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SHORT COMMUNICATION

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# Ultra-porous hollow particles

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**Abstract** Hollow particles with porous shells have been prepared by a simple modification to the surfactant-free polymerisation of styrene by the incorporation of water-soluble natural polymers and the use of high stirring speeds. The particle morphology has been characterised by scanning electron microscopy (SEM). When styrene is polymerised in the presence of either carboxymethyl cellulose (CMC) or sodium alginate at high stirring speeds, small homogeneous (solid) particles (diameter ~200 nm) and large porous particles (diameter~10 μm) are both formed. However, at low stirring speeds only the small homogeneous (solid) particles are formed. Further, only the small homogeneous (solid) particles are formed when non-adsorbing polymers such as starch and poly(vinyl alcohol) are present. In contrast, polymers that strongly adsorb onto polystyrene particles cause the polymerising mixture to flocculate. It is proposed that the porous character is a direct result of the polymerisation of a multiple emulsion in the presence of a depletion interaction. Moreover, addition of a high concentration of surfactant to the CMC system simply results in the spherical homogenous particles, suggesting that the surfactant removes the depletion effect.

**Keywords** Porous particles · Polymer adsorption · Interfacial polymerisation

## Introduction

Recently, control of the morphology of colloidal particles has become an important area in various fields of technology, and nowadays it is possible to prepare core-shell, micro-domain, interpenetrating network and hollow latex particles. The core-shell and hollow particles are more widely-used, as they can be used to protect environmentally-sensitive substances such as vitamins and flavours, to mask an odour or taste, to facilitate the safe handling of toxic materials, and to handle liquids as solids. Further, hollow latex particles impact on other health-enhancing technologies, such as drug encapsulation and controlled release.

Emulsion polymerisation is frequently used to prepare hollow particles by the polymerisation of a suitable monomer in the presence of a non-reactive oil phase [1, 2]. Bicontinuous microemulsion [3], the emulsion/solvent evaporation technique [4], spray drying [5], controlled phase separation [6], solvent swelling [7, 8, 9, 10, 11], incorporation of a blowing agent [12, 13], and coating techniques [14] have also led to hollow particles. Preparation of particles with ionisable cores also leads to hollow particles by osmotic swelling [15, 16, 17]. Further, it has been shown that the encapsulation and egress character of osmotically swollen particles can been improved via micro-voids in the core, connected by one or more channels to the surface of the particle [18]. Core-shell particles can be prepared by consecutive or sequential emulsion polymerisation with more than one monomer type [19] or via the polymerisation of monomers onto the surfaces of already formed silica particles [20, 21]. Further, a wide variety of nano-sized particle surface morphologies affectionately described as “confetti-like”, “raspberry-like”, “popcorn-like” and “void-containing” particles, “doublets” and “triplets” have been made by a two-stage surfactant-free emulsion polymerisation of styrene built on a cross-linked seed latex [22]. The same morphologies have also been made by heterogeneous combinations of two kinds of polymers [23, 24, 25]. Indeed, large composite particles of hollow or porous particles with radii 10–40 μm have been made by the suspension polymerisation of divinylbenzene and styrene in the presence of toluene [26].

Due to the lower density of hollow particles, these particles are used in the paper coating industry to enhance the sheet gloss and print gloss of coated paper [27, 28, 29]. Thermoplastic shell polymers can easily deform during the calendaring process, which leads to an improvement in the micro-smoothness of the sheet. Pigments such as $TiO_2$ are used for architectural coatings to hide the substrate, often in conjunction with extender pigments. Hollow latex particles cause an effective hiding effect due to their light scattering properties [30]. Here, we describe the synthesis of hollow particles with highly porous shells, which appear very much like “nano-golf balls”.

## Experimental

The monomer styrene, ammonium persulphate and sodium chloride were all obtained from Aldrich and used as received. The (polydisperse) polymers were obtained from various sources; low viscosity carboxymethyl cellulose CMC (Fisher), gelatin ($M_w = 100{,}000$; Kodak), poly(vinyl pyrrolidone) PVP ($M_w = 40{,}000$; Aldrich), poly(vinyl alcohol) PVA ($M_w = 14{,}000$; BDH), poly(acrylic acid) ($M_w = 230{,}000$; BDH), starch (Fisher), sodium alginate (Fisher) and $C_{12}E_4$ surfactant (Aldrich) were used as received.

### Synthesis of the latex

A series of polystyrene lattices were prepared by a simple modification to the established surfactant-free polymerisation method [31]. Into a three-necked, round-bottomed flask was placed 670 ml water, 73 g of styrene, 1.62 ml of 10% NaCl solution and a variable amount of the water-soluble polymer. The diameter of the round-bottomed flask is ~20 cm. This mixture was degassed for 1 h at 70 °C with stirring (stirrer blade diameter 45 mm) at speeds of 750 rpm, 1200 rpm and 1600 rpm. Then, 7.5 ml of 10% ammonium persulphate solution was added. After 48 h the resultant latex was filtered through glass wool and, where stated, also through a 10 μm nylon filter paper.

### SEM sample preparation

The samples were air-dried onto 12 mm carbon tabs (Agar Scientific) on 12 mm, Philips-type aluminium stubs (Agar Scientific), and gold sputter coated using an Emscope gold sputter coater. The samples were imaged using a XL-20 Philips Scanning Electron Microscope.

## Results

The preparation of solid particles by the emulsion polymerisation of water-insoluble monomer is well-established in the literature [32, 33, 34]. Recently, attention has focused on core-shell and hollow particles due to the added benefits these characters may introduce. Figure 1a shows SEM pictures from a polymerisation of styrene in water, in the presence of salt and the polymer CMC, and at high stirring speed. Figure 1b shows the result of

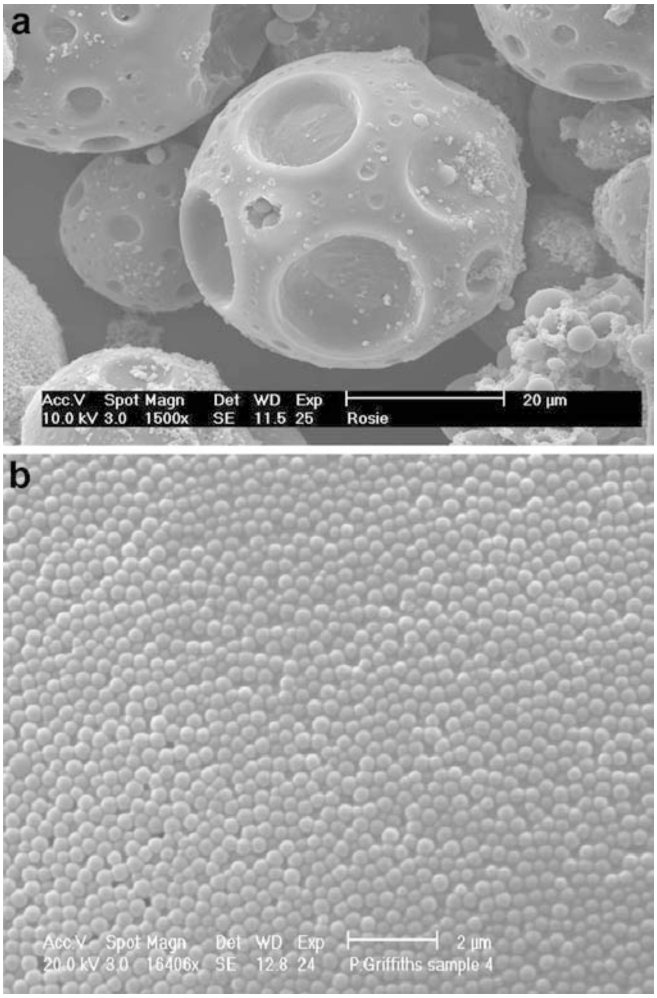

**Fig. 1** Particles resulting from the surfactant-free polymerisation of styrene in aqueous solution containing 1.62 ml of 10% NaCl solution and 2.25 g $L^{-1}$ carboxymethylcellulose (CMC) mixed at various stirring speeds. **a** The hollow, porous particles resulting from a stirring speed of 1600 rpm. Scale bar is 20 μm; the main particle has a diameter of ~40 μm. **b** The monodisperse, homogeneous particles resulting from a stirring speed of 750 rpm. Scale bar is 2 μm; average particle diameter is 250–350 nm

polymerisation at a more normal stirring speed, but otherwise identical conditions. A close inspection of the central particle displayed in Fig. 1a illustrates that these particles are actually hollow.

Figure 2 shows SEM pictures from a polymerisation of styrene in water, in the presence of salt and different quantities of the polymer CMC (Fig. 2b,c), at two different stirring speeds (Fig. 2a,c), and with sodium alginate at a speed of 1600 rpm (Fig. 2d). Clearly, the particles formed at the higher stirring speeds (Figs. 2a,b,c) have a very different morphology to those formed at the stirring speeds usually used in emulsion polymerisation (Fig. 1b). Similar conclusions can be drawn from the sodium alginate experiments. The "squashed" particles in Fig. 2d again illustrate the hollow character of these particles.

At the higher stirring speed, the particle size distribution is certainly bimodal (Figs. 2b,c), and contains, in addition to the homogenous mono-dispersed particles, a significant fraction (>20%) of larger hollow, porous particles.

Therefore, six different polymers have been examined, both those which adsorb strongly onto polystyrene latex surfaces (gelatin, PVP and PAA), those that do not (PVA and starch), and those where a depletion interaction occurs: carboxymethyl cellulose (CMC). The principle experimental variables have been the stirring speed and polymer concentration. Tables 1 and 2 summarise the main conclusions pertaining to the preparation of and the ultimate morphology of the particles.

It may be concluded that there is some critical stirring speed above which these particles are observed, but no

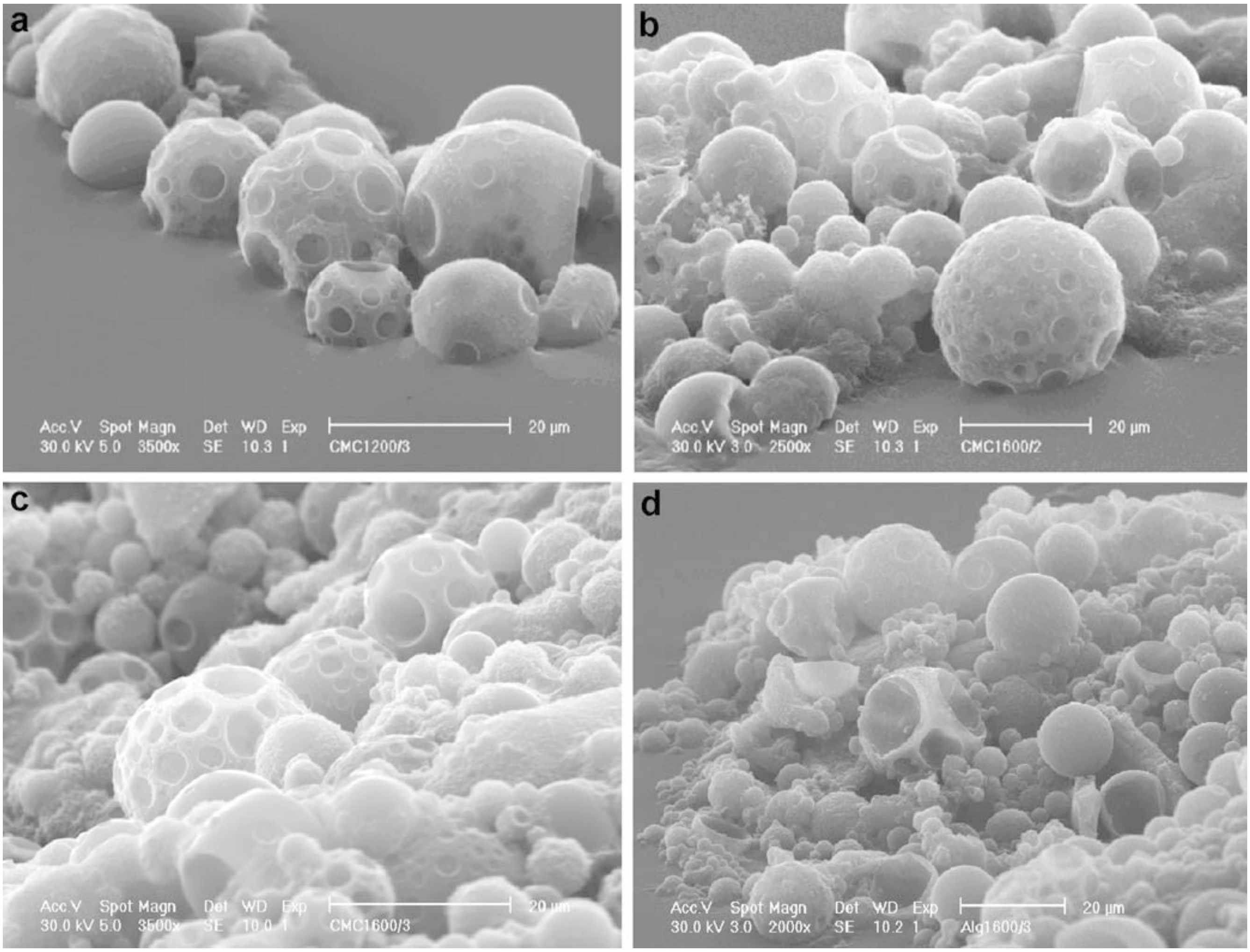

**Fig. 2** The hollow, porous particles resulting from the surfactant-free polymerisation of styrene in aqueous solution containing 1.62 ml of 10% NaCl solution with: **a** 7.4 g $L^{-1}$ sodium carboxymethylcellulose (CMC), mixed at a stirring speed of 1200 rpm (scale bar is 20 µm; the main particle has a diameter of ~20 µm); **b** 4.48 g $L^{-1}$ CMC, mixed at a stirring speed of 1600 rpm (scale bar is 20 µm; the main particle has a diameter of ~25 µm); **c** 7.4 g $L^{-1}$ CMC, mixed at a stirring speed of 1600 rpm (scale bar is 20 µm; the main particle has a diameter of ~20 µm); **d** 7.4 g $L^{-1}$ sodium alginate, mixed at a stirring speed of 1600 rpm (scale bar is 20 µm; the homogeneous particles have an average diameter of ~15 µm)

**Table 1** The effect of stirring speed on particle morphology in the presence of a fixed quantity of carboxymethyl cellulose CMC

| Speed (rpm) | CMC concentration (g $L^{-1}$) | Particle morphology |
|---|---|---|
| 750 | 2.25 | spherical, homogeneous particles ($r = 215$ nm) |
| 1200 | 2.25 | particle size 15–25 µm; pore size 2–10 µm |
| 1600 | 2.25 | particle size 10–30 µm; pore size 0.5–10 µm |

**Table 2** The effect of CMC concentration on particle morphology under conditions of constant shear

| CMC concentration (g $L^{-1}$) | Speed (rpm) | Particle morphology |
|---|---|---|
| 2.25 | 750 | monodispersed homogeneous particles |
| 7.4 | 750 | monodispersed homogeneous particles |
| 2.25 | 1200 | Particle size 15–25 µm; pore size 2–10 µm |
| 4.48 | 1200 | Particle size 5–40 µm; pore size 1.5–11 µm |
| 7.4 | 1200 | Particle size 12–18 µm; pore size 0.2–8 µm |
| 10.45 | 1200 | particle size 15–35 µm; pore size 0.3–15 µm |
| 4.48 | 1600 | particle size 5–20 µm; pore size 0.1–4 µm |
| 7.4 | 1600 | particle size 1–20 µm; pore size 0.5–1 µm |
| 10.45 | 1600 | particle size 8 µm; pore size 0.5–2 µm |
| 30 | 1600 | particle size 10–30 µm; no pores |

relationship of morphology to stirring speed or polymer concentration is obvious.

The nature of the polymer is, however, significant. CMC experiences a depletion interaction with a polystyrene surface. Gelatin [35, 36], PVP and PAA [37] which all adsorb strongly to polystyrene particles, cause flocculation of the dispersion during polymerisation. Starch and PVA [38], which do not adsorb to polystyrene surfaces, only show solid homogeneous small particles. Indeed, repeats of the CMC polymerisation experiments in the presence of a high concentration of the non-ionic surfactant $C_{12}E_4$ (Fig. 3a,b), show only the small spherical homogeneous particles.

## Discussion

The morphology only changes when a non-adsorbing polymer is present at low concentrations. Stirring speed is the most important parameter and therefore it is the interplay between the behaviour of the polymer and the effect this has on the structures present at high stirring speeds that determine the particle morphology.

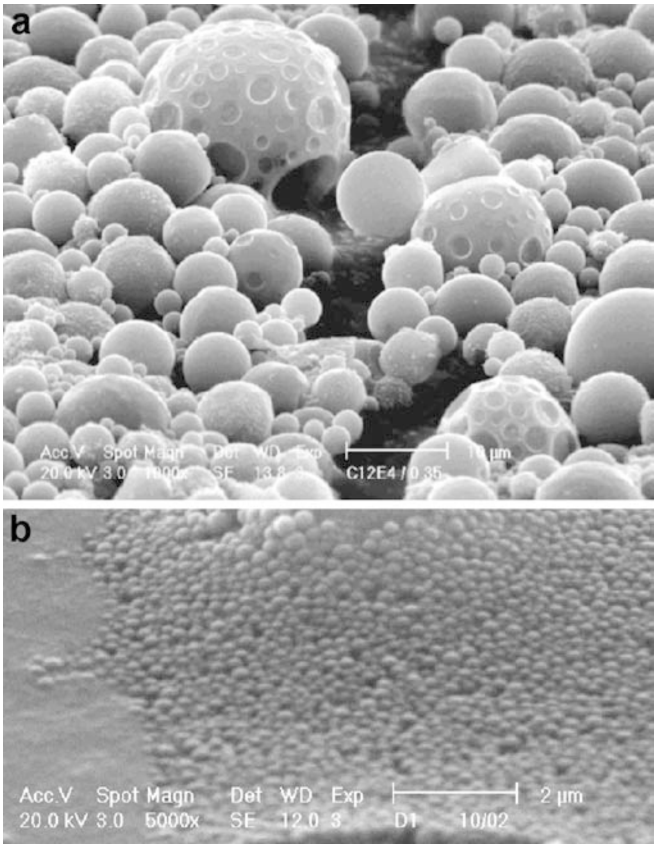

**Fig. 3** The hollow, porous particles resulting from the polymerisation of styrene in aqueous solution containing 1.62 ml of 10% NaCl solution, 7.4 g $L^{-1}$ sodium carboxymethylcellulose (CMC) and various amounts of $C_{12}E_4$, mixed at a stirring speed of 1600 rpm. **a** The hollow, porous particles resulting from using 1 g $L^{-1}$ of $C_{12}E_4$ (scale bar is 10 µm; the largest particle has a diameter of ~20mm); **b** the homogeneous particles resulting from using 3 g $L^{-1}$ of $C_{12}E_4$ (scale bar is 2 µm; the average particle diameter is ~150 nm)

We postulate that under these conditions of high shear, the styrene forms a multiple emulsion – small styrene droplets dispersed in water, which is in turn dispersed into large styrene droplets within the continuous aqueous phase. Accordingly, if the styrene forming the larger droplet is initiated, this will form a "shell", with interfacial tension acting to create the smooth character. However, this is a statistical process and not all of these larger droplets will be initiated; some merely act as a reservoir for the smaller droplets. These small droplets also polymerise, and form the smaller homogeneous particles. This simple picture will lead to a bimodal distribution of particles comprising smaller homogeneous particles enclosed with hollow particles.

The more interesting feature is the porous nature of the outer shell. This may have two origins:

1. A small $N_2$ bubble nucleated at the water/styrene interface due to the high stirring speed, much like the "dimples" reported by Sakau et al. [39], caused by their ultrasonic treatment. The porous character does increase with stirring speed.
2. A combination of a local depletion effect, localised viscosity variations, particle collision rates, and the kinetics of polymerisation.

The CMC flocculates polystyrene latex dispersions via a depletion measurement if present at sufficiently high concentration [40, 41]. Therefore, the CMC will be excluded from the styrene/water interface. The presence of this depletion zone is key, as those polymers that adsorb strongly to the polystyrene surface cause aggregation of the dispersion, while those that do not adsorb result in the same particle morphology as those where no polymer was added.

Further, the salt will reduce the electrostatic screening between the particles as they form, thereby facilitating some coalescence. These particles are a little "sticky", so if smaller polymerising droplet collides with a larger droplet, one can imagine a situation where some of the unpolymerised styrene in the larger droplet "drains" into the smaller one. However, only the styrene that is unreacted can do this, so the wall of the particle locally thins due to monomer loss. If the kinetics of polymerisation are comparable to the characteristic contact time, the result of a collision between a small particle and a large one will be a "footprint" of the smaller particle.

## Conclusions

By incorporating certain water-soluble polymers (carboxymethyl cellulose and sodium alginate) into a polymerising emulsion of styrene, porous hollow particles can be produced in moderate yields (>20%), along with small homogeneous polystyrene particles. A mechanism is proposed is which the coexisting particles arise due to the polymerisation of a multiple emulsion, and that a porous character results due to the impact of smaller particles on the pseudo-liquid surface of the large particles.

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