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Tuning the pore size and surface area of monodisperse Poly(Methyl Acrylate) beads via parallel seeded polymerisation

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Abstract

A library of 36 monodisperse Poly(Methyl Acrylate)(PMA) beads prepared by seeded polymerisation, for potential application in bio-separations and coatings, were synthesized in a high-throughput (HT) manner and analysed with respect to pore size, surface area and morphology. Beads with high porosity were obtained even with a minimum swelling time of 1 h. Both poly(vinyl alcohol) (PVA) and sodium *n*-dodecyl sulfate (SDS) were used as the surfactants to obtain particles with a high roundness index. The surface areas were essentially controlled by the ratio of the seed particles introduced in the system relative to the monomer, but did little to affect the average pore size. Increasing the swelling time from 1 to 48 h did not make any significant change in the particle morphology. High surface areas (84 m^2/g) and pore sizes up to 110 Å could be induced by judicious choice of solvent, while increasing concentrations of so called 'good solvents' increased the surface areas.
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1. Introduction

Combinatorial and high-throughput (HT) chemistry has seen a dramatic increase in application over the past decade. Major steps forward in the field of combinatorial polymer chemistry have been the development of parallel reactors [1], adapting multi-well plates for polymerisations [2], HT formulation optimisation for material discovery [3] as well as combinatorial screening techniques such as micro-array [4], high throughput gel permeation chromatography (GPC) [5], polymer gradients [6] and image analysis [7] to name but a few. However, only a few HT studies have targeted bead synthesis [1–3] although polymer beads have a wide variety of applications including carriers [8] of catalysts [9] and DNA [10], chromatographic separation materials [11] and biological screening devices [12].

Monodisperse or uniform porous particles are of great interest for various applications including chromatographic packing materials [13], ion exchange resins, [14] media for use in protein separation [15] and drug delivery [16]. In many cases, the porosity of the particles determines the efficiency of end use and Fréchet has carried out many studies on the effect of polymeric porogens in the creation of macroporous beads [13].

For many applications, polymeric particles are produced via classical suspension polymerisation [17] and the beads generally possess considerable variations in size.

Other techniques that can be used to produce beads are emulsion [18] and dispersion polymerisation [19], which can yield monodisperse particles less than 1 micrometer and up to 10 μm, respectively.

Various other methods to generate monodisperse particles are known and here, seed-based polymerisation was carried out in which seed particles with a narrow dispersity, obtained from emulsion or dispersion polymerisation were added to an emulsion of monomers, which then polymerise 'within' the seed [20,21]. Despite the often-complex experimental procedure, this technique is widely used to prepare micrometer-sized monodisperse particles. Since the seed particles can be made from relatively cheap monomers
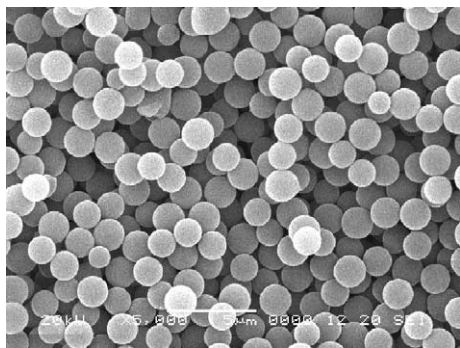
Fig. 1. SEM image of polystyrene seed particles produced by dispersion polymerisation (1.66 μm, SD 0.23 μm).

such as styrene and the shell from virtually any desired functional monomer, this technique is highly attractive, while the presence of a seed considerably reduces the amount of stabiliser required for polymerisation. A number of reports regarding the synthesis of monodisperse poly-(styrene-divinyl benzene) (PS-DVB) particles using this method can be found in the literature, [21–23] although monodisperse particles from other monomers such as methyl methacrylate [24] glycidly methacrylate [25], glycerol monomethacrylate [26] have also been reported.

Various methods of swelling the seed particles in monomer mixtures have been proposed including activated [27] and dynamic swelling [28]. Another technique put forward by Fréchet [29] uses a multiphase emulsion consisting of a monomer, soluble polymer particles (seeds), water and a stabiliser, while a single step swelling

Table 1
Preparation conditions for seed polymerisation of PS-PMA

No	Stabiliser	Monomer:seed		Swelling time	Porogen		Stirrer speed
	Name	w/w[a]	w/w	h	Name	vol/vol[b]	rpm
1	PVP	0.6	15/1	1	T/P	100/10	250
2	PVA	0.6	15/1	1	T/P	100/10	250
3	HPC	0.6	15/1	1	T/P	100/10	250
4	Tween 20	0.6	15/1	1	T/P	100/10	250
5	SDS	0.6	15/1	1	T/P	100/10	250
6	PVA/SDS	0.6/0.25	15/1	1	T/P	100/10	250
7	PVA/SDS	0.6/0.25	0	1	T/P	100/10	250
8	PVA/SDS	0.6/0.25	60/1	1	T/P	100/10	250
9	PVA/SDS	0.6/0.25	30/1	1	T/P	100/10	250
10	PVA/SDS	0.6/0.25	20/1	1	T/P	100/10	250
11	PVA/SDS	0.6/0.25	10/1	1	T/P	100/10	250
12	PVA/SDS	0.6/0.25	15/1	48	T/P	100/10	250
13	PVA/SDS	0.6/0.25	15/1	24	T/P	100/10	250
14	PVA/SDS	0.6/0.25	15/1	10	T/P	100/10	250
15	PVA/SDS	0.6/0.25	15/1	1	T/P	100/10	250
16	PVA/SDS	0.6/0.25	15/1	1	T/P	100/10	450
17	PVA/SDS	0.6/0.25	15/1	1	T/P	100/10	650
18	PVA/SDS	0.6/0.25	15/1	1	–	0	250
19	PVA/SDS	0.6/0.25	15/1	1	Th	100	250
20	PVA/SDS	0.6/0.25	15/1	1	H	100	250
21	PVA/SDS	0.6/0.25	15/1	1	Di	100	250
22	PVA/SDS	0.6/0.25	15/1	1	Dm	100	250
23	PVA/SDS	0.6/0.25	15/1	1	T	100	250
24	PVA/SDS	0.6/0.25	15/1	1	C	100	250
25	PVA/SDS	0.6/0.25	15/1	1	E	100	250
26	PVA/SDS	0.6/0.25	15/1	1	P	100	250
27	PVA/SDS	0.6/0.25	15/1	1	P	100	250
28	PVA/SDS	0.6/0.25	15/1	1	O	100	250
29	PVA/SDS	0.6/0.25	15/1	1	Do	100	250
30	PVA/SDS	0.6/0.25	15/1	1	C	100	250
31	PVA/SDS	0.6/0.25	15/1	1	Te	100	250
32	PVA/SDS	0.6/0.25	15/1	1	Et	100	250
33	PVA/SDS	0.6/0.25	15/1	1	P	50	250
34	PVA/SDS	0.6/0.25	15/1	1	P	100	250
35	PVA/SDS	0.6/0.25	15/1	1	P	200	250
36	PVA/SDS	0.6/0.25	15/1	1	P	400	250

T, Toluene; P, 1-Pentanol; Th, THF; H, Hexane; Di, Dioxane; Dm, DMF; C, Cyclohexanol; E, Etherl; O, Octanol; Do, Dodecanol; Te, Tetraethylene glycol; Et, Ethanol.

[a] Calculated based on the total aqueous phase (100%).
[b] Calculated based on the total monomer+cross-linker (100%).

Table 2
Composition of seed polymerisation phases

Seed dispersion	Organic phase	Aqueous phase
PS seed particles	Methyl acrylate	Water
Water	EGDMA	SDS
PVA	Initiator (BPO), Porogen, Co-solvent (1-Pentanol)	PVA

and polymerisation method was introduced by Ogino [30]. A variety of structured particles have thus been engineered over the past few years including: core-shell [31], microdomain [32] and interpenetrating networks [33], while depending on the type of core material used, encapsulated [34], voided [35] and movable core [36] particles can be produced.

Here, the synthesis of a library of highly cross-linked monodisperse porous polymeric particles, produced by the seeded polymerisation of methyl acrylate (MA) with a very short swelling time is reported, providing a detailed coverage and view of the effect of various factors impinging on the physical characteristics of the porous particles generated.

2. Experimental

2.1. Materials

All reagents were purchased from Sigma-Aldrich unless stated otherwise and used without further purification. Poly(Vinyl Alcohol) (PVA, M_w 9000–10,000, 80% hydrolysed) and Poly(Vinyl Pyrrolidone) (PVP, M_w 10,000) were used as stabilisers.

2.2. Particle characterisation

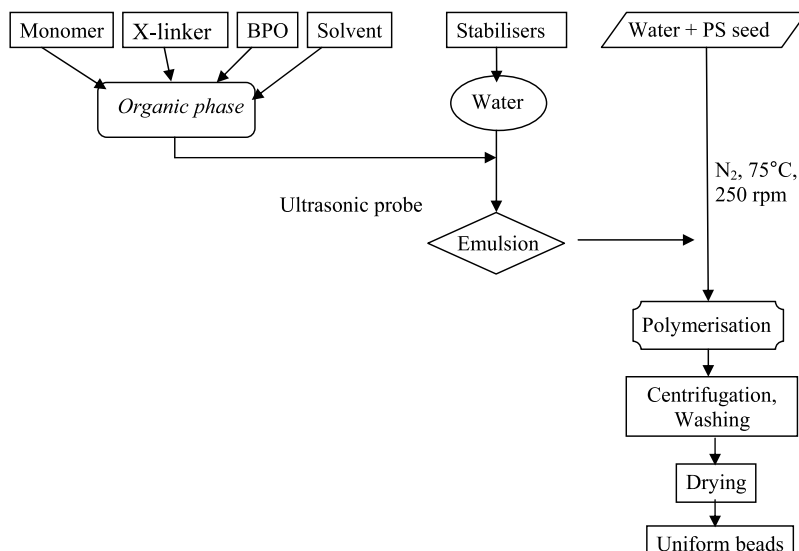Particle size distributions were determined on a Beckman

Coulter LS 230 with the particles suspended in water. Surface areas, pore sizes and pore volumes of the particles were determined by conventional BET analysis (nitrogen adsorption/desorption measurements) using a Quantachrome Nova 3000. SEM images were obtained on a JSM 5910 (Jeol) on samples coated with a thin layer of gold, to a depth of approximately 20 nm, under vacuum.

2.3. Dispersion polymerisation

Polystyrene seed particles were prepared (Fig. 1) by dispersion polymerisation of styrene using well established methods [19]. Briefly, polymerisation was carried out in ethanol (60 mL) initiated with benzoyl peroxide (BPO) (0.1 g, 1% w/w) and poly(vinyl pyrrolidone (PVP) as a stabiliser (0.7 g, 1% w/w) under a nitrogen atmosphere for 15 h at 65 °C. The beads were separated and washed by centrifugation (8000 rpm, 15 min) with water (2×50 mL) followed by methanol (2×50 mL). Purified seed particles were re-dispersed in water containing PVA (0.6%) with a particle content of 0.1 g/mL.

2.4. Seeded polymerisation

The synthesis of monodisperse polymer particles were carried out as previously reported [30]. In a typical experiment, polystyrene seed particles (0.2 g, 6.6% w/w with respect to reactants) were dispersed in water (10 mL) containing PVA (0.6% w/w) and the mixture stirred (250 rpm). A mixture of monomer MA (1.68 g) and cross-linker EGDMA (1.3 g, 25% w/w) containing BPO (0.1 g, 2% w/w) were added to 1-pentanol (0.3 mL) in toluene (3 mL) and allowed to stir until a homogeneous phase was obtained (250–650 rpm). Meanwhile, PVA (0.6% w/w) and SDS (0.25% w/w) were dissolved in water (55 mL) and added to the above mixture and emulsified using an

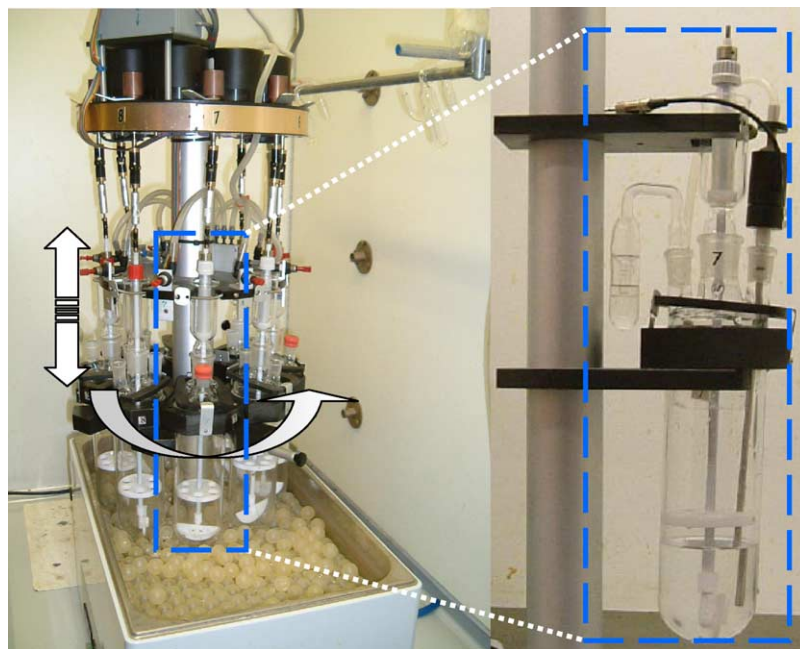Fig. 2. Schematic representation of polymerisation process [30].

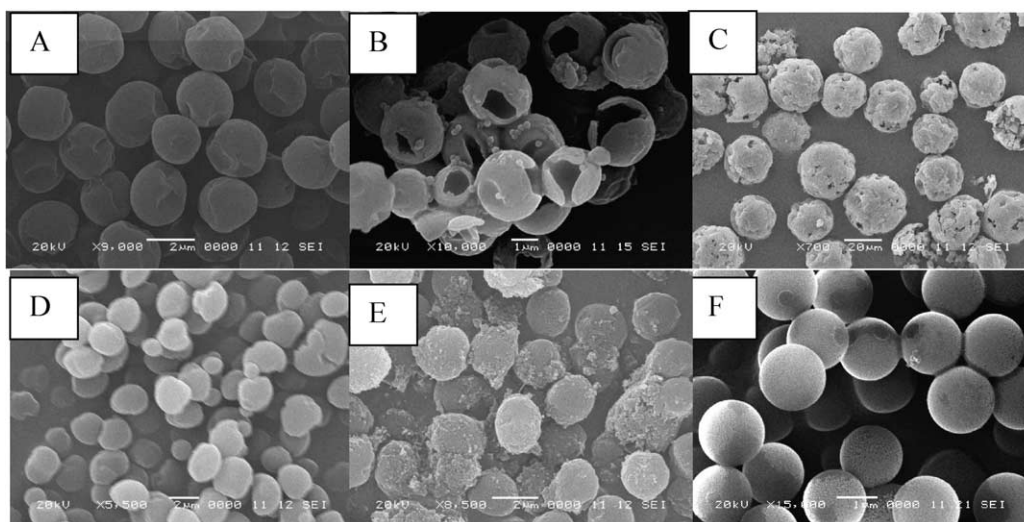Fig. 3. Parallel polymerisation apparatus used for seeded polymerisations.

Fig. 4. SEM images of beads synthesised using various stabilisers: (A) SDS, (B) HPC, (C) PVP, (D) PVA, (E) Tween 20, (F) PVA and SDS.

ultrasonic disrupter. One-third of the emulsion was added drop-wise to a stirred dispersion of the seed particles over 15 min. The second and third portions of the emulsions were added after 1 h intervals in the same manner. The mixture

Table 3
Stabilisers used and resulting diameters of beads obtained

Stabiliser	Diameter (µm)	SD (µm)
PVP	26.9	4.8
PVA	2.2	0.3
HPC	18.8	8.9
TWEEN20	7.0	7.5
SDS	2.2	0.3
PVA/SDS	1.6	0.3

was stirred at room temperature until the emulsified organic phase had been absorbed by the seed particles. The temperature was increased to 70 °C and polymerisation carried out for 15 h at a stirring rate of 250–650 rpm (see Tables 1 and 5). The resulting beads were purified by centrifugation (4000 rpm, 15 min), washed with water (3× 50 mL) and methanol (3×50 mL) and dried in a vacuum oven. Specific experimental conditions are given in Tables 1 and 2. A schematic representation of the process is given in Fig. 2.

Experiments were carried out in a multi parallel polymerisation apparatus (Ventacon®, UK), consisting of eight reaction vessels, each with a capacity of 500 mL and mounted on a rotating column [1]. Each vessel was
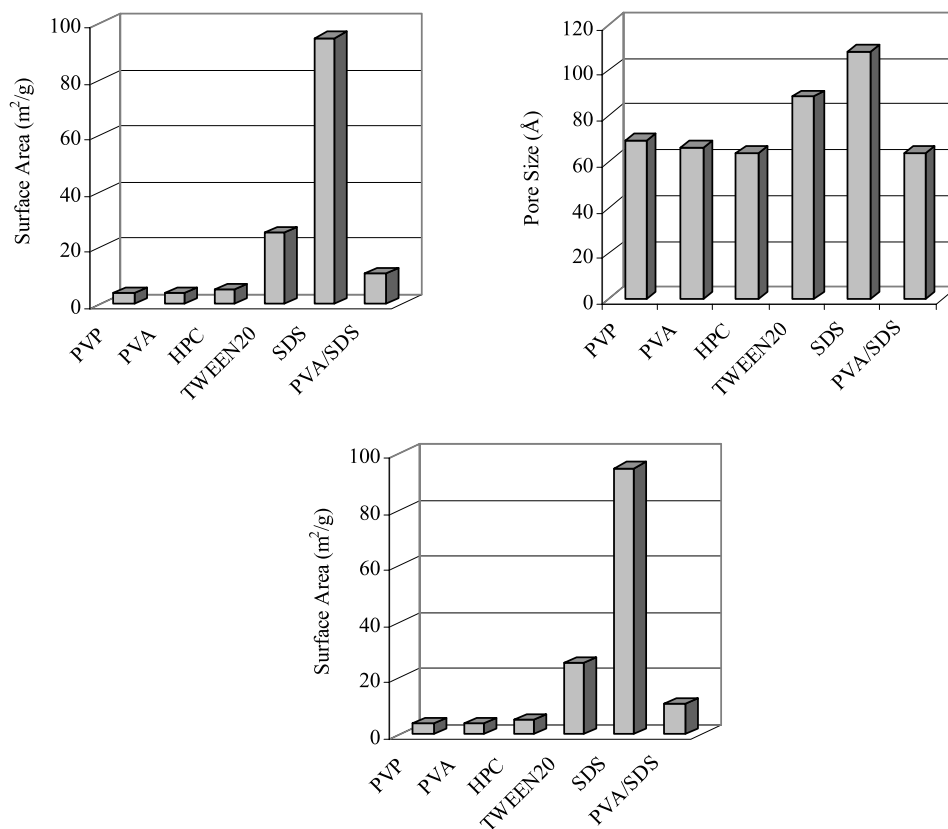
Fig. 5. Surface area, mean pore sizes and pore volume of particles obtained by seed polymerisation using various stabilisers.

individually mechanically agitated by means of an overhead stirrer with an individually controlled stirring speed for each reactor and with all vessels under nitrogen. Half-moon stirrers (diameter 55 mm, height 25 mm) made of poly-(tetrafluoroethylene) (PTFE) were used and were positioned close to the bottom of the vessel. The whole system was mounted to allow all eight vessels to be immersed in a common water-bath simultaneously (Fig. 3).

3. Results and discussion

3.1. Synthesis of monodisperse beads

Libraries of monodisperse particles were synthesised varying the porous structure of the beads while maintaining

Table 4
Size distribution of particles synthesised with varying monomer/seed ratios (see Table 1 entries 7–11)

Monomer/seed ratio	Particle diameter (μm)	SD (μm)
No seed	21	18.4
60/1	5.7	1.1
30/1	5.3	1.5
20/1	4.6	1.7
10/1	6.7	1.4

a high surface area. Ethylene dimethacrylate (EGDMA) was used as the cross-linker due to its structural similarity and comparable reactivity with MA, the cross-linking density was set at 25% in order to obtain good mechanical properties.

3.2. Effect of stabiliser

The effect of the type of stabiliser (PVP, PVA, Hydoxy-propyl cellulose (HPC), Tween 20, SDS and SDS/PVA mixtures) on particle formation was investigated (Table 1, entry 1–6), (Table 3). The morphology of the materials produced were found to be dramatically affected by the nature of the surfactants (Fig. 4), with beads synthesised with PVP being much larger and having a broader size distribution than with other stabilisers; while beads synthesised using HPC had a hollow structure (see Fig. 4(B)).

It was observed that particles synthesised using SDS had a high surface area/average pore size compared to the polymeric surfactants (Fig. 5), while combinations of PVA and the ionic surfactant SDS proved to be the most efficient in giving spherical particles with a narrow size distribution and hence was used in all further studies.

3.3. Controlling the surface area and pore size

3.3.1. Monomer: seed ratio

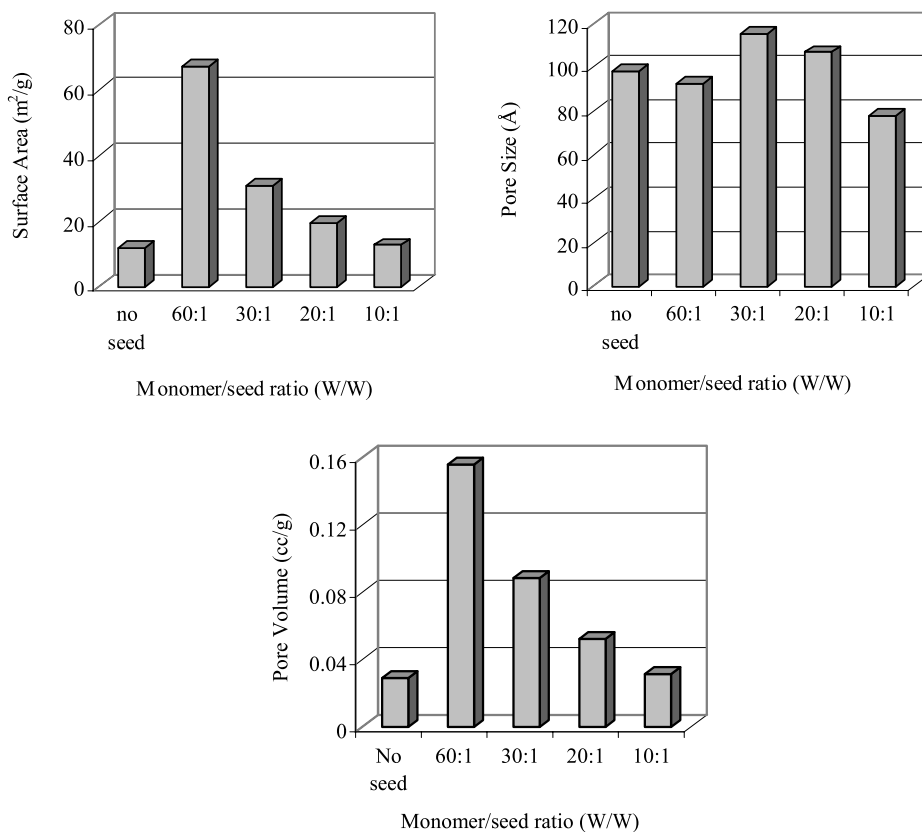Varying the monomer/seed ratio allowed the surface area

Fig. 6. Surface area, mean pore size and pore volume of particles synthesised when varying the monomer/seed ratio.

to be tuned (Table 1, entry 7–11), with high surface areas observed when the seed levels were low (Fig. 6) (the pore volume also found to follow this trend), while the average pore size was found to be in the mesoporous region (20–500 Å) although no specific correlations were observed.

Increasing the ratio of seed particles to monomer did not increase the average pore sizes, however, since the seed acts as a template during polymerisation, no seed resulted in polydisperse particles but little variation was observed in going from a seed ratio of 10/1 to 60/1 (Table 4).

3.3.2. Effect of swelling time and rate of agitation

The seed particles were allowed to swell with the monomer/solvent mixture for 1–48 h keeping the mono-mer/seed ratio fixed at 15/1 (Table 1, entry 12–15).

Monodisperse particles of 2 μm were obtained with no significant difference in properties (Table 5).

Although it was expected that the rate of agitation would have an influence on the size of the beads produced, however, this was ruled out as consistent particle sizes were obtained with varying degrees of shear (Table 1, entry 15–17). The rate of agitation did not have any significant influence on the particle characteristics such as surface area (Table 5).

3.3.3. Role of porogens in inducing high surface area and pore size

As the medium of transportation of the monomer droplets into the seed particles and the means of polymer solubilization, solvents play a key role in determining bead

Table 5
Size distribution, surface areas, pore sizes and pore volumes of particles synthesised with various swell times

Swelling time (h)	Stirring rate (rpm)	Diameter (μm)	SD (μm)	Surface area (m²/g)[a]	Pore size (Å)[a]	Pore volume (cc/g)[a]
48	250	2.27	0.17	9.2	68	0.016
24	250	2.24	0.26	10.5	64	0.017
10	250	2.26	0.26	9.3	63	0.015
1	250	2.14	0.23	4.45	73	0.008
1	450	2.32	0.15	7.91	60	0.012
1	650	2.35	0.31	13.6	51	0.017

[a] Determined by BET.

Table 6
Particle size distribution, surface area, pore size and pore volume of beads synthesised by seed polymerisation with varying porogen

Solvent[a]	Diameter (μm)	SD (μm)	Surface area (m²/g)	Pore size (Å)	Pore volume (cc/g)
None	2.16	0.26	–	69	0.002
THF	2.45	0.64	–	235	0.003
Hexane	2.23	0.28	–	96	0.002
Dioxane	2.12	0.27	–	648	0.002
DMF	2.18	0.28	–	69	0.002
Toluene	2.14	0.23	4.6	73	0.008
Cyclohexane	2.18	0.27	8.5	169	0.036
Et2O	2.08	0.27	10.4	127	0.033
1-Pentanol	2.73	0.92	84.5	81	0.171

[a] All the solvents were added 100% with respect to the reactants.

Table 7
Solubility parameters of various solvents used and polymers

Solvent	$\delta_{solvent}$ (MPa$^{1/2}$)	$\delta_{solvent} - \delta_{PMA}$
Cyclohexane	16.8	3.65
Cyclohexanol	23.3	−2.85
Dioxane	16.2	4.25
DMF	24.8	−4.35
Dodecanol	20.5	−0.05
Ether	15.1	5.35
Ethanol	26	−5.55
Hexane	14.9	5.55
Pentanol	21.7	−1.25
Octanol	21.1	−0.65
TEG[a]	20.3	0.15
THF	18.6	1.85
Toluene	18.2	2.25
MA	18.2	2.25
St	19	1.45
PMA	20.45	
PS	17.8	

[a] TEG-Tetra ethylene glycol.

morphology. A range of solvents were therefore selected, using a fixed monomer/seed ratio of 15/1 (Table 1, entry 18–32; Table 6). Monodisperse particles with pore size as high as 81 Å and with a surface area of 84 m²/g were obtained when 1-pentanol was used as the solvent (Figs. 7 and 8) (although similar pore sizes and surface area were achieved earlier (Fig. 6) the particles were not entirely spherical). Monodisperse particles were obtained with other solvents, but their surface area did not exceed 10 m²/g suggesting that 1-pentanol plays a crucial role in phase separation, thus creating the highly porous beads.

Generally, the seed particles were dispersed in water before the addition of the monomer-solvent mixture. If the porogen used solvates the polystyrene (PS) seeds, then the resulting particles would be a homogeneous mixture of polystyrene and PMA. However, if polymerisation takes place in a poorly solvated seed, the resulting particle may have a diffused core-shell structure due to the limited penetration of the monomers into PS matrix.

Pore formation is very complex due to the presence of multiple variables in the polymerising system. Solubility parameters of the various components are important factors in determining miscibility and phase separation that might takes place during pore formation, with solubility of the seed, the second monomer and polymer all being important. Generally two components are considered to be 'incompatible' when the difference between the solubility parameter is greater than 1.7 MPa$^{1/2}$ [37]. In the case of polymers, good solvents are those for which the solubility parameter is close to that of the polymer and as such a good solvent will enable a late phase separation, which leads to the formation of beads with a high surface area. This occurs as result of a large number
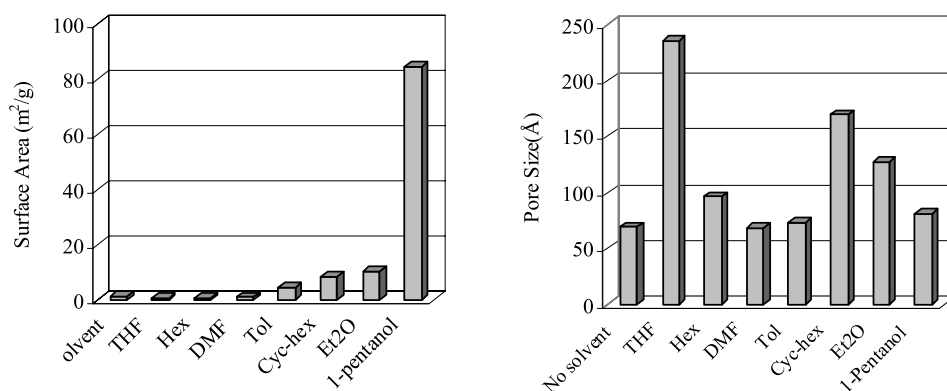

Fig. 7. Surface area and mean pore size of particles synthesised by varying solvents. The pore size was greatly influenced by the choice of solvent.
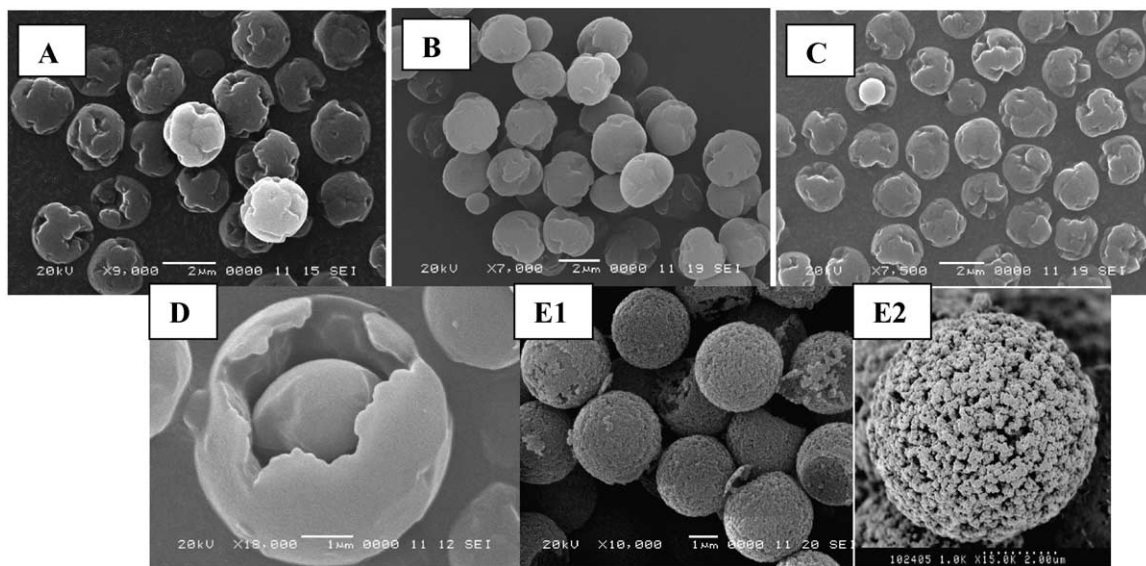
Fig. 8. SEM images of beads synthesised using (A) dioxane, (B) hexane, (C) DMF, (D) core shell particle from toluene and (E1, E2) 1-pentanol.

of small globules created during the phase separation which leads to the formation of pores of up to 100 Å [13]. In the case of the seeded polymerisation of MA, due to the solubility parameters of the porogen, phase separation would be expected to occur at different stages of the polymerisation. However, apart from the porogen, the polymerising monomer, MA, (Fig. 9) also needs to be considered as methyl acrylate is not a great solvent for PMA (Table 7) [38] and hence any unreacted monomer willt1
 also compete with the good solvent in phase separating the polymer (3 component system of porogen, MA and PMA).

From Table 7, it is apparent that higher alcohols with limited solubility in water can act as good solvents for the polymer allowing late phase separation. From the various experiments conducted so far, it was observed that 1-pentanol, which is a good solvent for PMA, has a major role in determining the porosity of the beads. Other alcohols
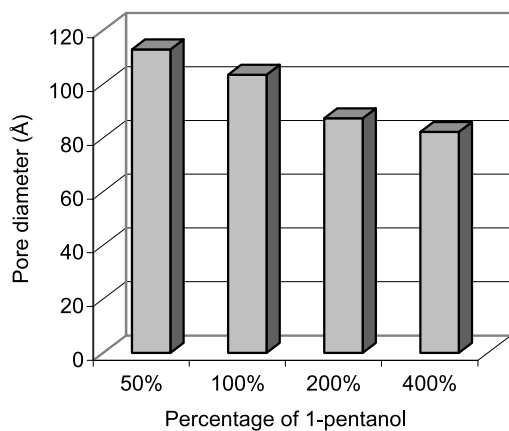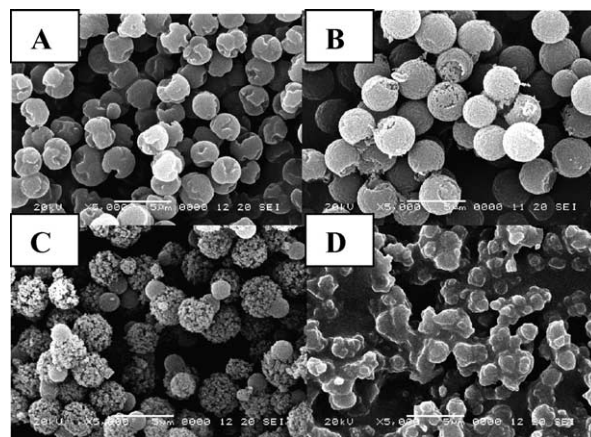

Fig. 10. SEM images of beads with (A) 50%, (B) 100%, (C) 200% and (C) 400% of 1-pentanol.

investigated gave higher pore sizes, with out any improvement in surface area (Table 8).

3.3.4. Effect of the amount of 1-pentanol on pore size

The level of 1-pentanol was varied from 50 to 400% (v/v with respect to the monomer) in the reaction mixture (Table 1, entry 33–36). As expected, the highest surface areas were observed for the sample which had the largest volume of

Fig. 9. Variation in the average pore size with increasing amount of 1-pentanol.

Table 8
Surface area, pore size and pore volume of particles synthesised with various alcohols

Solvent	Surface area (m^2/g)	Pore size (Å)	Pore volume (cc/g)
1-Pentanol	84.5	81.0	0.171
Octanol	14.9	117.6	0.044
Dodecanol	6.1	87.5	0.013
Cyclohexanol	3.7	137.3	0.013

porogen, while the mean pore size decreased with increasing porogen levels (Fig. 9), although the quality of the beads deteriorated with increasing levels of porogen (Fig. 10).

4. Conclusion

The solvents and choice of surfactants employed in the polymerisation process have proven to play an important role in determining the structural and physical properties of the beads synthesised in the two stage templated polymerisation described here. The combination of a polymeric and an ionic surfactant gave spherical particles, even with high-levels of cross-linking. In the case of PS(seed)-PMA(shell), it was found that beads synthesised using 1-pentanol as the porogen displayed a very high surface area compared to all other solvents, while, increasing the porogen quantity decreased the average pore size.

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