydrophobic particle will have a contact angle of $\theta < 90^\circ$ and the majority of the particle will be in the organic phase, while a hydrophilic particle will have a contact angle of $\theta > 90^\circ$ and majority of the particle will be in the aqueous phase.

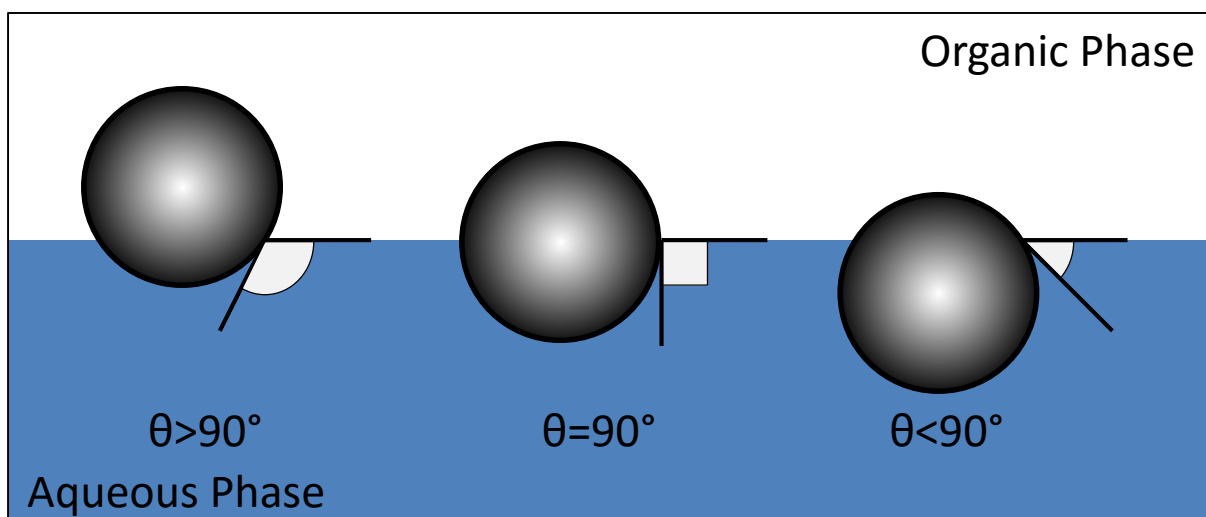


Figure 4. Three spherical particles of differing hydrophobicity at an aqueous/organic interface and the contact angles for each particle. The most hydrophobic particle (left) has a contact angle greater than 90° and resides mostly in the organic phase. While the reverse is true for the hydrophilic particle (right).

The energy (E) remove to remove a particle from an interface can be calculated from the formula [50] given in Equation 2 assuming spherical particles small enough that gravity is negligible and where r is the radius of the particle and γ in the interfacial tension.

$$E = \pi r^2 \gamma (1 \pm \cos \theta)^2$$

Equation 2

The sign in the bracket is negative for removal in to the aqueous phase and positive for removal into the organic phase. It is clear from this that the greatest particle removal energy occurs when the contact angle is 90° . It can be seen that as the term in brackets is squared that the energy of attachment will drop off rapidly as the contact angle is increased or decreased away from 90° therefore particles with very high or low contact angle will be ineffective at stabilising the interface and will remain dispersed in one of the phases. The value for the energy of attachment of a particle (for a standard water toluene system contact angle 90° [50]) is several orders of magnitude greater than the thermal energy of the system explaining why particle absorption is irreversible. The removal energy drops to roughly ten times the thermal energy at contact angles of greater than 160° or less than 20° or when particles reach sizes around 0.5 nm in diameter. In these cases the particles behave like surfactants constantly absorbing and desorbing from the interface. There can be contact angle hysteresis which becomes more pronounced the rougher the particle surface is and the less spherical it is [52].

Despite particles being attached most firmly when their contact angle is 90° it has been found that Pickering emulsions are best stabilised if the contact angle is slightly above or below this value [52, 53]. This is due the stability of the menisci surrounding the particles being greatest at 0° and 180° and least at 90° .

The wettability of a particle used to stabilise an emulsion also determine which phase will be dispersed/continuous. A hydrophobic particle used to stabilised an emulsion will strongly promote a W/O emulsion as the particle will mostly reside in the organic phase curving the interface such that the aqueous phase will be dispersed as droplets [48].

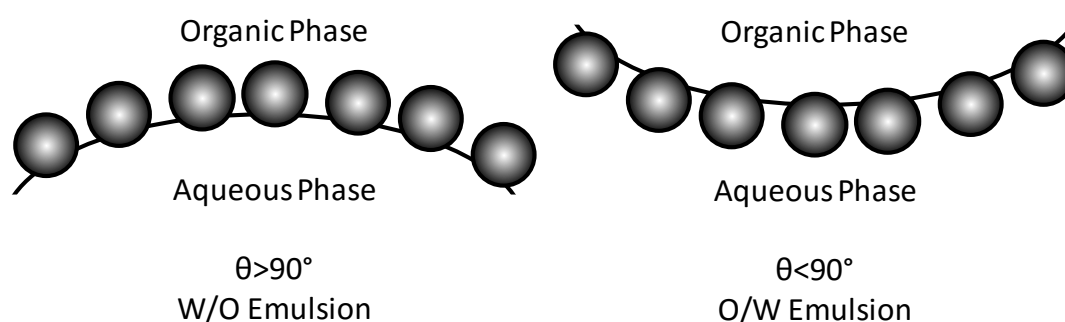


Figure 5. Diagram showing how the contact angle of a particle can be used to promote W/O emulsion or O/W emulsion. The contact angle of particle can be thought of as similar to the HLB of a surfactant.

In many applications steps are taken to modify the contact angle of a particle by modifying its surface to effect a change in hydrophobicity. Hydrophilic silica particles are commonly used to stabilised emulsions but they have been functionalised to be more hydrophobic, so they promote W/O emulsions, by physical absorption of oleic acid [54] or by silylation of their surfaces [53, 55]. It is also possible to create 'Janus particles' which have been heterogeneously coated such that the particles are amphiphilic similarly to surfactants [41, 56]. Currently many different types of particles have been used to stabilise Pickering emulsions including silica [40, 54, 57-59], titania [38], latex particles [60], carbon nanotubes [39] and clay particles [61].

1.3. Additional Factors affecting Emulsion Stability

The stability of an emulsion is mainly dependent on the use of an emulsifier (particle or surfactant) which has the correct properties (HLB, contact angle) and is present in a high enough concentration. It has been shown for all types of emulsifiers that an increase in concentration leads to greater stabilisation and smaller droplets sizes in the dispersed phase. The HLB or contact angle of the

emulsifier required to stabilise an emulsion depends on the polarity of the oil phase [27] and whether the emulsion is O/W or W/O. However the ability of the emulsifiers to stabilise the emulsion can also be affected by many other factors of a given system.

The pH of a system will in many cases affect the stability of an emulsion. For particles or surfactant containing ionisable groups changing the pH can affect the contact angle or HLB respectively. This can cause phase inversion or separation within an emulsion system.

Temperature can also affect emulsion stability [50]. This is much more evident in surfactant stabilised emulsions as due to their lower energy of attachment at the interface compared to particle stabilised systems as increased thermal energy perturbs the equilibrium such that less of the surfactant molecules are held at the interface thus decreasing emulsion stability. However due to the irreversible nature of absorption, of all but the smallest particles, Pickering emulsions show much greater thermal stability. Increased temperature also decreases the viscosity of an emulsion meaning droplets are more easily able to move into contact with each other increasing the rate of coalescence. Temperature can also affect the HLB of some surfactants due to dehydration of a polar head group.

The electrolyte concentration in the aqueous phase also has an important role to play in the stability of an emulsion. In general an increased electrolyte concentration will impart greater stability to an emulsion. They do this in the most part by inhibiting Ostwald ripening (coarsening). However changing electrolyte concentrations can affect the HLB of ionic surfactants and the contact angle of particles with ionisable surface groups. Vibration of an emulsion can increase the rate of phase separation so careful storage will prolong the life of many emulsions [62].

1.4. Phase Separation in Emulsions

The interface between the two phases is a high energy surface as immiscible molecules are forced into contact with one another. Therefore all macro-emulsions are thermodynamically unstable and will eventually break down unless stabilised by emulsifiers. Some thermodynamically stable microemulsions can form spontaneously [63].

Phase separation refers to the tendency of an emulsion to separate into two distinct layers of immiscible fluids as opposed to one phase being dispersed as droplets within the other. Several phenomena can contribute to the process of phase separation. Creaming and sedimentation [51] refer to phase separation due to the effects of buoyancy with the droplets of the dispersed phase rising or settling respectively dependent on the relative densities of the two phases. This leads to the

emulsion containing two distinct regions one containing a high concentration of dispersed phase droplets and another containing only continuous phase. However in some cases sedimentation has been deliberately used to create high internal phase emulsions [64]. Using phases with similar densities will decrease the rate of creaming and sedimentation as will increasing internal phase volume ratio, as tightly pack droplets move more slowly. Similarly to creaming and sedimentation flocculation can also lead to phase separation. Flocculation refers to the aggregation of dispersed phase droplets into clusters or flocs.

Creaming, sedimentation and flocculation all result in the droplets of the dispersed phase coming into closer contact with each other creating greater heterogeneity within the system however complete phase separation will result only when the individual droplets coalesce. When two droplets come into contact in an emulsion they are separated by a thin film of continuous phase [65]. If this thin film ruptures the two droplets will merge together to form a larger droplet eventually leading to phase separation. This coalescence is driven by the reduction in the high energy surface area between the two phases, for example two identical spherical droplets coming together reduce the total surface area by around 37%. The higher the interfacial tension between the two fluids the greater the driving force towards coalescence since the interface is less energetically favourable. Decreasing the rate of droplet coalescence can be achieved therefore by decreasing the interfacial tension with surfactant or by creating a steric barrier with particles. As well as the emulsion break down occurring in solution it should be noted that it can also occur heterogeneously at the wall of the vessel containing the emulsion [17].

Phase separation can also be caused by Ostwald ripening. This type of phase separation occurs due to the difference in chemical potential between the surface molecules in droplets of different diameters i.e. in a polydispersed system [66]. The larger the droplet the lower its curvature and therefore molecules on the surface of the droplet have less contact with the molecules of the continuous phase. This makes it less likely that these molecules will dissolve in the continuous phase. Therefore there will be a net movement of dispersed phase molecules from smaller droplets to larger droplets. This will result in larger droplets increasing in size at the expense of smaller droplets until the latter disappear entirely which can eventually lead to total phase separation. The greater the mutual solubility of the two phases the greater the risk of Ostwald ripening due to the larger rate of diffusion of internal phase molecules between droplets. Increased stabilisation of O/W emulsions can be achieved by increasing the concentration of ions in the aqueous phase of the emulsion [66], as this has the effect of reducing the solubility of the oil phase in the aqueous phase thereby reducing the rate of Ostwald ripening [67, 68]. However indefinitely increasing the concentration of

electrolyte can lead to emulsion instability as the surfactant can be salted out, forcing it into the oil phase thereby removing its stabilising effect [14].

1.5. Phase Inversion in Emulsions

Phase inversion refers to the switching of the dispersed and continuous phases of an emulsion from an O/W emulsion to a W/O emulsion or vice-versa. Phase inversion can be caused by two mechanisms [53] termed translational phase inversion and catastrophic phase inversion. It is distinct from phase separation as, if the system is still being agitated, it doesn't necessarily lead to the destruction of the emulsion just the reversal of the continuous and dispersed phases .

Catastrophic phase inversion, Figure 6, is the result of increasing the percentage volume of the dispersed phase until it reaches a critical value for the system whereupon it phase inverts [53]. It has only been observed in particle stabilised emulsions [69].

Translational phase inversion [47], Figure 6, is caused by a change in the HLB of a system such that the emulsion becomes unstable in its current form. This can be caused by the addition of additional surfactants, co-surfactants, salts [70], temperature changes [71], particles with different wettabilities [47] or by changing the pH of the system [27].

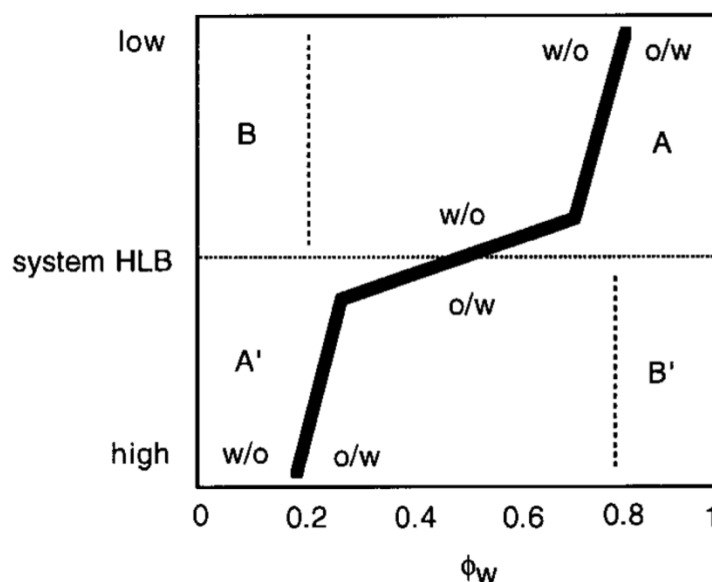


Figure 6. Graph representing both catastrophic and translation phase inversion for a water-toluene system stabilised by silica particles of differing wettabilities [53]. The catastrophic transition from B to A will occur in systems with hydrophobic silica particles whereas the transition from B' to A' occurs in the presence of hydrophilic particles.

1.6. Preparation of W/O High Internal Phase Emulsions

Several methods for the production of HIPEs have been developed. These can influence the final properties, such as the droplet size, of the emulsion. The most common method is to slowly add the dispersed phase to the continuous phase while gently agitating the mixture with an overhead mixer, (Figure 7) or laboratory vortex mixer [72]. Dispersed phase addition can be controlled by a number of methods such as a dropping funnel or syringe pump. Once all the dispersed phase has been added more vigorous agitation can be used to produce smaller droplet sizes [20, 73].

An alternate method is to mix the continuous and dispersed phases together with an appropriate emulsifier in the correct ratio in a single pot. Then the closed vessel is shaken either by hand or by a laboratory vortex mixer [72]. With this method the mixer undergoes a complex evolution during agitation, starting as an O/W emulsion before passing through a multiple W/O/W emulsion before finally forming the desired W/O HIPE.

HIPEs can also be formed by taking advantage of the phase inversion temperature (PIT) of a system [74], for example starting off with an O/W LIPE and agitating while rapidly heating it past the PIT to produce a W/O HIPE. This method reduces the mechanical energy required to produce the HIPE compared with the previous two methods. Again the greater the rate of agitation the smaller the size of the droplets formed in the final emulsion[74].

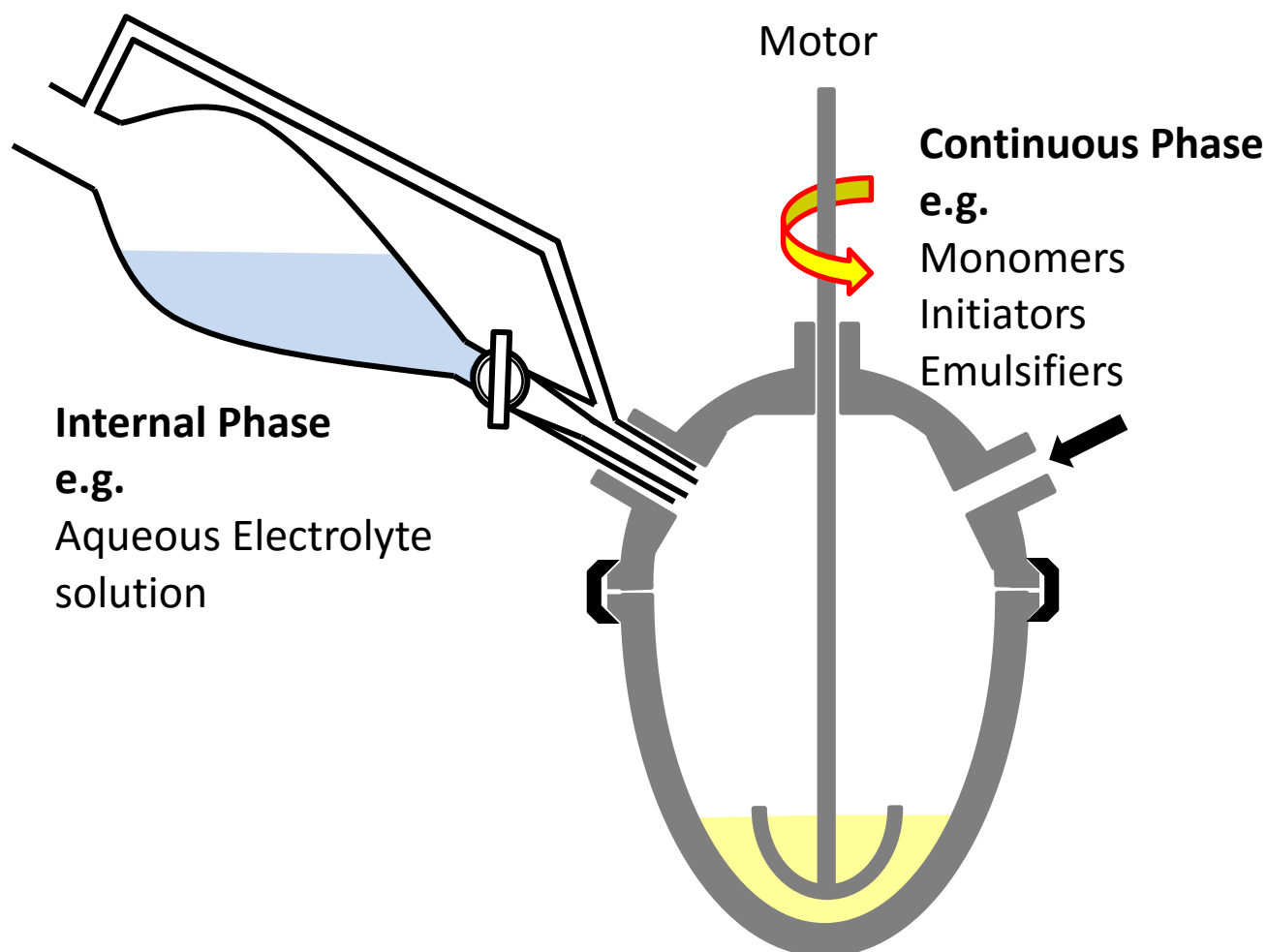


Figure 7. Diagram showing a common set up for the production of HIPEs. The continuous phase is added all at once to the vessel while the internal phase is added slowly from a dropping funnel. All the while the mixture is constantly agitated to produce, in this case, a W/O emulsion.

1.7. Rheological Properties of HIPEs

Unlike standard emulsions the high packing of internal phase droplets in a HIPE means their rheology is much more complex than a dilute emulsion. Dilute emulsions (<10% internal phase) exhibit Newtonian behaviour where their viscosity is determined by the composition of the continuous phase. HIPEs on the other hand are highly viscous and exhibit non Newtonian behaviour. They are characterised as Bingham fluids, this means that below a given yield stress they behave as an elastic solid and above the yields stress they flow, exhibiting sheer thinning behaviour [17].

As well as increasing with the internal phase volume the viscosity increases with increasing concentrations of emulsifiers. The diameter of the droplets of the internal phase also affects the viscosity of a HIPE with smaller droplets leading to higher viscosities [75]. Since the droplets are

usually created by agitation this means the rheological properties are often dependent on the conditions under which the HIPE was prepared.

1.8. Applications of HIPEs

HIPEs have been used for centuries in the form of mayonnaise [76] an O/W emulsion within an internal phase volume of up to 80% stabilised by the lecithin present in egg yolks. HIPEs have been considered for use as skin creams in both the cosmetic and pharmaceutical industries [77]. They have also been used to create fire resistant fuels for use in aircrafts [17] and in the production of nickel coated electrodes [78]. The main application of interest for this research is the use of HIPEs as templates to produce macroporous polymers which have a large range of applications in their own right.

2. Polymerised High Internal Phase Emulsions (polyHIPEs)

If the continuous phase of a HIPE is made up of monomers, the polymerisation of the emulsion will result in a highly porous structure termed a polymerised high internal phase emulsion (polyHIPE). Other names include emulsion template polymers [79], emulsion polymer foams [80] and emulsion template macroporous polymers [20]. Polymerisation of the dispersed phase of emulsions has also been used to produce polymer beads [81]. Polymerisation is usually achieved using a suitable free radical source, such as AIBN (2,2'-Azobis(2-methylpropionitrile)) [73], which is dispersed in one of the phases before mixing to form a HIPE. The HIPE is then left to polymerise at an elevated temperature, then if necessary purified and dried. Similarly to polyHIPEs, polyMIPEs and polyLIPEs have also been created and share the same definition as their respective HIPEs with respect to internal phase volume. Recently polyHIPE have been produced by solidifying polymers dissolved in the continuous phase of the template emulsion as opposed to polymerisation [82].

After polymerisation the dispersed phase droplets are left as cavities inside the rigid polymer foam, these cavities are termed pores [12]. The polyHIPE takes the form of the HIPE at the gel point of polymerisation [83]. The percentage volume that these pores represent in the overall structure is equivalent to the percentage volume they took up in the HIPE before polymerisation and represent the porosity of the polyHIPE. For example a HIPE with an internal phase volume of 80% will result in a polyHIPE of 80% porosity. Pore size in polyHIPEs therefore depends on the size of the droplets in the original HIPE; this can vary from below 2 μm [20] to well over 1000 μm . In general poly-Pickering-HIPEs, (polyHIPEs produced from Pickering emulsions) have larger pore sizes to those

produced from surfactant stabilised emulsions [50]. The density of a polyHIPE can either be represented by its skeletal density or its foam density. Skeletal density refers to the density of the polymeric material that makes up the polyHIPE whereas the foam density considers the total volume of the polyHIPE including the pores.

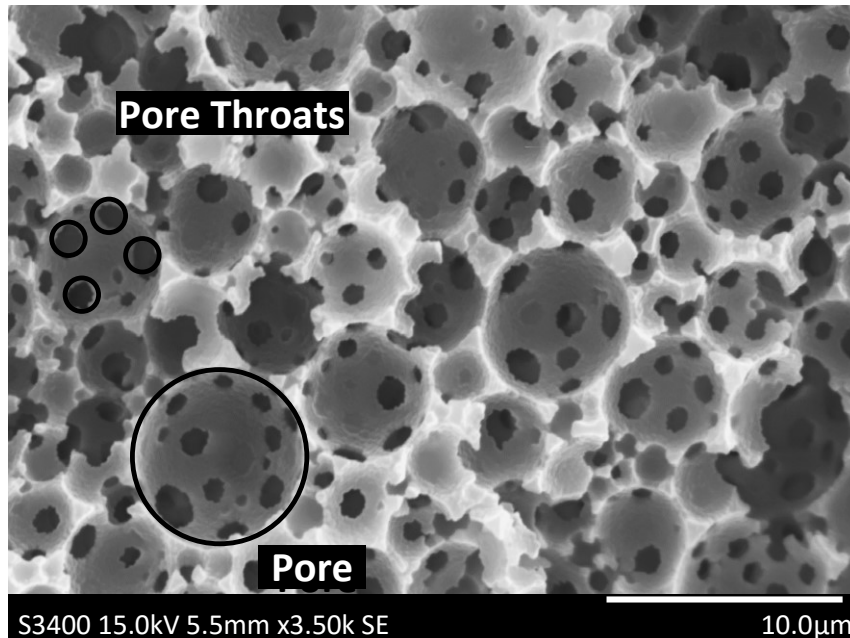


Figure 8. Surfactant stabilised S/DVB polyHIPE with 82% porosity. Pores and pore throats are clearly visible

Due to the close packing of droplets in a HIPE it is often the case that the thin lamellae between pores break down leading to connecting windows or pore throats [12] between pores. PolyHIPEs with interconnecting pores are termed open celled while if pore throats are not present the term closed celled is used.

PolyHIPEs are one of several similar porous media currently being investigated. The most common method for forming polymer foams is to use blown gas to create the voids or include a molten mixture species which breaks down to produce gas voids. However unlike using an emulsion template it can be harder to create interconnected pore structure of well-defined pore size. It has also been reported that polyHIPEs have superior mechanical properties to gas blown macroporous polymers [14] since smaller and more regular pore sizes are possible in a polyHIPE. Similarly interconnected systems to polyHIPEs are also seen in microcellular ceramic foams [84]. These are created using small sacrificial polymer beads to create the pores which are then burned out to give the porous structure.

2.1. PolyHIPE Permeability

The interconnected pores of an open celled polyHIPE mean it is a bicontinuous structure and will have a degree of permeability to fluid flow. Remarkably it was found that even polyMIPes and polyLIPes can have a degree of permeability and therefore must contain an interconnected pore structure [20]. The permeability of a porous material defines the ease at which fluid can flow through it given a driving force.

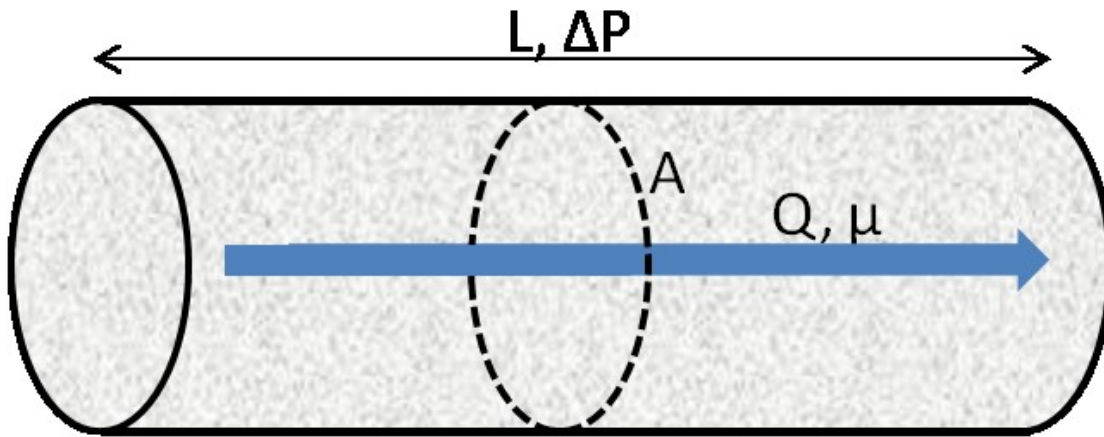


Figure 9. Diagram of porous material with the parameter that determine the permeability of the material.

Darcy' law (Equation 3) relates the flow rate of a liquid (Q) through a porous material to the viscosity of the (μ) liquid, the dimensions of the porous material (A and L for area and length respectively) and the driving pressure across the material (ΔP) using the permeability (k). This equation holds true for a linear horizontal flow of incompressible fluids and can be used to calculate the permeability in such cases.

$$Q = \frac{kA \Delta P}{\mu L}$$

Equation 3

Commonly the unit of permeability is the Darcy (D) while the SI units for permeability are m^2 , $1\text{D} = 10^{-12}\text{m}^2$.

For gas flows in porous media however a different set of equation is required to account for the change in velocity of the fluid in the porous media and the slip effect [85] which corresponds to flow along a stationary surface. These equations are given in Chapter 3 section 2.3.

PolyHIPEs with porosity of up to 2.6D [11] have been produced however a typical value for surfactant stabilised Styrene/DVB polymers is $\sim 0.5D$ [11]. There are many factors that influence the permeability of polyHIPEs such as the size and shape of the pore throats, porosity and degree of polydispersity present in the polyHIPE. Pore throats are often considered to be the factor limiting the porosity of a polyHIPE however increasing the size of pores and hence pore throats run the risk of weakening the polyHIPE [84]. Pore throats are commonly found in surfactant stabilised emulsion however Pickering emulsions are more likely to be closed celled and often require the addition of a surfactant to promote the formation of pore throats [86].

The formation of pore throats is a matter of debate in the polyHIPE community and is certainly a complex process affected by many factors. Cameron et al. [83] suggested that the pores throats form by the contraction of the thin films of continuous phase between dispersed phase droplets at the gel point of polymerisation. This conclusion was drawn by freezing the HIPE at several points during polymerisation, analysing them by Cryo-SEM noting at what point the pore throats were formed. However, Menner and Bismarck [18] dispute this noting that polyHIPEs with internal phase volumes of as high as 97% have been produced which are closed celled [87]. They speculate that pore throats are original formed as during polymerisation the surfactants are insoluble in the polymer as well as the aqueous phase. This forces the precipitation of surfactant in the thin films between droplets creating a weak point. However it is suggested the rupture of this film only occurs due to mechanical action during purification and drying. This mechanism is supported by pictures of intact and partially ruptured pore throats.

In both theories the concentration of surfactant is key, with higher concentrations promoting the formation of pore throats. This is due to higher concentrations of surfactant promoting the formation of smaller droplets which in turn leads to thinner solvent layers between individual droplets [83]. However pore throats have also be observed, although more uncommonly, in systems stabilised solely by particles so the formation of pore throats is not exclusively dependent on the concentration of surfactant [18].

2.2. Controlling the Properties of polyHIPEs

One major advantage of polyHIPEs is that it is possible to alter the structure such that they are suitable for a desired purpose.

2.2.1. Controlling Pore size

In the formation of a HIPE the dispersed phase is broken up into droplets by agitation, therefore the speed of and length duration of agitating the emulsion is important in determining the size of dispersed phase droplets and hence the eventual polyHIPE pore size. An increase in the rate of agitation leads to a decrease in the average droplet diameter. However as smaller droplets are less stable, leading to greater coalescence, a greater stirring rate causes non-uniform shear in the system increasing the range of droplet sizes (polydispersity) in the final polyHIPE [36]. Improper agitation can even result in emulsion break down [17]. This approach is thoroughly discussed in Chapter 3.

The temperature at which a HIPE is prepared must also be considered as emulsions undergo increased coalescence at high temperatures meaning the size of pores of the resulting polyHIPEs will also be increased. Surfactant HLB is also affected by temperature again resulting in larger pore at higher temperatures [30].

The pore throat size is of key importance in determining permeability of a polyHIPE. The size of pore throats is limited by pore size however actual size often depends on the conditions of preparation. It was found that as well as stabilising the emulsion against Ostwald ripening the electrolyte concentration in the aqueous phase can also dramatically increase the size of pores and pore throats at low rates of agitation [36]. In S/DVB poly-Pickering-emulsion it has been found that pore throat sizes can be dramatically increased from 1-3 μm to 19-26 μm by the addition of surfactant Hypermer 2296 [11]. This has a dramatic effect on the permeability of the material.

Surprisingly it is common for polyHIPEs to have a reasonably low surface area (3-20 m^2g^{-1} [35]) this makes it less attractive for applications like heterogeneous chemistry. However it is possible to increase the surface area [35, 88] by including a non-polymerisable component, such as toluene, in the organic phase as a porogen. This causes phase separation during polymerisation causing micropores within the walls of the pores vastly increasing surface area. Increasing the amount of time spent in purifying the polyHIPE has also been shown to increase the surface area [88]. However after some time a maximum surface area is reached after which further purification has no effect.

2.2.2. Mechanical Strength of polyHIPEs

One of the major problems associated with the use of polyHIPEs, due to their low foam density and high degree of interconnectivity, is mechanical weakness. However it has been reported that their properties are still superior to gas blown macroporous polymers due to the tighter packing of smaller droplets in polyHIPEs [14].

Several methods have been used to increase the mechanical strength of polyHIPEs. The simplest method is to decrease the internal phase volume so that walls between pores are thicker and foam density is increased [12]. However for applications where high porosity or high permeability is required this is not an attractive option.

Another method to improve the mechanical strength is to choose monomers that lead to a polymer with better properties for example by increasing the degree of crosslinking. For example a standard styrene-co-divinylbenzene (S/DVB) polyHIPE is easily shattered by a blow from a hammer, however by using polyethylene glycol dimethacrylate (PEGDMA) instead of DVB as a flexible crosslinker the resultant polyHIPE was able to withstand the blow [80, 89]. If a flexible monomer like 2-ethylhexylacrylate is used instead of some of the styrene an elastomeric polyHIPE can be produced [80]. However it was found that the resulting polyHIPEs were closed celled meaning that they are not appropriate for application where permeability is required.

As well as the stabilisation of emulsions addition of particles can also serve to improve the mechanical properties of polyHIPEs [73, 80]. It has been shown that for an S/DVB polyHIPE the crush strength can be increased 218% and the Young's modulus 280% through the use of silica particles modified with methacryloxypropyltrimethoxysilane (MPS) [90]. This allows the silica to be covalently incorporated into the polymer network.

Introducing hierarchy into the internal phase droplet sizes has also been shown to improve mechanical strength [91]. Many naturally occurring porous types of foam such as bone and wood used this approach to give structures with good mechanical strength. However it has been found that over purification can damage polyHIPE structure leading to a decrease in mechanical strength [88].

2.2.3. Further properties of polyHIPEs

The use of high amounts of conductive particles should make it possible to create electrically conductive polyHIPEs [73, 92]. Another method for creating electrical conductivity is to coat the polyHIPE with an electrically conductive polymer [93]. A material with a high electrical conductivity and surface area would be useful in the production of sensors.

It is also possible to functionalise the surface of polyHIPEs to give them specific chemical properties. This can be achieved by taking advantage of unreacted double bonds [94] or by using monomers with reactive side groups, such as vinyl benzyl chloride [95-97]. If particles are present in the pore wall it is possible that they can also be functionalised. Surface modification allows properties such

hydrophobicity, chemical resistance and catalytic activity of the polyHIPE to be controlled and manipulated.

3. Applications of Polymerised Emulsions

3.1. Non Separation Applications

Polymerised emulsions can be “cured” into any shape, such as monoliths or membranes by placing the template emulsion in to an appropriate mould before polymerisation. They can also be formed into macroporous beads [98-100]. The choice of monomers and reinforcement or adjusting the porosity allows control over mechanical properties and for the inclusion of desired functional groups, which can also be introduced by post-synthesis functionalization [101, 102]. This ease of functionalization is key to the wide range of possible applications of polymerised emulsions. The interest in possible polyHIPE applications is increasing resulting in several reviews in to various aspects of their nature being published in recent years [6, 103-109].

PolyHIPEs have been considered for many potential application including supports for cell cultures [110-112], bone grafts [113], setting cement for oil well cementing applications [114] and for chemical reactions [115, 116] as structural materials [117], porous electrodes [118], Self-sealing vessels [119] and separators in lithium ion batteries [120, 121].

There are many other possible applications for polyHIPEs including hydrogen clathrate storage [122] for use in hydrogen powered cars. PolyHIPEs have also been considered for use in tissue engineering applications [123] and ion exchange columns [92]. Poly-Pickering-HIPEs have been synthesised using renewably produced bacterial cellulose [124]; as petroleum based surfactants become more costly this may become a more attractive and environmentally friendly option. Currently there are no major commercial applications for the use of polyHIPE, this is mainly due to the limitations in their mechanical strength [37].

3.2. Filtration Applications

Due to their ability to be produced in any shape and their readily controlled pore size; polyHIPEs can be used as filters for both liquids and gases. Bhumgara [125] was able produce a filter device with 48 crossflow channels, by pumping a prepared HIPE into a mould before polymerisation. This device proved effective at filtering calcium carbonate (aragonite) particles ($D_{43} \approx 11 \mu\text{m}$). The polyHIPE filter was also found to be partially successful at filtering dispersions of double chain cationic surfactant (ArosurfTA-100) ($D_{43} \approx 1.4 \mu\text{m}$) once a surfactant gel layer had formed. This gel layer could be further stabilised by sulphonation of the polyHIPE increasing rejection to 55%, however the increased gel

layer also reduced permeate flowrate. Another important area in which PolyHIPEs could be used as filters is as a permeable barrier in oilwells, replacing traditional gravel packs. Ikem et al. [86, 126] were able to synthesise highly permeable (greater than 1 Darcy) poly-Pickering-HIPEs for this purpose with mechanical and thermal stability sufficient to withstand down hole conditions as the particulate emulsifier acts as effective reinforcement for the macroporous polymer [127]. PolyHIPEs have also be considered as aerosol filters [128]. Walsh et al. [129] showed that particles with sizes exceeding 1 μm were very effectively removed from an aerosol spray by a poly(styrene-divinylbenzene (S/DVB))HIPEs.

3.3. Membrane Applications

Casting polyHIPEs into membranes has opened up a wide range of applications in protein separation [130]. Membranes can be formed by moulding HIPEs between plates [92], slicing polyHIPE monoliths [131] or by spreading HIPEs on to a substrate using a casting blade [132]. Due to interaction between the mould/substrate and HIPE a low permeability skin [125] often forms on the polyHIPE and droplet coalescence in the polymerising HIPE results in the formation of pinholes, both causing problems for membranes. However, Krajnc et al. [133] reported polyHIPE membranes with thicknesses ranging from 30-500 μm with open porous surfaces by casting HIPEs on a glass substrate.

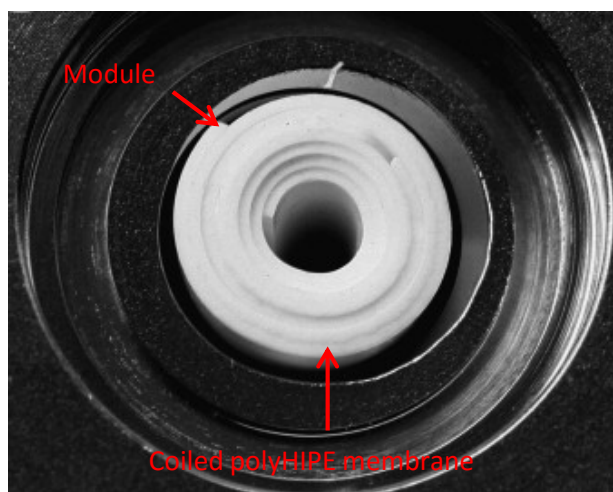


Figure 10. A flexible polyHIPE membrane wrapped around a frit in a module for use in protein separation. Reprinted with permission from Elsevier.

Separations membranes are required to be flexible and thin to withstand and reduce trans-membrane pressure drop, respectively. Conventional poly(S/DVB)HIPEs are chalky and brittle [12], therefore, Pulko et al. [132] used monomers, such as ethylhexyl acrylate as a plasticizing comonomer to increase the flexibility of polyHIPE membranes while retaining an interconnected permeable structure. In this way, it was possible to produce flexible enough polyHIPE membranes, which could

be wound into a module that could potentially be used for protein separation after surface modification (Figure 10). However it has been reported that addition of ethylhexyl acrylate can decrease pure water permeability [134].

Composite polyHIPEs, created by polymerising both the continuous and dispersed HIPE phases, have been explored as pervaporation membranes [135-137], showing high permselectivity to water. Composite polyHIPEs have also been used to create ion selective membranes [138].

Ion exchange modules were formed from sulphonated polyHIPEs [139]. The polyHIPE modules showed lower exchange capacity than commercial strong acid cation resins, however their superior hydrodynamics, due their open pore structure, resulted in higher break through capacities.

3.4. Chromatography Applications

PolyHIPE monoliths have inherently higher permeability than traditional packed beds [140], so their use as the stationary phase in chromatographic applications is the most thoroughly researched area of any polyHIPE application. Junkar et al. [141] found the pressure drop along polyHIPE monoliths could be accurately predicted by the representative unit cell model but not by traditional models for packed beds. PolyHIPEs often have lower surface areas ($\approx 5 \text{ m}^2\text{g}^{-1}$) than packed beds since they simply contain less material and often have smooth internal surfaces. However, their surface area can be dramatically increased by the introduction of non-polymerisable porogens into the continuous phase [35, 142] (Figure 11) or by swelling the polyHIPEs followed by hypercrosslinking [143]. Both operations create micropores, which dramatically increases the surface area available for solute absorption during chromatography to up to a claimed value of $1210 \text{ m}^2\text{g}^{-1}$ [143].

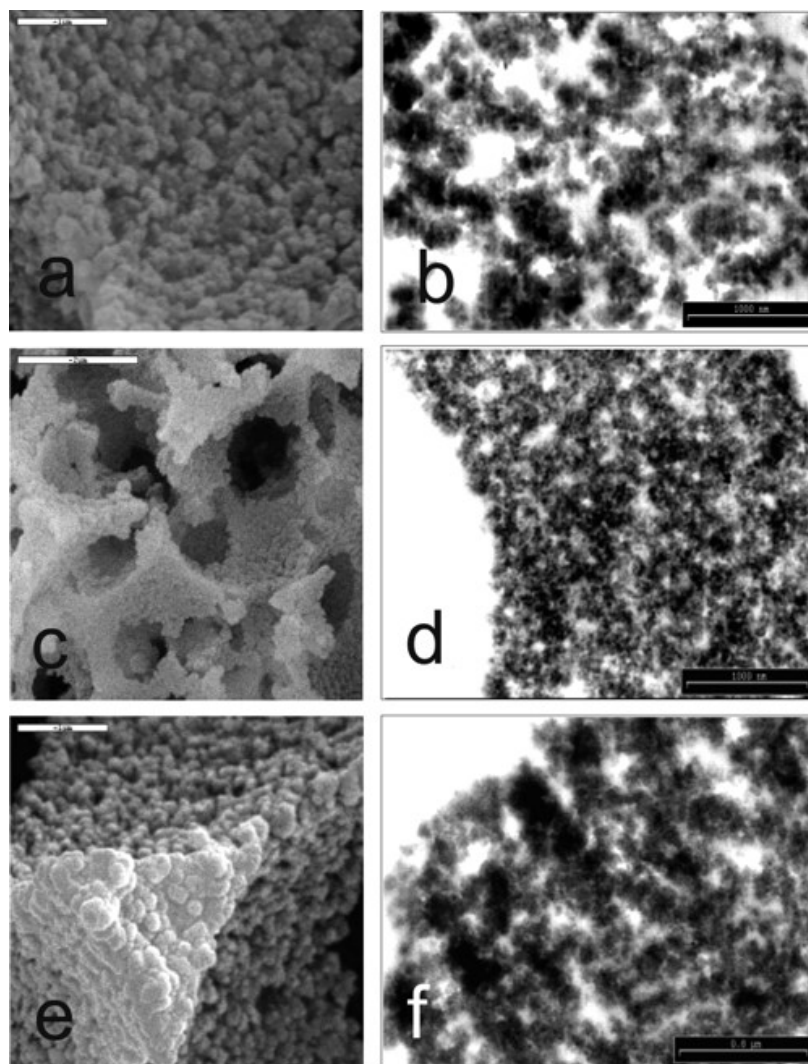


Figure 11. SEM and TEM images of poly(DVB)HIPEs with the inclusion of a porogen showing the increased surface area; (a and b) Toluene, (c and d) (2- chloroethyl)benzene, (e and f) 1,2-dichlorobenzene. Scale bars on images: (a and c) 2 μm ; (b, d and e) 1 μm and (f) 0.8 μm . Reprinted with permission from [33]. Copyright 2004 American Chemical Society.

Most polyHIPE chromatography publications are related to the separations of proteins and other biological molecules. The most common monomers used to produce polyHIPE monoliths for chromatography are methacrylates, such as glycidyl methacrylate (GMA) and methyl methacrylate (MMA), these have proven chromatographic capability and can be easily functionalized [144]. Krajnc et al. [130] were able to demonstrate that a poly(methacrylate)HIPE monolith was able to separate a typical mixture of proteins with similar efficiency to commercial monoliths. The polyHIPEs also showed good mechanical integrity up to porosities of 90%. Similar results were reported by Yang et al. [145] who were able to rapidly separate immunoglobulin from human plasma, as well as separating a protein mixture, also by using a methacrylate based (GMA with ethylene glycol dimethacrylate (EDMA) as crosslinker) polyHIPE monolith. They noted that the

monolith were suitable for high throughput elution and could be easily chemically modified. Similarly the functionalised methacrylate monoliths produced by Yao et al. [146] were shown to have a dynamic binding capacity for proteins, which are significantly higher than those of commercially available monoliths. When used to separate a mixture of proteins, the columns were found to be very efficient. Moreover, they did not exhibit any significant changes in separation performance or permeability over 300 runs or three months after production.

In addition to traditional chromatography the application of polyHIPEs in capillary electrochromatography (CEC) has also been examined [147]. Using a polyHIPE monolith with 90% porosity it was possible to separate alkylbenzenes by CEC with a high column efficiency [148]. It was also discovered that polyHIPE columns produced a strong electroosmotic flow without the addition of electroosmotic flow generating monomers. This was put down to ionisable sulphate groups present on polyHIPEs pore wall surfaces, which are created as by-product of the decomposition of the water-soluble initiator potassium persulfate. PolyHIPE monoliths have also been considered for use in ion chromatography [149].

It was recently reported by Hughes [150] that a poly(S/DVB)HIPE monolith was suitable for the size separation of nanoparticles by aqueous chromatography. It was possible to resolve 5 nm and 10 nm gold particles using this method; which is not possible with standard hydrodynamic chromatography.

3.5. Chemical Scavenging and Sorption Applications

The *in situ* removal of excess reactants and by-products from solutions is desirable as it can remove the need for downstream separations that are often the bottleneck for pharmaceutical processes. PolyHIPE supports have therefore been thoroughly investigated for use as chemical scavengers. Lucchesi et al. [151] produced amine scavenging polyHIPEs, which were shown to be effective in both batch and flow through operations. This was originally achieved by functionalization of pre-existing polyHIPEs with 4-vinyl-2,2-dimethylazlactone [152], however they can now be produced by a direct copolymerisation of (DVB) and *N*-(*p*-vinylbenzyl)-4,4-dimethylazlactone. Moine et al. [153] were able to produce amine scavengers by functionalising a polyHIPE with further methacrylate monomers (MMA or GMA). Such polyHIPEs were shown to be at least twice as effective at scavenging 1-hexylamine from THF solution as a commercial resin.

Krajnc et al. [96] used a functionalised polyHIPE containing amide groups to rapidly scavenge 4-chlorobenzoyl chloride from solution. Under flow through conditions (20 mL/h, monolith volume 3.5 mL) it was possible to scavenge 99% of the 4-chlorobenzoyl chloride in fewer than 10 min. Another

amine group bearing polyHIPE was produced by Tripp et al. [154] taking advantage of residual olefins, left after polymerisation, for functionalisation. The polyHIPE was able to scavenge 92% of phenyl isocyanate from THF solution in 49 min. The surface amine groups could be regenerated with hydrazine in THF, such that the monolith was reusable multiple times (**Figure 12**).

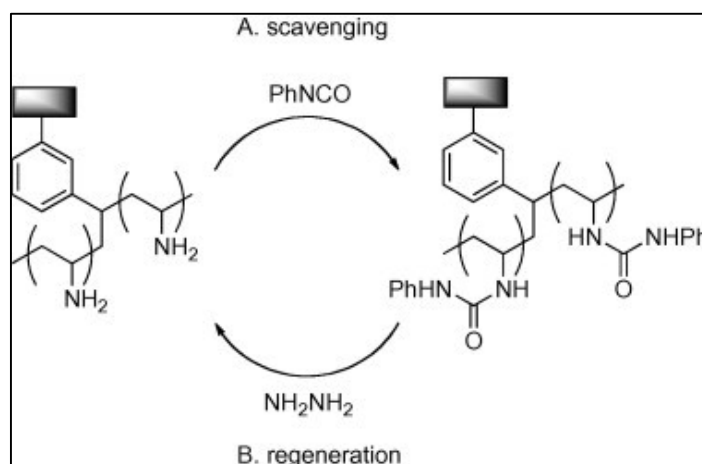


Figure 12. A polyHIPE functionalised to include amine groups scavenging phenyl isocyanate before the amine groups are regenerated using hydrazine. Reprinted with permission from Elsevier.

It was also demonstrated that the toxic herbicide atrazine could be removed from waste water by covalently bonding it to a polyHIPE containing secondary amines [155]. The same technique is likely to be effective for all triazine-based herbicides.

Methacrylate (hexadecyl methacrylate (HMA), MMA, trimethylolpropane-trimethacrylate with TMPTA as crosslinker) based polyHIPEs have also been examined as absorbent for trichloromethane, which is a non-biodegradable pollutant [156]. The most effective resin was found to absorb 34 g/g of pure trichloromethane. Similarly Sergienko et al. examined polyHIPEs as a sorbent for tribromomethane [157]. Katsoyiannis et al. [158] used poly(S/DVB)HIPEs coated with iron hydroxides, which were crushed into beads to remove arsenic anions from solution. The arsenic levels could be reduced below the 10 $\mu\text{g/L}$ maximum mandated by the United States Environmental Protection Agency (USEPA). These polyHIPEs were found to outperform a packed bed of iron oxide coated polystyrene beads in terms of maximum arsenic capacity before break through.

3.6. Breaking of emulsions

Ironically, polyHIPE membranes have been used to intensify the demulsification of water in crude oil emulsions in conjunction with conventional electrostatic demulsification. Conventional methods, such thermal, chemical and mechanical demulsification, are expensive, require long residence times and have to take place on shore. However by using a S/DVB based sulphonated polyHIPE membrane

in a crossflow setup Shakorfow [131] found that the rate of demulsification could be increased. Sulphonation was used to increase the polyHIPE's hydrophilicity. Separation was enhanced as the aqueous phase of crude oil emulsions was preferentially taken up at the emulsion-polyHIPE membrane interface, leading to the absorption of the surfactants on the polyHIPE, promoting coalescence of the water droplets. However the removed surfactants formed an oily layer on the surface of the membrane reducing permeate flux. Separately particles produced from sulphonated polyHIPEs were also used to intensify electrostatic demulsification of crude oil/water emulsions [159]. Almost complete crude oil/water separation was achieved in less than 10 min even with a high flowrate and low electric field strength, by addition of 0.5 g polyHIPE to 1 kg of emulsion. Here, the polyHIPE caused demulsification by the absorption of surfactants from solution.

4. Thesis Aims and Objectives

From a review of the publications relating to poly(merised)H/MIPes it is possible that their internal pore structure has a potential application as a low flow rate mixer. It is postulated that fluids passing through the pore structure will be divided and then recombined in a different orientation enhancing their mixing.

The aim of this work is to understand if macroporous polymers, produced by emulsion templating and commonly known as poly(merised)H/MIPes, can be used to effectively mix fluids that are being passed through them and to study the effect of variations in their pore structure on the mixing behaviour. The mixing behaviour of miscible liquids, immiscible liquids and gas-liquid mixing within the polyHIPE structure shall be investigated.

To meet this aims the following objectives will have to be achieved.

- 1) In order to pass fluids through a polyHIPE structure, suitable methods for the production of polyHIPE flow cells will be developed.
- 2) Methods to control the internal structure of polyHIPEs by manipulating the production of the template emulsions H/MIPes, by methods such as energy input during emulsification and dispersed phase percentage, will be explored.
- 3) In order to assess the mixing of miscible fluids within a polyHIPE structure, two methods will be used:
 - a) The residence time distribution for a pulse input through polyHIPE flow cells of differing pore throat size.
 - b) The 4th Bourne reaction will be carried out in polyHIPE flow cells, produced by polymerisation of emulsion templates stabilised by either surfactants or a mixture of particles and surfactants.
- 4) Immiscible liquid-liquid mixing within polyHIPEs shall be investigated by performing the liquid-liquid extraction of caffeine from water with ethyl acetate using the pore structure to generate significant interfacial area.
- 5) A three phase reaction shall performed within a palladium coated polyHIPE structure to assess their ability to perform gas-liquid mixing and the effectiveness of a polyHIPE catalyst support.

Chapter 2: General Experimental and Materials

1 Materials

The following materials were used during the course of this research: Styrene (S) ($\geq 99\%$), divinylbenzene (DVB) (80%), α, α' -azoisobutyronitrile (AIBN) (98%), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) ($\geq 99\%$), dimethoxypropane (DMP) (98%), sodium chloride (NaCl) ($\geq 99\%$), sodium hydroxide (NaOH) ($\geq 98\%$), hydrochloric acid (HCl) 37% solution, sodium hydrogen carbonate (NaHCO_3) ($\geq 99.7\%$), acetonitrile (CH_3CN) (99.8%), ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$) (99.8%), caffeine (99%) and 4-nitroacetophenone (98%) were purchased from Sigma Aldrich. Non-ionic ethoxylated ester-type surfactant Hypermer 2296 (HLB = 4.9) was kindly provided by Croda (USA). Palladium (II) Acetate (47.5% Pd) was purchased from Fisher Scientific. Hydrophobic pyrogenic silica particles HDK H20 were kindly provided by Wacker Chemie AG (Germany). Pressurized nitrogen (oxygen free) (99.998%) and hydrogen (99.995%) was purchased from BOC (UK). SPHEROMERS® CA10 (spherical polymer beads) were purchased from Microbeads AS (Skedsmokorset, Norway). Silicon carbide was purchased from Mineral Waters (Purfleet, UK). High temperature heat shrink tubing 9.9 mm bore, pro-Power Silicone Lubricant, Araldite® rapid adhesive and Araldite® 2020 were purchased from RS Components Ltd. (Corby, UK). Extruded polyacrylic tubing was purchased from Gilbert Curry Industrial Plastics Co Ltd (Coventry, UK). All materials were used as received.

2 Synthesis of Poly(merised) HIEs and Production of Flow cells thereof

2.1 Preparation of Emulsion Templates and Polymerisation to Produce polyHIEs

Emulsion templates were prepared in 50 ml batches agitated with a glass anchor attached to an overhead mixer (RW 20 Digital Mixer, IKA, Germany). All templates were W/O emulsions containing equal parts (by volume) of styrene (S) and divinylbenzene (DVB) as the polymerisable monomers in the continuous phase. α, α' -Azoisobutyronitrile (AIBN), the polymerization initiator, was present in the continuous phase, at a concentration of 1 mol.-% with respect to the monomers. The continuous emulsion phase also contained the emulsifiers, which were either the surfactant Hypermer 2296 (Croda, USA) or (in Chapter 5 only were stated) a mixture of Hypermer 2296 and hydrophobised pyrogenic silica particles HDK H20 (Wacker Chemie AG, Germany). Those produced with silica particles are identified as Pickering emulsions.

For emulsion templates stabilised solely by Hypermer 2296 the components of the continuous phase were placed in the agitation vessel in the ratio 2:2:1 S:DVB:Hypermer 2296, respectively. This mixture contained the AIBN. The mixture was then agitated slowly until all AIBN was dissolved and the mixture homogeneous. At this point the agitation speed was increased to 400 rpm and the aqueous phase added. The dispersed phase for all emulsion templates in this thesis was an aqueous solution of calcium chloride of concentration 0.27 mol dm^{-3} ($40 \text{ g dm}^{-3} \text{ CaCl}_2 \cdot 2\text{H}_2\text{O}$). The dispersed phase was added to the continuous phase using a syringe pump, with the exception of the emulsion templated polymers produced in Chapter 5 in which the dispersed phase was added using a calibrated dropping funnel. The rate of dispersed phase addition, in all cases, was 15 ml min^{-1} while the continuous phase was being continuously agitated at 400 rpm. After all the dispersed phase had been added the agitation rate was increased to 2,190 rpm (unless otherwise stated (chapter 3)) the maximum rotation rate of the overhead stirrer.

The continuous phase of the Pickering-HIPEs (Chapter 5 only) was prepared by taking a 1:1 mixture of styrene/DVB and adding 3% (w/v) of hydrophobised silica particles. This mixture was homogenised for 15 min at 15,000 rpm using a high-speed homogeniser (Kinematica POLYTRON PT 1600 E). The mixture was then placed in a glass mixing vessel containing 1 mol.-% AIBN and slowly agitated until all AIBN dissolved. The dispersed phase was added as described before under an agitation of 400 rpm. However after the addition of the dispersed phase was complete 5% by volume of Hypermer 2296 was added with respect to the continuous phase only. The modified Pickering HIPEs were then agitated at 2,190 rpm as before.

PolyHIPE monoliths were produced by drawing the emulsion template into cylindrical moulds with an internal diameter of 7 mm. If template emulsions were of high viscosity (due to lengthy agitation) they were transferred into the moulds using a syringe before being capped at both ends and place into a convection oven at 70°C to initiate polymerisation. However if the viscosity was too low to the emulsion would run out of the mould before it could be capped. In these cases the emulsion was slowly injected into the mould using a syringe taking great care to prevent the formation of air bubbles. The mould for the polymerised emulsion monoliths (both surfactant and Pickering) described in chapter 5, was a polyacrylic tubing with an internal diameter of 7 mm, while PTFE (polytetrafluoroethylene) cylinders with a 7 mm diameter hole drilled lengthwise through it was used as mould for the polyHIPEs described in chapters 4, 6 and 7. The PTFE moulds were superior to the polyacrylic moulds and were later in the thesis used as the monoliths could be more easily removed from the mould.

A volume of 15 ml of each batch was transferred into freestanding centrifuge tubes and polymerised. The resulting polyHIPE monoliths were later used for characterisation of the emulsion templated polymers. In all cases polymerisation was considered to be complete after 24 h in the convection oven at 70 °C. All moulds and centrifuge tubes containing emulsion templates were placed in to a secondary containment whilst in the convection oven to protect against solvent leaks.

2.2 Flow cell production

It was originally attempted to cast the polymerised emulsions directly into tubes to produce flow cells, however neither polyacrylic nor stainless steel tubing proved suitable for this. For both tube materials this was due fluid passing between the monolith and the inner wall of the tubing, when it was attempted to pass fluids through it, bypassing the internal structure. Therefore, it was necessary to produce thin cylindrical polyHIPE monoliths and fix them into the tubes to create the flow cells.

Flow cells were produced in two ways with the first method being used in chapter 5 only and the second method used in chapters 4, 6 and 7. The method presented in chapter 5 allowed for the introduction of two feed lines into the monolith, such that mixing only occurred within the pore structure of the polyHIPE (Figure 13b). It was also chronologically the first flow cell design produced during the research. However this method was inconsistently successful in preventing bypassing, had poorer long term stability and was more complex to produce than the method that replaced it in chapters 4, 6 and 7 (Figure 13a).

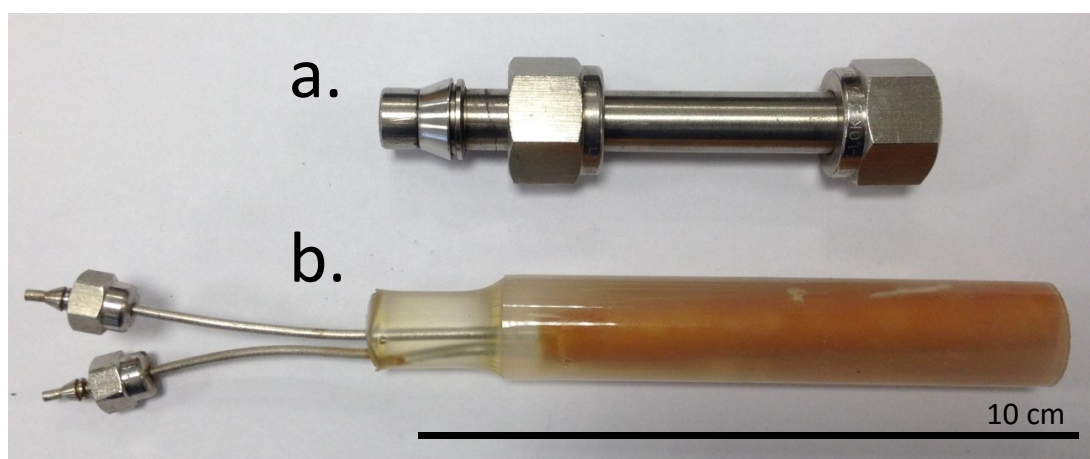


Figure 13. Photographs of the two designs of flow cell used during this research

2.2.1 Flow Cell Design used in Chapters 4, 6 and 7

After removal from the mould the polyHIPE monoliths were dried in a convection oven until constant mass (step 1 in Figure 14). In order to prevent fluid bypassing the polyHIPE monolith it was then dipped in to an epoxy adhesive (Araldite 2020) and the excess was wiped off the surface. The

monolith was then placed into the oven to cure the epoxy adhesive (step 2 in Figure 14). The low viscosity of the adhesive ensured that it was drawn by capillary action a short distance into the porous polyHIPE material where it provides a seal around the monolith. The coated monolith was then coated with rapid epoxy adhesive and inserted into a 3/8" stainless steel tube ($D_i=7.5$ mm such that the gap between the monolith and tubing was ≈ 0.25 mm) (step 3 in Figure 14). Care was taken to ensure no air bubbles were left entrapped in the process to avoid fluid shortcutting around the monolith. Once the epoxy resin was cured the ends of the flow cell were removed and the flow cell shortened to expose the ends monolith to allow fluids to be pumped through it (step 4 in Figure 14).

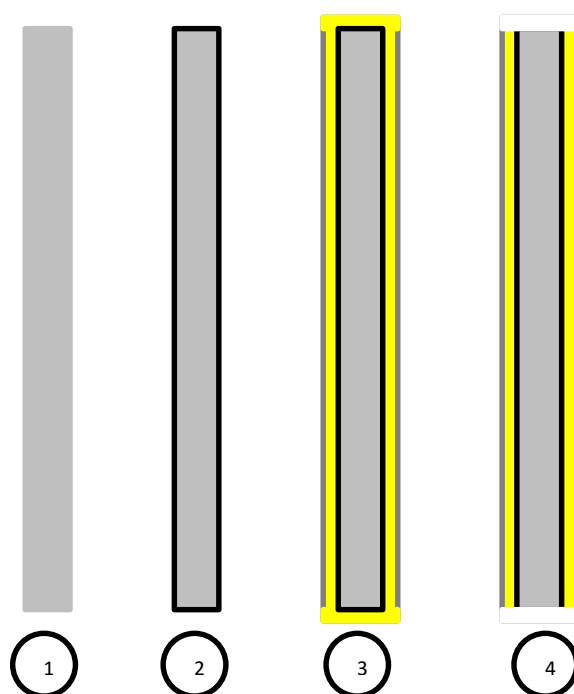


Figure 14. Diagrammatic representation of the production of polyHIPE flow cells used as co-current extractors. 1. PolyHIPE monolith is dried in a convection oven to remove water template; 2. Monolith is dipped in epoxy resin which infiltrates the surface pores creating an impermeable barrier once cured; 3. Monolith is glued into a steel tube; 4. Ends are removed to create a permeable passage for fluids.

Coating the surface of polyHIPEs (Figure 15) with an epoxy adhesive created a good seal without blocking the pore structure of it; three distinct layers can be observed (Figure 15a). The outside of the coated polyHIPE monolith was covered by a layer of epoxy resin about $60\text{ }\mu\text{m}$ in thickness (white arrow). This coating layer contained air bubbles that have been forced out of the macroporous polymer during the coating process but were trapped in the viscous resin. Underneath that, a layer

of macroporous polymer in which the pores have been filled with epoxy resin to depths of about 150 μm (black arrow) can be seen and this is finally followed by the normal polyHIPE. Figure 15b shows the boundary between the epoxy resin filled polyHIPE and normal polyHIPE. The epoxy filled region is non-porous and beads of epoxy resin can be seen in the shape of the pores. The epoxy adhesive did not fully penetrate the pore structure of the polyHIPE because its surface is covered by a less permeable thin skin [133]. The produced flow cells were shortened (step 4 of Figure 14) to ensure that the porous, permeable polyHIPE core was exposed.

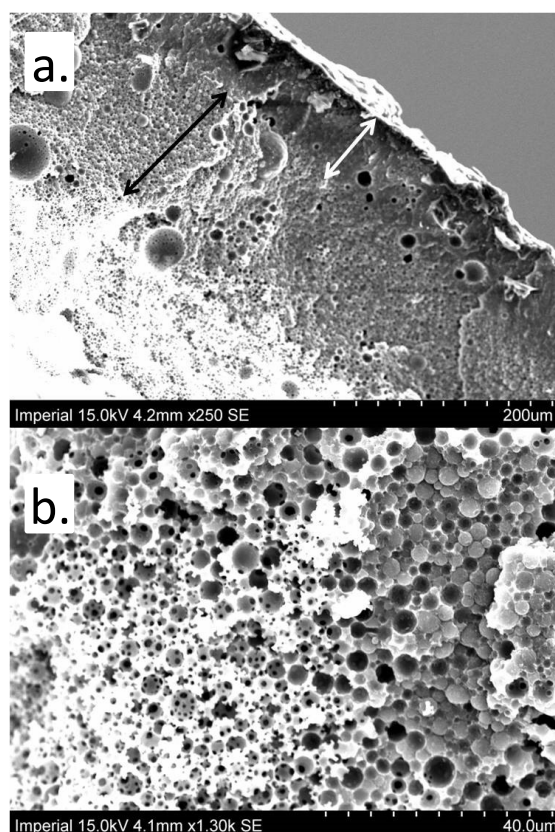


Figure 15. Scanning electron micrograph showing (a) a typical cross-section of a cylindrical polyHIPE monolith coated with epoxy resin and (b) the interface between the resin filled pores and the polyHIPE core.

2.2.2 Flow Cell Design used in Chapter 5

After polymerisation of the HIPE template the monoliths were removed from the mould and dried in a convection oven at 70°C until its mass is constant. In order to seal the polyHIPE monoliths they were then placed into a high temperature heat shrink tubing (RS Components Ltd. Corby, UK), whose inner surface was coated before inserting the polyHIPE with fast curing Araldite® Rapid adhesive, which has been shown to seal polyHIPEs effectively during gas permeability measurements (stage 2 in Figure 16)

Figure 16). The monolith was then exposed to a hot air from a heat gun, which causes the shrink tubing to contract onto the polyHIPE monolith sealing its sides. Care was taken not to trap any air bubbles (stage 3 in Figure 16) in the process. The ends of the polyHIPE were subsequently sealed with Araldite® Rapid adhesive. The monolith is then inserted in to an outer protective tubing (polyacrylic or steel) capped at one end, which is then filled with transparent Araldite® 2020 (RS Components Ltd. Corby, UK) covering the majority of the monolith. This assembly was then placed in to a convection oven at 70°C for at least 5 h to fully cure the Araldite® 2020. Afterwards, both ends of the flow cell were machined flat with one end being fully opened to the atmosphere (stage 4 in Figure 16). In to the other end two 1/16 inch feed holes were drilled in to the monolith to a depth of 5 mm. Into these holes 1/16 inch feed tubes were then inserted and sealed in place with a small amount of super glue. This prevents contact between the two solutions outside the structure of the emulsion templated macroporous polymer. After this, the feed tubes are additionally sealed in to 2 cm deep block of Araldite® 2020 and cured in a convection oven, with the superglue preventing the araldite from flowing into and blocking the feedholes (stage 5 in Figure 16)

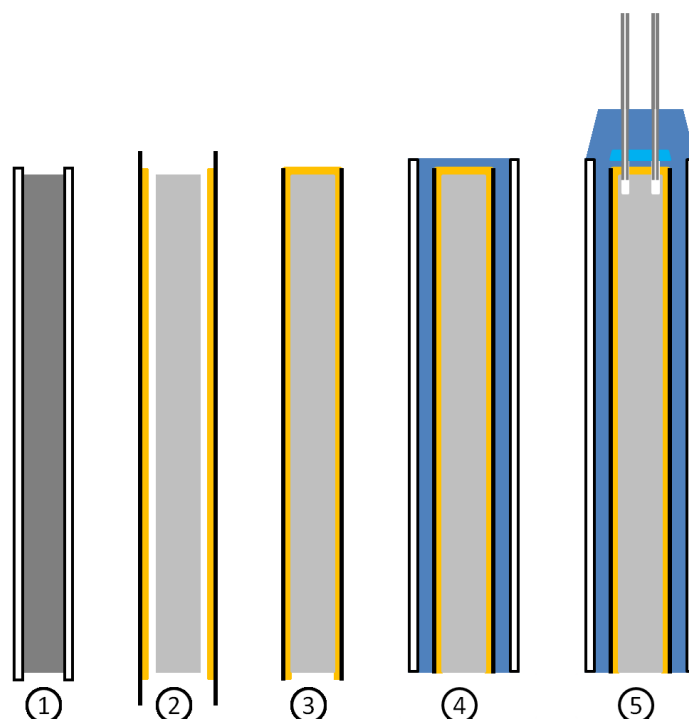


Figure 16. Stages in the production of flow cells for chapter 5; 1) Insert HIPE into rigid acrylic tubing and polymerise at 70°C in an oven; 2) Remove polyHIPE from acrylic tubing, dry the monolith in an oven and place into shrink tubing coated with rapid adhesive; 3) Heat the shrink tubing to force the adhesive into contact with the monolith and cure it; 4) Seal inside larger acrylic tubing with epoxy resin and machine both ends flat opening one to atmosphere; 5) Drill feed holes and insert feed tubes before sealing with super glue and more epoxy resin.

3 General Analytical Techniques

3.1 Characterisation of Pore Morphology by Scanning Electron Microscopy

The morphology of all produced emulsion templated polymers was characterised using scanning electron microscopy (SEM). The sample to be imaged was fractured from the monolith to prevent debris from obscuring the surface to be examined. Samples of approximately 1 cm³ were prepared for SEM by fixing them to SEM stubs using super glue. To ensure the samples were electrically conductive they were sputtering with gold for 20 s under vacuum using an Agar automatic sputter coater. A conductive path between the metallic SEM stub and the sample was ensured with a line of silver paint. The Hitachi S-3400N electron microscope was used to capture all images.

SEM was used to examine the surface and interior of the emulsion templated porous polymers to determine the pore and pore throat diameters and degree of pore interconnectivity. For the determination of the pore and pore throat diameter at least 100 measurements were recorded on samples taken from at least four different locations from a polyHIPE monolith. The measurements of individual pore and pore throat diameters were taken using the image analysis software Image J. These values were used to generate the average pore and pore throat diameters.

3.2 Characterisation of Polymer Density by Pycnometry

Pycnometry was used to determine the porosity of the dry polymerised emulsion monoliths in this thesis. Firstly the skeletal density (ρ_s), the density of the polymer, of the macroporous polymers was determined using Helium pycnometry (AccuPyc 1330, Micrometrics Ltd., Dunstable, UK). This involves placing the open celled polymer into a vessel of known volume under helium. A valve is then opened connecting the first vessel to a second also of known volume. Using the pressure drop in the system and the ideal gas law, the volume of the polymer is calculated and knowing the sample mass its skeletal density can be determined.

The foam density (ρ_f), also known as the envelope density, of the emulsion templated porous polymer including void spaces, was determined using an envelope density analyser (GeoPyc 1360, Micrometrics Ltd., Dunstable, UK). Firstly the volume of DryFlo[®] powder in a cylinder is determined. Then pieces of the emulsion templated porous polymer of known mass are placed into the cylinder and surrounded by the particles. The total volume of the particles and pieces of the emulsion templated polymer is then measured, allowing for the calculation of the volume of the emulsion

templated porous polymer. The porosity of the emulsion templated polymer was then determined using Equation 4.

$$Porosity(\%) = \left(1 - \frac{\rho_f}{\rho_s}\right) * 100$$

Equation 4

4 Equivalent Pore Throat Diameter in Packed Beds

In order to compare emulsion templated polymer flow cells with traditional packed beds (such as the HPLC columns used as control experiments) it was necessary to estimate the packed bed's equivalent pore throat diameter using the diameter of the particles filling composing the packed bed. The red region Figure 17 is the smallest possible interconnecting pore area between closed packed monodispersed spherical particles (D_p) and was taken as representative area equivalent to the pore throats in emulsion templated polymers (Figure 8). The area of the red region (A'_{pt}) (Equation 5) was calculated (Equation 6) and taken as an equivalent pore throat diameter (D'_{pt}).

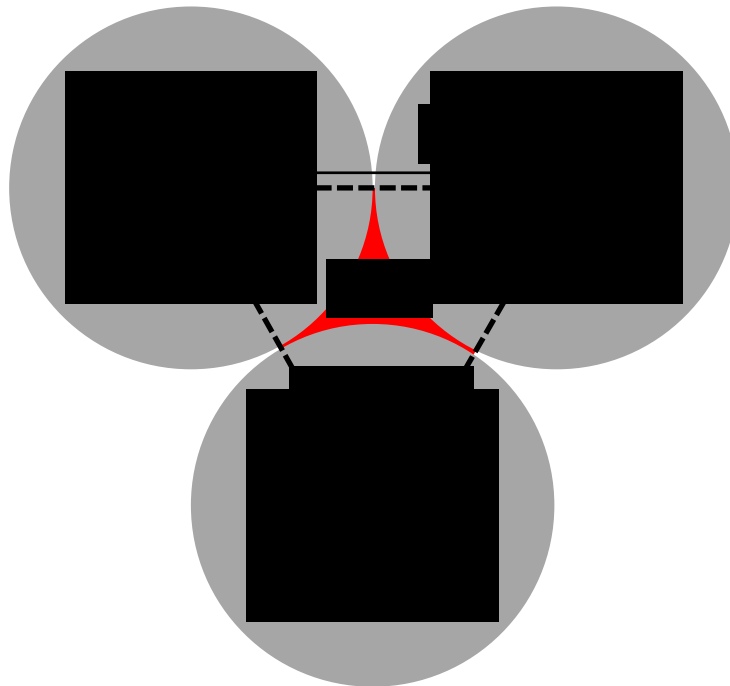


Figure 17. Schematic representing the interconnected area between particles in a packed bed

$$A'_{pt} = \frac{D_p}{2} \left(D_p^2 - \left(\frac{D_p}{2} \right)^2 \right)^{0.5} - \frac{\pi}{8} D_p^2 = \left(\frac{\sqrt{3}}{4} - \frac{\pi}{8} \right) D_p^2 \approx 0.04 D_p^2$$

Equation 5

$$D'_{pt} = \sqrt{\frac{4}{\pi} A'_{pt}}$$

Equation 6

This is the minimum area representing an interconnected pore present between closed packed particles of uniform size in a packed bed reactor, it does not quite reflect the reality as the particles in a packed bed are not monodisperse and packing is imperfect. A closed packed bed consisting of monodispersed spheres would have a porosity of $\approx 26\%$ [160]; in reality HPLC columns packed with nonporous particles have porosity's in the range of 35-45% [161, 162]. Therefore, the interconnecting pore throat approximations calculated represent only the smallest possible pore throats of the gaps between the particles in packed beds.

Chapter 3: Emulsion Templated Macroporous Polymers via Controlled Agitation

1 Introduction

One of the advantages of using concentrated emulsions as templates for the synthesis of macroporous polymers is the potential to control pore size and porosity via the template emulsion. Which allows for the production of macroporous polymers with desirable properties such as permeability [86, 126], surface area [35, 143] and mechanical strength [12] that can be tailored for desired tasks. Much work has been done on predicting the droplet size of emulsions produced in agitated vessels [163-166], it is therefore suggested that the morphology of emulsion templated macroporous polymers can be predicted in a similar fashion. This chapter therefore looks at how varying the energy input during the emulsification process to create the emulsion template via the rate and duration of agitation before polymerization of the template to form macroporous polymers allows for control of properties such as pore size and permeability. The main difference between droplet size in an emulsion and pore size in an emulsion templated polymer is that after emulsification and before the gel point of the polymerization is reached, coalescence of droplets can occur within the emulsion. This would lead to much larger pores than the original droplet size in the emulsion immediately after blending making it much less trivial to predict pore size of macroporous polymers produced by emulsion templating. Ostwald ripening (coarsening) [167] can also occur within the system leading to a hierarchal pore system, in which much larger pores are embedded in between much smaller ones [91, 168]. The rate of coalescence in emulsions was observed to increase at high temperatures [50] needed to typically initiate a free-radical polymerization. Such effects can make it more difficult to predict the morphology of macroporous polymers simply from the energy input during emulsification.

2. Experimental

2.1. Determination of energy input during emulsification

In order to calculate the specific energy (E_v) used for agitation in the system, the following three equations were used;

$$E_v = \frac{Pt}{V}$$

Equation 7

$$P = P_0 \rho_{ave} N^3 D_i^5$$

Equation 8

$$\rho_{ave} = \rho_d \Phi + \rho_c (1 - \Phi)$$

Equation 9

where E_v is the specific energy per volume, P the power, t the agitation time, V the volume of the emulsion template, P_0 the dimensionless power number relating inertial force to resistance force, ρ_{ave} the average emulsion density, N the rate of rotation of the impeller (rpm), D_i the impeller diameter, ρ_d and ρ_c the densities of the dispersed and continuous phases, respectively and Φ the internal volume ratio of the emulsion template. Reynolds numbers (Re) for the agitation of the emulsion template system were calculated using Equation 10.

$$Re = \frac{\rho_{ave} N D_i^2}{\mu_c}$$

Equation 10

Where μ_c is the viscosity of the continuous phase. All calculated Reynolds numbers were well over 1000 suggesting turbulent flow and hence a constant power number is a reasonable assumption [169]. Since the emulsion was agitated with an anchor impeller a power number of 0.22 was used, this value was taken from literature [170]. Since the power input is proportional to the cube of the rate of impeller rotation (Equation 8) the energy supplied to the system during emulsion preparation at 400 rpm is not considered in the final energy input. Losses of mass via evaporation and splashing were also considered to be negligible.

2.2. Sauter Mean Pore Diameter of Macroporous Polymers

Since the emulsion droplets provide the template for the pores in an emulsion templated macroporous polymer it is possible to predict pore size if the template droplet size is known. There are many equations used for the estimation of droplet sizes in an emulsion [163] however most of these are for steady state systems involving dilute emulsions (LIPES). In a steady state system the rate of droplet coalescence and droplet break-up are equivalent such that the average droplet size does not vary with time. Several equations [163, 171-173] relate some form of power or energy input (Wkg^{-1} or Jm^{-3}) to the Sauter mean droplet diameter. The equivalent in an emulsion templated macroporous polymer is the Sauter pore diameter (d_{32}) (Equation 11) as the pore size is determined by the droplet size at the gel point of the polymerization of the continuous phase.

The Sauter pore diameter d_{32} is defined as:

$$d_{32} = \frac{\sum_{i=1}^n d_{p_i}^3}{\sum_{i=1}^n d_{p_i}^2}$$

Equation 11

where d_p is the measured pore diameter. Equations relating Sauter mean droplet (pore) diameter to specific energy input are of a form similar to Equation 12:

$$d_{32} = cE_v^{-b}$$

Equation 12

where c is a constant dependent on the method of emulsification and method of droplet break-up, E_v the specific energy input ($J\ m^{-3}$) and b a constant dependent characteristic for the system used but usually having values varying between 0.35 and 0.47 but most commonly reported to be 0.4 [163].

2.3. Gas Permeability of Macroporous Polymers

The technique developed and described by Manley et al. [20, 86, 91] was used for measuring the gas permeability of the macroporous polymers. After removal from the 15 ml centrifuge tubes the macroporous polymers cylinders (≈ 14 mm in diameter) were coated using Araldite® rapid adhesive in order to seal the sides of the monolith against cross flow.

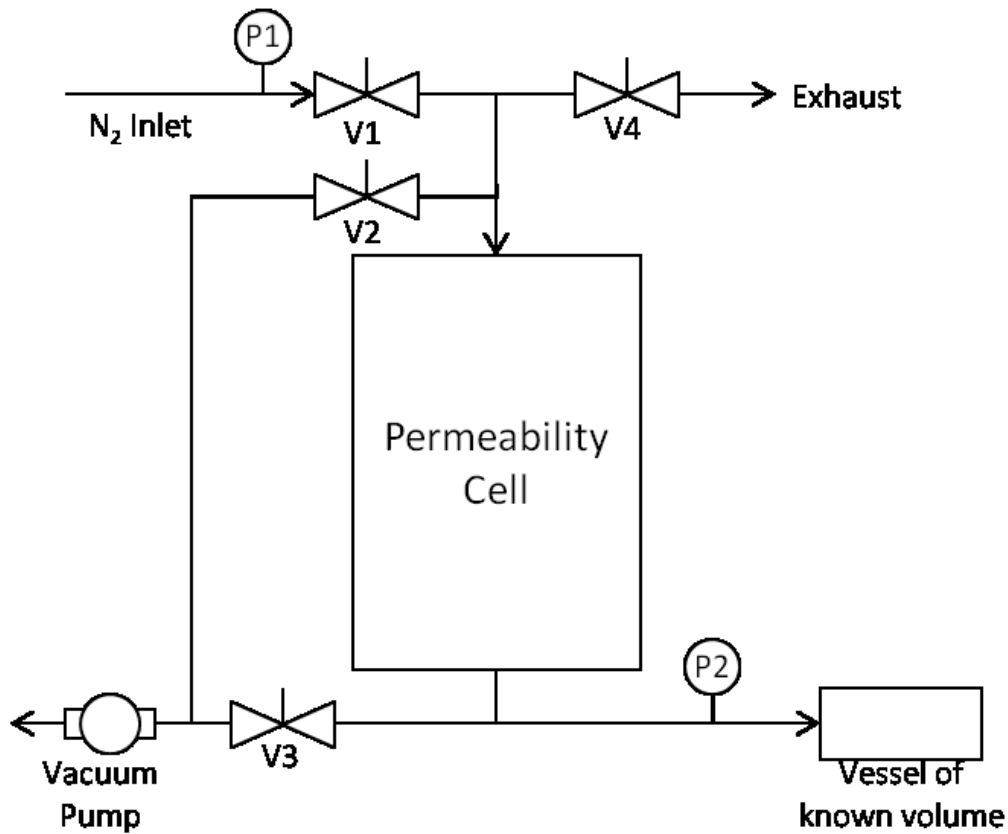


Figure 18. Schematic of the setup of the permeability cell used to determine the gas permeability of macroporous polymers.

The sample was then placed into a cylindrical PTFE mould (internal diameter 31 mm) to which a silicon release agent had been applied. The mould was then filled with Araldite 2020 epoxy resin and left to fully cure in a convection oven at 70 °C. The samples were then machined to a length of 25 mm ensuring the ends of the macroporous polymer were exposed to the atmosphere.

The samples were then tightly sealed into a homemade permeability cell, schematically shown in Figure 18. The system was first evacuated, using a vacuum pump by opening valves V2 and V3. Valve V2 was then closed and V1 opened allowing nitrogen of a set inlet pressure (measured at pressure sensor P1) to enter the cell. V3 was then closed and the rate of pressure rise at P2 measured using a stopwatch with the time taken between each 0.1 bar increment being measured. Each sample was tested three times at four different nitrogen inlet pressures (0.4, 0.6, 0.8 and 1 bar) and then the sample was turned over and the test repeated. The viscous permeability (k) was determined using the following equation [174]:

$$K = \frac{Q_2 p_2 L}{\Delta p A} = \frac{V \left(\frac{dp_2}{dt} \right)}{p_1 A} = \frac{k}{\mu} p_m + \frac{4}{3} K_0 \sqrt{\frac{8RT}{\pi M}}$$

Equation 13

where K is the permeability coefficient, Q_2 the downstream volumetric flowrate, p_1 and p_2 the upstream and downstream pressure, respectively, L the length of the porous sample, Δp the pressure drop across the sample, A the cross-sectional area of the sample, V the volume of nitrogen, t the time, p_m the mean pressure, μ the gas viscosity, K_0 the Knudsen permeability coefficient, R the universal gas constant, T the absolute temperature and M the molar mass of nitrogen.

The permeability coefficient (K) for the sample of interest was calculated using the rate of change of the downstream pressure (dp_2/dt) measured experimentally. Then by plotting a K as a function of mean pressure (p_m) the viscous permeability (k) was determined from the gradient (k/μ). The value reported is the average of the permeability reported for gas flow in both directions through the monolith.

Table 1. Summary of the template emulsification conditions and measured properties of the resulting polyHIPEs (PH) and polyMIPEs (PM) in this chapter.

	Template Emulsification conditions					Macroporous Polymer Properties				
Sample	Internal Phase Volume (%)	Agitation Speed rpm (±10)	Agitation Time (s)	Specific Energy input (kJm ⁻³)	Sauter Mean Pore Diameter (μm)	Average Pore Diameter (μm)	Average Pore Throat Diameter (μm)	Porosity (%)	Permeability (mD)	
PH-1	80	2190	10	0.66	12.3	10.0 ± 3.1	2.3 ± 0.9	81.6	464.8 ± 0.0	
PH-2	80	2190	30	1.98	7.9	6.8 ± 1.9	1.9 ± 0.6	81.4	212.5 ± 16.6	
PH-3	80	2190	60	3.95	6.0	5.0 ± 1.6	1.5 ± 0.4	81.3	283.0 ± 12.5	
PH-4	80	2190	120	7.91	4.9	3.7 ± 1.4	1.2 ± 0.4	81.2	60.2 ± 11.2	
PH-5	80	2190	300	19.78	3.3	2.7 ± 0.9	0.9 ± 0.3	82.1	56.0 ± 0.3	
PH-6	70	2190	10	0.66	17.1	11.6 ± 5.2	2.6 ± 1.0	74.7	293.0 ± 17.4	
PH-7	70	2190	30	1.97	9.6	7.7 ± 2.8	1.8 ± 0.5	74.6	127.7 ± 15.2	
PH-8	70	2190	60	3.93	6.5	5.4 ± 1.7	1.5 ± 0.4	73.7	115.7 ± 6.3	
PH-9	70	2190	120	7.86	5.5	4.4 ± 1.6	1.1 ± 0.3	73.7	44.3 ± 2.2	
PH-10	70	2190	300	19.64	3.7	3.0 ± 1.0	0.8 ± 0.2	73.1	19.1 ± 1.0	
PM-11	60	2190	10	0.65	16.7	13.4 ± 4.8	2.7 ± 0.8	70.9	278.1 ± 39.0	
PM-12	60	2190	30	1.96	10.6	8.8 ± 2.8	2.3 ± 0.7	68.3	225.8 ± 49.8	
PM-13	60	2190	60	3.91	8.0	6.6 ± 2.2	1.8 ± 0.5	67.6	86.9 ± 5.9	
PM-14	60	2190	120	7.83	6.5	5.3 ± 1.8	1.4 ± 0.4	68.4	126.3 ± 2.0	
PM-15	60	2190	300	19.54	4.43	3.7 ± 1.2	0.9 ± 0.3	66.2	13.5 ± 0.9	
PH-16	80	1000	10	0.06	34.6	23.4 ± 11.4	4.8 ± 2.2	77.9	552.8 ± 147.7	
PH-17	80	1000	30	0.19	21.6	17.0 ± 6.5	3.3 ± 1.3	79.3	971.1 ± 225.8	
PH-18	80	1000	60	0.38	17.16	13.9 ± 5.1	3.0 ± 1.0	81.0	906.4 ± 204.2	
PH-19	80	1000	120	0.75	15.9	12.4 ± 4.5	2.8 ± 0.9	81.4	640.8 ± 56.4	
PH-20	80	1000	300	1.88	11.2	9.2 ± 3.2	2.5 ± 0.7	79.8	483.9 ± 24.1	
PH-21	70	1000	10	0.06	46.0	27.9 ± 15.4	5.2 ± 2.0	77.5	786.8 ± 121.2	
PH-22	70	1000	30	0.19	25.5	19.5 ± 7.9	4.1 ± 1.7	79.0	1001. ± 182.6	
PH-23	70	1000	60	0.38	20.2	15.3 ± 6.3	3.4 ± 1.2	76.7	759.5 ± 120.4	
PH-24	70	1000	120	0.75	17.2	13.4 ± 5.3	2.8 ± 0.9	75.8	537.8 ± 33.2	
PH-25	70	1000	300	1.87	12.5	9.8 ± 3.8	2.54 ± 0.7	75.3	368.5 ± 13.3	
PM-26	60	1000	10	0.06	65.8	47.0 ± 30.1	7.5 ± 3.3	68.9	1067. ± 144.4	
PM-27	60	1000	30	0.19	41.0	28.0 ± 12.7	5.2 ± 2.2	72.6	747.8 ± 24.1	
PM-28	60	1000	60	0.37	27.6	20.5 ± 8.7	3.9 ± 1.3	66.6	324.5 ± 10.8	
PM-29	60	1000	120	0.75	21.4	16.7 ± 6.5	3.4 ± 1.2	67.4	238.2 ± 9.1	
PM-30	60	1000	300	1.86	14.0	9.9 ± 4.6	2.3 ± 0.8	69.5	215.0 ± 2.5	

3. Results and Discussion

3.1. Morphology of Macroporous Polymers

From *Table 1* and Figure 19 it can be seen that as expected the mean pore size of the macroporous polymers decreases with increasing energy input during the emulsification process. However in all of the samples 'pores' larger than those templated by the original emulsion droplets can be observed. These regions are seen in Figure 19 (images a, c, e, g and i). These are likely air bubbles entrained during emulsification as opposed to pore created by large coalesced droplets due to the large difference in size between them and the droplet templated pores. If coalescence was the cause there should be pores of intermediate size. Since the air bubbles decrease in size with increased energy input it is reasonable to assume that air entrainment occurs at the very beginning of agitation when the emulsion is least viscous. However in macroporous polymers produced from emulsions with low energy input (i.e. 1000 rpm and short agitation times) a wider range of pore sizes are seen suggesting that as well as air entrainment, coalescence also occurred. In measuring the pore and pore throat diameters reported in *Table 1* and Figure 20 air bubbles and coalesced regions (if they occurred) were ignored, to give a representation of the emulsion at the end of agitation. However the size of the pore throats in the walls of the larger pores, caused by droplet coalescence or by the entraining of air, are of a similar diameter to those in regions that did not undergo coalescence. This is because pore throats formed between two droplets are limited in size by the smaller of the two droplets. Therefore, unless two large droplets formed by coalescence are in contact during polymerization the pore throat size is determined by the droplet size produced at the end of the emulsification process. The effect emulsion template droplet coalescence on permeability is discussed in section 3.2 of this chapter. Further details of the HIPE templates compositions are presented in the Appendix (*Table 7*).

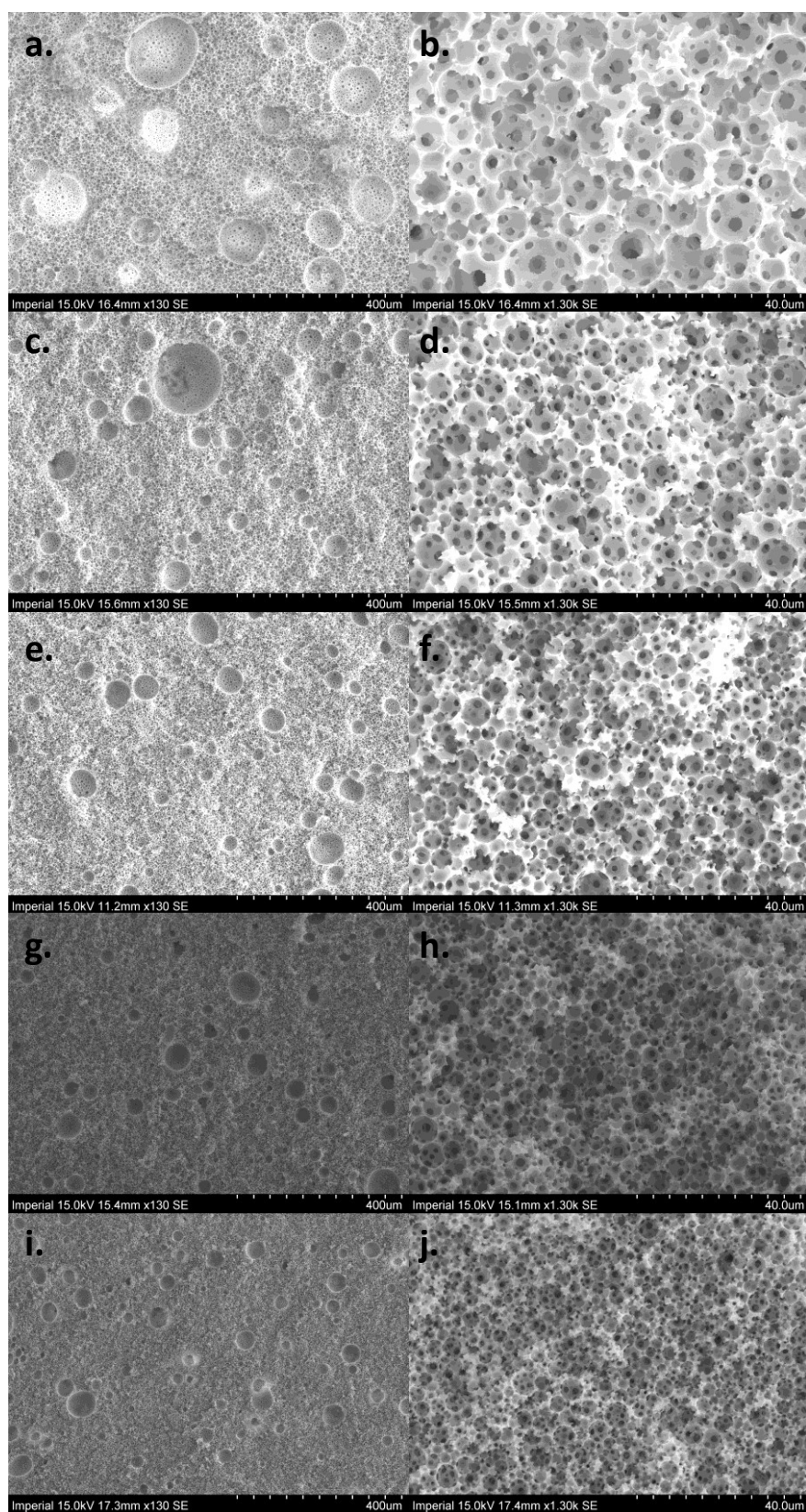


Figure 19. Representative SEM images of emulsion templated macroporous polymers produced from emulsion templates with an internal phase volume ratio of 80% agitated at 2190 rpm demonstrating how pore and pore throat diameter vary with increasing agitation time. a. and b. for 10 s (PH-1), c. and d. for 30 s (PH-2), e. and f. for 60 s (PH-3), g. and h. for 120 s (PH-4), i. and j. for 300 s (PH-5).

By plotting the value of the Sauter mean pore diameter, calculated from the measured mean pore diameter, against specific energy input (*Figure 20*) and fitting the data, it can be seen that the pore size of the emulsion templated macroporous polymers are well described by the power law Equation 12 [172], $R^2 \geq 0.97$, with values of b of close to 0.4. It was also observed that for all three internal phase volume ratios used (80%, 70% and 60%) the pore sizes produced are overlapping when a similar amount of energy (J m^{-3}) was introduced into the system at different rates of agitation. It should be noted that in all three graphs (*Figure 20*) those emulsion templates agitated at 1,000 rpm had a slightly larger Sauter mean pore diameter compared to those agitated at 2,190 rpm for similar specific energy input. However given the error range in Sauter mean pore diameter this cannot be conclusively stated. Also for polyMIPes produced from emulsion templates with internal phase volume ratios of 60% and 70% the overlap in average pore size is better than for those produced from HIPes with at 80% internal phase volume ratio. From all three graphs in *Figure 20* it can be seen that a steady state droplet size was not reached in the emulsion template since the Sauter mean pore diameter of the emulsion templated macroporous polymer was still found to be dependent on time even at the highest specific energy input used in this study ($\approx 2 \times 10^7 \text{ Jm}^{-3}$).

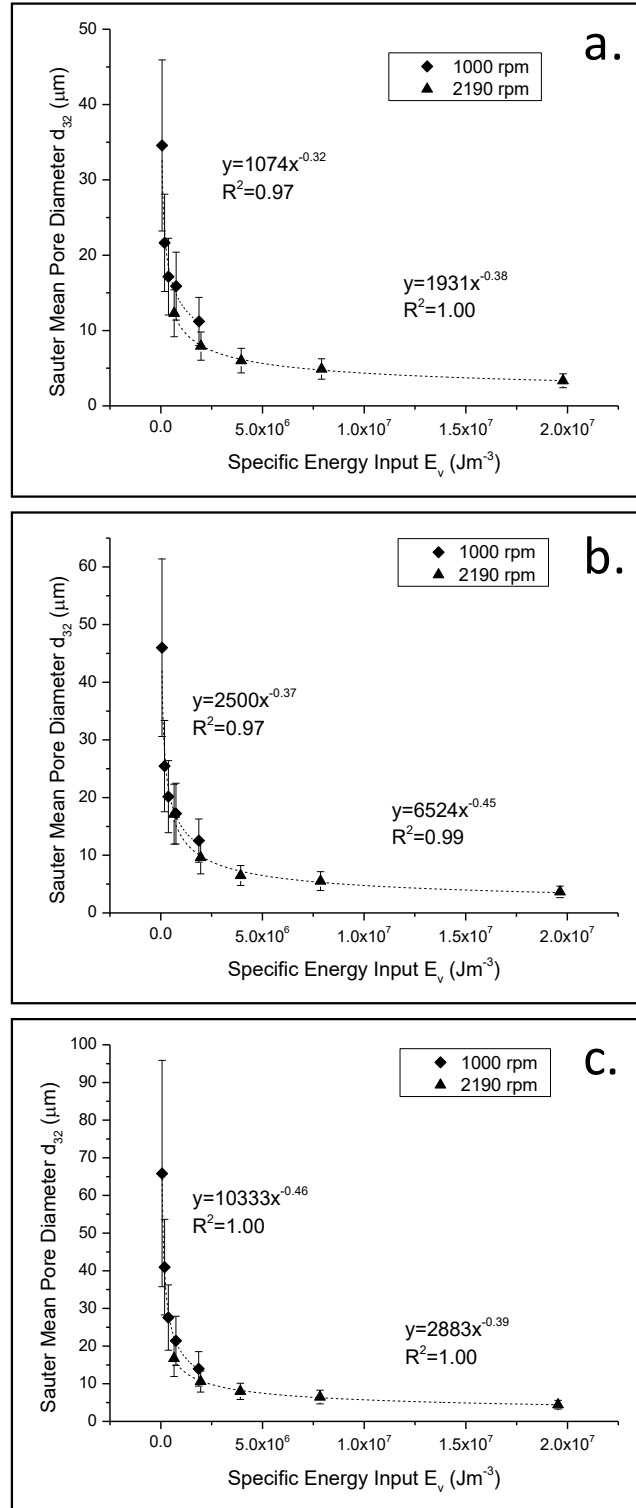


Figure 20. Sauter mean pore diameters of emulsion templated macroporous polymers, as a function of specific energy input introduced into the emulsion template. The emulsion templates were prepared at stirring rates of 1,000 and 2,190 rpm with internal phase volumes of a. 80%, b. 70% and c. 60%. Best fit curves of the form $y=cx^{-b}$ were then fitted to the results.

These results suggest that for control of pore sizes in emulsion templated macroporous polymers energy input during the emulsification process is a suitable method. It is most valid for macroporous polymers produced from emulsion templates prepared with high energy input and lower internal phase volume ratios, such that coalescence in the emulsion template is limited. If this is not the case a much wider pore size distribution was observed (see Appendix). For macroporous polymers produced from emulsion templates which underwent significant droplet coalescence prior to polymerisation energy input to the template emulsion is still useful for predicting average pore and pore throat size. The average pore size is particularly important in determining pore throat size, which most notably controls the permeability of the emulsion templated macroporous polymers.

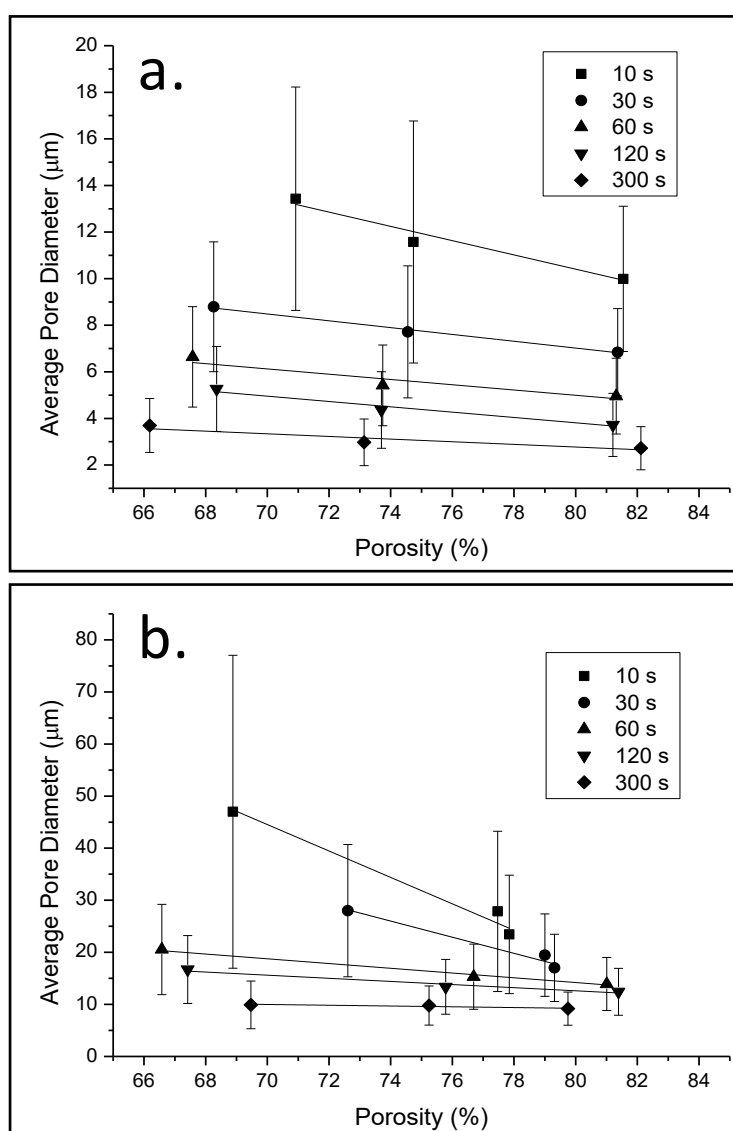


Figure 21 Average pore diameter of emulsion templated macroporous polymers varied between samples with the same agitation time but different final porosities. Template emulsion agitated at a. 2190 rpm and b. 1000 rpm.

Figure 21 clearly shows that for both agitation rates the average pore diameter decreased with increasing emulsion internal phase volume (indicated by porosity of the polymer) for the same agitation time. This is likely to be caused by the increase in the viscosity and average density of the emulsion templates with increasing internal phase volume. It has been reported that there are several factors affecting the viscosity of emulsions; emulsion viscosity increases with higher internal phase volume and decreasing droplet size [175]. However emulsions exhibit shear thinning behaviour which is more apparent the smaller the droplet size [176]. The average density of an emulsion is higher for water in oil emulsions with a higher internal phase volume ratio simply because the dispersed (internal) phase (aqueous calcium chloride solution) is denser than the continuous phase consisting of S, DVB and Hypermer 2296. The average emulsion densities (calculated from the individually measured densities of the two phases) were 969.2, 976.9 and 984.8 kgm^{-3} for emulsions with 60, 70 and 80% internal phase volume ratios, respectively. As both viscosity and average emulsion density increase with internal phase volume ratio, it took more energy to agitate emulsions with higher internal phase volume ratio at a given stirring rate. This increase in energy input led to smaller average pore diameters being formed in these systems, as seen in Figure 21 and Figure 22.

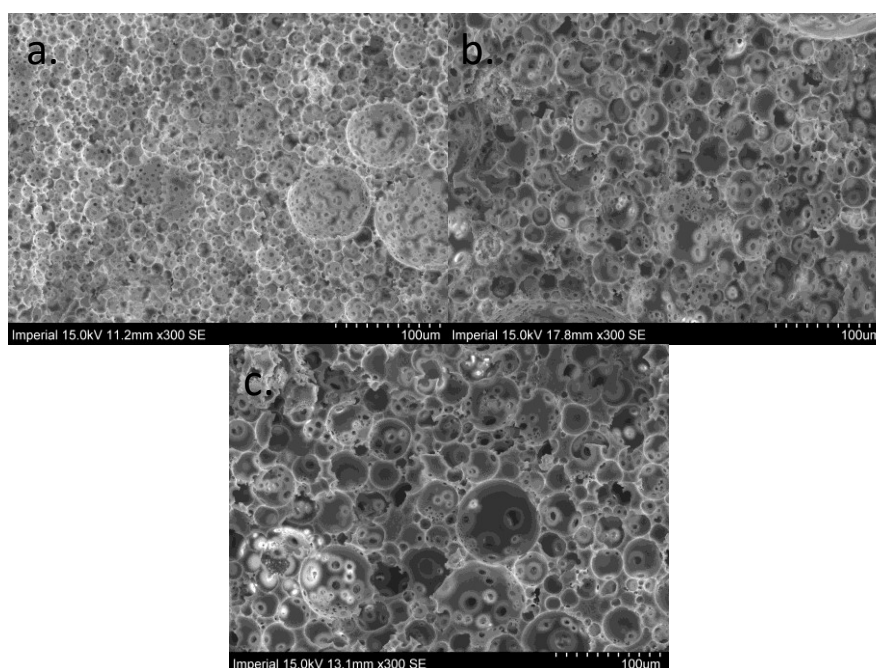


Figure 22. Representative SEM images of emulsion templated macroporous polymers to demonstrate the effect of the internal phase volume ratio of the template emulsion on the pore size of emulsion templated macroporous polymers. All emulsion templates were agitated for 30 s at 1000 rpm with an internal phase volume ratios of a. 80% (PH-17), b. 70% (PH-22) and c. 60% (PH-27) and then polymerized.

The porosity of the macroporous polymers often varies from the internal phase volume ratio used in the template emulsion (Table 1). In all cases the porosity is higher than the internal phase volume ratio used in the original emulsion would have predicted with the exception of samples PH-16, PH-17 and PH-20. This is due to the loss of surfactant and non polymerisable hydrocarbons (such as Diethylbenzene from the DVB) from the continuous phase during the purification and drying of the polymer monolith. Samples PH-16, PH-17 and PH-20 were produced from emulsions agitated at the lower rate of 1000 rpm with internal phase ratios of 80%. Their lower porosity than expected is likely due to the occurrence of some droplet coalescence and phase separation prior to polymerisation such at the gel point the emulsion had slightly less than 80% internal phase. This is corroborated by the formation of a thin film of non-porous polymer that form at the top these samples a degree of partial phase separation prior to complete polymerisation.

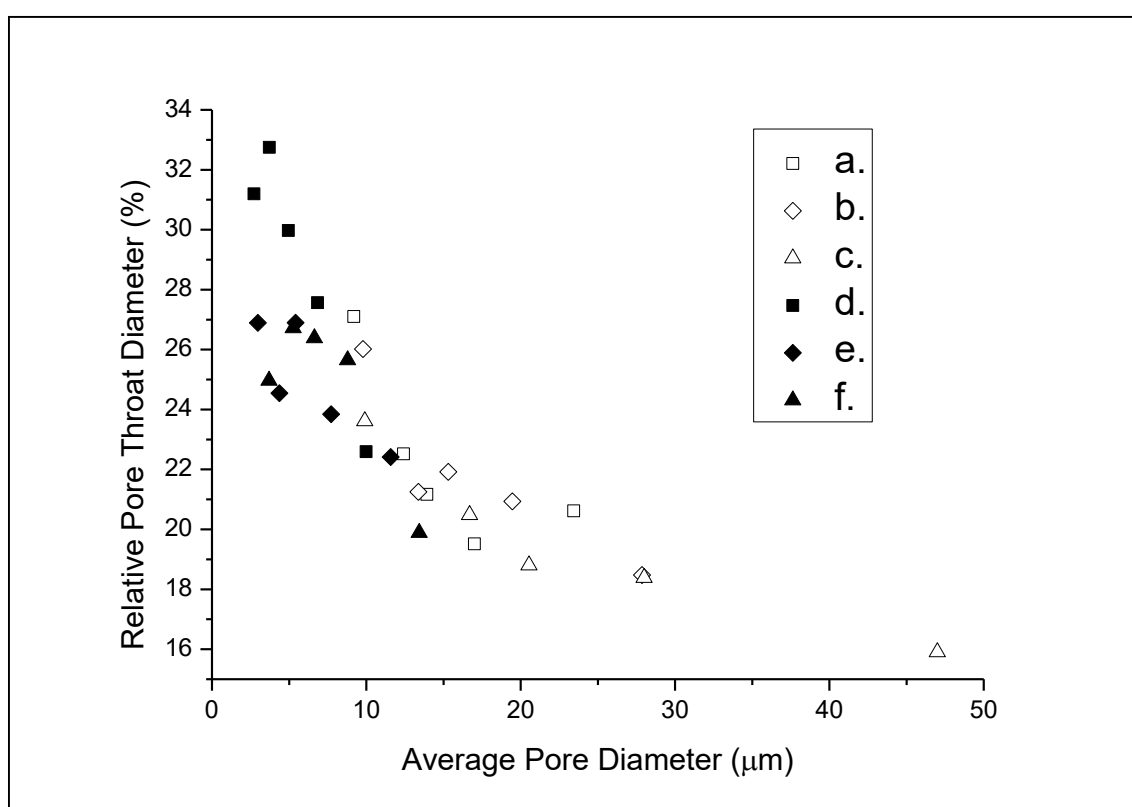


Figure 23. Relative pore throat diameter as function of average pore size. Template emulsification conditions a., b. and c. 1000 rpm with internal phase volume ratio 80, 70 and 60%, respectively and d., e. and f. 2190 rpm with internal phase volume ratio 80, 70 and 60%, respectively

For obvious reasons the larger the pores the larger the size of pore throats that can be formed (Table 1). However it was found that the relative size of the pore throats compared to the pores (Equation 14) is dependent on the size of those pores, as shown in Figure 23, the relative pore throat diameter ($d_{pt/p}$) was calculated using the following equation;

$$d_{pt/p}(\%) = \left(\frac{\bar{d}_{pt}}{\bar{d}_p} \right) * 100$$

Equation 14

where d_p and d_{pt} are the mean pore and mean pore throat diameter respectively. *Figure 23* shows that $d_{pt/p}$ was higher for emulsion templated macroporous polymers with smaller pores. It can also be seen in *Figure 23* (data set d.) that for the polyHIPEs made by polymerising an emulsion template with an internal phase volume ratio of 80% produced at 2,190 rpm the size of the pore throat relative to the pore is much greater compared to any of the other macroporous polymers. This increase in relative pore throat size is likely due to the increased droplet deformation, which had to occur during the production of HIPEs, creating larger thin film regions between droplets which eventually break to form the pore throats. Pore throat formation is either due to the thin film contraction during polymerisation [83] or due to mechanical action post synthesis [18]. However, for the same HIPE template with an internal phase volume ratio (80%) agitated at 1,000 rpm the relative pore throat size was similar to that of the other polyM/HIPEs with lower porosities. This is caused by the greater range of droplet sizes in these emulsions leading to more efficient droplet packing and hence less droplet deformation. Therefore, the key to producing the largest average pore throat size possible is firstly to increase pore size [86] (*Table 1*), secondly increase the porosity and thirdly to ensure droplets are as monodisperse as possible to maximise droplet deformation in the template emulsion (assuming internal phase volume ratio exceeds 74%) .

3.2. Permeability of Macroporous Polymers

The permeability of a macroporous polymer depends on the interconnecting pore throat size within the macroporous polymer and its porosity. It can be seen in *Figure 23* that the relationship between permeability and pore throat diameter is generally linear, as previously reported [20]. This proves that the energy input used to produce an emulsion template from which a macroporous polymer was produced does not of itself affect the gas permeability of the final macroporous polymer.

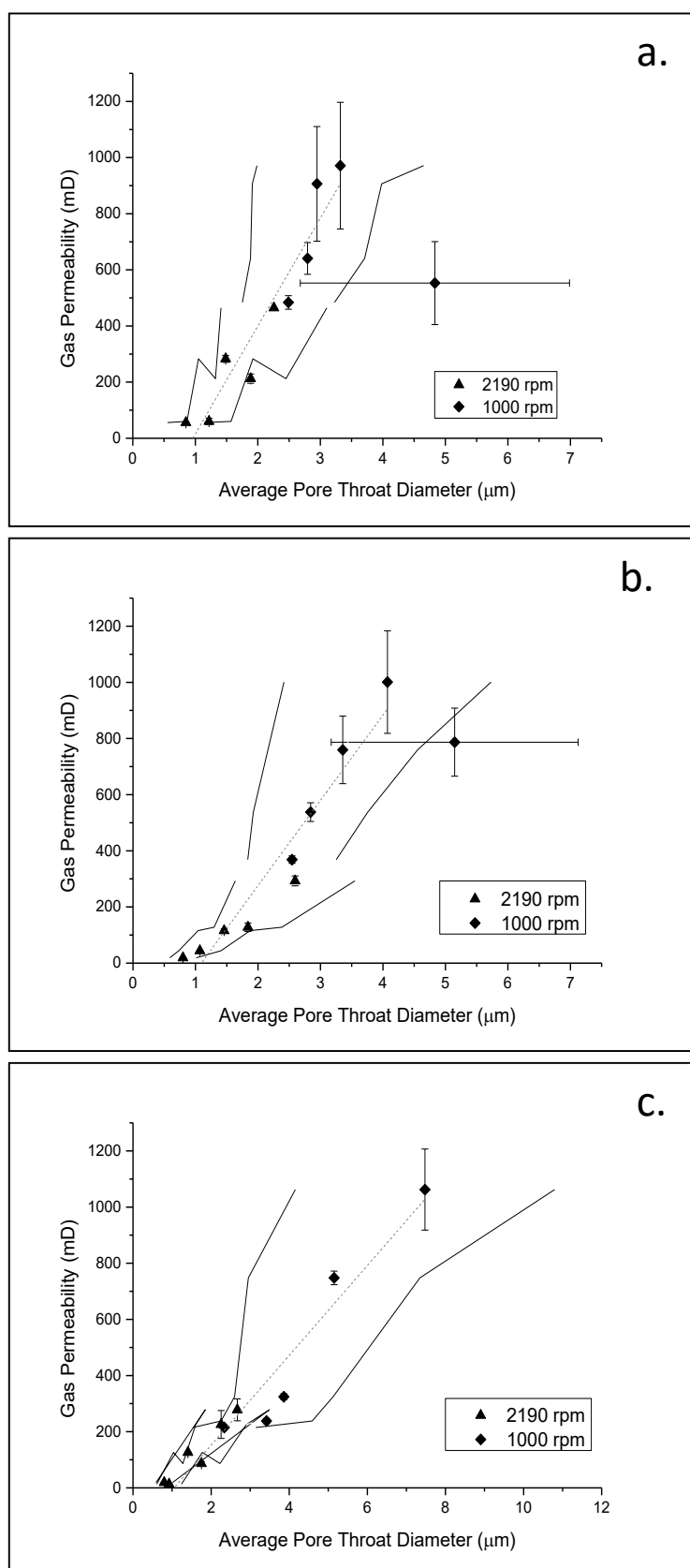


Figure 24. Gas permeability of macroporous polymers as a function of pore throat diameter. Macroporous polymers produced from an emulsion template with an internal phase volume ratio of a. 80%, b. 70% and c. 60%. Horizontal error bars shown as envelope around data points.

The average pore throat size (Table 1) generally does not vary significantly for the macroporous polymers synthesised from emulsions produced with similar energy input but different emulsion template internal phase volume ratios. However unsurprisingly those macroporous polymers with a greater porosity tended to have a higher permeability than those with lower porosity. This can be seen in *Figure 24* in the gradients of the graphs 8a, 8b and 8c being $385 \text{ mD } \mu\text{m}^{-1}$, $304 \text{ mD } \mu\text{m}^{-1}$, $160 \text{ mD } \mu\text{m}^{-1}$ respectively. The permeability increased with pore throat size of the macroporous polymers (*Figure 23*). However, this increase in permeability was much more pronounced for macroporous polymers produced from emulsion templates with higher internal phase volume ratio. This is especially marked when comparing the macroporous polymers produced from emulsion templates with 80 and 60% internal phase volume ratio created at a stirring rate of 2,190 rpm. It can be observed that the permeability of macroporous polymers produced by polymerising emulsion templates with an internal phase volume fraction of 60% and 70% are almost identical but by increasing the internal phase volume fraction of the emulsion template to 80% caused the permeability to increase significantly. This increase in permeability is likely due to larger pore throat diameter relative to pore diameter caused by the increase in droplet deformation in an 80% internal phase HIPE (*Figure 23*).

No macroporous polymer had a permeability much greater than 1 D; in fact the most permeable sample (PM-26 – 1,062 mD) was produced from an emulsion template with an internal phase volume of 60%. The reason for its high permeability was the large average pore throat size ($7.48 \mu\text{m}$) throughout the structure compensating for the lower porosity. However, PH-17 and PH-22 prepared by polymerisation of emulsion templates with an internal phase template of 80% and 70%, had similar permeabilities (971 mD and 1,001 mD, respectively) to PM-26. Their higher porosities compensating for the fact their pores and pore throats were half the size of those in PM-26, 3.32 and $4.07 \mu\text{m}$, respectively. The advantage of using an emulsion template with a lower internal phase volume, such a 60%, is that the resulting macroporous polymers have better mechanical properties compared to more porous polymers[90]. The permeability values reported are similar in magnitude to those reported by Ikem et al. [86] who were able to produce a polyHIPE with a permeability of $460 \pm 40 \text{ mD}$ (82% porosity, $d_{\text{pt}} = 1.5 \pm 0.5 \mu\text{m}$) using the same continuous and dispersed phases and agitation method.

However it is noticeable that there is a much larger experimental scatter in the permeability of the macroporous polymers produced by polymerisation of emulsion templates which were emulsified at a stirring rate of 1,000rpm for short lengths of time. This larger scatter was seen for all macroporous polymers produced from emulsions obtained after emulsification at 1000 rpm for 10s (PH-16, PH-21

and PH-26) and in those produced from emulsions agitated at 30 s and 60 s with internal phase template of 70% and 80% (PH-17, PH-18, PH-22 and PH-23). This is caused by a higher degree coalescence of the template emulsion before polymerization, creating pores which were much larger than those obtained at the end of agitation this makes the final structure more irregular. A similar result was found by Wong et al. [168]. Similarly air bubbles entrained into the emulsion will also be larger for a shorter agitation time of the emulsion template. The large coalesced regions and large trapped air bubbles meant the permeability of these emulsion templated macroporous polymer's varied significantly for different monoliths causing greater variations in their permeability compared to emulsion templated macroporous polymers produced from templates produced with a greater energy input. However this partial coalescence was not seen to significantly change the average permeability from the linear relationship between pore throat diameter and permeability expected, with the exception of PH-16 and PH-21. This suggests that even when some droplet coalescence occurs in the emulsion template prior to polymerisation the permeability is still a function of the size of the pore throats and its porosity, as pore throats diameters are determined by the smaller pores.

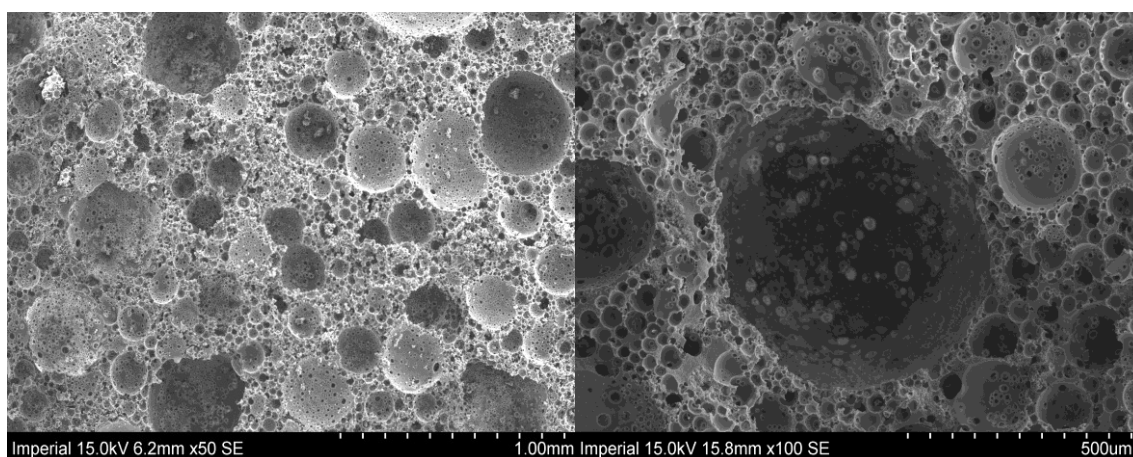


Figure 25. SEM images showing a. PH-21 and b. PH-26 to illustrate the large pores present including large areas without pore throats.

However for PH-16 and PH-21, produced from emulsion templates with an internal phase volume of 80% and 70%, respectively, emulsified for 10 s using a stirring rate of 1000 rpm, a significant negative deviation is observed in the permeability from the expected linear trend. It was expected they would have high permeabilities in excess of 1 D, due to their larger pore throats, in line with the linear relationships observed in *Figure 24a,b*. However there was a broad pore throat distribution present in PH-16 (*Figure 51*) and PH-21 (*Figure 52*) such that the larger pore throats had little bearing on the permeability this being limited by the smaller pore throats. However this does not explain why there was no negative deviation in permeability for PM-26 (*Figure 53*) which also had a wide pore throat size distribution. However as can be seen in *Figure 25* the walls of the coalesced

droplets are less open than typical for the pore structure of emulsion templated macroporous polymers which would decrease permeability. This suggests that the emulsion template of PM-26 was stable enough, due to its lower internal phase percentage, to prevent coalescence to the extent that the permeability of the final macroporous polymer was not decreased. However in PH-16 and PH-21 coalescence of the template emulsion occurred to the extent that permeability of the macroporous polymers produced thereof was compromised.

Chapter 4: Residence Time Distribution in PolyHIPEs Monoliths

1. Introduction

Residence time distribution (RTD) describes the probability of a fluid element leaving a chemical reactor or vessel after a given period of time after it was introduced into the system as such it is often used to characterise the mixing within a particular system. The residence time distribution is commonly determined by introducing a small pulse of inert tracer at the inlet of the system and measuring its concentration with respect to time at the outlet of the system. The spread of the tracer is described by the variance of the residence time distribution; a higher variance indicating greater mixing within the system. The residence time distribution behaviour falls between two ideal extremes, ideal plug flow and ideal continuously stirred tank behaviour [177].

Under ideal continuously stirred tank behaviour it is assumed that the moment a fluid element enters the system it is instantaneously and completely mixed with all other fluid within the system. If this is the case then the residence time distribution observed at the outlet will have exponentially decreased as the concentration in the system will be at its highest immediately after the tracer was introduced and decreases afterwards as the tracer is diluted in the system. This ideal model is most true for systems where the throughput is small compared to the volume, which is well mixed (for example using an impeller). Therefore, in an ideal continuously stirred tank the variance of the tracer pulse would be much higher at the outlet than the inlet

In ideal plug flow reactor a fluid element entering system is assumed to undergo no axial mixing when passing through the system, each fluid element can be seen as its own small continuously stirred tank. Therefore, a plug flow system is equivalent to an infinite series of continuously stirred tanks each having an infinite small volume. This being so the residence time distribution would be exactly the same at both the inlet and outlet of the system, with identical variance.

Here the aim was to determine the RTD of an inert tracer through a polyHIPE flow cell in order to investigate to what extent fluids are mixed when pumped through a polyHIPE mixing element. Also by creating monoliths with a range of pore and pore throat sizes by varying the energy input used during the preparation of the emulsion template, the effect of the internal polyHIPE structure on the RTD could be examined. Porous polymer monoliths have been studied before as static mixing elements for use in microfluidic systems [178, 179], however polyHIPEs have the advantage of a

higher porosity leading to low pressure drop. Moreover, the pore structure and pore and, therefore, pore throat size can be easily controlled.

One of the applications for which polyHIPEs were mainly considered is for chromatography columns [1, 146, 180]. This is due to the ability to tailor the properties of polyHIPEs; very high surface area polyHIPEs can be created for instance by the inclusion of porogens or post synthesis hypercrosslinking [142, 143]. However, conventional poly(S-co-DVB)HIPEs possess smooth internal surfaces and have surface areas of only $\approx 5 \text{ m}^2\text{g}^{-1}$ [142]. However by comparing the experimental mean residence time and hydraulic residence time it will be possible to determine if a chromatographic effect (if sorption is significant enough to slow the elution of the solvent) still occurs in unmodified poly(S-co-DVB)HIPEs monoliths.

2. Experimental

2.1. Residence Time Distribution Experimental Setup

The polyHIPE flow cells (Figure 14) were connected to a high performance liquid chromatography (HPLC) system, which pumped HPLC grade water at a rate of 1 ml min^{-1} through the flow cell into a UV detector (Jasco UV-975) attached to a computer. When the signal from the UV detector had stabilised and no air bubbles were observed at the flow cell outlet $100 \mu\text{L}$ of 0.12 gL^{-1} aqueous caffeine solution was injected into the inlet of the system. The caffeine solution passed through the flow cell and its concentration as function of time was determined using an UV detector (272 nm). Using image analysis software (Image J) the absorbance was recorded every 3.75 s (16 times a minute), and converted into the caffeine concentration in the detector at that point in time.

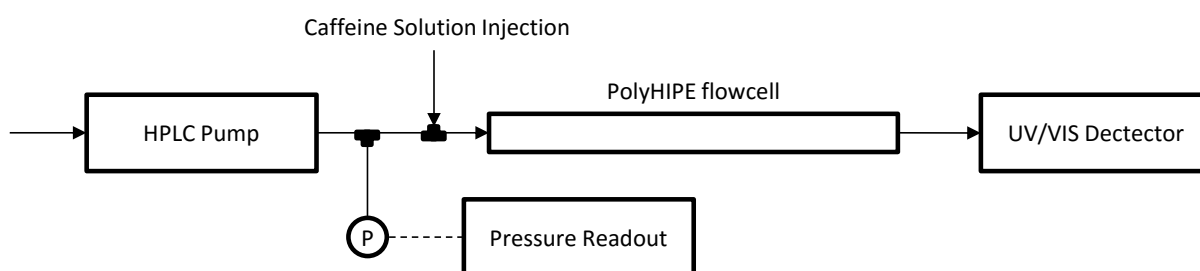


Figure 26. Schematic of the experimental setup used to determine the residence time distribution within polyHIPE flow cells

The variance of the caffeine pulse was also determined for a 12 element spiral static mixer and a HPLC column (Phenomenex Luna containing $5 \mu\text{m}$ c18 (2) particles with dimensions $4.6 \times 150 \text{ mm}$) both of which had similar internal volumes to the polyHIPE flow cells.

2.2. Determination of Variance

The following equations [181] were used to calculate the variance of the caffeine pulses at the exit of the flow cells and in an empty tube of the same dimensions (length 80 mm). These equations assume a steady state system of an incompressible fluid where fluid motion is due to advection only. The trapezium rule was used to approximate the integrals:

$$\bar{t} = \frac{\int_0^{\infty} tV dt}{\int_0^{\infty} V dt}$$

Equation 15

$$\sigma_{out}^2 = \frac{\int_0^{\infty} t^2 V dt}{\int_0^{\infty} V dt} - \bar{t}^2$$

Equation 16

where $\bar{t}$ is the experimentally measured mean residence time taken for the caffeine to pass through the flow cell (s), t the time (s), V the voltage recorded by the UV detector (mV) and σ^2 the variance of the caffeine pulse (s^2). The hydraulic residence time (t_h (s)) is the theoretical amount of time it takes a fluid element to pass through the flow cell in absence of dead volume or sorption occurring within the system as calculated using Equation 17:

$$t_h = \frac{V}{\vartheta} = \frac{V_m * Porosity}{\vartheta}$$

Equation 17

where V is the free volume of the flow cell (m^3), V_m the volume of the monolith (m^3) and ϑ the flow rate of the liquid through the flow cell (m^3s^{-1}). From the variance it is possible to calculate the number of ideal continuously stirred tanks the system represents [181]. This involves the change in variance ($\Delta\sigma^2$) of the caffeine pulse between the inlet and outlet of the flow cell, in all cases the inlet variance was taken to be that recorded in the absence of a flow cell. Since Equation 18 assumes that there is no chromatographic effect to distort the residence time of the tracer the hydraulic residence time was used as opposed to the mean residence time for the tracer pulse. As ideal plug flow can be thought of as infinite stirred tanks in series and represents no axial mixing, a system with fewer ideal continuously stirred tanks is indicative of better mixing.

$$Number\ of\ ideal\ continuously\ stirred\ tanks = \frac{t_h^2}{\Delta\sigma^2} = \frac{t_h^2}{\sigma_{out}^2 - \sigma_{in}^2}$$

Equation 18

2.3. Determination of Surface Area of polyHIPEs

The surface area of the polyHIPEs was determined using an automated gas adsorption analyser (TriStar 3000, Micromeritics). Nitrogen was used as the adsorptive for analysis of the sample and surface area reported was determined using the Brunauer–Emmett–Teller (BET) method.

2.4. Determination of Permeability of polyHIPE Flow Cells

The permeability of the polyHIPE flow cells was measured using a syringe used to pump deionised water through the flow cell with a pressure sensor at the inlet of the flow cell rather than using the pressure drop determined in the HPLC setup. This was due to the HPLC set up giving a pressure drop to the nearest bar whereas the pressure sensor gives the pressure drop to the nearest tenth of a bar. The permeability was then calculated using Darcy's law defined in Chapter 1 section 2.1.

3. Results and Discussion

Table 2. The effect of polyHIPE of pore structure on the variance of the caffeine pulse * Estimated equivalent pore throat diameter (Chapter 2 section 4)

Sample Number	Porosity (%)	Mean Pore Diameter (μm)	Mean Pore throat diameter (μm)	BET Surface Area (m^2g^{-1})	Permeability (mD) ± 0.5	Hydraulic residence time (s) ± 0.5	Mean Residence Time (s) ± 0.5	Variance (s^2) ± 0.5	Number of Ideal Continuously Stirred Tanks ± 0.5
RTD-1	82.0	8.9 $\pm$ 3.6	2.5 $\pm$ 0.8	2.09 $\pm$ 0.01	257	151	165	1555	16
RTD-2	82.4	6.0 $\pm$ 1.7	1.7 $\pm$ 0.5	3.12 $\pm$ 0.01	136	152	172	1688	15
RTD-3	83.4	4.8 $\pm$ 1.6	1.3 $\pm$ 0.4	3.94 $\pm$ 0.01	63	154	155	1934	13
RTD-4	81.7	3.6 $\pm$ 1.2	1.1 $\pm$ 0.3	4.90 $\pm$ 0.01	39	151	164	2257	11
RTD-5	82.4	2.8 $\pm$ 1.0	0.8 $\pm$ 0.2	6.40 $\pm$ 0.01	24	152	167	2487	10
Spiral Element Mixer	100.0	N/a	N/a	N/a	N/a	163	109	1933	15
HPLC column	49.0	N/a	1.1*	N/a	20	73	341	2232	3

3.1. Residence Time

As seen in *Table 2* the experimental mean residence times of all polyHIPE flow cells were found to be slightly greater than predicted by the hydraulic residence time (information on the HIPE templates can be found in *Table 8* in the Appendix). This suggests that despite the relatively low surface area of polyHIPEs ($2\text{--}6\text{ m}^2\text{g}^{-1}$, *Table 2* and *Figure 54*, Appendix) a small chromatographic effect was caused by the flow cells. However, despite compensating for the time the fluid spent in the pipework when calculating the mean residence time, there may have been small free volumes created at the ends of the flow cells where it was connected to the inlet and outlet, which would have increased the mean residence time recorded. Also if there was a chromatographic effect, the difference between the experimental mean residence time and hydraulic residence time should have increased with increasing surface area of the polyHIPE. However from the data in *Table 2* no such trend is observed. Especially when compared to the HPLC column, where there is a strong chromatographic effect leading to a significant difference between the mean residence time and the hydraulic residence time, unsurprisingly the chromatographic effect, if any, of the polyHIPE flow cells was almost negligible. However for the spiral mixer the mean residence time was lower than the calculated hydraulic residence time (*Table 2*) suggesting that, unlike the polyHIPEs or HPLC column there are stagnant zones within the mixer at this low flow rate increasing the rate at which the caffeine passed through the system.

3.2. Variance of Caffeine Pulse Input

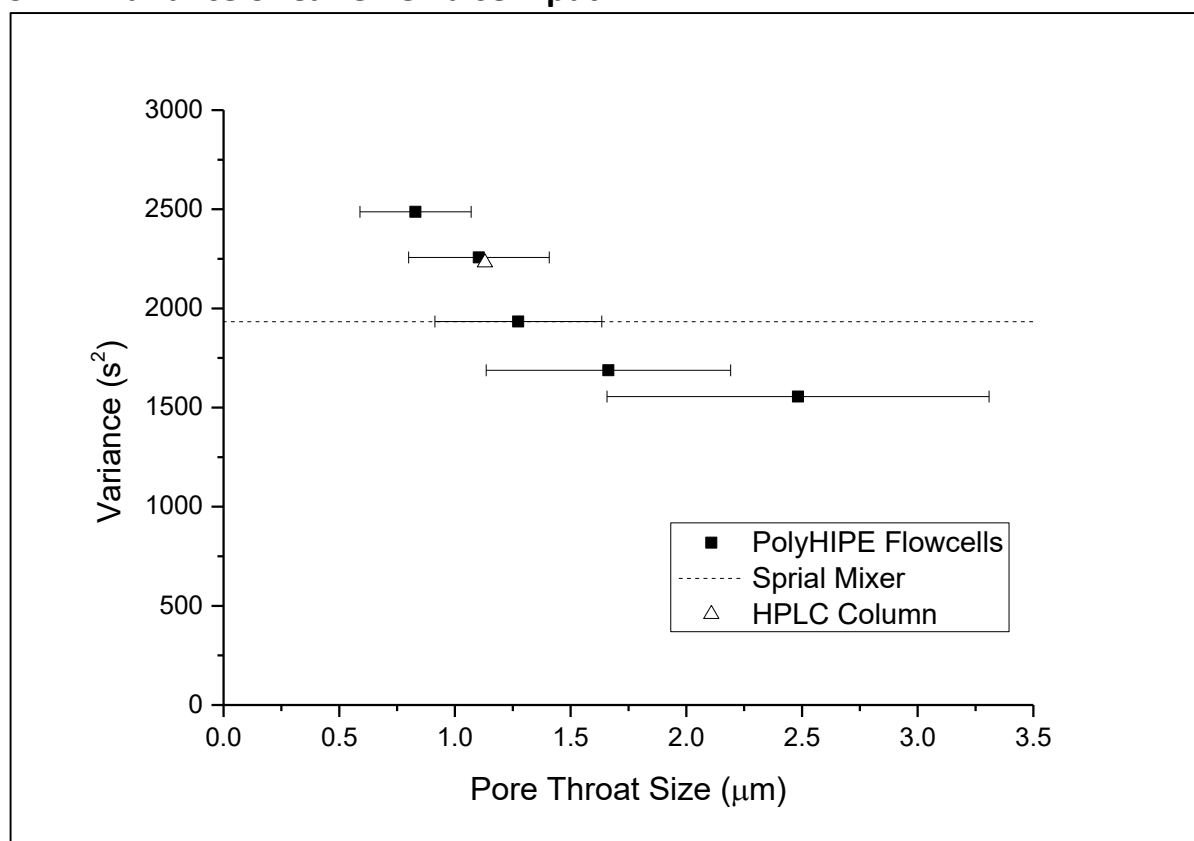


Figure 27. The variance of a caffeine impulse passing through polyHIPE flow cell as a function of polyHIPE pore throat size. Y-error smaller than data symbol.

The variance in the caffeine pulse was seen to increase with decreasing average pore throat size of the polyHIPE monolith. This suggests that smaller pore throats increased axial mixing of fluid elements. This is likely due to increased flow division and reorientation occurring within the structure. However it should be noted that as pore throat size decreased the variance levels off suggesting that there would still be a significant increase in variance for macroporous polymers with even larger average pore throat diameters. The RTD of the caffeine pulse after passing through the polyHIPEs was seen in all cases to contain just one peak, this is indicative of there being no bypassing within the column which would lead to additional peaks being present.

Comparisons were made between the polyHIPE flow cells and two commercially available systems of similar volume, a spiral static mixer and a HPLC column. However these did not have precisely the same dimensions as the polyHIPE flow cells. The HPLC column gave a similar variance to the polyHIPE columns with comparable pore throat size however at the cost of a much lower permeability. The spiral static mixer provided a variance similar to the polyHIPEs but almost no pressure drop.

3.3. Number of Stirred Tanks Represented by the PolyHIPE Flow Cells

When measured in the absence of any flow cell, the variance of the caffeine pulse at the inlet (σ_{in}^2) was found to be 106 s^2 , this value was used to calculate the number of ideal continuously stirred tanks represented by the polyHIPE flow cells (Equation 18).

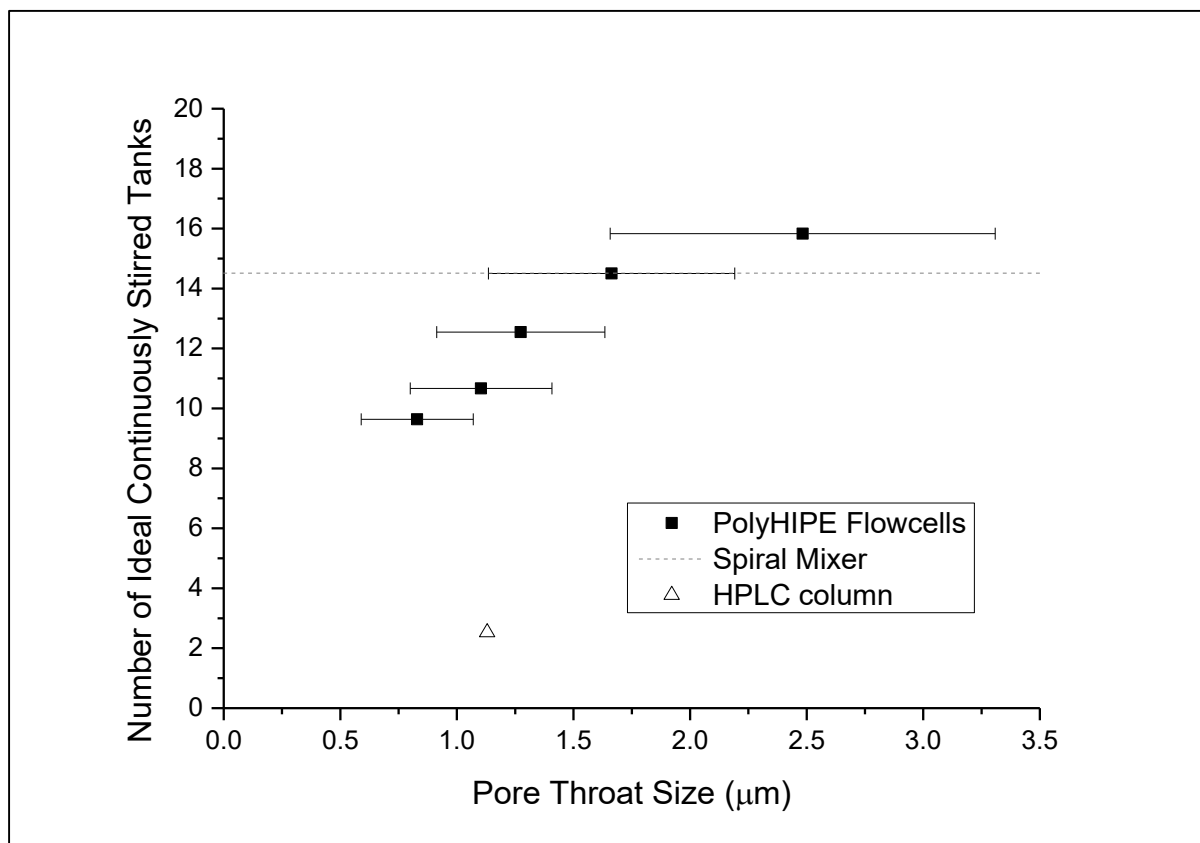


Figure 28. The number of ideal stirred tanks represented by polyHIPE flow cells as a function of polyHIPE pore throat size. Y-error smaller than data symbol.

From Figure 28 it can be seen that the number of ideal continuously stirred tanks represented by the polyHIPE flow cells decreased with average pore throat size, which is indicative of increased mixing of fluid elements. However, due to its lower porosity leading to a lower hydraulic residence time, the HPLC column represented far fewer ideal continuously stirred tanks than the polyHIPE flow cells, suggesting it is the more effective mixer, but again resulting in a much higher pressure drop across the column.

3.4. Permeability of PolyHIPE Flow Cells

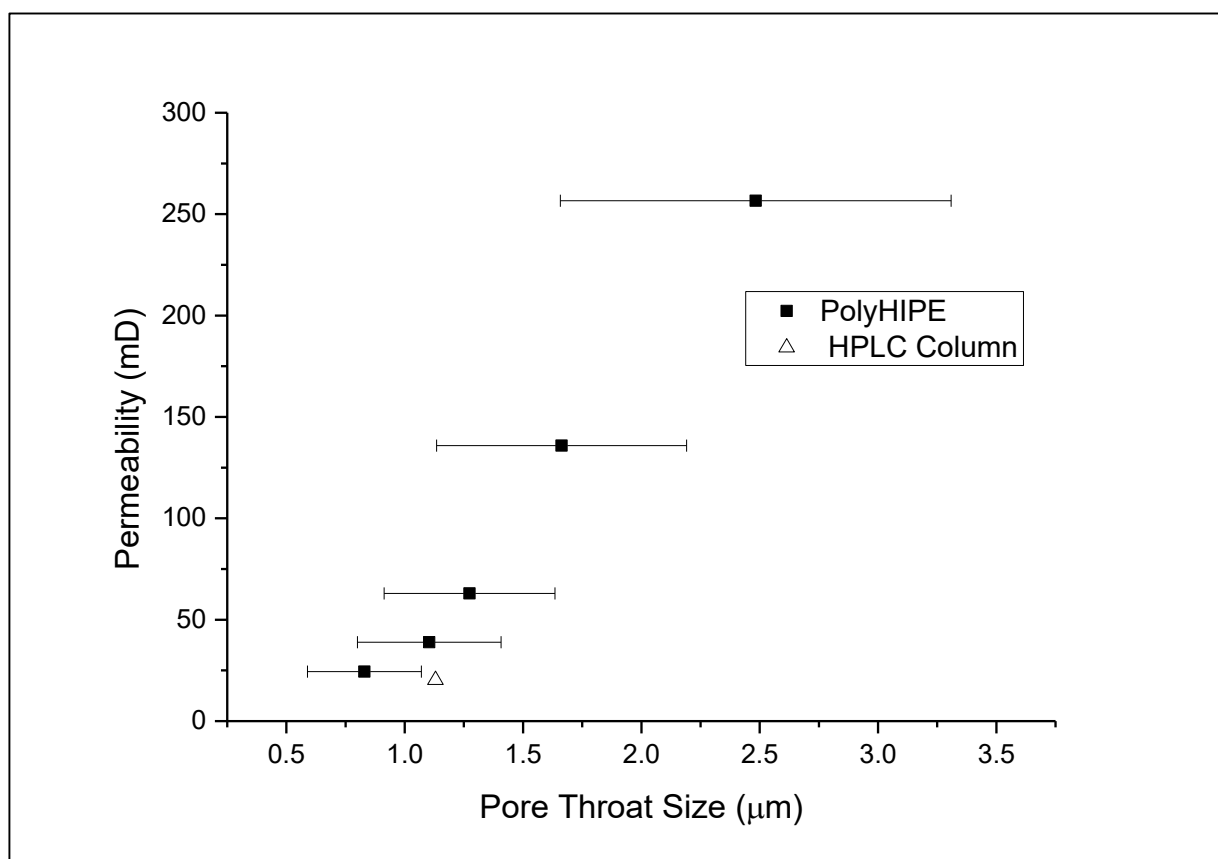


Figure 29. The permeability of polyHIPE flow cells as a function of pore throat size. Y-error smaller than data symbol.

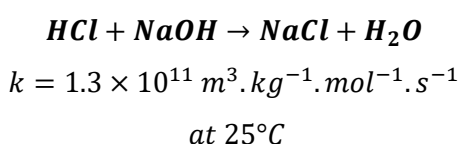
The permeability of polyHIPEs monoliths increased linearly with increasing average pore throat diameter. It can also be seen that they are significantly more permeable than the HPLC column used as a comparison, due to their significantly greater porosity.

Chapter 5: Micromixing in Emulsion Templated Macroporous Polymers characterised by the Bourne reaction

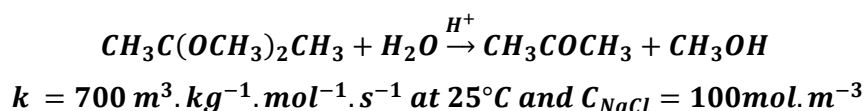
1. Introduction

Here we consider the use of polyHIPEs as homogenous micromixing elements, postulating that their intricate internal structure will result in effective mixing when fluids are forced through them, as the continuous reorientation of the fluids could lead to rapid contact between fluid elements at much lower flowrates than would be required for traditional static mixers [182] or impingement thin liquid sheets mixers [183] and at lower shear than a rotor-stator mixer [184]. This could be of significance in areas, such as pharmaceutical production with trends towards continuous production at lower flowrates [5].

In order to assess the effect on homogeneous mixing of a fluid flow through an emulsion templated macroporous polymer a mixing sensitive homogeneous reaction was used. These usually consist of two competitive reactions, which proceed at very different rates such that the extent of one reaction is dependent on the extent of micromixing in the system [185]. The fourth Bourne reaction [186, 187] was used to assess the micromixing within macroporous polymers due to its ease of use. The 4th Bourne reaction consists of two reactions that are competitive and parallel; the neutralisation reaction between sodium hydroxide (NaOH) and hydrochloric acid (HCl) and the acid catalysed hydrolysis of dimethoxypropane (DMP) to acetone and methanol [187, 188]:



Equation 19



Equation 20

From

Equation 19 and Equation 20 it can be seen that reaction coefficients (k) differ by many orders of magnitude meaning that in the event of rapid mixing of fluid elements the neutralisation reaction will move rapidly to completion before significant DMP hydrolysis can occur. As the sodium hydroxide is present in slight excess the reaction mixture is alkaline once neutralisation is complete,

so no further acid catalysed DMP decomposition does occur. However in the event of slower, less effective mixing more DMP molecules will encounter local regions of low pH, causing a greater yield of hydrolysis products to be observed. The effectiveness of micromixing within the polyHIPE structure can therefore be assessed by analysis of the concentration of the products of the hydrolysis reaction and comparing this with control samples.

2. Experimental

2.1. Micromixing Experimental setup

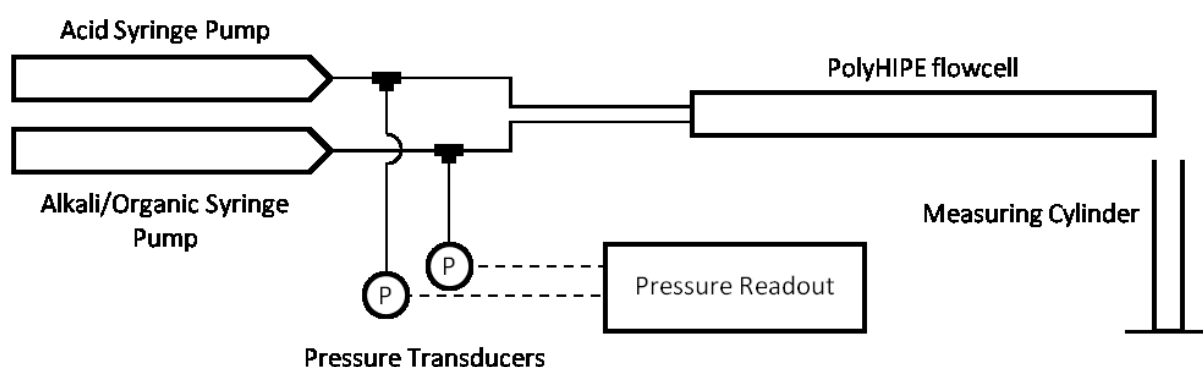


Figure 30. Experimental setup used to determine the pressure drop and mixing characteristics of polyHIPEs

The experiments to quantify micromixing using the Bourne reaction were performed in the setup schematically shown in Figure 30. The flow cell was connected to two syringe pumps, one containing hydrochloric acid (360 mol m^{-3}) and the other containing a solution of sodium hydroxide (380 mol m^{-3}), DMP (200 mol m^{-3}) and NaCl (100 mol m^{-3})[188]. These solutions were then pumped into the flow cell via the separate 1/16 inch tubes displacing the air from the monolith. The NaOH and DMP (stable at high pH) in aqueous solution are mixed with the HCl solution within the macroporous polymer structure with the NaOH being in slight stoichiometric excess. The pressure up stream of the flow cell was measured using two pressure transducers, one on each feed line, which were connected to a digital readout. Since the far end of the flow cell was open to the atmosphere so that the pressure drop across the polyHIPE was known.

The permeability k of the samples was calculated using Darcy's law, which relates the volumetric flowrate Q of a liquid of known viscosity μ through a porous sample with a cross-sectional area A and length L with the pressure difference across the sample ΔP . The permeability k is given in units of Darcy's where 1 Darcy is equivalent to 10^{-12} m^2 . Darcy's law is given in Chapter 1 section 2.1.

The pressure drop was measured by pressure transducers in both the acidic and alkali feed lines. The dimensions of the polymer monolith were measured after manufacturing the flow cell, taking in to account the 5 mm depth of the drilled feedholes. It was assumed that the viscosity of the reaction mixture was constant and equal to that of water (10^{-3} Pa.s).

However when used for the first time, the initial breakthrough of liquid from the polyHIPE flow cells often produces a small amount of polymer fragments before the liquid begins to run clear. These fragments were examined using SEM and found not to be of a porous structure typical of emulsion templated polymers suggesting that they are not pieces of polymer that have broken off by the fluid flow. These fragments are most likely debris left over from the machining of the polyHIPE (stage 4 in Figure 16 in Chapter 1). Samples were never taken until all polymer fragments had been flushed out.

Samples of liquid were taken at the outlet of the polyHIPE flow cell after at least three pore volumes of liquid had passed through the flow cell in order to ensure steady state. The flowrates of the two liquids were always identical to ensure that the NaOH was always in excess of the acid. After the experiment was complete the flow cells were stored for a month before the experiment was repeated.

2.2. Determination of Effectiveness of Micromixing

The extent of the decomposition of the DMP was quantified using high performance liquid chromatography (HPLC) to determine the concentration of acetone at the exit of the flow cell. The amount of acetone detected is indicative of the effectiveness of the micromixing as poorer mixing will cause greater DMP decomposition and hence a higher acetone concentration will be detected.

The HPLC mobile phase used was a 2:1 mixture of water and acetonitrile buffered to a pH of 9.2 with NaHCO_3 to prevent further DMP decomposition within the HPLC. A mobile phase flowrate of 1 ml/min was used and the injected sample volume was 30 μl . The sample was analysed by UV detection at a wavelength of 270 nm as acetone is the only UV active species. The column used was a Phenomax 5 μm C18 packed bed column 4.6 mm $\varnothing$ x 250 mm. The feeds were also analysed to confirm decomposition did not occur before the experiment was run.

Table 3. Effect of the pore structure of macroporous polymers on permeability and the extent of acid catalysed decomposition of DMP. ml/min

Sample	Porosity (%)	Average Pore Diameter (μm)		Average Pore Throat Diameter (μm)	Permeability (mD)	Steady State Yield of DMP Decomposition (%)	Reynolds Number (Re)
S-1	75	3.4	± 1	1	± 0.3	19.9 ± 0.0	5.60×10^{-4}
S-2	81	3.5	± 1.1	1.2	± 0.4	14.7 ± 0.8	6.50×10^{-4}
S-3	81	4.5	± 1.3	1.7	± 0.6	21.6 ± 1.2	8.90×10^{-4}
S-4	83	6.4	± 2.2	1.9	± 0.6	20.8 ± 2.4	9.80×10^{-4}
S-5	80	6	± 2	2.1	± 0.6	21.1 ± 0.3	1.10×10^{-3}
S-6	83	13.5	± 4.3	3.6	± 1.2	21.6 ± 0.2	1.90×10^{-3}
S-7	83	20.6	± 8.4	3.8	± 1.3	22.3 ± 0.3	2.00×10^{-3}
P/S-1	78	4.1	± 1.9	0.6	± 0.2	12.2 ± 0.0	3.10×10^{-4}
P/S-2	85	5.2	± 2.3	1.3	± 0.4	17.7 ± 0.0	6.50×10^{-4}
P/S-3	85	8.2	± 2.6	1.6	± 0.6	20.2 ± 0.2	8.40×10^{-4}
P/S-4	84	8.8	± 2.6	2.2	± 0.7	19.3 ± 0.9	1.10×10^{-3}
P/S-5	91	12.6	± 4	3.2	± 1.3	22.5 ± 0.1	1.50×10^{-3}
P/S-6	85	39.8	± 18.3	9.2	± 4.4	21.2 ± 0.3	4.70×10^{-3}
P/S-7	81	86.8	± 34.3	22.2	± 9.9	23.1 ± 0.0	2.70×10^{-2}
Blank Tube	100	N/a		N/a		26.2 ± 0.9	3.03
Spiral Static Mixer**	≈ 65	N/a		N/a		22.9 ± 1.6	4.66
HPLC Column***	49	N/a		1.13		22.9 ± 0.3	3.30×10^{-3}

* Permeability could not be accurately determined. ** Helical static mixer with twelve 6 mm helical elements in 6.5 mm ID tubing. *** An equivalent pore throat size was estimated from the area between tightly packed 5 μm spheres, porosity from personal communication with M. Whitmore, 2013.

3. Results and Discussion

3.1. Effect of internal structure on micromixing

Macroporous polymers produced from emulsions stabilised by surfactants or both particles and surfactants (composition Table 9, Appendix) possess the interconnected pore structure expected of emulsion templated macroporous polymers (Figure 31). By stabilising HIPEs with both particles and surfactants it was possible to greatly increase the pore size, typical for poly-Pickering-HIPEs, yet the concentration of surfactant was enough to induce the formation of pore throats thereby creating a very permeable structure. The porosity, average pore and pore throat diameters are summarised in Table 3. By varying the agitation time and internal phase volume ratio of the emulsion template it was possible to produce macroporous polymers with a range of porosities and pore/pore throat sizes as can be seen by comparing the length scales in Figure 31.

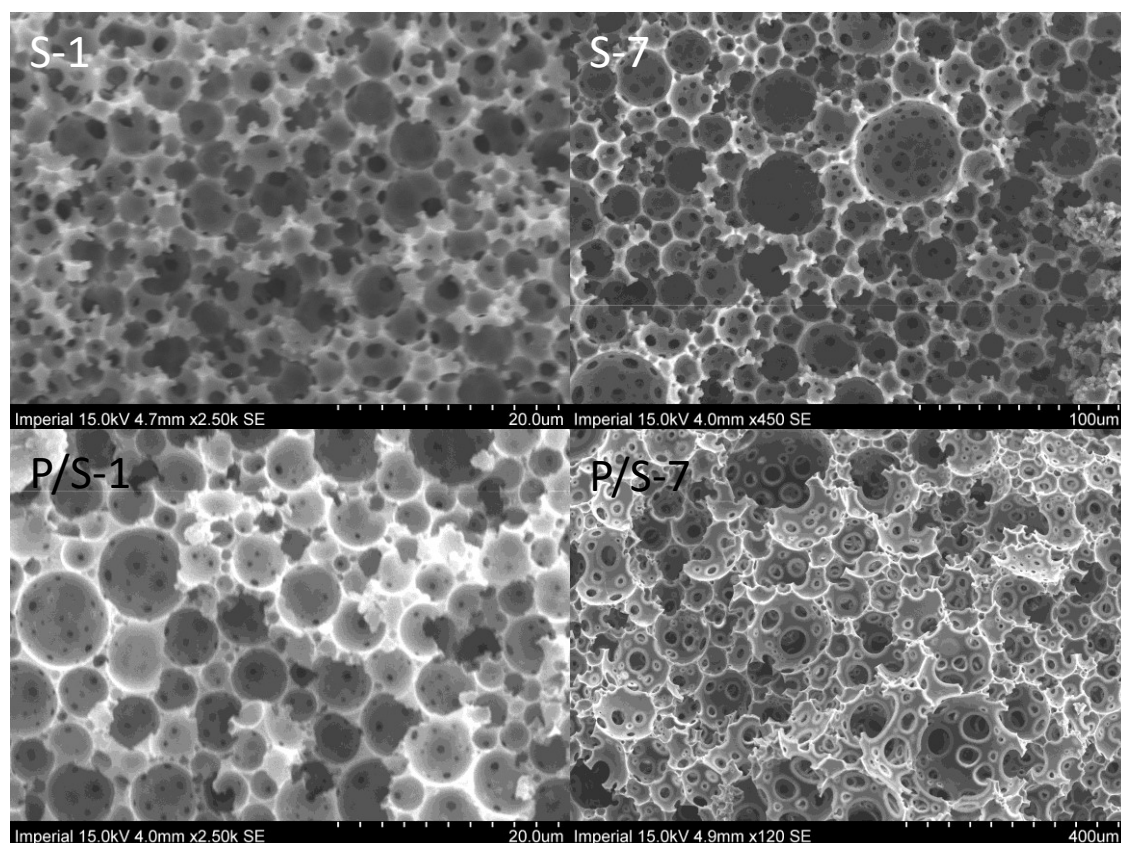


Figure 31: Representative SEM images of polyHIPE samples S-1 and S-7 produced from surfactant stabilised HIPEs as well as P/S-1 and P/S-7 produced from particle stabilised HIPEs.

It can be seen that the extent of DMP hydrolysis is lower in all cases where the reaction mixture is passed through a macroporous polymer compared to an empty tube with an internal diameter 7 mm at a total flowrate of 1 ml/min. All but sample P/S-7, with the largest average pore throat diameter, produced a similar or lower DMP hydrolysis yield compared to the spiral static mixer used as control

mixer. However, it should be noted that the range of hydrolysis yields was generally much narrower for the flow cells than either the spiral static mixer or the blank tube. This is because at such a low flowrate (1 ml/min with $Re < 0.1$) fluid elements in the spiral mixer and blank tube are larger leading to greater variation in the determined hydrolysis yields. Whereas after being mixed within the pores of macroporous polymers the fluid is more homogeneous hence a more consistent hydrolysis yields were found. The HPLC column containing 5 μm particles (a particle size similar to the pores in the emulsion templated polymers such that it could be considered to be an inverse polyHIPE) gave a hydrolysis yield similar to the spiral static mixer and many of the polyHIPE flow cells, however it was much less permeable than most of the emulsion templated macroporous polymers. The HPLC column was included to simulate a packed bed system. Overall it was found that there was no marked difference in decomposition yields between similar macroporous polymers produced by polymerisation of surfactant and particle/surfactant stabilised HIPEs.

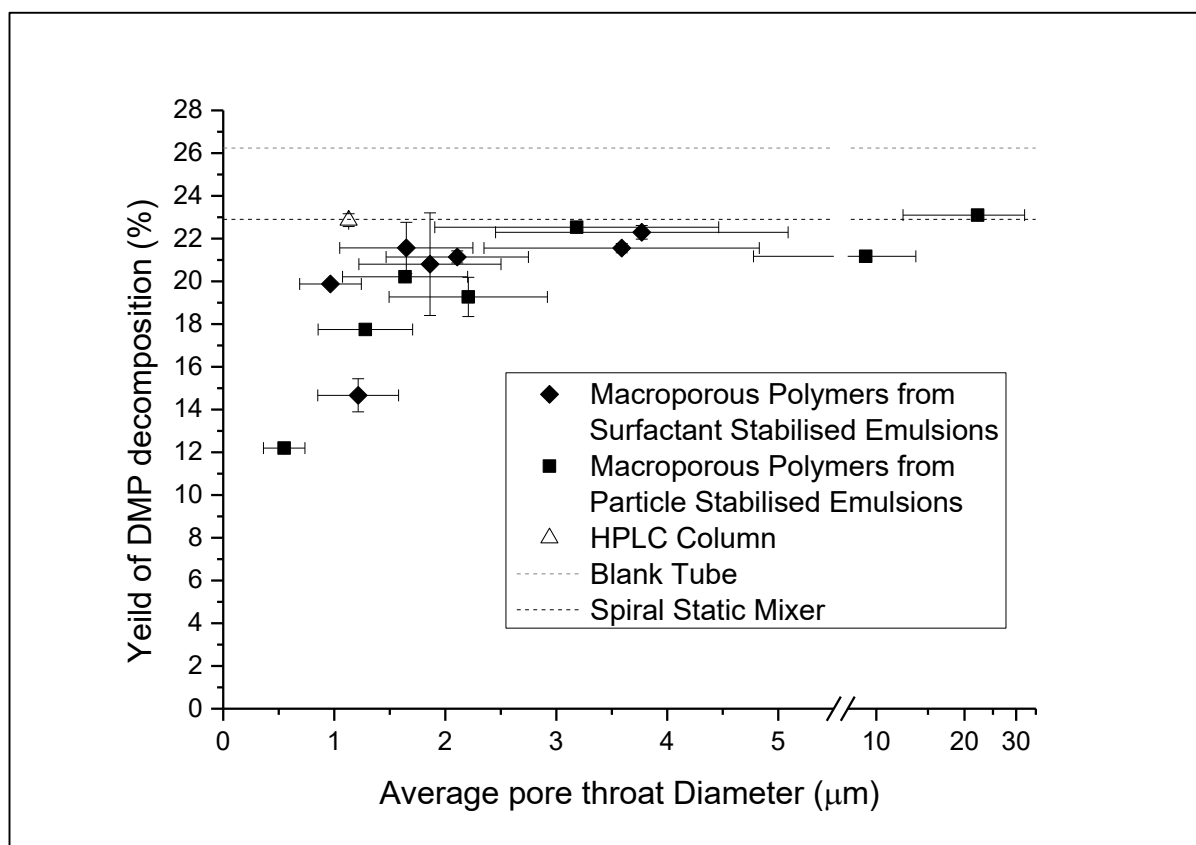


Figure 32: Yield of the acid catalysed DMP decomposition as function of the pore throat size of the macroporous polymers produced from surfactant stabilised emulsions and particle/surfactant stabilised emulsions. Shown for comparison are the yield of DMP decomposition for a blank tube, spiral static mixer and HPLC column.

It was generally observed that hydrolysis yields decreased when using macroporous polymers with smaller pore throats as micromixers. This was most noticable for samples S-2 and P/S-1; these were

able to decrease the product of the hydrolysis reaction by up to 50% compared to an empty tube. It can also be seen from Figure 32 and samples P/S-6 and P/S-7 in particular that the effectiveness of the flow cells at preventing DMP decomposition levels off, giving hydrolysis yields similar to that of the spiral static mixer, when the pore throat size increases to above 3 μm . This suggests that even very permeable macroporous polymers would still be able to give improved micromixing comparable to that of a packed bed HPLC column yet at a much lower pressure drop. For example the hydrolysis yield in sample S-7 was 22.3% similar to the HPLC column (22.9%) however the monolith had a permeability over 10 times greater (190 mD) compared to that of the packed particle bed (18 mD). However comparing literature results, the mixing within the monoliths was much less effective than in spiral static mixers at their designed Reynolds numbers [187] this is due to the much high energy input per volume to the system resulting in effective turbulent mixing. Comparable hydrolysis yields to those reported here were attained in microreactors [182].

When the total flowrate was increased from 0.2 ml/min to 2 ml/min it was found that this had no effect on the yield of hydrolysis reaction in the polyHIPE flow cells. The yield of decomposition products and hence the effectiveness of micromixing within the polyHIPEs appeared to be a characteristic of the pore structure, specifically the pore throat size. Therefore, it is suggested that the micomixing within polyHIPEs is a result of extensive flow division and reorientation within the pore structure, the extent of which is increased by smaller pore throats. It is unlikely that turbulence plays any role in the micromixing due to the low flowrates involved and the small pore sizes inhibiting the formation of turbulent eddies [189]. The Reynolds number (Re) for each sample was calculated using mean pore throat diameter (D_{pt}) as the characteristic unit of length. Where u is the fluid velocity in interior of the flow cell calculated from the fluid velocity entering the flow cell (U) divided by the permeability.

$$Re = \frac{\rho u D_{pt}}{\mu}$$

Equation 21

$$u = \frac{U}{P}$$

Equation 22

All Reynolds numbers were small ($Re < 0.1$) and as the flow still obeyed Darcy's Law and, therefore, it is safe to assume lack of turbulence in the system[189]. The extent of micromixing was found to be greatest (lowest DMP decomposition yeilds) in macroporous polymer flow cells with smaller pore throats and therefore one would expect, if mixing was due to turbulence, these samples to have the

highest Reynolds numbers whereas the opposite is true. Over the range of porosities examined in this work there was no clear link between porosity of the macroporous polymer and the extent DMP decomposition (Table 3).

The length of polyHIPE required for effective micromixing was investigated by performing the Bourne reaction in a flow cell followed by reducing its length and repeating the experiment. As an example the results for sample P/S-1 are shown in Figure 33, demonstrating that essentially the acid base neutralisation is complete after passing the reaction mixture through only 30 mm of the monolith at a flow rate of 1 ml/min. If an ideal plug flow reactor[190] had perfect mixing (7 mm diameter at a flowrate of 1 ml/min) the neutralisation should be 99.99% complete within $3.2 \cdot 10^{-11}$ mm and the hydrolysis yield should be virtually zero. The reason it takes 30 mm for complete neutralisation is due to the time it takes for the acid and base to fully mix first within the polyHIPE structure. A similar mixing length was found by Fréchet e. al.[179] using porous polymer monoliths in microfluidic channels. As the length of the macroporous polymer monolith decreased towards zero the yield of the hydrolysis reaction unsurprisingly rises to levels observed for the empty tube, most likely because the neutralisation reaction is incomplete when the fluid leaves the macroporous polymer monolith. This suggests that even a small length of macroporous polymer can effectively act as micromixer, in this case preventing an extra 10% of the total DMP molecules from being decomposed.

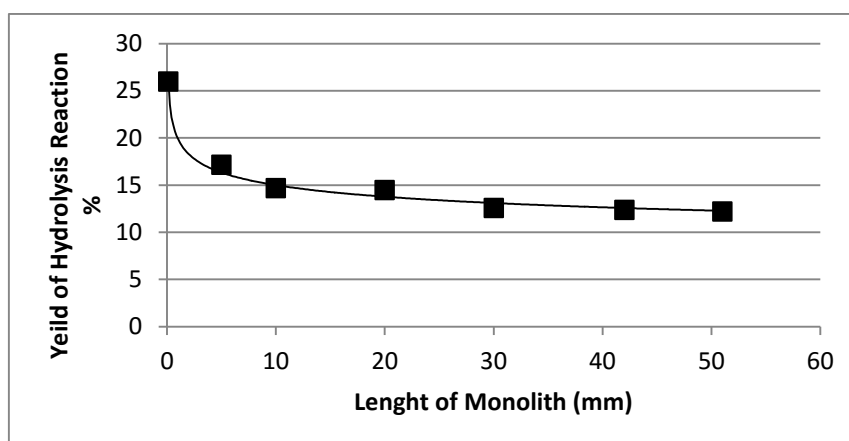


Figure 33: Yield of DMP hydrolysis within polyHIPE monolith P/S-1 as a function of its length. This shows that neutralisation of the acid is complete within the first 30 mm of the monolith as no further reduction in DMP yield is seen at greater lengths.

3.2. Effect of PolyHIPE Internal Structure on Permeability

However the downside to being able to increase micromixing by decreasing the average pore throat size and porosity is that this inevitably also leads to a decrease in permeability and higher pressure

drops across the flow cells. The most important factor in determining the permeability of the polymer monoliths is the size of the pore throats (Figure 34). In varying the flowrate it was found that the macroporous polymer monoliths obeyed Darcy's law with the pressure drop increasing linearly with volumetric flow. It should also be noted that macroporous polymers also offer a larger surface area than spiral static mixers with at least the same degree of micromixing. This surface area could be used to support a catalyst or for other forms of surface chemistry. The permeabilities recorded were consistent with values previously reported [20, 86]. It should be noted that when comparing the liquid permeabilities reported here to literature gas permeabilities there will be a small discrepancy but this is not significant unless pore diameters are lower than the gas mean free path ($\approx 0.1\mu\text{m}$) [191] which they are not for the polyHIPEs in this work.

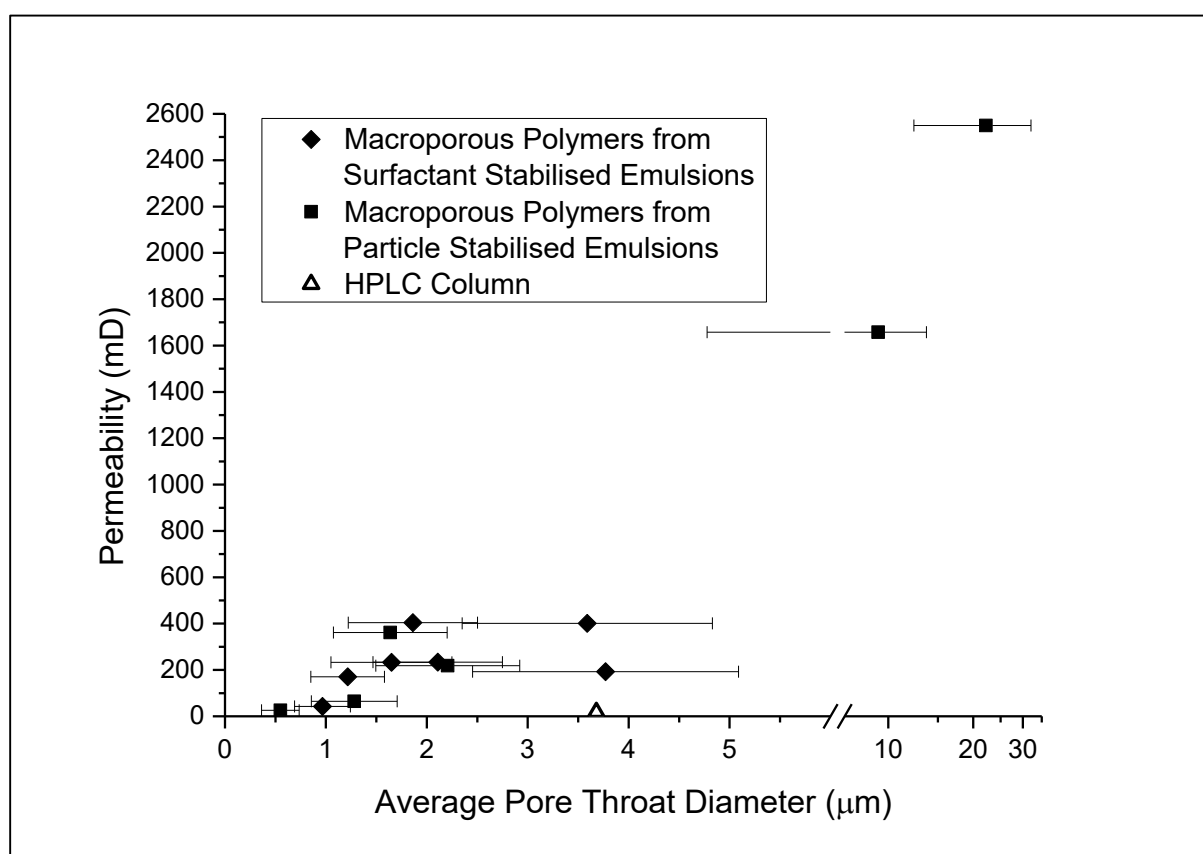


Figure 34: Permeability of macroporous polymer monoliths as function of mean pore throat diameter. Y-error smaller than data symbol.

3.3. Durability of Macroporous Polymer Flow cells

The polyM/HIPE flow cells were stored for one month before being retested under the same conditions to examine if they maintained the same level of performance. For most samples the yield of the hydrolysis reaction rose after storage, for some by a considerable extent, this was accompanied by an increase in permeability. However over half of the samples showed an increase

in hydrolysis yield of less than 10% compared to the first experiment and all samples were still more effective mixers than an empty tube.

SEM micrographs taken of the flow cells after use were analysed to evaluate if the increase in permeability was due to damage caused by the passage of the reaction solution. The SEM showed that the average pore throat size remained constant and no obvious damage could be seen to the polymer structure. This implies that there is no significant damage to the polymer structure by fluid action at the flowrates investigated in this study.

With the breakdown of the internal pore throat structure of the polyHIPE ruled out, the cause the increase permeability is likely to be the breakdown of the bond between the polymer and the Araldite® Rapid epoxy adhesive. This would cause bypassing of the polymer monolith and maybe mixing to occur on the outside of the polyHIPE structure. This is supported by the fact that the permeability of most samples increased after use and storage. It is noticeable that those samples that had the greatest percentage increase in hydrolysis operated at higher pressures (low permeabilities). This high pressure could result in the fluid being forced between the monolith and adhesive layer causing mixing to occur outside of the polyHIPE monolith. The smaller pore sizes of the lower permeability samples would also have contributed to poorer adhesion by preventing the adhesive penetrating the material and hence forming a weaker “mechanical interlocking” bond with the monolith. The majority of the samples showed an increase in permeability one month after production with the average permeability of those increasing by 11.5%.

In order to assess the micromixing caused by the internal structure of the polymer it was necessary to drill into the monolith a small way, this ensured that the two feed streams only ever made contact with in the pores of the material. However, it did mean that the two flows were only separated at the inlet by a segment of porous polymer two millimetres across. This resulted in damage to several samples when high pressure difference between the two feed legs occurred, for example if at the end of an experiment one side was suddenly depressurised. When this occurred the small section of polymer in between the two inlets ruptured allowing premature contact between the two fluids. This could lead to poorer contact between the two liquids contributing to the increase in DMP decomposition seen after use.

Chapter 6: Mixing Two Immiscible Liquids in Emulsion Templated Polymers

1. Introduction

This chapter explores the potential and effectiveness of macroporous polymers in promoting liquid–liquid extraction (LLE). The extraction of caffeine from an aqueous solution using organic solvents, similarly to the indirect method historically used for the decaffeination of coffee beans [192], was used as a model process. It can be anticipated that the intricate internal structure of polyHIPEs could lead to effective separation and reorientation of fluid elements creating a high interfacial area between the immiscible phases for mass transfer to occur. This technique could have importance in areas such as pharmaceutical production where flowrates are expected to be low and separation is often the process bottleneck [5].

In its most basic form LLE involves contact between two immiscible liquid phases (usually water and an organic solvent), one phase containing a solute that has a degree of solubility in both phases such that, when the two phases are in contact, it partitions between the two. Industrially this is most commonly achieved in mixer-settlers [193], centrifugal contact separators [194], extraction columns [195], microfluidic contactors [196], rotor-stator mixers [197], membrane enhanced methods [198] and static mixers [199]. The process described in this work differs from supported liquid extraction [200], where the aqueous phase is absorbed on to a high surface area substrate and batches of the organic phase are passed over it to effect extraction, whereas in this process both phases continuously pass through the monolithic support which itself acts to promote extraction.

2. Experimental

2.1. Caffeine Partition and Mass Transfer Coefficients

The partition coefficient P is defined as the ratio of the concentration of a solute in the two immiscible phases at equilibrium as can be seen in *Equation 23*. In order to calculate the partition coefficient (P) 10 ml of an aqueous caffeine solution (1 gL^{-1}) was agitated with 10 ml of ethyl acetate using a vortex mixer. The system was allowed to reach equilibrium and then settle before samples of both phases were taken. The caffeine concentration in each phase at equilibrium was then determined using (C_{aq}^* and C_{org}^*) using UV-Vis spectroscopy (PerkinElmer, Lambda 35).

$$P = \frac{C_{org}^*}{C_{aq}^*}$$

Equation 23

The mass transfer coefficient (k_{org}^0) was calculated by following the extraction in a stirred vessel. 20 ml of 1 gL⁻¹ aqueous caffeine solution saturated with ethyl acetate was contacted with 80 ml of ethyl acetate saturated with water in a cylindrical vessel agitated with a Rushton turbine at 275 rpm. Using a micropipette 50 µl samples of the organic phase were taken as the extraction progressed. The caffeine concentration in the continuous phase (organic) could then be followed by UV-Vis spectroscopy.

The data from the extraction were then used to calculate the overall mass transfer coefficient ($k_{org}^0 a$) using the following equation (as derived in the Appendix):

$$C_{org} = \left(\frac{1}{1 + \alpha} \right) P C_{aq}^{init} \left(1 - e^{-(1+\alpha)k_{org}^0 a \cdot t} \right)$$

Equation 24

with

$$\alpha = \frac{V_{org} P}{V_{aq}}$$

Equation 25

where C (mol m⁻³) is the caffeine concentration, V_{org} and V_{aq} are the volume (m³) of organic and aqueous phase, respectively, t (s) the time and 'a' the interfacial area per unit volume (m² m⁻³). The interfacial area per volume (a) was calculated from the Sauter mean droplet diameter ($\bar{d}_{32}$), as given by the correlation for Rushton turbines reported by Chen and Middleman[201].

$$\frac{\bar{d}_{32}}{D} = 0.053 We^{-0.6} = 0.053 \left(\frac{\rho_c N^2 D^3}{\sigma} \right)^{-0.6}$$

Equation 26

$$a = \frac{6\theta}{\bar{d}_{32}}$$

Equation 27

where D is the impeller diameter (m), ρ_c the density of the continuous phase (kg m⁻³), N the rate of impeller rotation (s⁻¹), σ the interfacial tension (N m⁻¹) and θ the dispersed phase volume.

By plotting the natural logarithm of the caffeine concentration as function of time (see Appendix), the overall mass transfer coefficient ($k_{org}^0 a$) for the extraction could be calculated from the gradient, this was then divided by the interfacial area per volume (a) to give the mass transfer coefficient for

this solvent solute system (k_{org}^0). Once the mass transfer coefficient is known the interfacial area per volume generated within the macroporous polymers could be calculated.

2.2. Caffeine Extraction in PolyHIPE Flow cells

2.2.1. Experimental setup

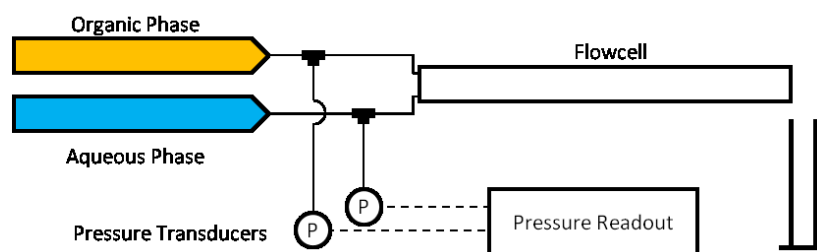


Figure 35. Experimental setup for the extraction

An aqueous solution of 10 gL^{-1} caffeine was prepared using deionised water that had been saturated with the ethyl acetate beforehand. The ethyl acetate used to extract the caffeine was also saturated with deionised water before the experiment; this was to ensure that there was no change in the volume of solvents during extraction since water and ethyl acetate have a degree of mutual solubility. Using a double syringe pump (PHD Ultra, Harvard Apparatus, UK) the two phases were passed together into the polyHIPE flow cell and allowed to mix within the pore structure of the polyHIPE at a flow rate of 0.2 mL min^{-1} (total flow rate of 0.4 mL min^{-1}). The pressure of the fluid was recorded using pressure sensors allowing the permeability (k) of the flow cell to be calculated using Darcy's Law (as described in Chapter 1 section 2.1).

After waiting for at least three residence times (pore volumes), the two phase mixture from the flow cell was collected for 2 min in a measuring cylinder where very rapid phase separation occurred. A $50 \mu\text{L}$ sample of one phase was then taken from the measuring cylinder using a micropipette. The $50 \mu\text{L}$ sample was placed into 10 ml of already prepared solvent; the sample was then placed into a fridge to prevent any solvent evaporation. This was repeated at least 3 times for each solvent to ensure reproducibility. For comparison a blank tube, spiral static mixer and a HPLC column were also used to conduct the extraction. The HPLC column was an Agilent Zorbax SB-C8 $4.6 \times 75 \text{ mm}$, packed with $5 \mu\text{m}$ hydrophobised silica particles simulating a packed bed. In order to calculate an equivalent pore throat diameter for the HPLC column, the minimum area between the silica particles was used.

2.2.2. Determination of Overall Mass Transfer Coefficient and Stage Efficiency

In order to assess the ability of macroporous polymers to promote liquid-liquid extraction the overall mass transfer coefficient (k_{org}^0) had to be determined. As the polyHIPE flow cell acts as a co-current

contactor the mass transfer coefficient was calculated from the mass balance of caffeine in the aqueous phase, where Q_{aq} is the flow rate of the aqueous caffeine solution.

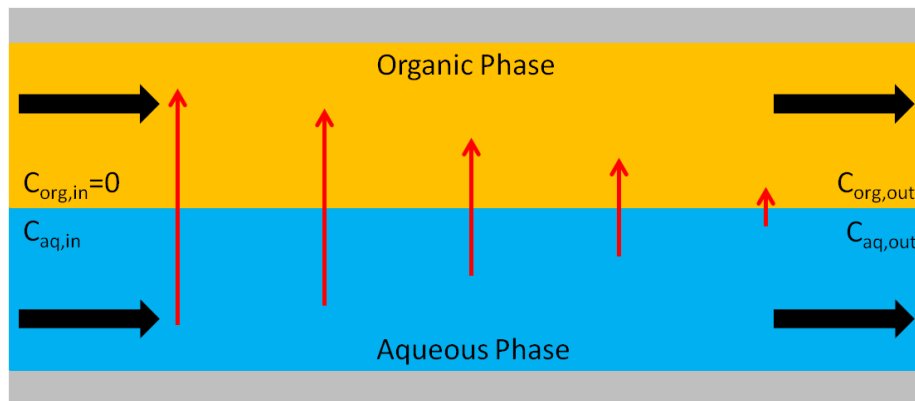


Figure 36. Diagrammatic representation of liquid-liquid extraction in co-current contactor. Thick arrows represent the direction of liquid flow while thin arrows represent the rate of mass transfer.

$$k_{org}^0 a V_{mix} LMCD_{Co-current} = Q_{aq} (C_{aq,in} - C_{aq,out})$$

Equation 28

The logarithmic mean concentration difference for a concurrent extractor ($LMCD_{co-current}$) is being defined as:

$$LMCD_{Co-current} = \frac{(C_{aq,in} - C_{org,in}/P) - (C_{aq,out} - C_{org,out}/P)}{\ln \left(\frac{(C_{aq,in} - C_{org,in}/P)}{(C_{aq,out} - C_{org,out}/P)} \right)}$$

Equation 29

and

$$V_{mix} = V * \text{Porosity}$$

Equation 30

where V_{mix} is the volume in which the extraction took place, this being equal to the volume of the monolith multiplied by the porosity calculated using Equation 4. It was assumed the volume of the macroporous polymer taken up by the epoxy resin used to seal the monolith was negligible. The stage efficiency, representing how close the system came to equilibrium within the flow cell, was also calculated.

$$\text{Stage Efficiency (\%)} = \frac{C_{org,out}/C_{aq,out}}{P} * 100$$

Equation 31

3. Results and Discussion

3.1. PolyHIPE Structure and Properties

By changing the internal phase volume ratio and agitation time of the emulsion templates (Table 10, Appendix) it was possible to create a range of polyHIPEs with different porosities, pore and pore throat diameters. The difference in the range of pore throat size produced can be seen in *Figure 37*. It is also apparent that the decrease in porosity caused by a reduction of internal phase template from 80 % to 70 % leads to a decrease in pore throat frequency, i.e. the number of interconnects between adjacent pores.

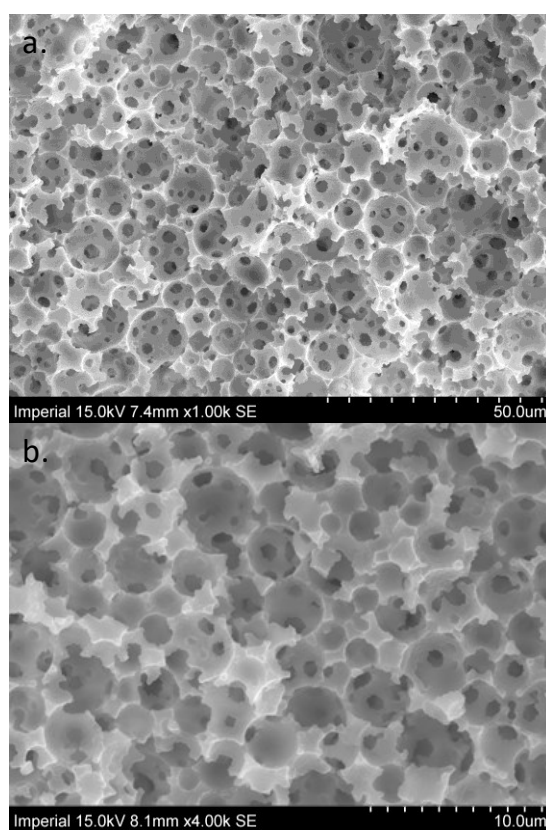


Figure 37. Representative SEM images of polyHIPEs produced by polymerization of different internal phase templates, which were agitated at 2190 rpm for different lengths of time. a. 80% internal phase template agitated for 10 s (LLE-1) average pore size 9.7 μm b. 70% internal phase template agitated for 300 s (LLE-10) average pore size 2.8 μm

The small pore throats in the polyHIPEs mean that there is a substantial pressure drop across the flow cells compared to a blank tube and static mixer. Unsurprisingly, those polyHIPEs with higher porosity were found to have a higher permeability for a similar mean pore throat diameter. Also, the smaller the mean pore throat diameter the lower the permeability. However, the permeability was considerably higher for polyHIPE flow cells than for the HPLC column (*Figure 38*). Samples LLE-3 and

LLE-8 have a similar pore throats size (1.56 μm and 1.53 μm , respectively) compared to the equivalent pore throat size of the HPLC column (1.13 μm), however their permeability is much higher than that of the HPLC column because of their higher porosity (*Table 4*).

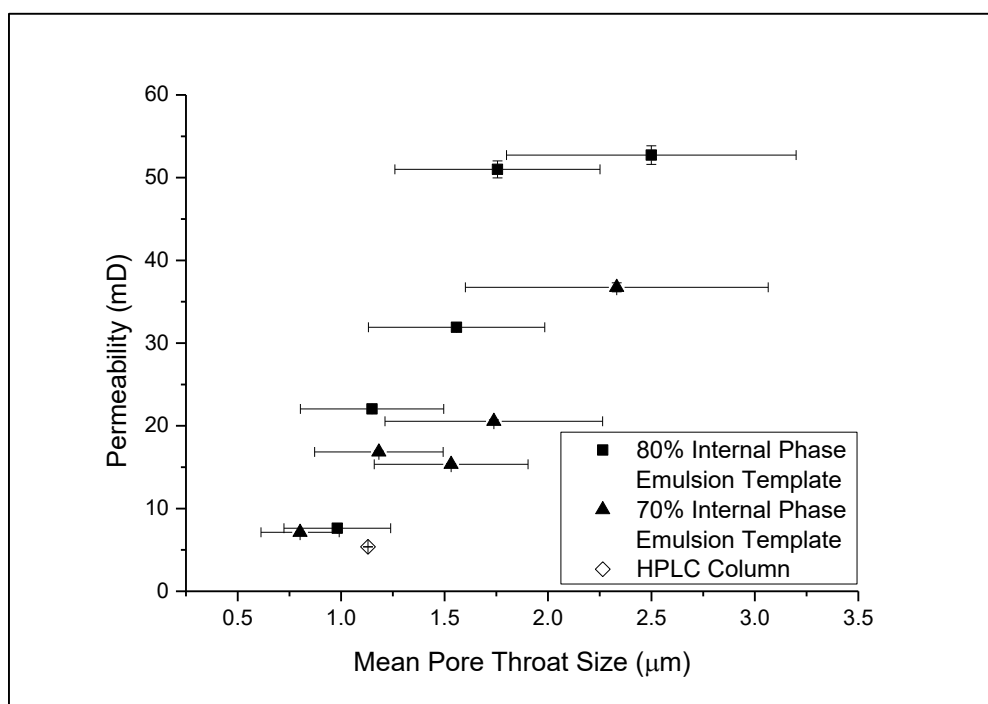


Figure 38. Permeability of the polyHIPE extractor as function of mean pore throat diameter.

Table 4. Effect of emulsion templated macroporous polymers pore structure on the extent of caffeine extracted within it * Porosity given by manufacturer.

Sample	Templating Conditions		Macroporous Polymer Properties			Extraction Results			
	Internal Phase Volume Ratio	Agitation Time (s)	Average pore size (μm)	Average pore throat size (μm)	Porosity (%)	Permeability mD	$k_{\text{org}}^0 \cdot 10^{-3}$ (s-1)	Stage efficiency (%)	$a \cdot 10^4$ (m^2/m^3)
LLE-1	80	10	9.7 $\pm$ 3.1	2.5 $\pm$ 0.7	83	52.7 $\pm$ 1.1	1.18 $\pm$ 0.02	68.0 $\pm$ 0.9	1.09
LLE-2	80	30	6.3 $\pm$ 2.0	1.8 $\pm$ 0.5	84	51.0 $\pm$ 1.0	1.40 $\pm$ 0.19	75.8 $\pm$ 5.8	1.29
LLE-3	80	60	5.0 $\pm$ 1.6	1.6 $\pm$ 0.4	82	31.9 $\pm$ 0.4	1.49 $\pm$ 0.26	77.5 $\pm$ 6.4	1.37
LLE-4	80	120	4.1 $\pm$ 1.2	1.2 $\pm$ 0.4	82	22.0 $\pm$ 0.2	1.53 $\pm$ 0.08	78.3 $\pm$ 2.3	1.40
LLE-5	80	300	3.1 $\pm$ 0.9	1.0 $\pm$ 0.3	82	7.6 $\pm$ 0.0	1.92 $\pm$ 0.02	86.7 $\pm$ 0.4	1.76
LLE-6	70	10	9.9 $\pm$ 3.6	2.3 $\pm$ 0.7	75	36.7 $\pm$ 0.5	1.16 $\pm$ 0.10	62.9 $\pm$ 3.7	1.07
LLE-7	70	30	6.6 $\pm$ 2.3	1.7 $\pm$ 0.5	70	20.6 $\pm$ 0.2	1.44 $\pm$ 0.03	69.0 $\pm$ 0.9	1.33
LLE-8	70	60	5.6 $\pm$ 1.8	1.5 $\pm$ 0.4	74	15.3 $\pm$ 0.1	1.46 $\pm$ 0.27	72.5 $\pm$ 7.1	1.35
LLE-9	70	120	3.8 $\pm$ 1.2	1.2 $\pm$ 0.3	76	16.8 $\pm$ 0.1	1.50 $\pm$ 0.18	74.6 $\pm$ 5.5	1.38
LLE-10	70	300	2.8 $\pm$ 0.9	0.8 $\pm$ 0.2	76	7.1 $\pm$ 0.0	1.64 $\pm$ 0.19	78.2 $\pm$ 4.4	1.51
Blank	N/a	N/a	N/a	N/a	100	> 2000	0.45 $\pm$ 0.05	N/a	0.42
Spiral Static Mixer	N/a	N/a	N/a	N/a	100	> 2000	0.69 $\pm$ 0.08	N/a	0.64
HPLC Column	N/a	N/a	N/a	1.13	39*	5.4 $\pm$ 0.0	1.57 $\pm$ 0.05	N/a	1.45

3.2. Liquid-Liquid Extraction Mass Transfer Characteristics of PolyHIPE flow cells

As the two phases exited the flow cells it was observed that an emulsion had been formed suggesting the two immiscible phases did undergo mixing and reorientation within the polyHIPE structure. However the two phases extremely rapidly phase separated such that only a very small amount of mass transfer could have occurred after exiting the flow cell compared to the mass transfer that occurred within it. Moreover the droplets in the emulsion produced at the exit of the flow cell were rather large. This also suggests no surfactant leached from the surface of the polyHIPE into the extraction mixture as this would have stabilised the emulsion. No evidence of surfactant was observed in the UV/Vis spectra of either phase (see Appendix) and if any surfactant was lost by the polyHIPE was likely removed by the first pass through of fluid through the flow cell.

The stage efficiency was used as a measure of how near the system came to reaching equilibrium within the polyHIPE flow cell that had a length of 70 mm and a diameter of 7 mm ($\approx 2.7 \text{ cm}^3$). Since the dimensions of the HPLC column and spiral static mixer used as controls were different to the polyHIPE flow cells the only fair comparison that could be made between them and the polyHIPE flow cells was by calculating the overall mass transfer coefficient, so the stage efficiency is not reported for the control experiments.

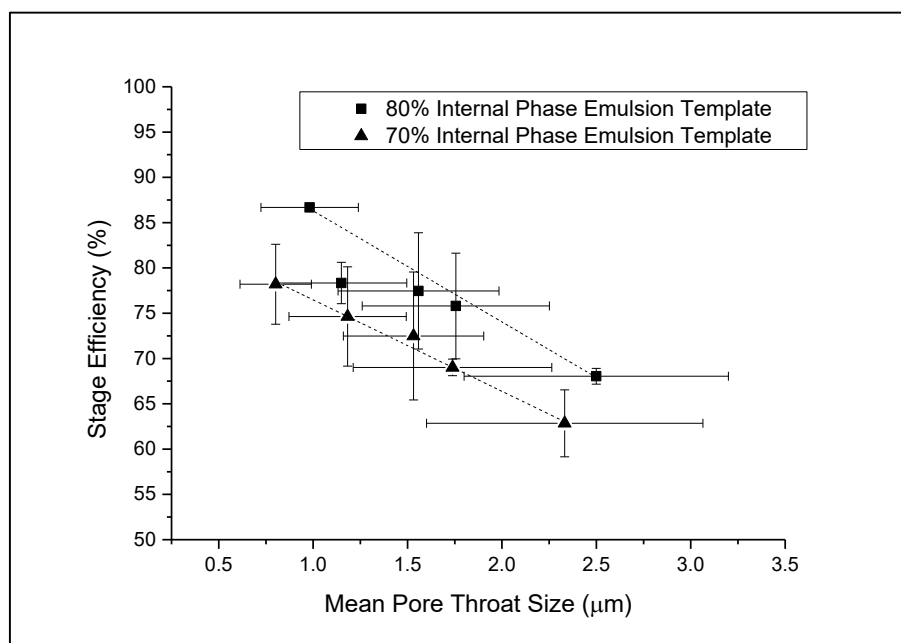


Figure 39. Stage efficiency of the extractor varies with the size of pore throats of emulsion templated macroporous polymers.

It is clear that the smaller the pore throat the closer the system came to reaching equilibrium within the polyHIPE flow cell (Figure 39). This is due to the smaller mean pore throats forcing the fluid to

separate into smaller fluid elements. This increases the interfacial area between the two phases across which extraction takes place. If the system was required to reach equilibrium than the length of the flow cell should be increased. Compared to a blank tube the polyHIPEs all provide an increased overall mass transfer coefficient of at least 100%. For the same flow rate the spiral static mixer gave a slight increase in overall mass transfer coefficient compared to the blank tube but it was still significantly lower than the worst performing polyHIPE flow cells (samples LLE-1 and LLE-6), i.e. the ones with the largest pore throats.

The polyHIPE flow cells produced from an emulsion template with 80 % internal phase volume ratio showed a higher stage efficiency than those produced from templates with 70% internal phase volume ratio as can be seen clearly in *Figure 39*. The difference is explained by the difference in the extractor volume since this is equal to the total volume of the flow cell multiplied by the porosity of the polyHIPE (pore volume). As the flow rate into all the flow cells was constant a greater porosity resulted in an increased residence time within the polyHIPE increasing the stage efficiency of those with greater porosity.

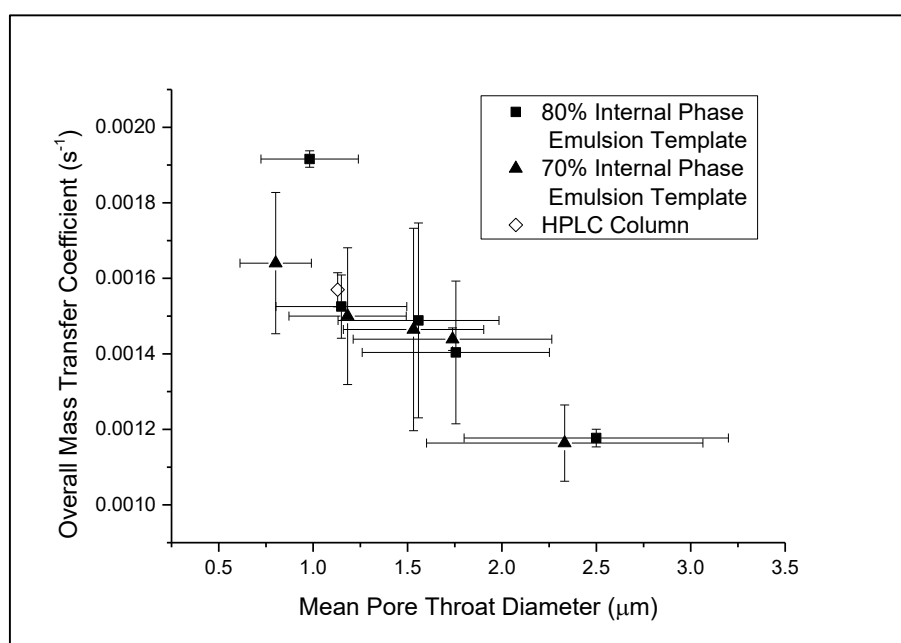


Figure 40. Overall mass transfer coefficient for the extraction of caffeine from aqueous solution by ethyl acetate within a polyHIPE as a function of mean pore throat diameter. polyHIPEs produced from 80% and 70% internal phase templates are compared.

However when the overall mass transfer coefficient (k_{orga}^0) for the extraction was calculated it was found that the results for those polyHIPEs produced with internal phase templates of 70 % and 80 % were remarkably similar (*Figure 40*). This suggests that the porosity of a polyHIPE has a minimal effect on the interfacial area per volume generated within its internal structure. The calculation

(Equation 28 and Equation 30) of the overall mass transfer coefficient takes in to account the porosity of the polyHIPE allowing a fair comparison between polyHIPEs of differing porosities. Figure 40 suggests a strong correlation between the overall mass transfer coefficient and the mean pore throat size for liquid-liquid extraction; polyHIPEs with smaller pore throats resulting in the largest mass transfer coefficients. It was possible to increase the overall mass transfer coefficients by over 50% by changing the agitation time of the emulsion template used to produce the polyHIPEs from 10 s to 300 s (comparing samples LLE-1 and LLE-5 for example). Decreasing porosity has the effect of decreasing residence time and permeability (Figure 38). The overall mass transfer coefficient increased with decreasing pore throat size, which suggest that an effective polyHIPE extractor should have small pore throats but high porosity.

Compared to a blank tube all the macroporous polymers more than doubled the overall mass transfer coefficient (and hence interfacial area generated). Also most polyHIPE flow cells had an overall mass transfer coefficient almost double that of the spiral static mixer. By estimating an equivalent pore throat size for the HPLC column filled with 5 μm diameter particles, it can be observed that a similar mass transfer coefficient compared to the polyHIPEs was achieved but also a much greater pressure drop (Figure 38).

From experiments carried out in a stirred tank (section 2.1) the mass transfer coefficient (k_{org}^0) was determined to be $1.08 \times 10^{-7} \text{ ms}^{-1}$. From this and the calculated overall mass transfer coefficients ($k_{org}^0 a$) it is possible to evaluate the interfacial area per volume (a) produced in each macroporous polymer. For example sample LLE-5 was able to produce an interfacial area per volume of $17,600 \text{ m}^2 \text{ m}^{-3}$. Then by using Equation 27 and assuming the extraction occurring in an emulsion with a dispersed phase volume fraction of 50% an equivalent drop size can be calculated to determine how small the droplets would have been if this extraction were performed in a stirred tank. This gives for sample LLE-5 a Sauter mean droplet diameter (d_{23}) of 170 μm . Clearly from the size of the pores (Table 4) in the polyHIPEs a stirred vessel can achieve droplets much smaller than 170 μm and hence create a much larger interfacial area per volume than a polyHIPE flow cell. However this is within the standard operating droplet size range ($10 \mu\text{m} < d_{23} < 1,000 \mu\text{m}$) [202] in stirred tank operations. Centrifugal contact separators also work within a similar droplet diameter range[203] and static inline mixers are commonly able to produce droplets in the range of $10 \mu\text{m} < d_{23} < 200 \mu\text{m}$ [202], however the spiral static mixer used in this work was unable to match this since the overall flow rate was much lower than it was designed for. However, for smaller scale liquid-liquid dispersion methods such as rotor stator mixing and ultrasonic mixers, Sauter mean droplet diameters of $1 \mu\text{m} < d_{23} < 50 \mu\text{m}$ [204] and $0.1 \mu\text{m} < d_{23} < 10 \mu\text{m}$ [205] are achieved, respectively.

There are several advantages of using polyHIPEs for performing liquid-liquid extractions. They can produce a reasonable surface area per volume compared to existing methods, such as static mixers, however they do this at much lower flow rates. They are also low shear which means they can be used to extract shear sensitive molecules, such as DNA [206] or proteins [207]. Another benefit is that polyHIPEs have a decent surface area, which can be increased by hypercrosslinking [143] or use of porogens [142]. This surface area of polyHIPEs can be modified post-synthesis to suit many potential applications [153, 208, 209]. This could allow the production of tailored reactive-extraction systems [210]. The same could in principle be achieved with packed bed systems, however the polyHIPE flow cells were shown to accomplish this at lower pressure drop due to their higher porosity (*Figure 40*).

Chapter 7: Gas-Liquid Mixing for Heterogeneous Catalysis in Emulsion Templated Polymers

1. Introduction

This chapter presents the ability of palladium coated polyHIPEs to catalyse the three phase nitroreduction of 4-nitroacetophenone and investigates the effect of the structure of the polyHIPE on the conversion of the reaction. The complex internal structure of a polyHIPE is anticipated to create a sufficiently large interfacial area between a liquid and gas which concurrently pass through it while preventing bypassing and reducing the high back pressure associated with packed bed systems [211-213].

Hydrogenations of organic compounds are one of the most common and important industrial chemical reactions, however several challenges need to be overcome to ensure they proceed successfully. Firstly hydrogen does not commonly react with organic compounds at low temperatures ($> 450^{\circ}\text{C}$) without the presence of a catalyst, commonly heterogeneous palladium on carbon (Pd/C) [214], which form metal hydride compounds with hydrogen allowing it to react with the organic compounds. Secondly if the organic compound is present as a solute hydrogen must diffuse through the liquid film to reach the catalyst surface so a high interfacial area between the gas and the liquid phases must be maintained. In hydrogenations commonly the rate at which the hydrogen diffuses through the liquid film is significantly lower than the rate at which it could be consumed at the catalyst surface, as such these reactions are often mass transfer limited [215]. In this work the hydrogenation examined was the nitroreduction of 4-nitroacetophenone to 4-aminoacetophenone catalysed by palladium deposited on internal pores surface within polyHIPE monoliths (Figure 41).

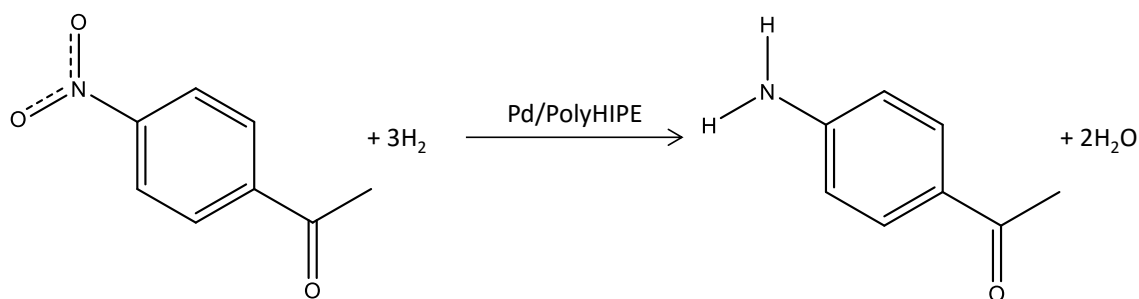


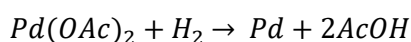
Figure 41. Nitroreduction of 4-nitroacetophenone by hydrogen to 4-aminoacetophenone with a palladium on polyHIPE catalyst.

2. Experimental

2.1. Catalyst Loading

The flow cells (Figure 14) of length 80 mm are then flushed with deionised water to remove calcium chloride left over from synthesis of the polyHIPEs. If this is not done the palladium acetate reacts with the calcium chloride and prevents even distribution of palladium metal within the polyHIPE. The flush water was then removed by passing compressed air through the flow cell followed by drying the polyHIPE monolith in a convection oven at 70 °C until its mass is constant.

Palladium acetate [216] in ethyl acetate, at concentration 11 gL⁻¹ (see Appendix), is then passed through the flow cell using a syringe pump until the void space is totally filled. The flow cell is then placed in a convection oven at 70 °C to remove the ethyl acetate precipitating the palladium acetate within the polyHIPE pore structure. Gaseous hydrogen is then passed through the flow cell at 1 ml min⁻¹ at 80 °C and atmospheric pressure for one hour in order to reduce the palladium acetate to zero-valent palladium (Equation 32) [217]. The theoretical loading of the palladium on the polymer was 2 wt%.



Equation 32

A packed bed control was created using polymethylmethacrylate (PMMA) spheres of 10 µm diameter (SPHEROMERS® CA10) as packing with grit-24 (≈ 700 µm) silicon carbide particles as a diluent [218]. A 1:1 mixture by mass of the PMMA spheres and silicon carbide particles was carefully loaded in to an empty stainless steel tube of the same type as used to produce the flow cells and sealed in place with stainless steel frits. The palladium acetate solution was then loaded, precipitated and reduced using the same method as for the polyHIPE flow cells

2.2. Measurement of Catalyst Loading

The weight percentage of catalyst on the polyHIPEs was measured using an Optima 2000 DV inductively coupled plasma mass spectrometer (ICP). Samples of the palladium impregnated polyHIPE of known mass were digested in aqua regia (3:1 mixture of nitric acid and hydrochloric acid) for 24 h. After digestion any remaining solids were filtered out, the remaining solution diluted with deionised water and the concentration of palladium ions in solution quantified using ICP. Knowing the volume of the solution containing the palladium ions and the original mass of the polyHIPE sample the palladium loading on the polyHIPE was calculated.

The same method was used to assess the reactor effluent to ascertain the extent of palladium being lost from reactor during the operation of the flow cell. A known volume of reactor effluent was allowed to evaporate in a sample tube before the remaining residue, containing any lost palladium, was digested as described above and analysed by ICP. From this the concentration of palladium in the reactor effluent was calculated.

2.3. Nitroreduction Experiment

2.3.1. Experimental Setup

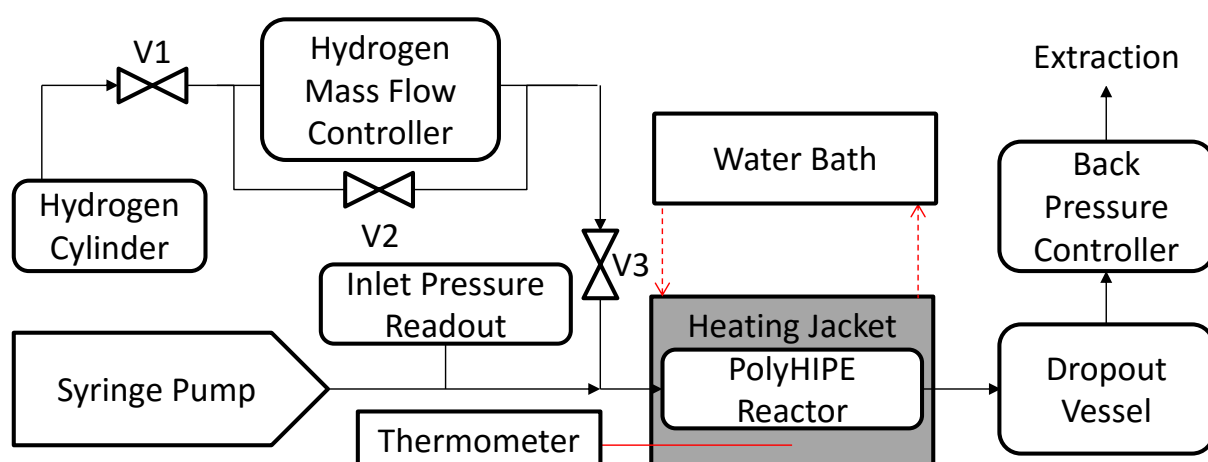


Figure 42. Schematic of the experimental setup for the nitroreduction of 4-nitroacetophenone with hydrogen using palladium catalyst supported on a polyHIPE monolith. Where V1 is the hydrogen control valve, V2 the reactor pressurisation valve and V3 the liquid check valve.

Before the experiment the water bath is turned on to bring the reactor to 60 °C, as determined using a thermometer. Hydrogen (BOC, UK) was supplied to the reaction mixture from a cylinder through valve V1. The entire system was then pressurised by opening and then closing valve V2 to allow hydrogen to flow through the reactor. The backpressure controller then allows the pressure in the system to decrease to 5 bar (at both the reactor inlet and outlet) and maintains that pressure at the exit of the reactor throughout the experiment. The mass flow controller then sets the flow of hydrogen into the reactor to 0.5 ml min⁻¹; the system is allowed to settle allowing both mass flow rate and back pressure to reach their set values. The syringe pump is then used to pump the ethyl acetate containing 0.5 mmol L⁻¹ 4-nitroacetophenone into the reactor at a rate of at 0.5 ml min⁻¹. The 4-nitroacetophenone is reduced by hydrogen in the presence of the palladium catalyst to form 4-aminoacetophenone. The pressure required to force the two fluids through the polyHIPE flow cell

is recorded at the entrance of the reactor allowing the calculation of the pressure drop across the reactor. By assuming a linear pressure drop along the reactor the mean reactor pressure was also calculated. After exiting the reactor the reaction mixture flows into the dropout vessel where the liquid ethyl acetate is collected for sampling. After use each sample had any remaining ethyl acetate removed by passing compressed through the flow cell.

2.3.2. Analysis of Extent of Reaction via High Performance Liquid Chromatography

The samples containing 4-aminoacetophenone in ethyl acetate were analysed by high performance liquid chromatography (HPLC) in order to determine the extent of the reaction via the concentration of product. The column used contained Luna 5 μ m C18(2) particles and had dimensions of 4.6 mm $\varnothing$ x 150 mm. The mobile phase comprised 40% methanol 60% aqueous phosphate buffer solution (pH 3) passed through the column at 1.2 ml min⁻¹. Sample injection volume was 5 μ l and this was analysed at wavelength of 292 nm.

3. Results and Discussion

After precipitation of the palladium acetate and passing hydrogen through the flow cell a colour change from the white of the original polyHIPE to grey/black was observed as the palladium was reduced (Figure 43).



Figure 43. PolyHIPE within a flowcell before (left) and after (right) impregnation with palladium metal. Flow cell internal diameter 7 mm.

It can be seen in Figure 44 that there is a clear difference between the surface of the pores before and after the introduction and reduction of the palladium salt. The surfaces of the pores of the as produced polyHIPEs are smooth (Figure 44a), typical of a S/DVB polyHIPE produced without porogens [219]. However, after the deposition and reduction of the palladium acetate, the pore surfaces were roughened by deposition of palladium metal (Figure 44b).

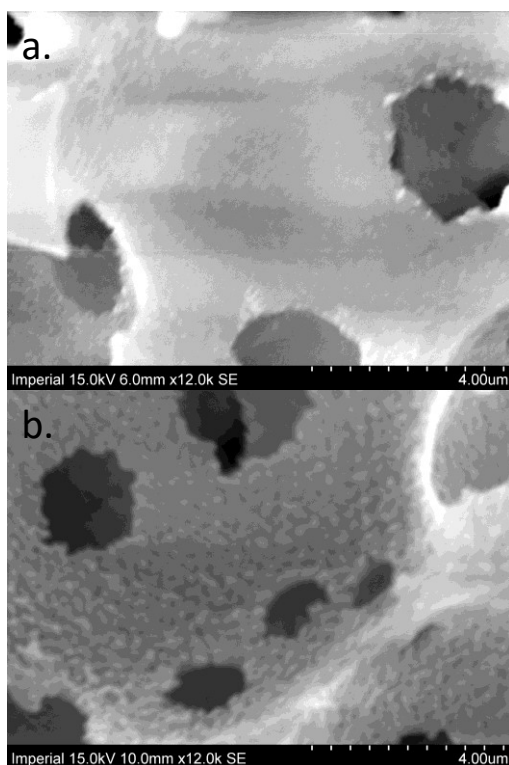


Figure 44. High magnification SEM Image of polyHIPE surface (a.) before and (b.) after impregnation with palladium metal.

Using the incipient wetness method to impregnating the palladium directly into a flow cell provided several advantages over other methods described in the literature [220-222]; It allowed easy filling of the void space with the palladium acetate solution using a simple syringe pump setup as opposed to a vacuum system. Also as the palladium acetate reduction could be carried out with gaseous hydrogen it removed the need for reducing agents, such as sodium borohydride, which are expensive to purchase and to dispose of. At the temperatures and pressures used in this investigation there was no evidence seen in the HPLC analysis for reduction of the carbonyl group present in 4-nitroacetophenone. Only a single product peak relating to 4-aminoacetophenone was observed.

Table 5. How the properties of palladium containing polyHIPEs effect the nitroreduction of 4-nitroacetophenone to 4-aminoacetophenone.

Sample Number	Mean Pore Diameter (μm)	Mean Pore Throat Diameter (μm)	Porosity (%)	Palladium Weight Percentage (%)	Initial Use		Secondary Use	
					Reaction Conversion (%)	Pressure drop (bar)	Reaction Conversion (%)	Pressure drop (bar)
HC-1	8.9 ± 3.0	2.2 ± 0.7	82.2 ± 1.3	2.7 ± 0.3	18.0 ± 0.2	0.9 ± 0.1	24.9 ± 0.1	0.9 ± 0.1
HC-2	5.7 ± 1.9	1.6 ± 0.4	81.4 ± 0.1	2.3 ± 0.3	22.5 ± 0.3	1.6 ± 0.4	23.1 ± 0.1	1.6 ± 0.4
HC-3	4.4 ± 1.5	1.3 ± 0.4	83.2 ± 1.3	3.3 ± 0.2	24.5 ± 0.1	1.9 ± 0.2	29.2 ± 0.6	1.9 ± 0.2
HC-4	3.4 ± 1.2	1.0 ± 0.3	81.7 ± 0.6	3.2 ± 1.9	28.1 ± 0.2	1.8 ± 0.4	27.4 ± 0.0	2.0 ± 0.0
HC-5	2.6 ± 0.9	0.8 ± 0.2	82.6 ± 1.6	3.0 ± 1.3	30.5 ± 2.2	2.8 ± 0.1	31.5 ± 0.0	3.1 ± 0.0
Packed Bed Control	N/a	2.3*	53.0*	0.8 ± 0.0	22.5 ± 0.3	11.7 ± 0.1	11.6 ± 1.3	5.5 ± 0.0

*Equivalent packed bed pore throat diameter calculated from the minimum area between 10 μm spheres, packed bed porosity from the mass and density of the packing material and flow cell volume. PolyHIPE recipes can be seen in Table 11, Appendix.

3.1. Conversion of 4-nitroacetophenone in Pd/PolyHIPE reactors

The reaction conversions reported for each sample in Table 5 are an average of at least two different flow cells containing polyHIPEs produced with the same agitation time (energy input) to prepare each emulsion template. The conversion of 4-nitroacetophenone to 4-aminoacetophenone follows a linear relationship as a function of mean pore throat diameter (Figure 45). With small pore throat diameters resulting in higher conversions. This suggests that the nitroreduction remained mass transfer limited even in polyHIPE reactors with the smallest pore throats. If the increase in interfacial area between the hydrogen and ethyl acetate (containing the 4-nitroacetophenone) was increased to an extent that the reaction became non-mass transfer limited it would be expected that the reaction conversion would cease to increase with decreasing pore throat size, which it does not.

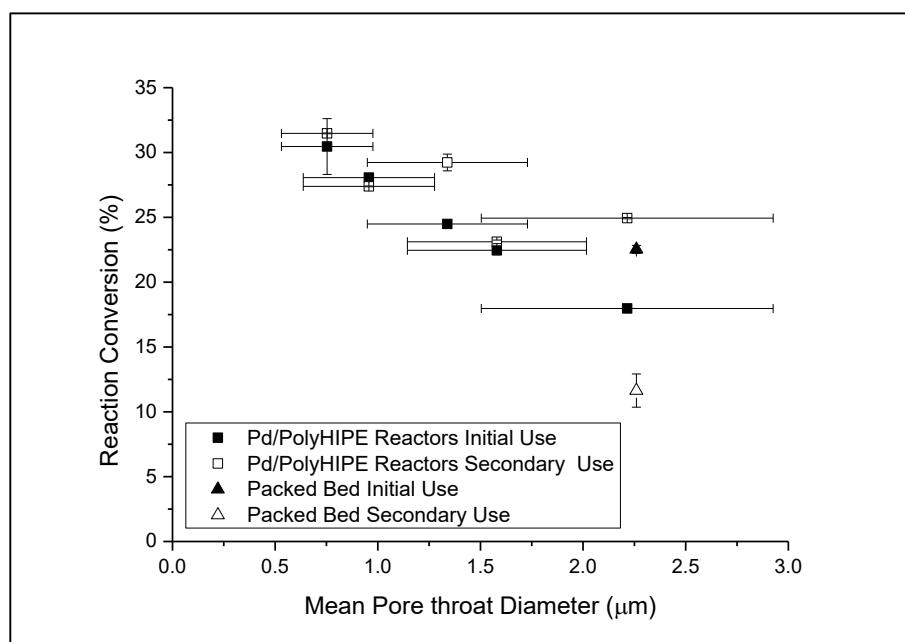


Figure 45. Conversion of 4-nitroacetophenone to 4-aminoacetophenone by hydrogen varied as a function of polyHIPE pore throat size in a Pd/PolyHIPE reactor.

The palladium weight percentage is not constant between flow cells (Table 5), varying between 2.3% and 3.3%. This is further evidence for the reaction remaining mass transfer limited as the reaction conversion does not correlate with the amount of palladium catalyst deposited in to the polyHIPE reactors, suggesting that the mass transfer from the gaseous phase to the liquid phase is still significantly slower than the reaction at the catalyst surface. Therefore, the variation in palladium loading had no effect on the observed conversion. The palladium loading for every sample is higher than the 2% predicted from the concentration of palladium acetate (11 g L^{-1}) in ethyl acetate precipitated within the polyHIPE despite in each case the porosity being slightly higher (81.4%-83.2%) than the 80% used in the calculation (see Appendix). This suggests that in filling polyHIPE

flow cells with the palladium acetate solution some palladium acetate is absorbed on to the surface of the polyHIPE increasing its loading within the flow cell before reduction. The weight percentage of palladium in the packed bed was significantly lower than in the polyHIPE, however due to the greater mass of material contained in the packed bed this equates to an equivalent overall mass of palladium between the reactors.

When repeating the nitroreduction within the flow cells it was seen that, with the exception of sample HC-2, the reaction conversion increased upon repeated use. It was observed that during the first set of reductions carried out in the flow cells generally the reactor effluent was not clear but cloudy. This was caused by impurities formed during the reduction of the palladium acetate, such as acetic acid, that were not removed from the flow cell by the hydrogen stream as well as particles of palladium that detached from the polyHIPE's surface. The removal of these impurities is likely to be behind the increased conversion on reuse.

In comparison the packed bed as support for Pd-catalyst resulted in a slightly higher conversion than the Pd coated polyHIPE flow cell with a similar pore throat diameter on first use. However, on repeated use the conversion dropped significantly, from 22.5% to 11.6%. This was accompanied by a significant reduction in mean reactor pressure, as seen in Figure 46. bed reducing both pressure drop (hence mean reactor pressure) and reactant conversion.

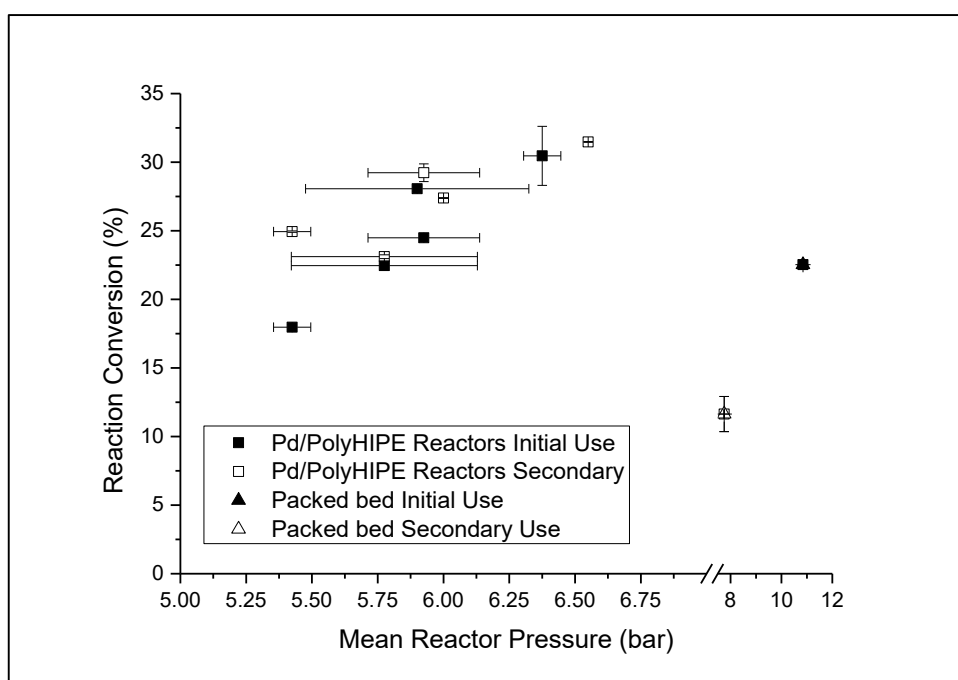


Figure 46. Conversion of 4-nitroacetophenone to 4-aminoacetophenone by hydrogen as a function of mean reactor pressure.

This suggests that channelling occurred within the packed bed upon reuse for a second reduction reaction as the particles within the bed compacted creating wider channels for the reactant to flow through bypassing the catalyst

Since the reaction is mass transfer limited it is unsurprising that there is a first order relationship between the 4-nitroacetophenone conversion and mean reactor pressure. The increase in reaction conversion with decreasing mean pore throat diameter therefore is explained not by the increase in gas-liquid interfacial area but by the increased back pressure caused by the lower permeability of polyHIPEs with smaller average pore throat size (Figure 47). The increased mean reactor pressure increased the rate of the hydrogen mass transfer into the liquid phase increasing the conversion within the reactor. However despite the significantly higher mean reactor pressure the packed bed control did not achieve as high conversions as the polyHIPE flow cells. This is partly explained by a lower residence time within the packed bed, due to its lower porosity, and partly by channelling meaning the fluid leaving the reactor passed through less of the catalyst pack than expected.

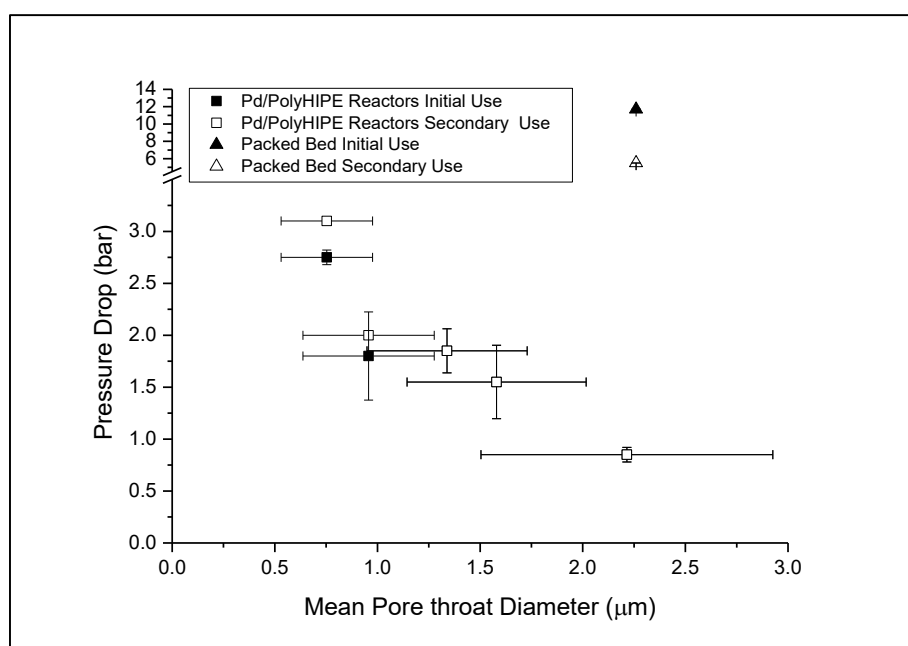


Figure 47. Pressure drop across a Pd/PolyHIPE reactor as a function of polyHIPE average pore throat size when fluid flow was comprised of a two phase mixture of 0.5 ml min^{-1} hydrogen gas and 0.5 ml min^{-1} ethyl acetate.

For the polyHIPE flow cells the pressure drop across the reactor decreased linearly with decreasing average pore throat diameter. It can also be observed that the pressure drop of the Pd/polyHIPE flow cells is significantly lower than that of the packed bed. Comparing the Pd/polyHIPE with the smallest mean pore throat diameter (greatest pressure drop) to the packed bed, it can be noted that

the pressure drop across the polyHIPE is still twice as low. The lower pressure drop of the Pd/polyHIPE flow cell is due to their greater porosity (Table 5). Comparing initial and secondary use there is minimal change in pressure drop between the experiments, the majority showing no measurable change at this level of accuracy (0.1 bar). The pressure drop across the polyHIPE reactor also confirms that gas liquid mixing within the polyHIPE structure, as if the two phase were segregated the gas would rapidly bypass the liquid within the reactor and no measurable difference in pressure between the two ends of the reactor would have been observed .

3.2. Palladium Catalyst Loss

Since palladium was reduced directly on to the surface of the polyHIPE the reactor effluent was analysed to determine if catalyst was lost during the nitroreduction. Each use saw 16ml of ethyl acetate passed through the reactor.

Table 6. Palladium catalyst lost from the reactors during the nitroreduction

Sample Number	Percentage Catalyst Lost (%)	
	Initial Use	Secondary Use
HC-1	0.15	0.04
HC-2	0.16	0.01
HC-3	0.11	0.04
HC-4	0.14	0.02
HC-5	0.01	0.01

Less than 0.2% of catalyst was lost for all samples during both combined uses (Table 6). Also for all samples, with the exception of HC-5, the amount of palladium present in the effluent was significantly lower after for the second nitroreduction. This is most likely due to the palladium most poorly bonded to the polyHIPE pore walls being removed primarily during the first use. The percentage of catalyst lost showed no trend when compared to pore or pore throat size and is likely to be solely a function of the reduction conditions of the palladium acetate and the flow rate though the flow cell. Since the palladium loss is minimal it is suggested that the incipient wetness method is an effective way to impregnate polyHIPEs with catalytic metals.

Chapter 8: Conclusions and Future Work

1. Conclusions

The following chapter summarises the results of the experimental work on polyHIPE mixers as presented in Chapters 3, 4, 5, 6 and 7

1.1. Chapter 3: Very Permeable Emulsion Templated Macroporous Polymers via Controlled Agitation

The effect of energy input in to the emulsion templates, used to synthesise macroporous polymers, on average pore diameter, pore throat diameter and permeability of these emulsion templated macroporous polymers was assessed. Macroporous polymers were produced from emulsion templates with internal phase volume ratios of 80, 70 and 60% produced at agitation rates of 1,000 and 2,190 rpm and for agitation times of from 10 s to 300 s. It was seen that the average pore size decreased with increasing energy input into the emulsion template in line with what would be expected from an emulsion especially at higher rates of agitation. This suggests that controlling the energy input is an effective means of tailoring properties, such as permeability, of emulsion templated macroporous polymers. However at the lower end of the range of energy input (emulsion templates agitated at 1,000 rpm for 10 or 30 s) an increase in the amount of droplet coalescence, which occurred in the emulsion template was observed, resulting in porous polymers with distinct large pores. It was found that for similar energy inputs during the emulsification process the average pore size was smaller in the macroporous polymers produced from more concentrated emulsions. This was due to the increased density and viscosity of the emulsion templates with higher internal phase volume ratios requiring increased energy input to agitate them for a set impeller speed. The size of pore throats was dependent mainly on the size of the pores; however the average pore throat size relative to the pore size increased with decreasing pore size. Relative pore throat size was also larger for macroporous polymers obtained by polymerisation of emulsion templates with higher internal phase volume ratios. This was most noticeable for macroporous polymers produced from emulsion with 80% internal phase volume ratio at higher rate of agitation, due to increased droplet deformation. Porosity and pore throat size both significantly affect the permeability of emulsion templated macroporous polymers. It was possible produce very permeable polyMIPes, even with an internal phase template volume ratio of 60% due to the larger droplet sizes producing larger pore throats in the resulting porous polymers. For macroporous polymers produced with low energy input (10 s agitation at 1,000 rpm) and high internal phase volume ratio we observed pore hierarchy,

which was caused by significant droplet coalescence in the template emulsion before polymerization, in the most extreme cases this caused a significant reduction in permeability.

1.2. Chapter 4: Residence Time Distribution in PolyHIPEs Monoliths

The effect of polyHIPE pore throat size on the residence time and variance of a caffeine pulse passing through a monolith was examined in order to assess their potential as static mixers. From the residence time of the caffeine it was seen that the polyHIPEs exhibited a very limited chromatographic effect, this is due to their low surface areas ($2\text{-}6\text{ m}^2\text{g}^{-1}$). The smaller the average pore throat size in the polyHIPE, the greater the variance of the caffeine pulse detected at the outlet. A single caffeine peak was observed for every polyHIPE. The variance of the pulse was found to be comparable to that of a chromatographic column and spiral static mixer. However, the number of ideal stirred tanks represented by the polyHIPE monoliths was significantly higher than the packed bed chromatography column due to their higher porosity. However this did mean the polyHIPE monoliths had a significantly higher permeability than the chromatography column

1.3. Chapter 5: Micromixing in Emulsion Templated Macroporous Polymers characterised by the Bourne reaction

Macroporous polymers produced from particle stabilised and surfactant stabilised emulsions were produced with a range of porosities and pore sizes. It was found that, compared to an empty tube and helical static mixer, all macroporous polymer flow cells resulted in a lower hydrolysis yield for the 4th Bourne reaction indicating better micromixing. With the most effective sample (P/S-1) reducing the yield by 50%, although a 13% reduction in yield was more common. It was found that the characteristic that most influenced the yield of hydrolysis was the size of the interconnecting pore throats; with smaller pore throats producing lower hydrolysis yields. Smaller pore throats decrease the permeability of the polymer monoliths, with the polyHIPEs with the smallest pore throats being over an order of magnitude less permeable than those with the largest pore throats. It is suggested that these factors decrease the yield of the hydrolysis reaction by causing significant flow division and reorientation so that the neutralisation can proceed rapidly to completion, reducing the opportunity for acid catalysed hydrolysis.

It was possible to achieve greater reduction of the hydrolysis yield with an emulsion templated macroporous polymer than with a HPLC column, acting as a packed bed, while still maintaining a higher permeability. It was found that altering the flowrates did not affect the hydrolysis yields, suggesting that the internal polyHIPE structure determines the intensity of micromixing. It was also determined that the acid base neutralisation is complete after a short length of monolith, in the

order of 30 mm. Monoliths shorter than this resulted in an increase in the hydrolysis yield due to incomplete neutralisation within the macroporous polymer monolith.

1.4. Chapter 6: Immiscible liquid-liquid mixing in Emulsion Templated Polymers

The ability of emulsion templated macroporous polymers to create interfacial area within an immiscible liquid system has been assessed by using polyHIPE flow cells to perform the extraction of caffeine from an aqueous solution with ethyl acetate. It was found that the overall mass transfer coefficient (k_{orga}^0) of the extraction within the polyHIPEs increased with decreasing the pore throat size. This is because as the two phases pass through the complex interconnected pore structure of polyHIPEs, they are broken up into fluid elements creating more interfacial area between the two phases. The size of these elements is likely to be a function of the pore throat size, with polyHIPEs with smaller pore throats creating higher interfacial area. The pore throat size could be decreased by increasing the length of time for which the emulsion template was agitated as this decreased the size of the droplets in the emulsion template. The overall mass transfer coefficient of the extraction was found not to be dependent on the porosity of the polyHIPE. However an increased porosity does increase the stage efficiency due to the increased residence time within the flow cell. Compared to both an empty tube and a spiral static mixer the polyHIPE flow cells resulted in significantly higher overall mass transfer coefficients. A HPLC column was able to provide a similar value for the overall mass transfer coefficient as the polyHIPE flow cells. However the pressure drop across the polyHIPE flow cells was found to be significantly lower than for a conventional packed bed HPLC column.

By calculating the interfacial area per volume generated within the polyHIPE flow cell it was shown that many conventional methods of generating interfacial area, such as stirred tanks, are able to produce a higher interfacial areas per volume. However there are several advantages to using polyHIPE flow cells as extractors such as their ability to operate at very low flow rates and their potential for use in reactive-extraction systems due to their high surface area.

1.5. Chapter 7: Heterogeneous Catalysis in Emulsion Templated Polymers

Catalyst containing polyHIPEs were assessed for use as three phase reactors to carry out a heterogeneously catalysed nitroreduction of 4-nitroacetophenone to 4-aminoacetophenone, thus showing their potential as monolithic reactors. By changing the agitation time of an 80% internal phase template emulsion a range of poly(S/DVB)HIPEs were produced with varying average pore throat diameters, these were used to create flow cells. Palladium was then inserted into the pore structure of the polyHIPEs using the incipient wetness method by precipitating palladium acetate from solution and then reducing it to the native palladium in gaseous hydrogen. As a comparison a

palladium containing packed bed of spherical particles of similar dimensions to the polyHIPE pores was also examined. It was discovered that the mixing of the gas and liquid phases of the within the polyHIPE pore structure was not efficient enough to prevent the nitroreduction of 4-nitroacetophenone to 4-aminoacetophenone from being mass transfer limited. However the reduction did proceed within the polyHIPEs suggesting gas-liquid contact did occur within the polyHIPE pore structure and that the two phases are not segregated. The conversion of 4-nitroacetophenone increased linearly with decreasing mean pore throat diameter of the polyHIPE, this was due to the lower permeabilities of these reactors increasing the mean reactor pressure and thus the amount of hydrogen in the ethyl acetate. The reactors maintained the same or higher levels on conversion upon reuse. In comparison the packed bed reactor produced a similar conversion of 4-nitroacetophenone to the polyHIPE reactors but suffered from channelling such that conversion significantly reduced upon reuse. It also had a significantly higher pressure drop than any of the polyHIPE reactors.

Small amounts of palladium were found to be lost from the polyHIPE reactors during the nitroreduction reactions. However the amount lost was found to reduce upon repeated use suggesting the remaining catalyst was securely attached showing effective palladium deposition.

1.6. Overall Conclusion

As stated at the beginning of this work the aims of this work were to understand if macroporous polymers are capable of mixing fluids being passed through them and to investigate the effect of variations in their pore structure have on the mixing behaviour. This aim has been met with insight gained into miscible liquid, immiscible liquid-liquid and gas-liquid mixing within the polyHIPE structure. It has been shown that there is significant mixing caused by passing fluids through a polyHIPE's intricate internal structure caused by division and reorientation of fluid elements for all three systems. However the extent of mixing in the examined gas-liquid system was not significant enough to overcome the mass transfer limitation of a three-phase reaction. The mean pore throat diameter seems to determine the intrinsic mixing ability of the polyHIPE flow cells at low flow rates examined. For miscible liquid and immiscible liquid-liquid mixing reducing the mean pore throat diameter, in all cases studied here this was achieved by increasing the energy input during the production of the emulsion template, intensified the mixing characteristics. However at the same time decreasing the mean pore throat diameter results in a decrease of the permeability of the polyHIPE flow cell.

2. Future Work

The applications described in this thesis lay the groundwork for other potential research that could be performed with polymerised high and medium internal phase (ratio) emulsions.

The polyHIPE flow cells were produced during the course of my PhD and explored for various fluid mixing applications. The polyHIPE monoliths produced had all mean pore diameters, which did not vary along its length. However, gradient polyHIPEs could be produced [223]. For example a flow cell could be produced by filling a tube with certain amounts of HIPE that were agitated for slightly longer times. Such a flow cell would contain a polyHIPE whose pore size steadily decreases along its length. Such flow cells with a pore size gradient could find applications as reactive filters [224, 225]. They could also, for example, be impregnated with colloidal silver particles [226] to impart antibacterial properties while having higher permeability than traditional filters.

The possibility of creating interfacial area between immiscible liquids, comparable to that found in conventional mixer settlers [202], was demonstrated and so it would be desirable to study if liquid-liquid reaction could be performed within a polyHIPE flow cell. A suitable reaction could be the nitration of an aromatic compound such as benzene [227] with an aqueous solution containing nitric and sulphuric acids. The harsh reaction conditions would test the robustness of polyHIPE flow cells. These reactions are often mass transfer limited and also can produce significant heat. Recent research into these types of reactions focused on capillary microreactors [227, 228]. It was reported that the narrower the channel size the higher the conversion of the reaction [229] due to the decrease in diffusion distance. However the capillary diameters were of the order several hundred micrometres and so much larger than the pores and pore throats of polyHIPEs. It can be expected that a greater flow division and fluid element reorientation occurs within polyHIPEs as compared to capillaries due to the interconnecting pore structure of polyHIPEs. Therefore carrying out these nitration reactions, or other two-phase reactions, within a polyHIPE flow cell could reduce diffusion distances further increasing conversion while allowing simple temperature control of the reaction using a heating/cooling jacket.

It was possible to perform both liquid-liquid extraction and chemical reactions within a polyHIPE flow cell and, therefore, it is very reasonable to assume that a reaction coupled with extraction could be performed. Reactive extractive processes have been less investigated than reactive distillation however they are important in biotechnology [210, 230, 231], for example for the extraction of antibiotics, such as penicillin.

It was observed (Chapter 6) that by passing two immiscible phases through a polyHIPE flow cell they be dispersed in each other, however these ‘emulsions’ were not stabilised by an emulsifier and so rapidly phase separated. However if suitable emulsifiers were present in the system it would be possible to produce emulsions using this method. Emulsions produced this way could even then be polymerised to produce polymer particles or polyHIPE beads, similar to those produced using microfluidic techniques [232-234]. It would be interesting to determine the relationship between the droplet diameter of the produced emulsion and the pore and pore throat diameters of the polyHIPE used to prepare any emulsion.

PolyHIPEs have great scope for the creation of multifunctional reactors [235, 236] allowing the intensification of chemical processes. By creating polyHIPE monoliths containing two or more functional groups, for example a metal catalyst and an acidic functional group [237], multiple series reactions could be carried out within the same flow cell. Monoliths tailored to a specific chemical process could be created with each section of polyHIPE performing a specific purpose. A flow cell could possess a catalytic section followed by a sorption section to remove by-products before another catalytic section. In this way a multifunctional reactor could be produced into which the reactants are introduced, several chemical processes could take place and the product is formed. This could also be performed at a much smaller scale allowing the production of specialty chemicals such as tailored medicines [238].

In creating catalytic polyHIPE reactors, described in Chapter 7, the catalyst produced in situ after depositing the catalyst precursor using the incipient wetness method. It would require fewer steps to produce the catalytic reactor if the palladium could be incorporated during the emulsification step. One way of doing this would be to replace the salt in the dispersed phase (here calcium carbonate used to inhibit coarsening) with the palladium salt, which after the monolith is dried could be directly reduced on to the polyHIPE surface. This method would have the advantage of allowing facile control of the weight percentage of catalyst within the system and requires only one simple post synthesis step. The reason this method was not used in Chapter 7 is due to the inherently wasteful method of polyHIPE production meaning that the majority of produced HIPE was not used to produce polyHIPE flow cells. An alternative method for the production of catalytically active polyHIPEs would be to create poly-Pickering-HIPEs using the catalyst particle itself as the emulsifier so it is present in the pore wall after polymerisation. However the particle would need to have the correct wetting behaviour in order to create stable HIPE templates meaning that the catalyst particles would most likely need to be surface modified before it could be used as an emulsifier [239]. Unfortunately, this would most likely inhibit the particles final catalytic properties.

The process of producing polyHIPE flow cells needs to be improved if the technology is to be commercialised, as the methods used in this thesis would be unsuitable. It would be ideal to polymerise the template HIPE directly in a stainless steel tube or another container as opposed to creating the monolith separately and fixing it into a container. This could be achieved by pre-treating the container surface so that the polyHIPE adheres to the surface after polymerisation, unlike poly(S/DVB)HIPEs, which do not adhere to steel. If more commercial niches are to be found it is important that they are researched as part of a larger system containing other unit processes. They also need to be run continuously for extended periods of time to further analyse how they degrade under real conditions.

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Appendix

Chapter 3: HIPE Template Composition

Table 7. Composition of template HIPEs used in Chapter 3.

Sample	Continuous Phase Composition				Internal Phase Composition		Agitation Speed rpm (±10)	Agitation Time (s)
	Styrene (ml)	Divinyl-Benzene (ml)	Hypermer 2296 (ml)	AIBN (g)	40 g/L Calcium Chloride Solution aq (ml)	Internal Phase Volume (%)		
PH-1	4	4	2	0.13	40	80	2190	10
PH-2								30
PH-3								60
PH-4								120
PH-5								300
PH-6	6	6	3	0.195	35	70		10
PH-7								30
PH-8								60
PH-9								120
PH-10								300
PM-11	8	8	4	0.26	30	60		10
PM-12								30
PM-13								60
PM-14								120
PM-15								300
PH-16	4	4	2	0.13	40	80	1000	10
PH-17								30
PH-18								60
PH-19								120
PH-20								300
PH-21	6	6	3	0.195	35	70		10
PH-22								30
PH-23								60
PH-24								120
PH-25								300
PM-26	8	8	4	0.26	30	60		10
PM-27								30
PM-28								60
PM-29								120
PM-30								300

Chapter 3: Pore Size Distributions of PolyH/MIPes

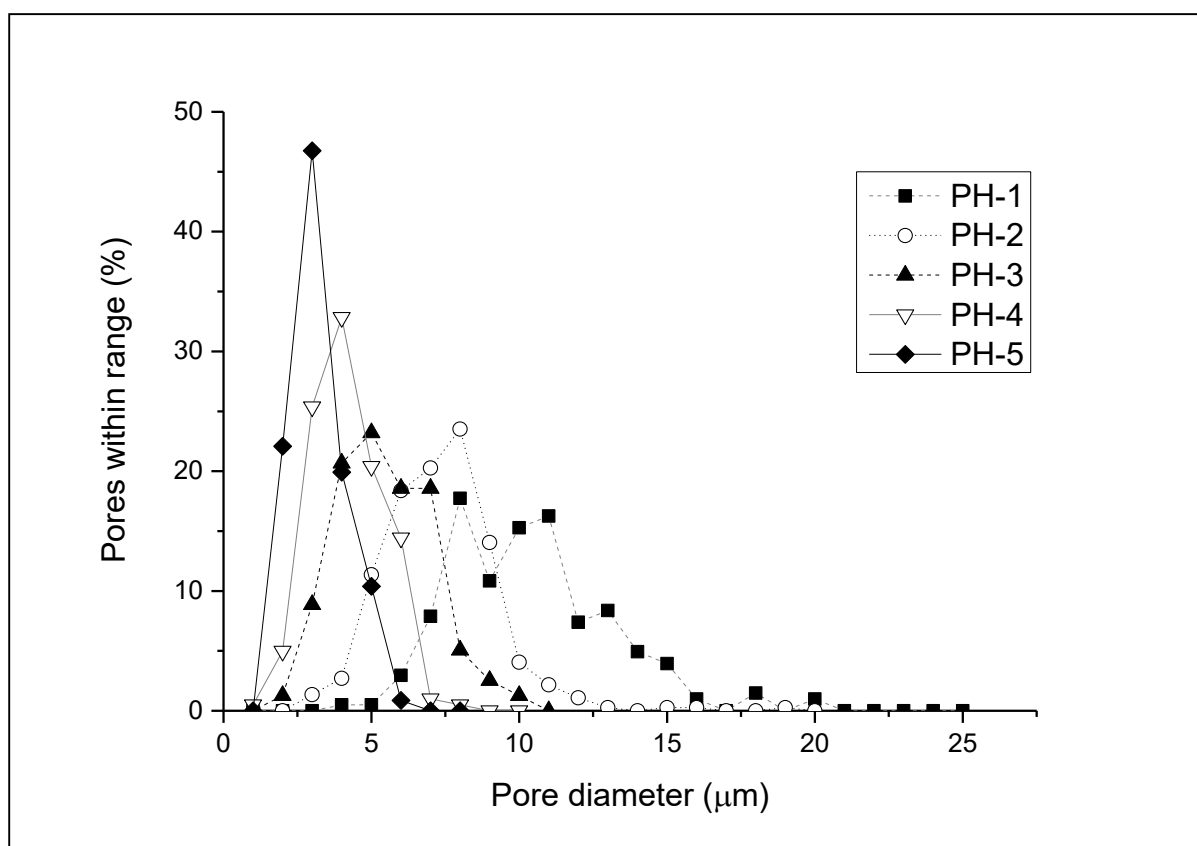


Figure 48. Pore size distributions for PH-1, 2, 3, 4 and 5, histogram bin range 1μm

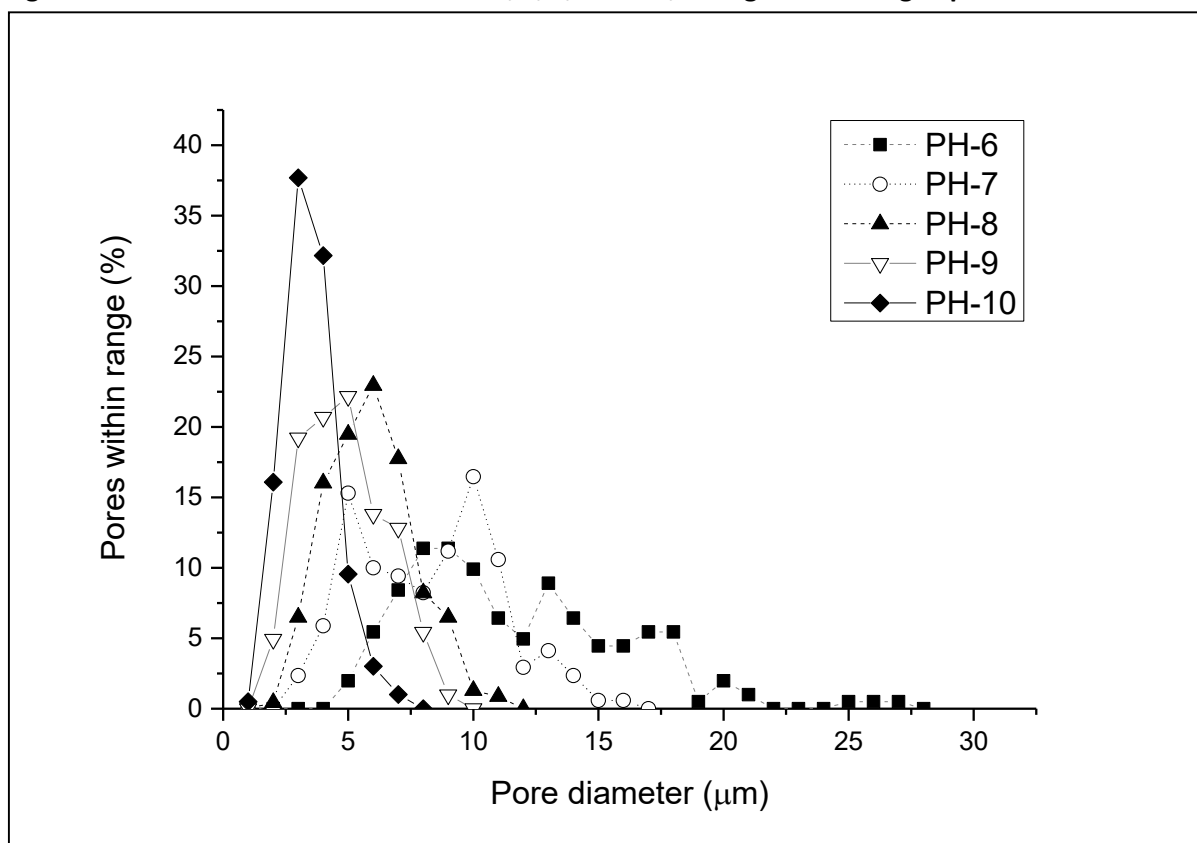


Figure 49. Pore size distributions for PH-6, 7, 8, 9 and 10, histogram bin range 1μm

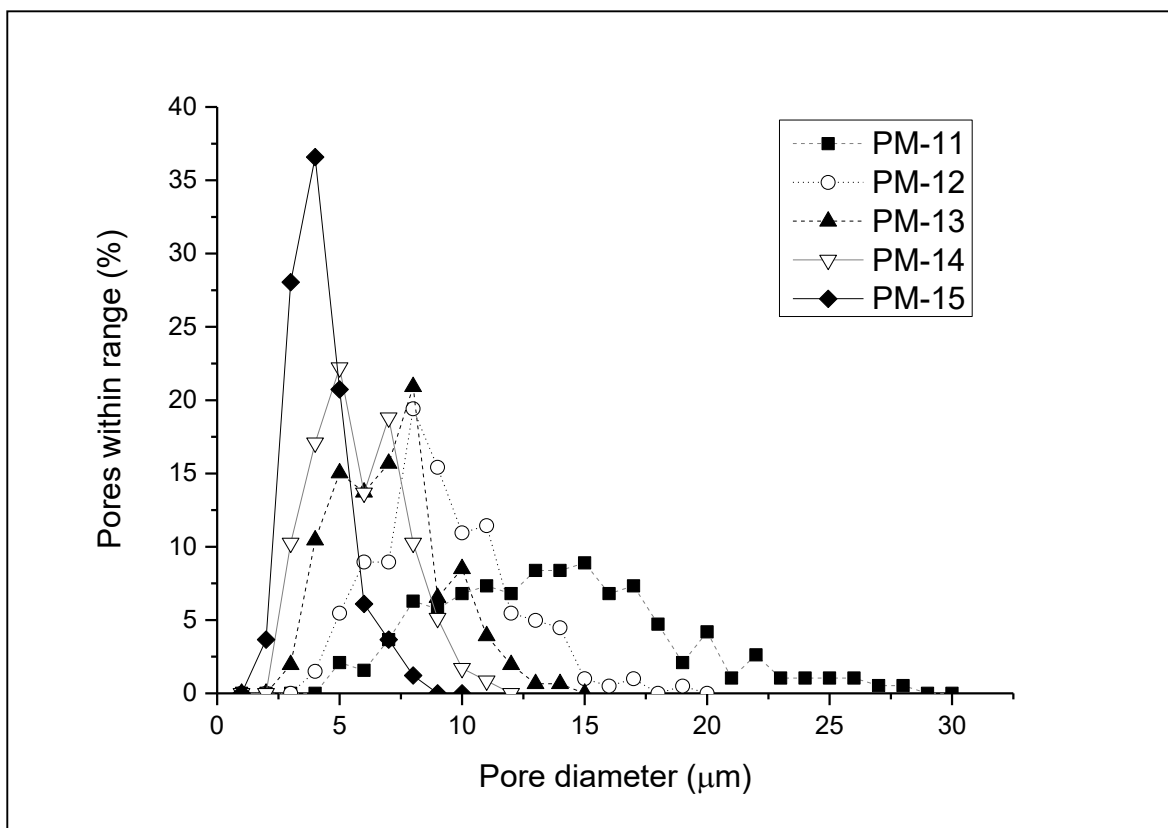


Figure 50. Pore size distributions for PM-11, 12, 13, 14 and 15, histogram bin range 1μm

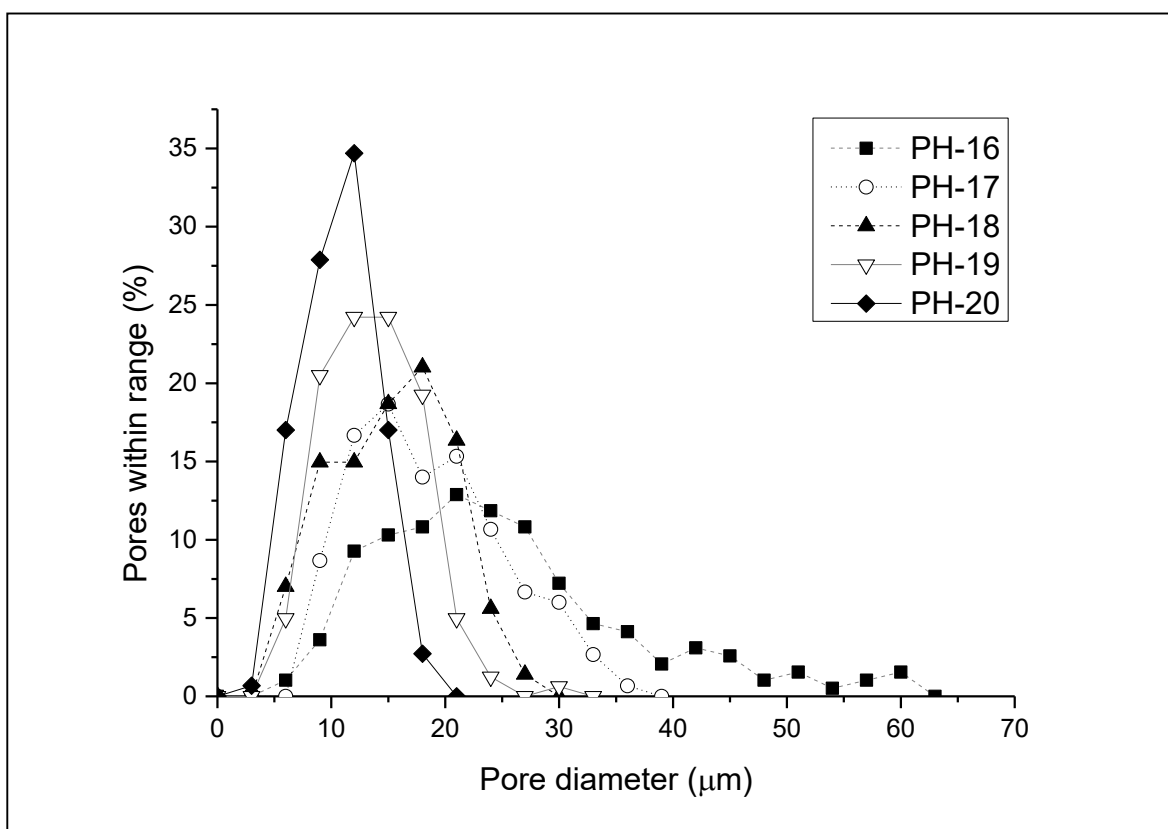


Figure 51. Pore size distributions for PH-16, 17, 18, 19 and 20, histogram bin range 3μm

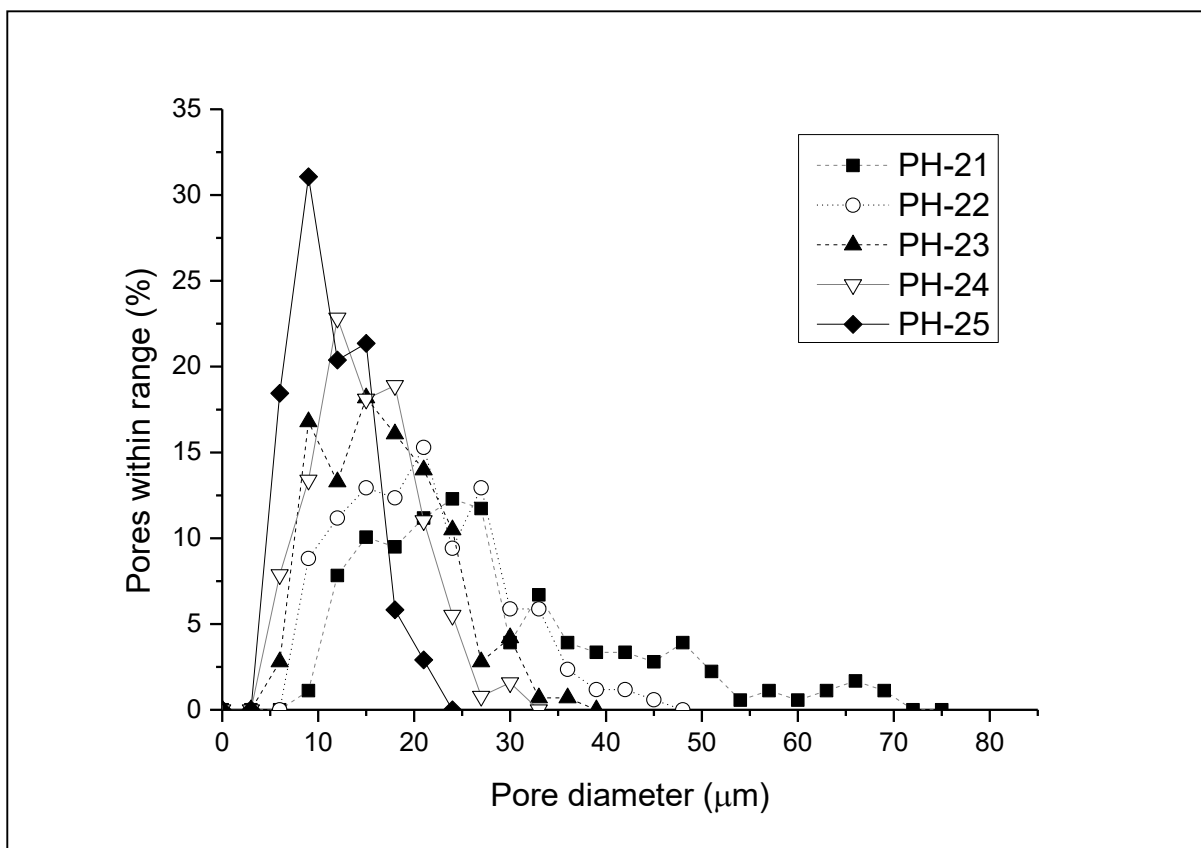


Figure 52. Pore size distributions for PH-21, 22, 23, 24 and 25, histogram bin range 3μm

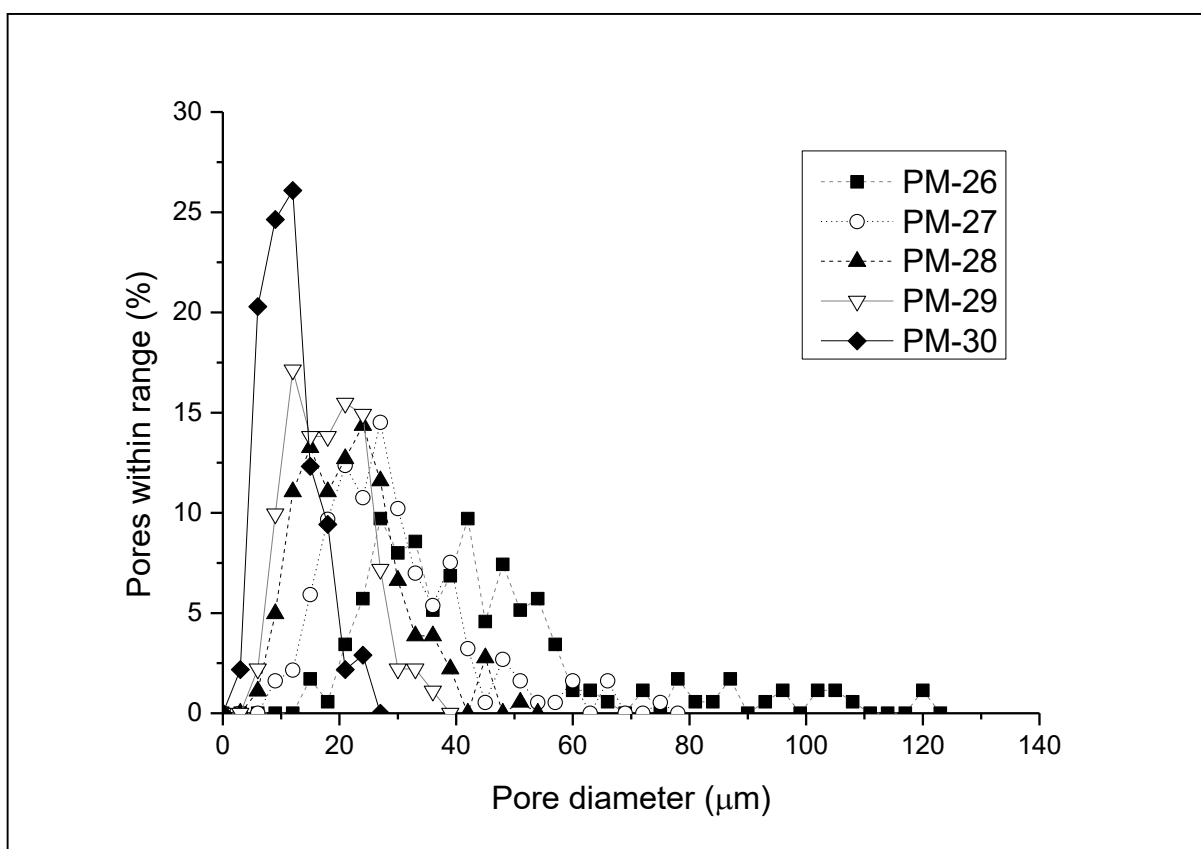


Figure 53. Pore size distributions for PM-26, 27, 28, 29 and 30, histogram bin range 3μm

Chapter 4: HIPE Template Composition

Table 8. Composition of template HIPEs used in Chapter 4.

Sample Number	Continuous Phase Composition				Internal Phase Composition		Agitation Speed rpm (± 10)	Agitation Time (s)
	Styrene (ml)	Divinyl Benzene (ml)	Hypermer 2296 (ml)	AIBN (g)	40 g/L Calcium Chloride Solution aq (ml)	Internal Phase Volume (%)		
RTD-1	4	4	2	0.13	40	80	2190	10
RTD-2								30
RTD-3								60
RTD-4								120
RTD-5								300

Chapter 4: PolyHIPE Surface Area

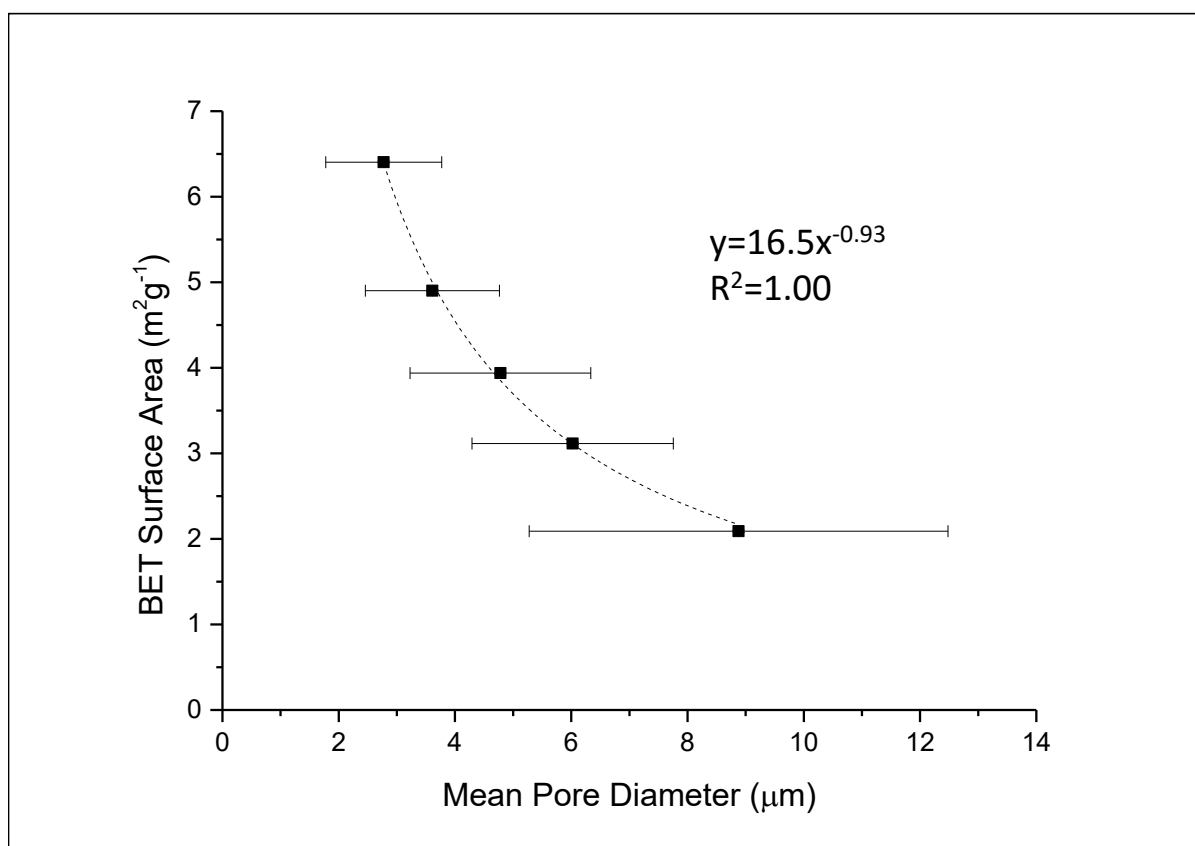


Figure 54. How the BET surface area of S/DVB polyHIPE varied as a function of pore diameter

Chapter 5: HIPE Template Composition

Table 9. Composition of template HIPEs used in Chapter 5.*Added after initial agitation

Sample	Continuous Phase Composition					Internal Phase Composition	Agitation Speed rpm (± 10)
	Styrene (ml)	Divinyl Benzene (ml)	Hypermer 2296 (ml)	Hydrophobized silica particles (g)	AIBN (g)	40 g/L Calcium Chloride Solution aq (ml)	
S-1	5	5	2.5	0	0.16	37.5	2190
S-2	4	4	2	0	0.13	40	
S-3	4	4	2	0	0.13	40	
S-4	4	4	2	0	0.13	40	
S-5	4	4	2	0	0.13	40	
S-6	4	4	2	0	0.13	40	
S-7	4	4	2	0	0.13	40	
P/S-1	6.25	6.25	0.625*	0.375	0.2	37.5	
P/S-2	5	5	0.5*	0.3	0.16	40	
P/S-3	5	5	0.5*	0.3	0.16	40	
P/S-4	5	5	0.5*	0.3	0.16	40	
P/S-5	2.5	2.5	0.25*	0.15	0.08	45	
P/S-6	5	5	0.5*	0.3	0.16	40	
P/S-7	5	5	0.5*	0.3	0.16	40	

Chapter 6: HIPE Template Composition

Table 10. Composition of template HIPEs used in Chapter 6.

Sample	Continuous Phase Composition				Internal Phase Composition		Agitation Speed rpm (±10)	Agitation Time (s)
	Styrene (ml)	Divinyl Benzene (ml)	Hypermer 2296 (ml)	AIBN (g)	40 g/L Aqueous Calcium Chloride Solution (ml)	Internal Phase Volume (%)		
LLE-1	4	4	2	0.13	40	80	2190	10
LLE-2								30
LLE-3								60
LLE-4								120
LLE-5								300
LLE-6	6	6	3	0.195	35	70		10
LLE-7								30
LLE-8								60
LLE-9								120
LLE-10								300

Chapter 6: Derivation of Equation 24

$$\begin{aligned} N_{Caffeine} &= k_{aq}(C_{aq,b} - C_{aq,i}) \\ N_{Caffeine} &= k_{org}(C_{org,i} - C_{org,b}) \end{aligned}$$

Assuming equilibrium at interface

$$P = \frac{C_{org,i}}{C_{aq,i}}$$

Substituting and rearranging

$$N_{Caffeine} = k_{org}^0(C_{aq,b}P - C_{org,b})$$

Where

$$\frac{1}{k_{org}^0} = \frac{P}{k_{aq}} + \frac{1}{k_{org}}$$

It follows that

$$\frac{dC_{org}}{dt} = k_{org}^0 a(C_{aq}P - C_{org})$$

Knowing that no caffeine is destroyed and that there is no caffeine originally in the organic phase and assuming the surface of the polyHIPE is saturated with caffeine, the following mass balance can be written

$$V_{aq}C_{aq}^{init} = V_{aq}C_{aq} + V_{org}C_{org}$$

Rearranging and substituting for the concentration in the aqueous phase

$$\frac{dC_{org}}{dt} = k_{org}^0 a(PC_{aq}^{init} - \left(1 + \frac{V_{org}P}{V_{aq}}\right)C_{org})$$

This is then integrated to give Equation 24

Chapter 6: Determination of k_{org}

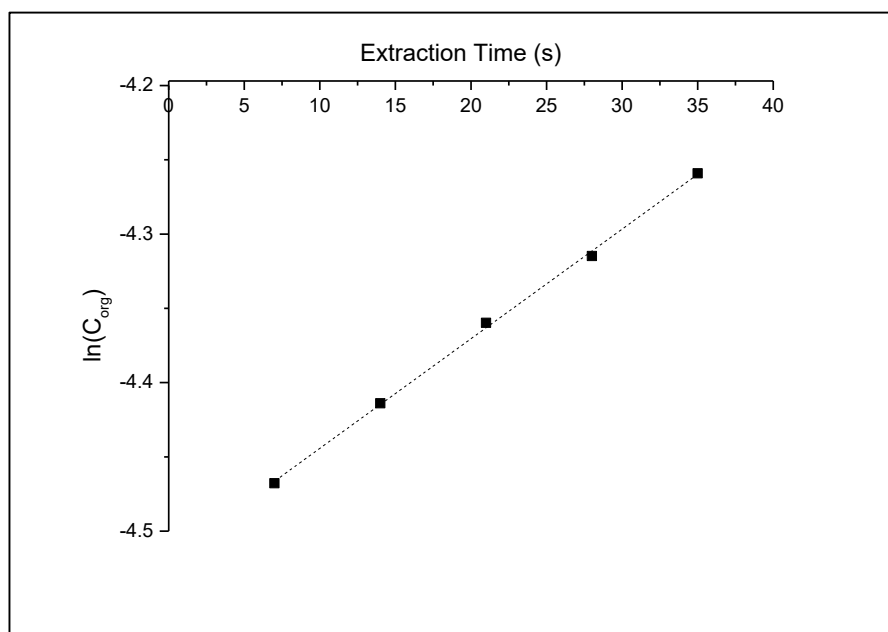


Figure 55. *Determination of k_{org} in a stirred tank, showing how the concentration of caffeine in the organic phase varied with extraction time.*

Chapter 6: Relative UV/Vis Spectra of Hypermer 2296 and Caffeine in Ethyl Acetate

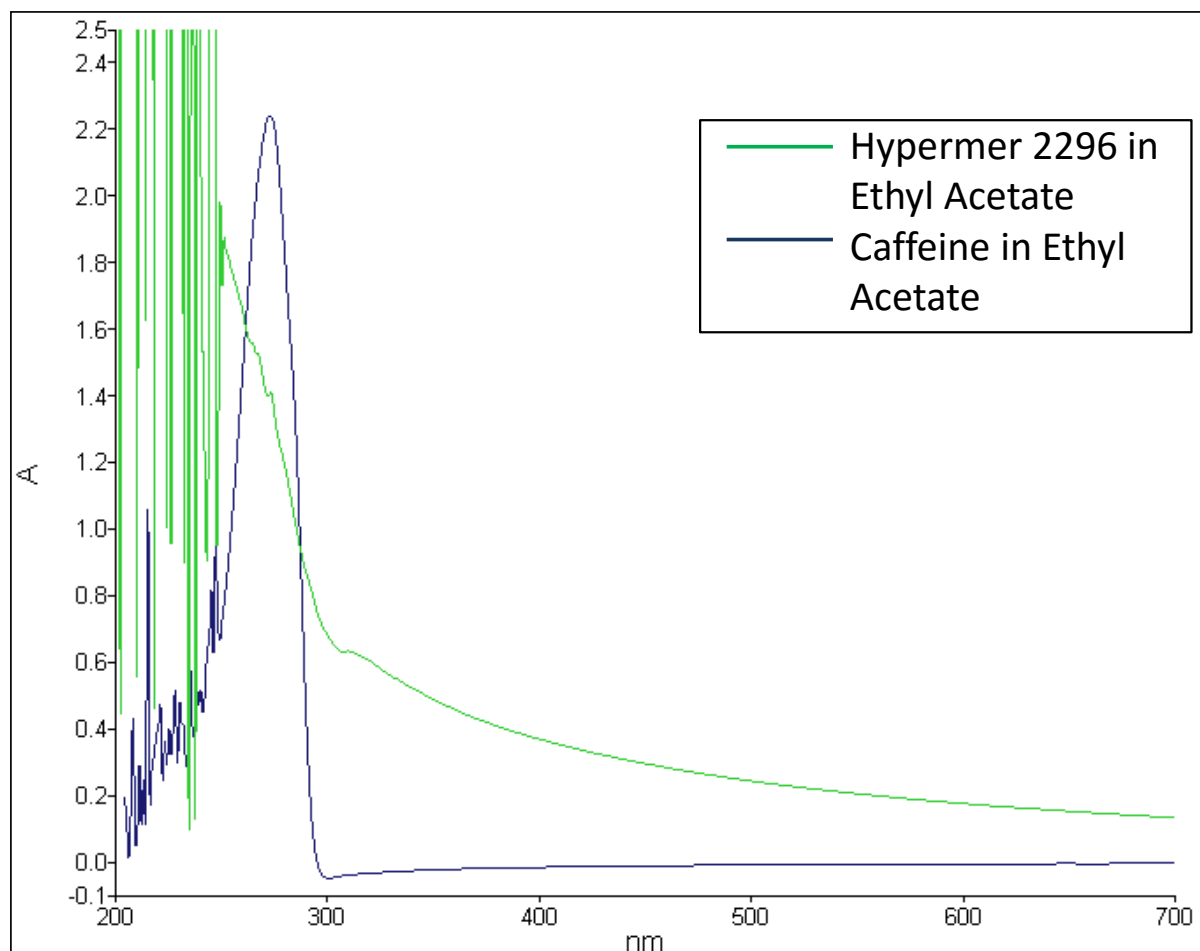


Figure 56 A comparison of the UV/Vis spectra of hypermer 2296 (1 wt%) and Caffeine (0.05 gL^{-1}) in Ethyl Acetate. In all the experimental samples taken there was no indication of any hypermer 2296 leeching from the polyHIPE only a single peak for caffeine was observed.

Chapter 7: HIPE Template Composition

Table 11. Composition of template HIPEs used in Chapter 7.

Sample Number	Continuous Phase Composition				Internal Phase Composition		Agitation Speed rpm (± 10)	Agitation Time (s)
	Styrene (ml)	Divinyl Benzene (ml)	Hypermer 2296 (ml)	AIBN (g)	40 g/L Calcium Chloride Solution aq (ml)	Internal Phase Volume (%)		
HC-1	4	4	2	0.13	40	80	2190	10
HC-2								30
HC-3								60
HC-4								120
HC-5								300

Chapter 7: Determination of Palladium Loading in PolyHIPE Flow Cells

In order to achieve a 2 wt% loading of Pd⁰ within the polyHIPE reactor with 80% porosity;

Monolith volume = 2.69 cm³ (7mm Diameter 80mm Length)

Typical Foam Density for 80% porosity S/DVB polyHIPE = 0.206 gcm⁻³

Therefore Mass of polyHIPE = 2.69 cm³ * 0.206 g/cm³ = 0.55g

Therefore Mass of Pd⁰ required = 0.55 g * 0.02 = 0.011 g

Therefore Mass of Pd(CH₃COO⁻)₂ required = 0.011 g * (224.5 g mol⁻¹ / 106.4 g mol⁻¹) = 0.023 g

(Molar mass of Pd⁰ = 106.4 g/mol, Molar mass of Pd(CH₃COO⁻)₂ = 224.5 g mol⁻¹)

Pore volume of polyHIPE = 2.69 cm³ * 0.8 = 2.15 cm³

Therefore the Concentration of Pd(CH₃COO⁻)₂ needed for 2 wt% loading = 0.023 g / 2.15 cm³ = 0.011 g/cm³ = 11 g/L