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New Evidence for the Mechanism of the Pore Formation in Polymerising High Internal Phase Emulsions or Why polyHIPEs Have an Interconnected Pore Network Structure

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Summary: We present new evidence that the formation of pore throats (windows) or pore interconnects in polymerised High Internal Phase Emulsions (polyHIPEs) is most likely due to a mechanical action exerted during the post-synthesis processing of the porous polymer monolith. We would like to invite researchers interested in this field to reopen the discussion on the mechanism which lead to the formation of pore throats during the polymerisation of concentrated emulsion templates.

Keywords: foams; High Internal Phase Emulsion (HIPE); macroporous polymers; radical polymerisation; structure

Introduction

Lissant classified emulsions having an internal phase volume fraction of at least 70% as High Internal Phase (Ratio) Emulsions (HIPEs).[1–4] However, HIPEs are usually referred to as emulsions having an internal phase volume fraction of at least 74%.[5] The internal phase of HIPEs consists of closed packed but undistorted spheres until its volume exceeds 74 vol.-%. A further increase of the internal phase leads to the deformation of droplets, i.e. the enclosed droplet spheres flatten in the area of contact points with neighbouring droplets. At volume fractions between 74% and 94%, the internal phase droplets arrange in a rhomboidal decahedral packing whilst above 94 vol.-% the geometric configuration of truncated octahedrons is preferred.[2–4] HIPEs consist most commonly but not necessarily[6] of an organic continuous and an aqueous internal phase. Such emulsions are commonly stabilised by large amounts of non-ionic surfactants, such as span 80 (sorbitan monooleate, Sigma Aldrich, Gillingham, UK)[5,7] or Hypermer 1070 an polyalkanolamine compound (UNIQEMA, Wirral, UK).[8–10] The addition of salt, such as $CaCl_2$, to the aqueous phase enhances the stability of the emulsions by suppressing Ostwald ripening.[5,7] Following the Unilever patents by Barby and Haq in 1982[11,12], HIPEs containing monomers within the organic phase have gained increasing interest due to the fact that they can act as template for highly porous polymer foams with an open porous interconnected pore network structure. The polymerisation of the continuous phase of HIPEs leads to the formation of porous polymer monoliths, so called polyHIPEs (Figure 1).

Because of their unique properties, polyHIPEs are considered for numerous applications, such filter media[13], ion exchange modules[14], monolithic polymer supports for catalysis[15] and even as scaffolds for tissue engineering applications.[16–18] However, the limited mechanical stability of highly porous polymer foams produced by the polymerisation of the continuous phase of concentrated emulsions has so far hindered any real world applications of these materials.

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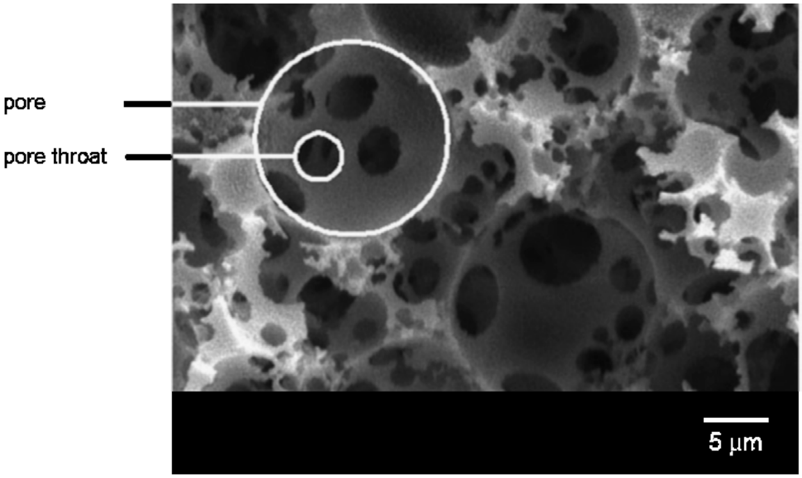

Figure 1.
Definition of pores and pore throats of polyHIPEs.

Observations and Discussion

Williams et al.[19–22] studied in detail the polymerisation of HIPEs containing divinylbenzene (DVB) and styrene as monomers within the organic phase. They could show that the degree of pore interconnectivity strongly depends on the surfactant level rather than on the internal phase volume. Is the surfactant level less than 5 vol.-% relative to the organic phase volume fraction, polymer foams with a closed-cell pore structure are produced even if the internal phase of the HIPE occupies 97 vol.-% of the total volume of the emulsion.[19] The increase of the surfactant concentration leads to a significant reduction of the droplet size of the internal phase. Consequently, this causes thinning of the continuous organic phase film, which separates individual internal phase droplets, because the overall surface area of the droplets is dramatically increased. The reduced thickness of the polymerisable phase film, which is expected to be especially thin in the area of contact points of deformed neighbouring droplets, seemed to be crucial in order to produce open porous polymer foams during the polymerisation of the continuous phase of HIPEs.[19–22] Williams and Wrobleski[20] state "*styrene/divinylbenzene (1:1) emulsion foams produced with 20–50% sorbitan monooleate (based on monomer) are the best at every monomer level.*"

The formation of the pore throats is a complex phenomenon, which depends on many parameters, such as the volume fraction of the internal phase, the concentration of the surfactant, the droplet size, the tendency for Ostwald ripening and the nature of the polymer forming during the polymerisation. Cameron et al.[23] investigated the formation of pore throats during the polymerisation of common styrene/DVB HIPEs with 88 vol.-% internal phase via cryo-SEM. Samples of the original HIPE and the HIPE polymerising for 130 min, 160 min, 240 min and 300 min, respectively, were frozen in liquid nitrogen and SEM images were taken at $-210\,^{\circ}$C. In order to identify the pore structure of the HIPE at different states of the polymerisation, the internal phase was removed by sublimation in vacuum prior to recording of the SEM images. The first pore throats just appeared after a polymerisation time of 130 min. Only if the polymerisation was allowed to continue further, a highly interconnected pore structure characteristic for polyHIPEs develops. Cameron et al.[23] could show that the structure of the HIPE acts as template for the resulting polyHIPE and, moreover, that dramatic changes occur within the organic phase during polymerisation. These changes lead to the formation of pore throats at the gel point of the polymerisation. It was suggested that the observed formation of pore throats is a result of the volume contraction on conversion of monomer to polymer, which is indeed a well-known phenomenon of vinyl polymerisation chemistry. Cameron et al.[23] argued that the polymer network, which forms during polymerisation, provides sufficient structural integrity to prevent the collapse of the forming polymer foam whilst the thinner monomer/polymer films, i.e. the faces in the area of contact points between neighbouring droplets, shrink internally towards the plateau borders. Their argumentation seemed to be supported by the fact that no significant shrinkage is observed during the polymerisation of the HIPE template but they shrink during the drying process.[5,23–26] Not even polyHIPEs without closed surface skin do shrink.[13] However, this description is in direct contrast to our own observations. Figures 1 and 2 show SEM images of different areas of the same polyHIPE. This polyHIPE was synthesised by the polymerisation (at 70 °C for 24 h) of a HIPE containing 80 vol.-% internal phase. The polymerisable organic phase consisted of 30 vol.-% styrene and 50 vol.-% DVB as monomers and 20 vol.-% Hypermer 1070 as surfactant. The resulting polymer foam possesses the characteristic morphology of polyHIPEs (Figure 1) consisting of pores, whose diameter ranges from 9 μm to 19 μm. These pores are interconnected via almost perfectly spherical pore throats with diameters ranging form 2 μm to 7 μm. However, we can find many pore throats, which are still partially sealed by thin polymer films (see arrow in Figure 2).

It seems as if polymer films once covered these ‘‘holes’’ entirely. This finding implies that the aqueous internal phase droplets of a HIPE are completely enclosed by the organic phase during the entire polymerisation and the pore throats *only* appear during the purification and removal of the locked in internal phase from the synthesised polyHIPE. This purification process usually includes Soxleth solvent extraction (with acetone or methanol) of the polymer foam and drying at elevated temperatures under reduced pressure.[7,10,27] A possible explanation for the pore opening is that the thin films covering the individual internal phase droplets simply rupture (pop open like a pull-back bottle opening) during the purification and drying process. However,

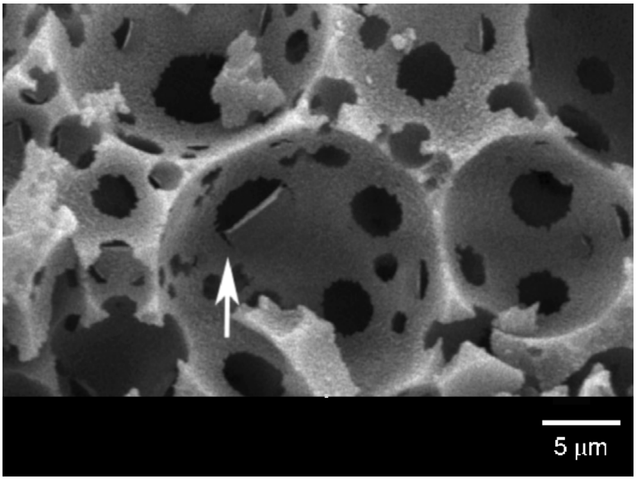

Figure 2.
polyHIPE having pore throats partial covered with a thin solid film.

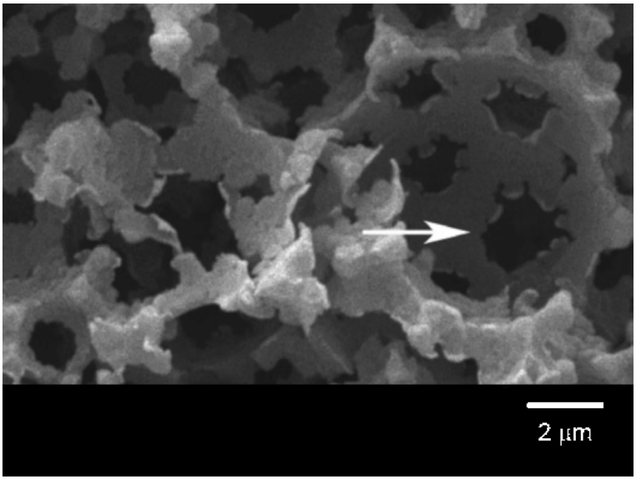

Figure 3.
polyHIPE with burst polymer films, which were initially covering the faces between to adjacent aqueous droplets.

the formation of very spherical pore throats could be supported by a phase separation occurring in the polymerising organic phase. The organic phase of this emulsion consisted of the 80 vol.-% monomers and 20 vol.-% surfactant. The solubility of this water insoluble surfactant (Hypermer 1070) in the organic phase might decrease with progressing polymerisation. This would lead to the formation of two organic phases; a polymer rich and a surfactant rich phase during the progressing polymerisation, i.e. the surfactant is being pushed out of solution towards the oil/water interface in the contact area between neighbouring droplets of the aqueous phase. This

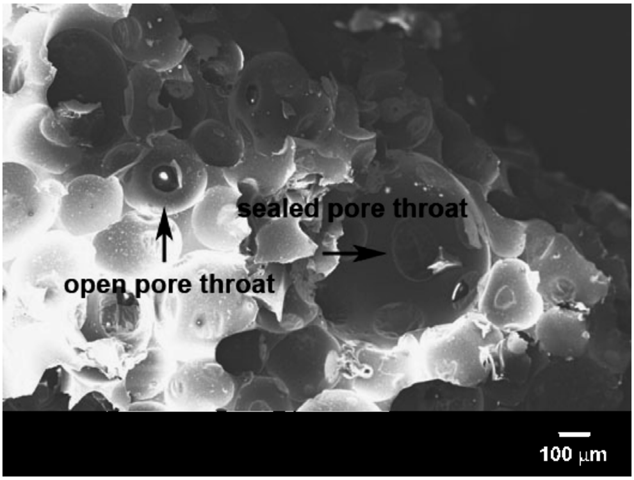

Figure 4.
Pickering polyHIPE with partial open porous structure.

process could lead to the formation of a weak point that fractures during the polyHIPE purification process. Our hypothesis can explain, why the surfactant concentration is so crucial for the formation of an interconnected pore structure and why no 'external' shrinkage is observed during the polymerisation of HIPEs. The surfactant rich phase might first appear as small droplet in the area of contact points of neighbouring internal phase droplets and grow during the polymerisation forcing the forming polymer to retreat towards the plateau areas of the HIPE. Consequently, the film surrounding individual internal phase droplets remains intact. This also means the polymerising HIPE cannot shrink 'externally', since the internal phase consists of an incompressible liquid. The formation of the pore throats is eased if indeed the solubility of the surfactant decreases in the monomer phase and a structurally weak surfactant phase forms within the polymerising organic phase. After the polymerisation the pore throats will be still covered by a thin film mainly consisting of surfactant and probably a weak polymer network. This film might be peeled off during the purification of the polyHIPE either by dissolving the surfactant during solvent extraction or, more likely, during the following drying process under vacuum.

It was commonly assumed that for the synthesis of open porous polyHIPEs the maximum continuous phase level is limited to 26 vol.-%, which causes the extremely low foam density of the resulting polyHIPE. However, we have shown that open porous polymer foams can also be produced via the polymerisation of emulsion templates with an internal phase volume fraction as low as 60 vol.-%.[8–10] In this case also 20 vol.-% surfactant Hypermer 1070 with respect to the total volume of the organic phase was used to stabilise the emulsion.

Figure 3 shows an SEM micrograph of the resulting porous polymer monolith. It seems that the pore throats simply burst open. The changed mechanism could be explained by the increased thickness of the pore walls, which also contributes to the improved mechanical strength of the produced polymer foam.

More recently we succeeded in preparing HIPEs which were solely stabilised by nanoparticles.[1] We used these so called Pickering HIPEs as templates to synthesise highly porous polyHIPEs. The polymerisation of the organic phase of the Pickering HIPE results in a partially open porous polymer foam. Figure 4 shows an SEM of such a Pickering polyHIPE. It can be seen that a thin film still covers the region between two droplets but others are partially open, i.e. the thin film is about to rupture.

Conclusion

Our observations show that the formation of the open porous structure of polyHIPEs is a complex process. However, it seems that the actual formation of the pore throats is primarily caused by a mechanical action, which leads to the rupture of the thin polymer films covering the faces between the closest neighbouring droplets. Besides the known fact that the presence of large amounts of surfactant supports the formation of interconnects *it is not an imperative* for the formation of pore throats as demonstrated by the fact that pore throats also form in solely particle stabilised polymerisable concentrated emulsion templates.

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