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High internal phase emulsions (HIPEs) containing divinylbenzene and 4-vinylbenzyl chloride and the morphology of the resulting PolyHIPE materials

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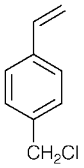
The cell size of DVB–VBC PolyHIPEs decreases with increasing VBC content, which appears to be due to the adsorption of VBC at the emulsion interface leading to a lower interfacial tension and a smaller droplet size.

High internal phase emulsions (HIPEs) are defined as emulsions in which the droplet phase occupies greater than 74.05% of the emulsion volume, this figure representing the maximum volume occupiable by uniform spheres. Such systems have been known for many years, and features such as their preparation, stabilisation, structure and rheology have been investigated in detail.[1] Our interest[2] in HIPEs, and that of several other groups,[3] lies in their ability to be used as templates for the production of highly porous polymers. Such materials, known as PolyHIPEs using Unilever's nomenclature,[4] are prepared by polymerising the thin monomer films that surround the droplets of inert solvent-in-monomer solution HIPEs. Subsequent removal of the droplets produces a highly porous material (Fig. 1).

During the course of our work on developing novel PolyHIPE materials we undertook the preparation of species containing 4-vinylbenzyl chloride (VBC, **1**). This monomer is sufficiently hydrophobic to allow successful HIPE preparation, and results in materials possessing reactive chloromethyl functionalities that are amenable to functionalisation, potentially leading to a wide range of derivatised highly porous materials. VBC has been used previously to prepare HIPEs where it was present in either the droplet[5] or the continuous[6] phase, leading to the production of agglomerates of particles or foams, respectively. However, the influence of VBC on the emulsion and resulting polymer morphology was not described.



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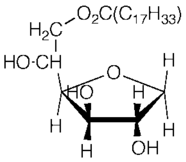

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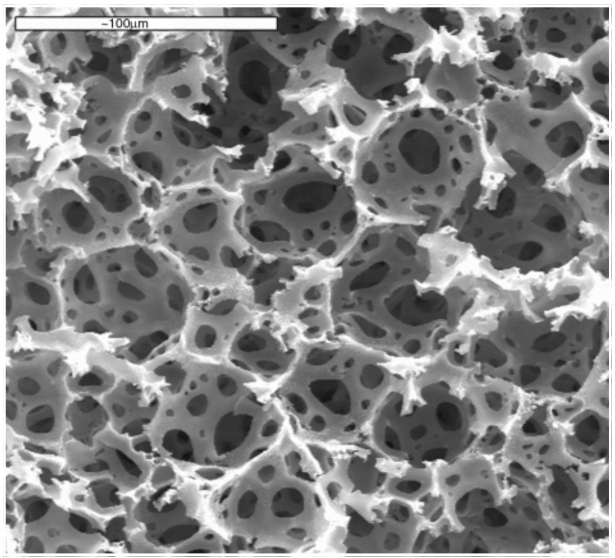

Fig. 1 SEM of a S–DVB PolyHIPE foam (pore volume *ca.* 90%, nominal crosslink density *ca.* 15%). Scale bar = 100 μm.

VBC-containing materials were easily prepared by addition of an aqueous solution of $CaCl_2.2H_2O$ and $K_2S_2O_8$ to a mixture of monomer(s) plus surfactant, using conditions optimised for the production of styrene–divinylbenzene (S–DVB) PolyHIPEs.[4,7] The ratio (wt%) of VBC to DVB[8] was varied, to give a range of foams, each with a pore volume of 90%. To our surprise, the resulting materials had smaller average cell sizes than those obtained from styrene and DVB (*e.g.* Fig. 1). SEM photographs (Fig. 2) clearly show that increasing the VBC content in the formulation causes a decrease in average cell size from 10 μm [Fig. 2(*a*)] to less than 5 μm [Fig. 2(*e*)]. Interestingly, the foam composed entirely of polyVBC [Fig. 2(*f*)] has no discernible cell structure. Previously, Williams[9] found that increasing the DVB concentration in styrene–DVB PolyHIPEs from 0 to 100% resulted in a decrease in average cell diameter by about 10 μm. He reasoned that DVB,

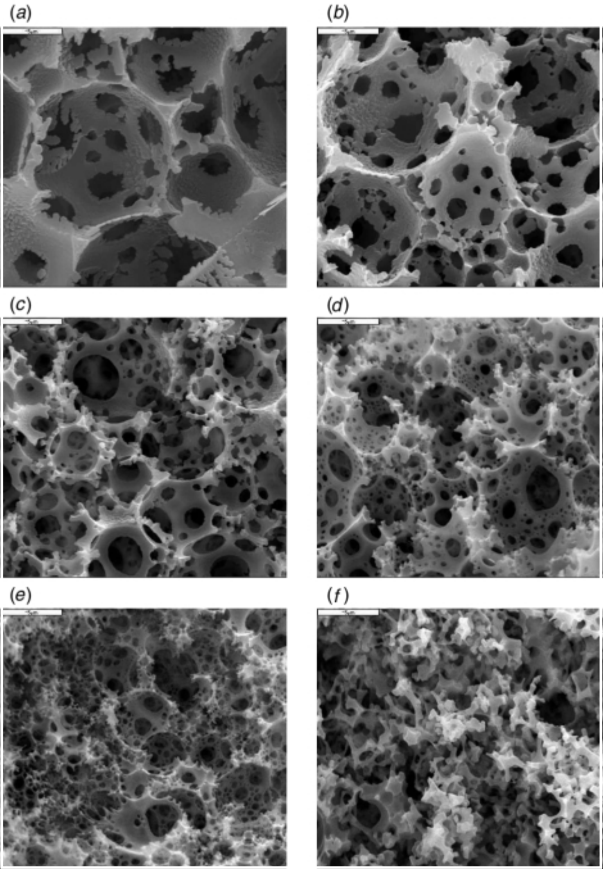

Fig. 2 SEMs of VBC–DVB PolyHIPE foams (ref. 16): (*a*) X80PV90; (*b*) V12.5X70PV90; (*c*) V37.5X50PV90; (*d*) V62.5X30PV90; (*e*) V87.5X10PV90; (*f*) V100X0PV90. Scale bar = 5 μm.

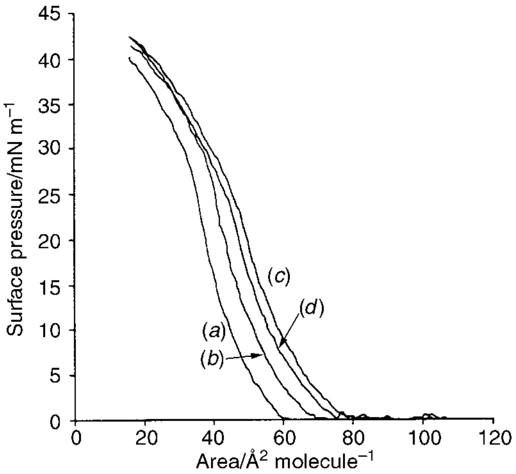

Fig. 3 π–A curves for films containing Span 80 alone (*a*) and Span 80 (17 mol% relative to total oil phase) plus DVB (*b*), VBC (*c*) and DVB–VBC (50:50 mol. mixture) (*d*).

being more hydrophobic, was leading to more stable emulsions. It is well known that droplet size decreases with increasing emulsion stability since the surface energy per unit area is lower. A decrease in emulsion droplet size leads to a decrease in PolyHIPE cell size since the foam is effectively a replica of the emulsion structure immediately prior to gel formation.

In our case, with VBC–DVB foams, increasing DVB concentration causes an increase in average cell size of the resulting foam. This implies that VBC leads to more stable emulsions than DVB. Emulsion stability is influenced by such factors as temperature, surfactant nature and concentration, phase composition and viscosity. Since the surfactant used was Span 80 (sorbitan monooleate, **2**) in each case, at constant concentration (20 wt% relative to monomer content), the polymerisation temperature was constant and emulsion preparation conditions were identical, the different behaviour must be due to differences in the physical chemistries of DVB and VBC. Both species being low molar mass entities, one would not anticipate tremendous differences in the viscosities of VBC and DVB.[10] We therefore concluded that the marked difference in their behaviour must be as a result of different interfacial properties. In particular, we wondered whether VBC could be concentrating at the interface and acting as a cosurfactant with Span 80.

It is well known that small molecules bearing polar and non-polar functionalities can adsorb at the interface of emulsions, the polar group locating in the aqueous phase and the non-polar group in the organic phase. Additionally, small molecule surface-active species can co-adsorb with surfactants possessing large head-groups, such as Span 80, leading to a better-packed interfacial film and consequently a more stable emulsion.[11] The presence of an aromatic moiety in the hydrophobic part of the cosurfactant may enhance its adsorption at the interface.[12]

Using a Langmuir trough, we measured the surface pressure against area (π–A) curves of films of Span 80 alone, and Span 80 with DVB, VBC and a 50:50 mixture of DVB and VBC.[13] The interfacial behaviour of the various components can be inferred from their π–A curves (Fig. 3). Span 80 [Fig. 3(*a*)] displays the behaviour of a typical surfactant; surface pressure is low and constant until critical film compression is reached, whereupon it increases drastically. The area corresponding to this compression represents the area of the condensed interfacial film where the surfactant molecules are densely packed. Adsorption of the other species (VBC, DVB) at the interface will cause greater crowding and lead to an increase in π at higher area (lower compression), which is indeed observed. From fig. 3 it can be inferred that DVB [Fig. 3(*b*)] is slightly adsorbed at the interface, but VBC [Fig. 3(*c*)] is adsorbed to a significantly greater extent. Therefore, VBC is co-adsorbed with Span 80 at the interface and leads to a more dense film. These results appear to confirm our hypothesis that VBC is acting as a cosurfactant. Williams[14] previously investigated the influence of 22 cosurfactants on the stability of S–DVB HIPEs and found that none enhanced stability.[15] However, all but three of those additives were alcohols and none possessed halide residues.

Further information on the interfacial behaviour of systems containing VBC can be deduced from closer inspection of Fig. 3. The curve of the film containing a 50:50 mixture of VBC and DVB [Fig. 3(*d*)] lies nearer to that of VBC [Fig. 3(*c*)] than to that of DVB [Fig. 3(*b*)], indicating that the greatest changes in interfacial properties occur on initial addition of VBC. This behaviour can also be inferred from the morphology of the PolyHIPE materials (Fig. 2); the decrease in cell size is more dramatic up to addition of 30% VBC [Fig. 2(*c*)], after which the cell size decreases only slightly. This implies that the interface is close to saturation at a VBC concentration in the HIPE of around 30%.

To conclude, we have prepared reactive PolyHIPE materials from VBC and DVB. These possess smaller average cell sizes than corresponding materials prepared from styrene and DVB. This phenomenon appears to be due to the adsorption of VBC at the interface, which lowers the interfacial tension, leads to a more stable emulsion with smaller droplets and therefore to the production of a foam with a smaller average cell diameter. The ability to control the morphology of these porous materials is crucial to their technological development.

Notes and references

1 See N. R. Cameron and D. C. Sherrington, *Adv. Polym. Sci.*, 1996, **126**, 163; E. Ruckenstein, *Adv. Polym. Sci.*, 1997, **127**, 163; and references therein.

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10 Viscosities of VBC and DVB (55%) at 25 °C are 1.830 and 1.007; from: *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., ed. J. I. Kroschwitz, Wiley, New York, 1991.

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12 M. J. Rosen, *Surfactants and Interfacial Phenomena*, 2nd edn., Wiley, 1989, p. 6.

13 Film compositions were chosen to reflect as closely as possible the composition of the HIPE organic phase. In each case, 30 µl of a $CHCl_3$ solution ([Span 80] = 2.33×10^{-3} mol dm^{-3}, [additive] = 1.17×10^{-2} mol dm^{-3}) was spread on an aqueous solution of calcium chloride (0.075 mol dm^{-3}).

14 J. M. Williams, *Langmuir*, 1991, **7**, 1370.

15 One example, Brij 78, was found to produce a bimodal cell size distribution, the smaller of which were smaller than those commonly observed in S/DVB foams.

16 PolyHIPE coding system: V*a*X*b*PV*c*, *a* = wt. % of VBC relative to total monomer phase; *b* = nominal crosslink density (wt. % of actual DVB in monomer phase); *c* = pore volume (vol. % internal phase of HIPE).

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