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Reversibly collapsible macroporous poly(styrene-divinylbenzene) resins

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Abstract

A series of poly(styrene–divinylbenzene) (poly(PS–DVB)) resins have been prepared by suspension polymerisation of styrene–DVB mixtures with DVB contents of 1–12 mol%. In each case 2-ethyl-hexan-1-ol was used as a porogen. Those resins prepared with <10 mol% DVB collapsed to clear glassy particles on drying from dichloromethane or toluene. However, on drying these resins from acetone, methanol and $scCO_2$ some opacity was retained. The surface area of each dried species was measured by applying the BET theory to N_2 sorption isotherms. Those resins containing ≤ 6 mol% DVB and dried from the former two solvents indeed have negligible surface area and superficially are very like gel-type resins. All the resins dried from the latter group of solvents have significant surface area which decreases systematically with fall in DVB mol%. The resin with 6 mol% DVB and negligible surface area dried from toluene was re-swollen in acetone and re-dried. This process re-established the pore structure and surface area. Using inverse size exclusion chromatography the porosity of all the resins was investigated when swollen in tetrahydrofuran. In all cases significant surface area (110–250 $m^2 g^{-1}$) was detected. This group of resins are therefore macroporous but, depending on the solvent and drying procedure, the porous morphology can be collapsed reversibly to form dry resins superficially similar to gel-type species. However, in practice these novel resins retain a latent pore structure which is readily re-established on treatment with suitable solvents. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(styrene–divinylbenzene) resins; Porous morphology; Collapsible

1. Introduction

The ever-increasing use of polymer supports in combinatorial chemistry [1,2] parallel synthesis and various solid phase extraction procedures, coupled with the re-emergence of these materials in the immobilisation of catalysts and other reactive species [3–5] has focussed attention on the molecular and morphological structure of the suspension polymerised styrene–divinylbenzene (styrene–DVB) resins most often exploited in this role [6]. Two groups of resins are most commonly described. The first, referred to as gel-type species, are lightly crosslinked, typically employing 0.5–2 mol% DVB, and rely upon solvation of individual polymer chains by a thermodynamically good solvent to swell the polymeric network and allow access to the support (Fig. 3A). In the swollen state such resins are soft and compressible and relatively fragile in shear. The second, referred to as macroporous species, are usually more highly crosslinked, and possess a complex system of permanent pores created by employing a porogen (usually an organic solvent) in the polymerisation. The pore system can be accessed by thermodynamically poor solvents as well as good ones, and these resins are more rigid even in contact with solvent. They can therefore be employed in packed columns. Unfortunately in order to generate stable macroporous structures it has become common practice to use levels of crosslinker typically ≈ 15–80 mol%. As a consequence the polymer or gel phase within these macroporous resins is usually relatively impenetrable, and reactions within this phase are often mass transfer limited. A potentially improved morphology would be one which is macroporous but with the gel phase only lightly crosslinked.

2. Experimental

2.1. Resin syntheses [7]

These were performed in a 1 l parallel-sided jacketed glass baffled reactor with metal stirrer carrying two propeller-type blades driven at 700 rpm in a downward direction. Typically (for 5 mol% crosslinker) an organic phase

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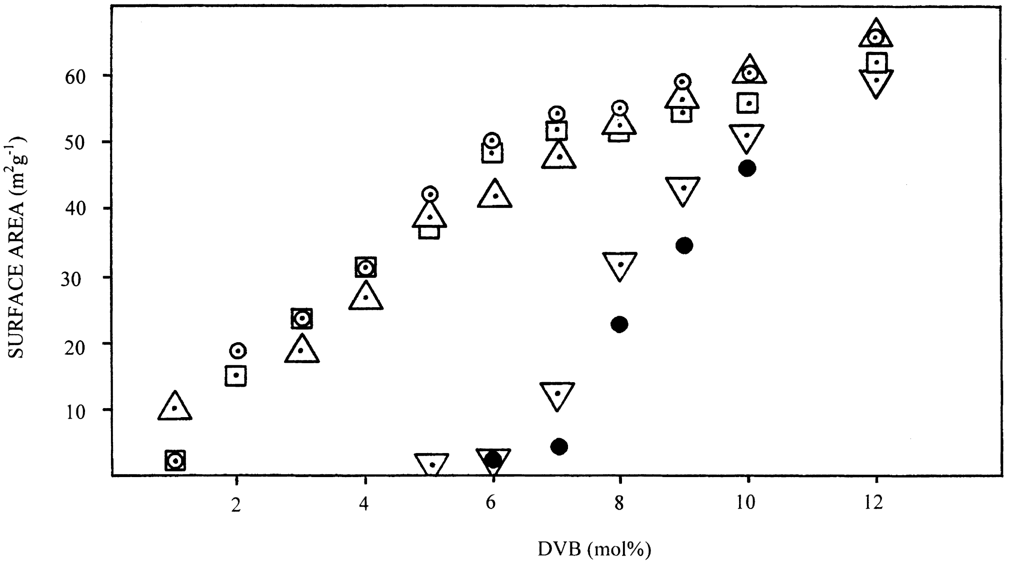

Fig. 1. Dry state surface area data for collapsible macroporous Poly(styrene–DVB) resins prepared with varying levels of DVB crosslinker. Resins dried from: ◬; scCO$_2$; ⊡, acetone; ⊙ methanol; ▽ toluene; ●, dichloromethane.

comprising styrene (20 g), commercial divinylbenzene (1.64 g, ≈80% grade), azobisisobutyronitrile (0.21 g) and 2-ethyl-1-hexanol (25 ml) was added to an aqueous phase (900 ml) containing xanthan gum (1.16 g), cellosize (0.11 g), boric acid (15.5 g) and NaCl (180 g). The suspension was purged with N_2 and the inert atmosphere maintained during polymerisation. The latter was carried out at 80°C for 6 h. The polymer beads were washed copiously with water by successive decantation and then with methanol. Finally, they were extracted with acetone in a Soxhlet for 12 h before being dried under vacuum at 60°C overnight. The yield of high quality beads was ≈85% with a particle diameter range ≈75–300 μm.

2.2. Drying procedures

For the organic solvents resin samples swollen overnight were dried at 60°C for 24 h in a vacuum oven. A separate sample of each resin was also extracted and dried from $scCO_2$ at 40°C for 1 h using a flow-rate of sfc grade CO_2 of 4 $cm^3\ min^{-1}$ at 200 bar [9].

2.3. Surface area measurements

Surface areas of dry resins were determined from conventional N_2 sorption isotherms utilising the BET Theory [10,11]. The instrument employed was a Micromeritics ASAP2010 with dedicated software. Surface areas of resins swollen in tetrahydrofuran were deduced from inverse size exclusion chromatography (ISEC) [14] in which the resin was used as the stationary phase (4 ml swollen volume) and the elution volumes of standard solutes (C5-C30 alkanes and polystyrenes of molecular weight 580–1 800 000) were measured (flow rate = 1 ml min^{-1}; Waters 510 hplc pump; Differential refractometer detector RIDK 101, Laboratorni Pristroje).

Porosity data was evaluation from the molecular weight/elution volume profiles by applying a model due to Ogston [15] and in-house generated software [14,16].

3. Results and discussion

We now report on our synthesis and evaluation of reversibly collapsible poly(styrene–DVB) resins prepared with DVB contents of 1–12 mol% and employing 2-ethyl-1-hexanol as a thermodynamically poor porogen. Each resin was prepared by suspension polymerisation using a procedure already reported in detail in the literature [7]. The volume ratio of comonomers, styrene and DVB, to 2-ethyl-1-hexanol was 1:1, and the mole ratio of the comonomers was adjusted to provide a (real) DVB content of 1–12 mol%, respectively. (In practice a commercial grade of DVB was used containing ≈80 mol% of DVB isomers, the balance being ethylstyrene isomers; account was taken of the real DVB content in formulating polymerisation mixtures).

A separate sample of each resin was contacted overnight with each of the following solvents:acetone, methanol, dichloromethane and toluene, and then each exhaustively dried in a vacuum oven at 60°C for 24 h. A separate sample of each resin was also swollen, extracted and dried from supercritical $scCO_2$ [8] at 40°C for 1 h [9]. Interestingly those resins such as the 4, 5 and 6% DVB-containing species dried from toluene and dichloromethane appeared transparent and glassy under the optical microscope, whereas the same resins dried from acetone and methanol were opaque.

The surface area of each resin sample was determined

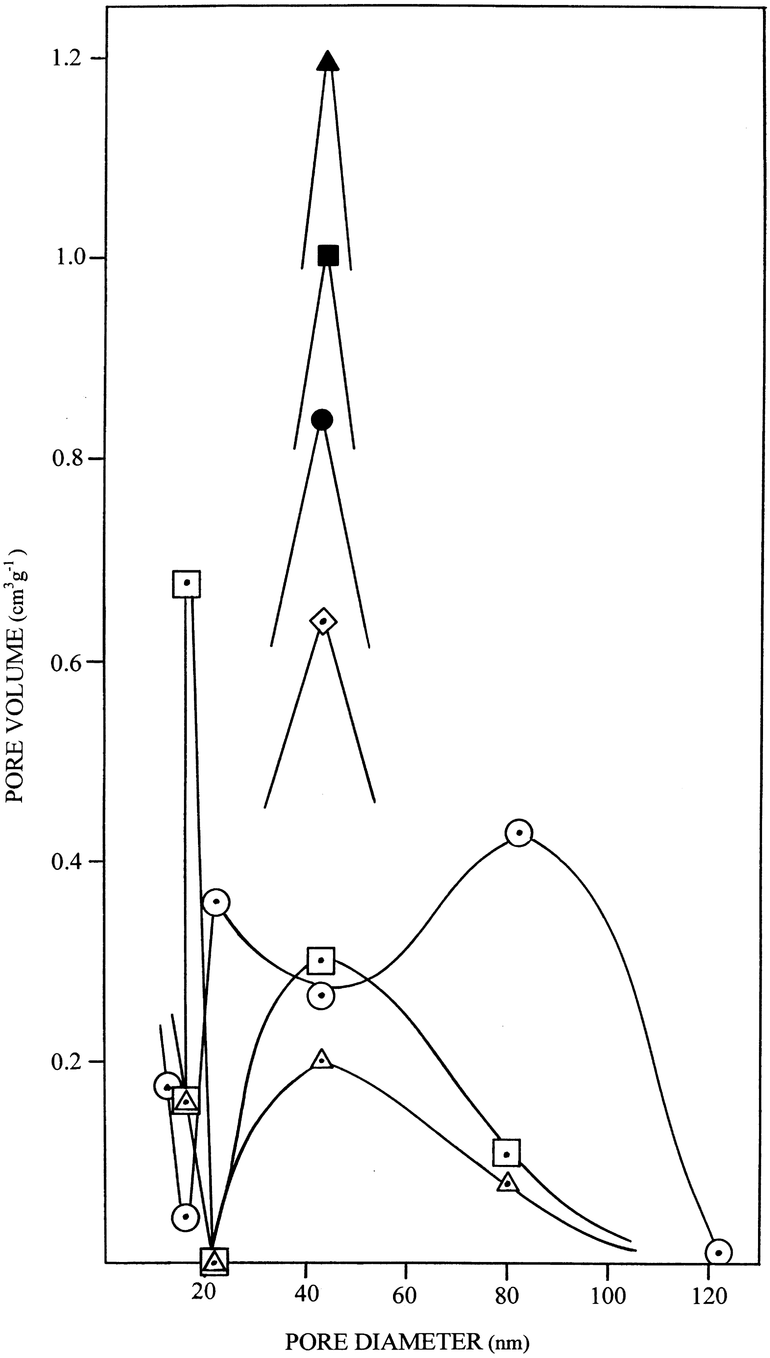

Fig. 2. Pore size distribution data for resins in the tetrahydrofuran swollen state: ⊙, 3% DVB; △, 4% DVB; ⊡ 5% DVB; ◈, 6% DVB; ●, 7% DVB; ■, 8 and 9% DVB; ▲, 10% DVB.

from the N_2 sorption isotherm by application of the BET theory [10,11]. The data obtained are shown in Fig. 1. The 12% DVB-containing resin displays a surface area of $\approx 60\ m^2\ g^{-1}$ irrespective of the solvent from which it is dried. This is typical of the value expected when employing a precipitating porogen such as 2-ethyl-1-hexanol and this resin is a permanently porous species routinely described as macroporous. For the remaining resins employing $<12\%$ DVB the surface area depends markedly on the solvent from which the resin is dried. Two solvent groups can be identified. The first comprise dichloromethane and toluene which are thermodynamically good solvents for poly(styrene–DVB) networks. Clearly drying from these solvents results in a collapse of the pore structure of the resins and a concomitant loss of surface area (Fig. 1). The collapse becomes increasingly serious as the %DVB falls to seven, and is essentially total for all resins with $\leq 6\%$ DVB. These species are clear and glassy and superficially look identical

Table 1
Porosity characteristics of collapsible macroporous poly(styrene–DVB) resins when swollen with tetrahydrofuran (determined via inverse size exclusion chromatography [14,15])

Resin DVB content (mol%)	Macropore volume ($cm^3 g^{-1}$)	Macropore surface area ($m^2 g^{-1}$)	Swollen gel volume ($cm^3 g^{-1}$)
3	1.29	176	2.26
4	0.60	112	2.46
5	1.25	250	2.00
6	1.16	154	1.88
7	1.45	187	1.03
8	1.37	136	1.21
9	1.36	128	1.37
10	1.45	131	1.14

to gel-type resins of low (≈0.5–2%) DVB content. Drying from these solvents therefore appears to be via an equilibrium process during which the polymer network gradually folds. The second group of solvents comprise acetone, methanol and $scCO_2$. All of these are rather thermodynamically poor solvents for poly(styrene–DVB) networks and it appears that drying from these solvents occurs in a non-equilibrium fashion such that some or all of the porous structure remains “frozen-in”. The level of porosity which is retained falls as the %DVB falls and at 1% DVB the network is incapable of retaining any pore structure. Progressive change, indeed loss, of pore structure is reflected in the steady fall of surface area for resins with say <7% DVB content. Drying from $scCO_2$ involves rapid depressurisation and has been shown to be a very effective method for inducing porosity in a wide range of polymeric substrates [12,13]. In addition, the low viscosity and high diffusivity of $scCO_2$ make it a very efficient medium for removal of the last traces of porogen. In the present case, drying from $scCO_2$ and freezing of the pore structure is achieved in ≈1 hour relative to ≈24 h for conventional poor solvents. In order to confirm that the observed collapse of porosity is reversible, the 6% DVB-containing species which had been collapsed by drying from toluene (surface area = 2.3 $m^2 g^{-1}$) was re-saturated with acetone, then dried from this solvent. This re-established the pore structure and the new surface area (45.3 $m^2 g^{-1}$) was within experimental error the same as that obtained for the original sample of this resin dried from acetone (48.3 $m^2 g^{-1}$).

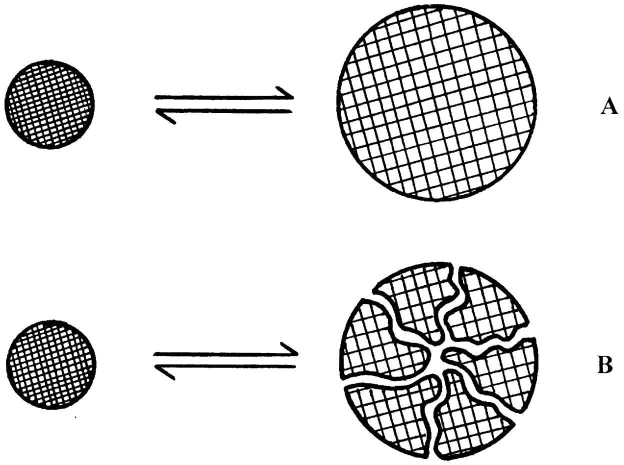

Fig. 3. (A) Schematic representation of swelling/deswelling of a gel-type resin; and (B) a collapsible macroporous resin.

Interestingly those resins which collapsed on drying from toluene to yield optically clear glassy beads in the dry state became rather opaque on re-sorbing solvents. This confirms the reformation of a discrete pore structure with refractive index discontinuities of the same order of magnitude as visible light, and therefore capable of efficient scattering. In order to confirm the presence of a discrete pore structure in the swollen state (as opposed to a uniform solvated gel network as is the case with gel-type resins) ISEC [14] was performed on the resins swollen in tetrahydrofuran [14]. Applying a standard model [15] to the molecular weight/elution volume profiles yields information both on macropore and swollen polymer gel morphology. Some data obtained are shown in Table 1. Bearing in mind the imprecision of the ISEC technique the surface areas and macropore pore volumes of all the resins examined in the tetrahydrofuran swollen wet state fall within a relatively narrow range. This is almost certainly because all the resins were prepared with the same level of the same precipitating porogen, and with a narrow range of DVB levels, albeit the latter proves crucial regarding the collapsibility of the resins. The pore size distribution curves in Fig. 2 show that some differences do arise at a finer level. The resin containing 3% DVB exhibits a rather wide pore size distribution with pore diameters ≈12–80 nm. With increase of crosslinking to 4 and 5% the distribution narrows with a maximum developing around 40 nm and a second maximum ≈15 nm. Beyond 5% DVB the distribution becomes unimodal around a sharpening maximum at 40 nm.

Somewhat as expected, the volume of swollen polymer mass decreases with increase of the DVB content. The total swollen polymer gel volume seems to be similar to that determined by ISEC in the case of gel-type resins of similar %DVB content, for example gel-type resins containing 3.5 and 5% DVB exhibited swollen volumes of 2.39 and 2.03 $cm^3 g^{-1}$ in tetrahydrofuran, respectively [16].

However, the present macroporous resins seem to have a more heterogeneous density in the swollen polymer matrix than conventional gel-type resins.

To our knowledge a clear and readily accessible identification and characterisation of the reversibly collapsible macroporous resins described here has not previously been made in the literature. However, a careful examination of publications primarily originating from the Bayer Company shows that sulfonic acid resin species with properties similar to those disclosed here have been prepared, characterised and marketed [17–19]. We suspect that other ion exchange resin companies are also familiar with the technical advantages offered by these species.

Reversibly collapsible macroporous resins (Fig. 3B) therefore offer novel scope for exploitation in, e.g. solid phase combinatorial chemistry and as supports for catalysts. To some extent they are likely to combine the advantages of gel-type and macroporous species within a single morphology. The somewhat higher overall %DVB content makes these species more mechanically robust than simple gel-types. The latent pore structure is also likely to allow facile ingress and egress of solvent minimising the likelihood of osmotic shock during swelling and deswelling. Furthermore, in the swollen state the macroporous structure will allow rapid diffusion of reagents, reactants and products within resin particles. At the same time the polymer gel phase is only modestly crosslinked and much less likely to impose local mass transfer limitations than is the case with resins with conventional macroporous morphologies. In addition our use of $scCO_2$ shows that porogen and other residual fragments can be removed very rapidly and efficiently at near ambient temperatures. We ourselves are currently exploring further the exploitation of these species as improved resin catalyst supports.

Acknowledgements

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