Open cellular reactive porous membranes from high internal phase emulsions†

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High internal phase emulsions (HIPEs) incorporating styrene, 4-vinylbenzyl chloride, divinylbenzene and ethylhexyl acrylate were applied to prepare reactive, cross-linked porous membranes with open cellular architecture and thicknesses between 30 and 500 μm.

High internal phase emulsions are emulsions where the volume fraction of the internal phase exceeds 74.05%. Water in oil type HIPEs especially have become an established media for porous polymer preparation.[1] A unique morphology of a polyHIPE material makes it suitable for a variety of applications, especially where macro porosity is necessary for convective mass transfer. Known applications include solid phase organic synthesis, separation of biomacromolecules, biocatalyst supports, water purification, sensors material, filtration, sorption *etc*.[2]

A three-level porosity can be observed within the polyHIPE materials; larger pores due to the droplets of the non-polymerizable internal phase, smaller interconnecting pores and the porosity of the polymer film itself. The formation of interconnecting pores is not yet fully understood. A higher density of the polymer compared to the monomer mixture could cause the shrinkage and rupture of the polymer film, thus forming the pores. Investigations by cryo-SEM at various stages of formation HIPEs during the polymerisation support this theory,[3] while some findings suggest that interconnecting pores might be formed as a result of the post polymerisation treatment.[4] All level pore size distributions can be affected by the choice of appropriate conditions, most notably phase volume ratio, surfactant structure, phase polarity differences, porogen additions, and the cross-linking degree.[5] The possibility of pore size tuning is therefore another feature of polyHIPE materials which makes them attractive for exploration in various fields. Most of the reports on polyHIPE materials describe monolithic forms where emulsions are polymerized in appropriate moulds. A monolithic piece can be formed into a desired shape, for instance into disks for chromatography,[6] rods for flow-through synthesis support[7] or it can be ground if powder is a more desired form. HIPEs can also be suspended into the third phase, producing a multiple emulsion, resulting after the polymerisation in polyHIPE beads.[8]

Thin films with an open porous structure are another form of porous material with a wide array of possible applications. Ruckenstein reported in 1989 the use of high internal phase emulsions for the preparation of composite membranes for the separation of mixtures of solvents.[9] Cameron *et al*. reported the preparation of polystyrene membranes with the aid of HIPE templates.[10] The moulding of a HIPE emulsion in between PTFE plates using spacers is described, however problems regarding the collapse of emulsion resulting in pinholes and non porous membrane skin are mentioned. The supporting substrate and the amount of the surfactant seem to be the most important factors influencing this. We were experimenting with a different approach for the preparation of membranes using HIPEs. It resulted in membranes being completely open porous even on the surface and almost pinhole free. Herein we report polyHIPE membrane preparation based on styrene (St), divinylbenzene (DVB), vinylbenzyl chloride (VBC) and ethylhexyl acrylate (EHA).

As porous membranes have a wide spectrum of applications and concentrated emulsions are an established media for the preparation of porous polymers, polyHIPE membranes are an attractive material for further exploration. Furthermore, possessing such a membrane with functional groups for chemical modifications and cross-links for insolubility would be useful in the fields of applications such as separation (membrane chromatography), solid phase synthesis (modules for flow through techniques), sensoring, *etc*. The styrene–divinylbenzene system is probably the most studied system in the area of polyHIPE preparation. Parameters defining the stability of the emulsion and consequently the morphology of the resulting polymeric material are well known.[5c,f] To prepare styrene–divinylbenzene polyHIPE membranes, a concentrated emulsion containing 75–85 vol% of the aqueous phase, sorbitan monooleate as a surfactant and 1 to 5 mol% of divinylbenzene in the oil phase, was used. But rather than pouring it into a thin mould (as done by Cameron *et al*.), a casting blade was used to spread the emulsion onto a polished glass substrate (see ESI for details†). The spread of the emulsion was carefully covered with another glass plate and heated to 60 °C for 24 h. Several other types of support were tested, such as PTFE plates, PTFE foil, and aluminium foil. However, none of these produced satisfactory results. With the glass plate, and the use of a stainless steel casting blade, polymerised films had generally very few pinholes. The thickness of the resulting membrane depended on the thickness of the layer determined by the opening on the casting blade. Upon examination of the membranes by scanning electron microscopy, the typical polyHIPE structure is evident (Fig. 1). The largest pores,

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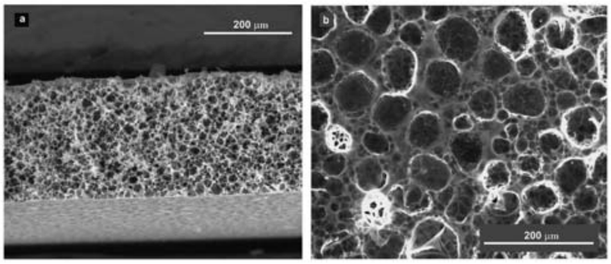


Fig. 1 SEM images of styrene–DVB polyHIPE membrane A2 (a-cross-section, b-surface).

Table 1 Synthesised membranes

	Monomers					
Membrane	St (%)	DVB (%)	VBC (%)	EHA (%)	Water phase (%)	Thickness[a]/µm
A1	80	20	—	—	80	270
A2	95	5	—	—	80	205
A3	98	2	—	—	80	240
A4	99	1	—	—	80	215
A5	95	5	—	—	75	30
A6	98	2	—	—	75	255
A7	98	2	—	—	85	230
A8	96	4	—	—	75	175
A9	96	4	—	—	85	285
A10	86	4	—	10	75	345
A11	76	4	—	20	75	405
A12	66	4	—	30	75	250
B1	47.5	5	47.5	—	80	375
B2	88	2	10	—	80	200
B3	78	2	20	—	80	220
B4	73	2	25	—	75	225
B5	86	4	10	—	80	215
B6	76	4	20	—	80	215
B7	71	4	25	—	75	230
B8	66	4	20	10	80	385
B9	56	4	20	20	80	430

[a] Average thickness variation data can be found in the ESI.

which are the result of the droplets of the aqueous phase, are *ca.* 20 µm in diameter, while interconnecting pores are *ca.* 3.5 µm in diameter.

Usually, when preparing monolithic polyHIPE materials in moulds, a non porous skin is formed on the surface or at the contact with the mould. In the case of a monolithic piece that is subsequently reshaped, this poses no particular problem, however in the case of membranes, the collapse of the HIPE structure on the surface would cause a change in characteristics and our target was to avoid this. There are quite a few characteristics of the supporting substrate influencing the morphology of the polyHIPE at the phase border, hydrophilicity/hydrophobicity probably being the most important. While Cameron *et al.* found that PTFE was the best mould material; we on the other hand found that PTFE plates were not so useful for the casting technique. It should however be said that this finding may also be due to the use of a different emulsion spreading procedure. Besides the cross section of the produced membrane, the surface was also examined by SEM (Fig. 1). The image clearly shows the open cellular structure on the surface of the membrane produced with glass substrate. The flux of water through the membranes was measured using the AMICON 8400 membrane cell. High volume fluxes, up to 44 mL cm^{-2} min^{-1} at 0.5 bar were observed, which is very high compared to dense membranes of comparable thickness, suggesting a convective rather than diffusive mass transfer and therefore an open structure. The mechanical flexibility of membranes is also important in view of various applications where membranes are positioned in modules. The addition of some acrylates to the monomer mixture is known to decrease the glass transition temperature and therefore increase the mechanical flexibility of the polyHIPE material.[11] This effect is due to the introduction of a different monomer resulting in a bigger free volume and thus more flexibility. Another factor influencing the mechanical stability is the cross-linking degree. We found that a percentage of DVB higher than 20% resulted in rather stiff membranes that broke upon bending of over 45 degrees, while membranes with less than 2% of DVB swelled in DCM and toluene to such a degree that they became difficult to handle. 4 mol% of DVB was found to be the optimum amount of cross-linker in terms of mechanical properties (*vis.*). In the case of styrene–DVB polyHIPE membranes, the optimization of DVB content was sufficient to achieve the desired mechanical properties. Different casting blades were used to obtain membranes with various thicknesses. Very reproducibly, blades produced membranes with approx. half the thickness of the nominal (blade opening). There were slight variations which can be ascribed to different viscosities of the emulsions. The cast thicknesses were lower than the nominal casting blade opening would suggest, which is due to the emulsion flow following spreading.

In order to obtain polyHIPE cross-linked membranes with functional groups, 4-vinylbenzyl chloride (VBC) was introduced into the oil phase of the precursor emulsions. VBC based polyHIPE monoliths have been described and utilized in solid phase organic synthesis techniques.[7,12] PolyHIPE beads with VBC chemistry have also been described,[8c] however VBC based polyHIPE membranes have not yet been reported in the literature. With regards to the substrate for membrane preparation, no dramatic difference was observed. The exchange of some of the styrene with VBC resulted in the same optimum casting and curing procedure, using glass substrate and casting blades. Membranes with 10, 20, 25 and 47 mol% of VBC were prepared (Table 1), with 75 vol% or 80 vol% aqueous phase and with 2 or 4% of cross-linking degree. The open cellular interconnected structure, similar to styrene–DVB polyHIPE can be seen also in this case (Fig. 2). Pores and interconnecting pores are smaller, *ca.* 5 µm (pore diameter) and 1 µm (interconnecting pore diameter). The flexibilities of VBC based

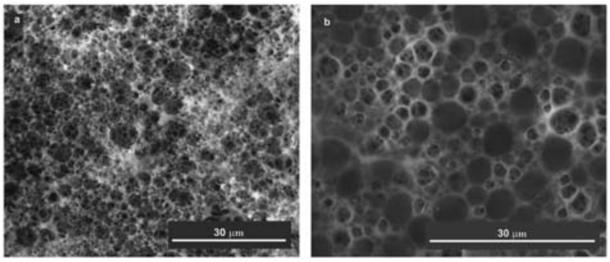
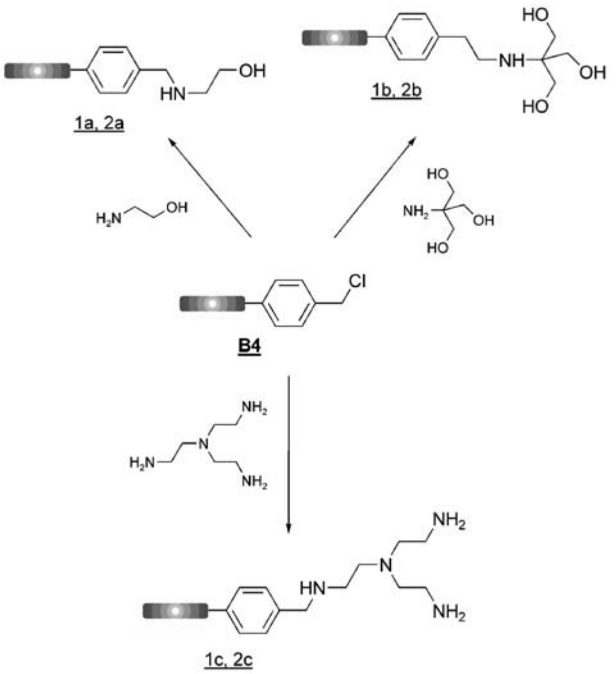


Fig. 2 SEM images of cross-section (a) and surface (b) of VBC polyHIPE membrane B1.



Scheme 1 Functionalisation of polyHIPE membranes with amines.

Table 2 Functionalisation of polyHIPE membranes

Polymer	Reaction temp./°C	Calc. % N	Found % N	Calc. % Cl	Found % Cl	Conversion (%)
B4		—	—	6.9	6.9	—
1a	60	2.6	1.8	—	2.2	68
1b	60	2.3	1.7	—	1.9	70
1c	60	7.8	4.0	—	3.0	54
2a	90	2.6	2.3	—	0.8	89
2b	90	2.3	2.1	—	1.7	73
2c	90	7.8	4.9	—	1.6	74

polyHIPE membranes were substantially lower than the flexibility of styrene based ones. Thus the introduction of ethylhexyl acrylate, which improved the mechanical flexibility (*vis.*); the addition of 10 mol% of EHA was found enough to prepare very flexible membranes that were easily wrapped around a 1 cm diameter tube. Reactions with amines were used to briefly test the reactivity of the membranes and accessibility of reactive sites (Scheme 1). The membranes were simply immersed in a solution of an amine for a certain amount of time and analyzed *via* FTIR (surface and bulk) and elemental analysis. Flow through modules will be used in the future.

The conversions (see Table 2) are comparable to those achieved with monolithic polyHIPEs under flow conditions.[7] The percentages, calculated from the remaining chlorine and the incoming nitrogen in the membranes, range from 57 to 89, which we believe is very high considering the method of functionalisation. In the case of tris(2-aminoethyl)amine, there is probably some additional cross-linking *via* the second amino groups since the amounts of nitrogen are lower than expected considering the remaining chlorine. This phenomenon has been observed also in the case of monolithic VBC polyHIPEs.[7] The reactions with amines illustrate the ease of functionalisations and therefore the wide possibilities of applications.

In conclusion, open cellular porous membranes of thicknesses between 30 and 500 μm with polyHIPE architecture and that are pinhole free can be prepared by casting HIPEs onto glass substrates. VBC can be incorporated in order to obtain functionalities and such membranes are mechanically stable, flexible, and permeable and can be functionalized with nucleophiles, for instance amines. The thickness can be controlled by the use of the appropriate casting blade and mechanical flexibility by the degree of cross-linking and the addition of ethylhexyl acrylate. We believe that the areas of application of such membranes are very wide due to the possibility of morphology tuning of polyHIPE materials. PolyHIPE membranes with other chemistries, functionalisations and applications are under investigation.

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