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Comparison of the effect of pore architecture and bead size on the extent of plasmachemical amine functionalisation of poly(styrene-*co*-divinylbenzene) permanently porous resins

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Abstract

Poly(styrene-*co*-divinylbenzene) (PS/DVB) permanently porous resins suitable for plasmachemical modification with allylamine were prepared by suspension polymerisation. Experimental design methods were employed to investigate simultaneously the influence of crosslinker content, porogen type and porogen level on the surface area, pore volume and pore diameter of the resins. From this, it was found that the porogen has a greater influence than the crosslinker. Variation of porogen type and level while keeping crosslinker level constant then lead to the maximisation of each parameter of interest, resulting in a set of samples with a wide range of values. Six samples were then chosen, representing high and low values of each property, and were subjected to plasmachemical modification with allylamine. It was found that pore volume had the greatest influence on the extent of modification. However, subsequent experiments indicated that the extent of modification is much greater for smaller beads. It is concluded that plasmachemical functionalisation occurs mainly on the external surface of the beads.

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1. Introduction

Permanently porous[1] polystyrene-*co*-divinylbenzene (PS/DVB) resins were invented in the 1950s and are widely used as ion-exchangers, polymeric absorbents, chromatographic separation media and as solid supports for organic synthesis [1]. They are now a well-known alternative to gel-type supports for a variety of applications, and in particular for solid-phase chemistry, in which their advantages have been confirmed by a number of groups [2]. Various applications of polymer supports in organic synthesis require careful design and control of the porous structure of the support [3]. Polymer beads with fixed pores can be obtained by suspension polymerisation, which is particularly suited to the production of large spherical beads typically in the range 5–1000 μm [4].

By careful choice of porogen (and crosslinker type/concentration), a wide range of porosities can be produced (according to IUPAC definition [5]—micropores: <20 Å; mesopores: between 20 and 500 Å; macropores: >500 Å). The conditions for obtaining a permanently porous structure have been reviewed in great detail [3]. It has been established that the porosity and surface area of the beads are strongly influenced by the polymer synthesis conditions, including porogen composition, porogen concentration (degree of dilution), crosslinking degree and reaction temperature [6,7]. A high concentration of crosslinker is necessary to produce permanent porosity with a high surface area; materials prepared with insufficient crosslinker, even in the presence of a porogenic solvent, are essentially non-porous [3].

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[1] The term ‘macroporous’ is avoided as it implies pores of >50 nm in diameter.

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There is a demand for improved higher loading solid-supported reagents and scavengers with easily accessible reactive sites, for use in organic synthesis applications. One method of potential use to introduce surface functionality to permanently porous resins is plasmachemical modification [8]. Plasmas are often divided into three groups: plasmas in thermodynamic equilibrium; plasmas in local equilibrium; and non-equilibrium, or so-called cold, plasmas. In the latter type, which normally are produced in low-pressure discharges, the electron temperatures (10^4–10^5 K) are much higher than those of the heavy particles (the overall temperature of the gas can be as low as room temperature). Thermodynamic equilibrium is not reached even at a local scale; and physical interactions and chemical reactions can be initiated at relatively low temperatures within these non-equilibrium plasmas.

In the present work, porous PS/DVB beads with no functional groups were treated with an allylamine cold plasma, to load the surface with amine groups. Using a small set of commercial resins, it was found previously that both the pore architecture of the bead and bead size were important in determining the extent of functionalisation [9]. However, with that limited sample set it was not possible to separate the relative contributions of each characteristic to the extent of functionalisation. Further work [10] confirmed a strong influence of bead size, but this involved only one resin so the influence of pore architecture was not obvious. Therefore, it was decided to prepare a set of PS/DVB resins in which features such as the surface area, pore diameter and pore volume were varied in a well-defined manner.

Several studies on the effect of concentration and type of porogen, used at different levels of crosslinker, on the physical properties (mainly surface area) of porous beads have been performed with PS/DVB resins [11,12]. It is found that a good thermodynamic solvent for the growing polymer network leads to a greater proportion of micropores and thus higher surface areas. However, to our knowledge a complete study on the effects of synthesis conditions, simultaneously, on the surface area, pore volume and pore diameter of permanently porous resins has not been conducted. Furthermore, all of the previous studies deal with relatively low levels of DVB, whereas our work involves resins of 72% nominal crosslink density. The first objective of the research therefore was to define synthesis conditions (crosslinker content, porogen type and porogen content) that control the parameters of interest, namely surface area, pore diameter and pore volume. In order to maximise the information provided from the minimum number of experiments, multivariate analysis was used. The results from this were then used, in an iterative process, to maximise independently each variable, leading to a set of well-defined materials. Appropriate samples from this set were then treated with an allylamine plasma and the extent of modification quantified by elemental analysis and chemical methods (Fmoc number determination). Thus, the influence of pore architecture on surface modification by plasmachemical means was studied. Furthermore, simple fractionation of a sample by sieving allowed the investigation of bead size on extent of modification.

2. Experimental

2.1. Materials

Divinylbenzene (80% tech. grade, Aldrich) and styrene (Aldrich) were freed of inhibitor by washing with 1% aqueous sodium hydroxide (Aldrich) solution, followed by several washes with deionised water. Toluene (Fisher Scientific), heptane (Aldrich), dodecane (Aldrich), 2,2′-azo-bisisobutyronitrile (AIBN, BDH), poly(vinyl alcohol) (M_w 85,000–146,000, 87–89% hydrolysed, Aldrich), sodium chloride (Avocado) and all other solvents were used as received.

2.2. Instrumentation

The porosity and surface area of the products were determined by nitrogen adsorption/desorption analysis and mercury porosimetry. The instrument utilised for nitrogen sorption analysis was a Micromeritics TriStar 3000 Surface Area and Porosimetry Analyser. Prior to each experiment, the samples (~0.2 g) were degassed at 50 °C for 12 h. The specific surface area of the dry resins was determined using the nitrogen sorption BET technique [13] and the pore size distribution was determined by the BJH model [14]. Mercury porosimetry was carried out using a Micromeritics AutoPore III 9420 instrument. Elemental CHN analysis was performed with a CE440 elemental analyser (Exeter Analytical Inc).

2.3. Suspension polymerisation

The porogen concentration is expressed as a percentage of the total volume of the monomers and the aqueous/organic phase ratio was kept constant (4:1). In a typical experiment, styrene (5 ml, 43 mmol, 12 mol% of total monomer content) and divinylbenzene (45 ml, 253 mmol actual DVB, remainder 62 mmol ethylstyrene, 71 mol% actual DVB) were mixed thoroughly with porogen (50 ml) and AIBN (0.5 g, 3.0 mmol, 0.8 mol% relative to total monomer content). The stabiliser, comprising PVA (2 g) and sodium chloride (2 g, 34 mmol), was dissolved in water (400 ml) before being transferred to a 500 ml suspension polymerisation reactor (with four baffles on the walls of the reactor and a metal stirrer with two propeller-type blades). The mixture of monomers, heptane and AIBN was then added rapidly to the aqueous phase at a stirring speed of 800 rpm. Thereafter, the reaction vessel was flushed with nitrogen gas for 10 min and the water bath temperature raised to 80 °C and maintained for a period of 6 h. After 6 h, the beads were collected by suction filtration and washed with hot distilled water. The beads were then transferred to a Soxhlet thimble and extracted with water then acetone for 24 h each. After this, the beads were allowed to air-dry at room temperature before being further dried at 50 °C under vacuum to constant mass. Fractions of different particle sizes of each batch were collected by sieving via six Endecotts' test sieves of different aperture sizes (20–300 μm) with the aid of a sieve shaker (Endecotts' Minor Sieve Shaker).

2.4. Experimental design

Experimental design was employed to plan a series of experiments for the preparation of porous PS/DVB beads, to determine which conditions affect the surface area, pore volume or pore diameter of the resins. The experiments were set up as a 2^3 factorial design. The three experimental variables investigated were as follows:

1. difference in solubility parameter of PS/DVB and porogen ($\Delta\delta$) (x_1)
2. amount of porogen (x_2)
3. divinylbenzene concentration (x_3)

The 'high' and 'low' levels of each parameter used for the experiments are shown in Table 1. Eight batches of polystyrene beads were prepared under different conditions, representing the experimental set-up for a 2^3 factorial design (Table 2). The surface area, pore volume and pore diameter for each resin were measured by nitrogen sorption and mercury porosimetry.

As seen from the results reported in Table 3, the porogen has a critical effect on the porous properties of the resulting beads. The specific surface areas are quite large when the mixture of toluene and heptane (1:1) is used as the porogen (480–544 m^2/g) whereas lower surface areas result when using heptane (366–499 m^2/g). The opposite is found with the pore volume and pore diameter where toluene/heptane produces smaller pore volumes and diameters (0.53–0.83 ml/g, 48–82 Å respectively), and with heptane larger pore volumes and diameters (0.68–0.94 ml/g, 81–112 Å, respectively).

The surface area, pore volume and pore diameter results are employed as the response variables for the multivariate data analysis (Table 3). The regression coefficients of the experimental variables were calculated by means of multiple linear regression using MATLAB 5.3. Regression analysis of the experimental data is shown in Figs. 1–3.

Table 1
'High' and 'low' levels used for making porous polystyrene beads

Experimental variable[a]	'Low' level (−)	'High' level (+)
x_1[b]	1.35 MPa$^{1/2}$	2.9 MPa$^{1/2}$
x_2	67 vol%	100 vol%
x_3	49 mol%	72 mol%

[a] See text for definitions.

[b] See Table 4 for δ values of solvents and PS/DVB.

Table 2
Compositions of experiments for 2^3 factorial design (0.8 mol% AIBN, PVA as stabiliser at 80 °C for 5 h and 800 rpm stirring speed)

Experiment	$\Delta\delta$ (MPa)$^{1/2}$ (x_1)	Amount of porogen (%vol) (x_2)	DVB concentration (%mol) (x_3)
1	1.35	67	49
2	2.9	67	49
3	1.35	100	49
4	2.9	100	49
5	1.35	67	72
6	2.9	67	72
7	1.35	100	72
8	2.9	100	72

From Fig. 1, it is seen that the experimental variable of x_3 (DVB concentration) has a positive regression coefficient when the response variable is surface area. This infers that employing higher DVB concentrations (72% mol) will increase the surface area of the bead. Meanwhile, the other two experimental variables x_1 (solubility parameter difference, $\Delta\delta$) and x_2 (amount of porogen) reveal negative regression coefficients on the surface area of the beads, with the effect of $\Delta\delta$ being stronger. These results suggest that the surface area will be enhanced if toluene/heptane (1:1) at 67% dilution with 72% mol DVB are employed as synthesis conditions (i.e., from Table 3, resin 5–544 m^2/g). The polynomial from which the regression coefficients are obtained is

$$y = 467.6 - 41.6x_1 - 13.6x_2 + 20.1x_3 \qquad (1)$$

Fig. 2 indicates that all three experimental variables produced positive regression coefficients with pore volume as the response, however the effect of DVB concentration (x_3) is small. Pore volume is thus enhanced if heptane at 100% dilution is used as the porogen to prepare the beads, together with a crosslinker content of 72% mol (i.e., from Table 3, resin 8–0.94 ml/g). The effect of degree of dilution is highly significant on the pore volume. The polynomial

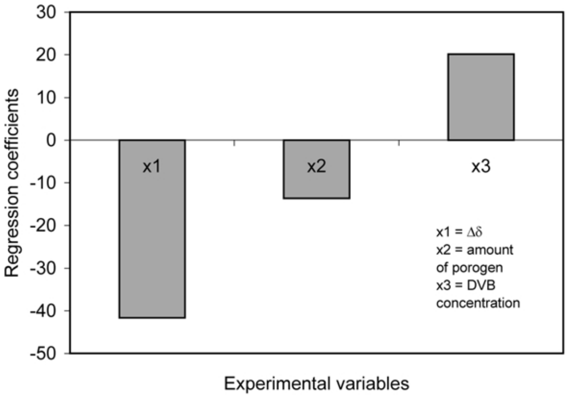


Fig. 1. Multivariate analysis regression coefficients of poly(styrene/DVB) beads using surface area as the response.

Table 3
Surface area and porosity results for multivariate analysis experiments

Experiment	BET surface area[a] (m^2/g)	BJH pore volume[a] (ml/g)	BJH pore diameter[a] (Å)	Pore size range[b] (Å)
1	517	0.53	59	20–5,000
2	366	0.68	97	20–10,000
3	497	0.83	83	20–20,000
4	411	0.92	112	20–50,000
5	544	0.53	48	20–300
6	499	0.74	81	20–20,000
7	480	0.79	71	20–500
8	429	0.94	110	20–20,000

[a] Determined by N_2 adsorption analysis.
[b] Determined by a combination of N_2 adsorption analysis and Hg porosimetry.

from which the regression coefficients are obtained is

$$y = 0.7441 + 0.0751x_1 + 0.1254x_2 + 0.0028x_3 \tag{2}$$

From Fig. 3, it can be observed that the experimental variables of x_1 ($\Delta\delta$) and x_2 (amount of porogen) have positive regression coefficients and x_3 (DVB concentration) has a small negative regression coefficient. The interpretation here is that the pore diameter will be enhanced if heptane at 100% dilution with 49% mol DVB are employed (i.e., from Table 3, resin 4–112 Å). The polynomial from which the regression coefficients are obtained is

$$y = 82.6 + 17.4x_1 + 11.4x_2 - 5.1x_3 \tag{3}$$

2.5. Plasmachemical functionalisation

Plasmachemical modification with allylamine was performed on a 250 mg scale, in a rotating glass reactor at 0.4 mbar pressure with a continuous wave plasma ignited at 20 W for 20 min. Detailed experimental procedures are given elsewhere [9].

2.6. Reactive amine loading determination by Fmoc number

Quantification of the number of accessible amine groups introduced by plasmachemical functionalisation was achieved by measuring the Fmoc loading [15], Scheme 1. This entailed washing the treated beads (~30 mg) in fritted tubes with methanol (10 × 2 ml), and then diethyl ether (2 × 2 ml) in order to remove any loosely bound material. 2 ml of a solution of 9-fluorenylmethyl chloroformate (Fmoc-Cl) dissolved in THF (10 equiv.) was added to each tube with diisopropylethylamine (DIPEA). These tubes were then placed onto an orbital shaker (Vibrax VXR) for one hour, allowing the Fmoc-Cl coupling reaction to proceed to completion. Excess solvent was removed by pumping on a vacuum block, and the remaining material was washed successively with methanol (10 × 2 ml) and diethyl ether (2 × 2 ml). Finally, the samples were dried under vacuum.

Deprotection of the Fmoc-amine groups involved weighing 10 mg of each dried polymer sample into individual 5 ml volumetric flasks, followed by the addition of 200 μl of a 20% piperidine/*N*,*N*-dimethylformamide (DMF) solution, and allowing the samples to stand for 30 min. Each solution was diluted with methanol to make a total of 5 ml, and the absorbance at 300 nm associated with the piperidine adduct deprotection product was measured using a UV/VIS spectrometer (Unicam) in conjunction with a reference solution consisting of 0.8% (v/v) of 20% piperidine/DMF in methanol. The Fmoc loading for each sample was calculated using the Beer–Lambert law.

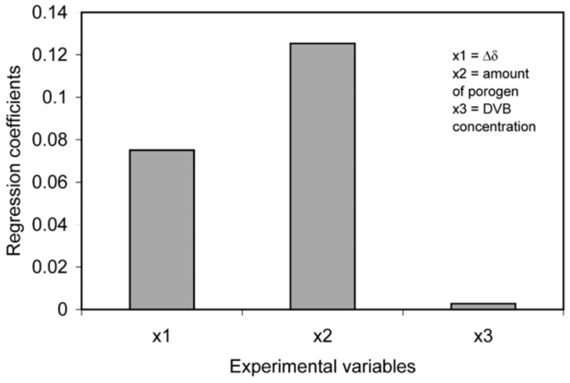


Fig. 2. Multivariate analysis regression coefficients of poly(styrene/DVB) beads using pore volume as the response.

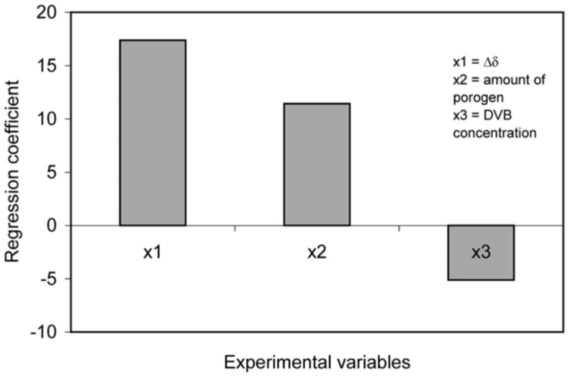
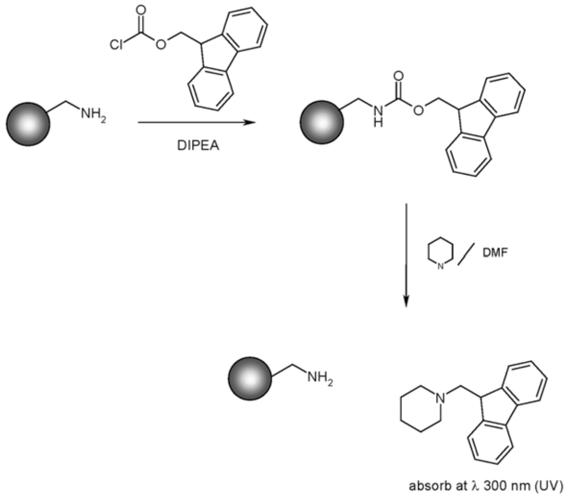


Fig. 3. Multivariate analysis regression coefficients of poly(styrene/DVB) beads using pore diameter as the response.



Scheme 1. Derivatisation of amine groups on plasmachemical-functionalised polymer beads with 9-fluorenylmethyl chloroformate (Fmoc-Cl), followed by deprotection to obtain the piperidine adduct.

2.7. Raman imaging microscopy

The procedures for sample preparation, coupling with 4-cyanobenzoic acid, Raman imaging and data processing have been described in detail elsewhere [10].

3. Results and discussion

The type of porogen and the degree of dilution used to prepare permanently porous resins have a critical effect on the porous properties of the resulting materials, although it is believed that the total pore volume is controlled largely by the amount of porogen employed and is less influenced by the nature of the porogen [3]. The porogens employed in suspension polymerisation for the production of porous copolymers can be classified into three types: solvating, nonsolvating and linear polymers or mixtures thereof, which will generate different profiles of pore size distributions [7].

During polymerisation, phase separation between the porogen and the growing polymer network takes place [3]. When a porogen with an affinity for the polymer is used (e.g., toluene/heptane), the polymer network remains fully solvated up to high conversion of monomers into polymer. When phase separation finally occurs the resulting microgel particles are small and contain only a small amount of residual monomer and crosslinker. The separate porogen phase now will contain a lower concentration of unreacted monomer and crosslinker. Further polymerisation in the porogen phase creates a small amount of additional polymer, which acts to fuse microgel particles. The microgel particles, therefore, tend to retain their individual identity and the network of micro- and mesopores, generated between the microgel particles when first formed, is essentially retained. Such resins therefore have large surface areas. On the other hand, when a precipitating porogen is used (e.g., heptane), the phase separation occurs at low conversion. Microgel particles, now swollen with a high concentration of monomer and crosslinker, are formed and the separate porogen phase contains significant levels of monomer and crosslinker. A great deal more copolymer is therefore formed after the phase separation process in both the porogen and the droplet/particle phases, which has the effect not only of fusing the microgel particles but also of causing significant in-filling of small pores between these. In an extreme case, the individual particles can lose their identity and form aggregates producing a labyrinth mainly of macropores. Such resins are formed with a low surface area and a pore size distribution broadened towards the macropore region.

The effect of a porogen can be explained in terms of its solubility parameter, δ [16] (Table 4). The lower the difference between the solubility parameters of the resin and the porogen, the higher the affinity between these two species [11]. The solubility parameters for styrene-DVB copolymers [16] range from 17 to 18.6 $\mathrm{MPa}^{1/2}$. In a relatively recent study, Errede found that δ for PS/DVB resins increased with crosslink density to a value of 17.8 $\mathrm{MPa}^{1/2}$ for a 20% crosslinked resin [17]. Consequently, we have assumed a value of 18 $\mathrm{MPa}^{1/2}$ for our more highly crosslinked resins. From the data in Table 4 it can be said that the affinity between the polymer network and the diluents increases if the solvent is changed from heptane to the toluene/heptane mixture.

The results of the regression analysis indicate that porogen type and content in general have a greater effect on the response factors than DVB concentration, and that a higher DVB content leads to an increase of two of these parameters (surface area and pore volume). Therefore, it was decided to investigate further the influence of porogen type and concentration on the response factors, keeping crosslinker content constant at 72%. This allowed the maximisation of the surface area, pore diameter and pore volume for the resins. Conditions were also varied to obtain a series of resins with lower values of each of the response factors, in order to produce a wide spread of values. Ordering the resins by increasing value of each response factor (see Fig. 4 for surface area as an example) allowed the choice of resins for plasmachemical modification. From each response factor, two samples were chosen—one high and one low value for the parameter under consideration. In order to avoid samples with extreme values, only those within the limits of 33 and 66 percent of the maximum value

Table 4
Solubility parameters of different porogens [16] and PS-DVB

Porogen	Solubility parameter/($\mathrm{MPa}^{1/2}$)
Heptane	15.1
Toluene/heptane (1:1)	16.65
Poly(styrene/DVB)	18[a]

[a] See text for origin of this value.

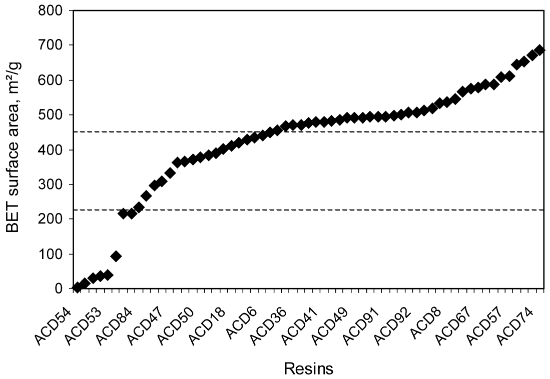


Fig. 4. Resins listed in order of increasing surface area. The dotted lines represent 33 and 66% of the maximum value.

Table 6
Extent of plasmachemical modification for the investigated samples

Resin	Nitrogen loading (mmol/g)	Fmoc loading (mmol/g)
ACD84	0.94	0.05
ACD68	1.68	0.07
ACD37	1.03	0.04
ACD48	1.23	0.04
ACD29	1.16	0.04
ACD47	1.01	0.04

were considered. Table 5 shows the ‘low-value’ and ‘high-value’ resins chosen for each of the three categories, together with their preparation parameters and properties. It should be pointed out that the ‘low’ and ‘high’ resins were chosen in order to obtain, as much as possible, a variation of one parameter while keeping the others constant, to study the effect of each parameter in isolation.

Elemental analysis (CHN) and determination of Fmoc number were used to characterise the plasmachemically modified samples (Table 6). Elemental analysis gives an indication of the total amount of nitrogen that is incorporated onto the polymer surface, while the Fmoc number is a measure of the number of *reactive* amine groups. Quite high levels of modification are obtained by elemental analysis, however it can be seen that the vast majority of these are unreactive to Fmoc attachment and therefore inaccessible for further chemical elaboration. The results also indicate that a high surface area together with pore volume (resin ACD 68) give rise to the highest level of modification. The importance of pore volume is revealed by comparison of this resin with ACD29, which has a slightly higher surface area but much lower pore volume and consequently has a much lower Fmoc loading.

A further parameter that could influence the extent of plasmachemical modification is bead size [10]. Consequently, it was decided to plasma-treat a whole resin sample and a daughter sample that had been sieved to below 53 μm diameter. The results are shown in Table 7. It is evident that the bead size has a greater influence on the extent of modification. The increase in the extent of plasmachemical modification for the sieved compared to the whole sample is much greater than the spread of values in Table 4. A similar influence of bead size on extent of modification was reported in our previous work [9,10]. However, the present study demonstrates conclusively that bead size is the dominant factor determining the extent of plasmachemical modification with allylamine. The results presented above suggest that the modification of the beads occurs mainly on the external surface. Smaller beads give rise to a greater external surface area (plasma-solid interface), so their extent of modification is greater. This conclusion is verified by Raman imaging microscopy (Fig. 5), which indicates the presence of a highly functionalised outer shell approximately 3 μm deep. It should be pointed out that plasmachemical amine functionalisation of the available surface could be expected throughout the bead, as the internal porous architecture is easily penetrated by gases. This could also occur in the absence of swelling solvents (as is the case here)—functionalisation only occurs at the surface, however there is available surface *throughout* the bead due to its high and permanent porosity. Therefore, the observation of a predominance of amine groups near the bead circumference is not simply due to the inability of the bead to swell in the reaction medium. It should be pointed out that the modification with 4-cyanobenzoic acid and Raman imaging only shows the reactive amine groups, which are present in a much lower concentration than the total amount of nitrogen (Table 6). Therefore, it cannot be concluded that the plasma

Table 5
The ‘low-value’ and ‘high-value’ resins for the variables that were investigated

Resin	DVB (%mol)	Porogen[a]	Dilution (%)	BET SA[b] (m^2/g)	BJH Vp[c] (ml/g)	BJH D[d] (Å)	Classification
ACD84	36	Hep	100	235	0.72	188	Low SA
ACD68	72	Tol/Dod (1:1)	200	454	1.31	112	High SA
ACD37	72	Hep	150	389	0.50	82	Low Vp
ACD48	66	Hep	100	401	0.99	118	High Vp
ACD29	72	Tol/Hep (1:1)	100	480	0.79	71	Low D
ACD47	54	Hep	100	333	0.74	125	High D

[a] Hep = heptane, Tol = toluene, Dod = dodecane.

[b] Surface area, determined by the BET method [13].

[c] Pore volume, determined by the BJH method [14].

[d] Average pore diameter, determined by the BJH method [14].

Table 7
Preparation conditions, characterisation data and extent of plasmachemical modification for a whole and size-fractionated resin

Resin	DVB (%mol)	Porogen	Dilution (%)	BET SA (m^2/g)	BJH Vp (ml/g)	BJH D (Å)	[N] (mmol/g)	Fmoc (mmol/g)
ACD30	72	Heptane	100	429	0.94	110	0.87	0.075
ACD30 (<53 μm)	72	Heptane	100	429	0.94	110	1.30	0.17

has only penetrated to a shallow depth from the bead exterior surface.

The production of beads with a highly functionalised shell could have advantages in areas such as reagent scavenging. The high concentration of exterior functionality could result in scavenging beads with superior kinetics to traditional gel-type or permanently porous supports, which can be slow to react [18]. Our studies on the use of these beads in solid phase organic synthesis (SPOS) and scavenging applications will be reported elsewhere.

4. Conclusions

Experimental design has been used to investigate simultaneously the influence of crosslinker level, porogen type and porogen level on the surface area, pore volume and pore diameter of permanently porous poly(styrene-*co*-divinylbenzene) beads. It was found that porogen type and level have a greater effect in each case than crosslinker content. This information was used to maximise each of the properties under consideration, resulting in a set of samples with a wide spread of values for each property. Six samples representing ‘high’ and ‘low’ values of each property were then chosen and treated with allylamine plasma after which the level of functionalisation was assayed by elemental analysis and Fmoc number determination. The results indicate that pore volume has the greatest influence on the extent of plasmachemical modification with allylamine. Finally, the influence of bead size was investigated by comparing the degree of functionalisation of a sample sieved to below 53 μm with that of the parent sample. It was found that the sample containing the smaller beads was modified to a significantly higher level. The interpretation of these results is that the majority of the modification with allylamine occurs towards the external surface rather than throughout the bead.

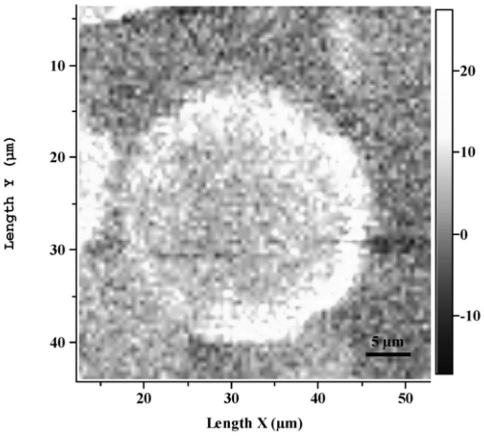


Fig. 5. Raman microscopy image of allylamine treated PS/DVB bead (diameter <53 μm) after coupling with 4-cyanobenzoic acid. The bright regions correspond to the integrated cyanoband intensity (2210–2260 cm^{-1}).

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