Polymer Bulletin 44, 179–186 (2000)

Polymer Bulletin

Porosity analysis of some poly(styrene/divinylbenzene)beads by nitrogen sorption and mercury intrusion porosimetry

H. Deleuzel[1,*], X. Schultze[1], D.C. Sherrington[2]

[1] Laboratoire de Chimie Organique et Organométallique, UMR 5802-CNRS, Université Bordeaux I,
351 Cours de la Liberation, 33405 Talence, France
[2] Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street,
Glasgow, G1 1XL, UK

Received: 10 December 1999/Revised version: 5 February 2000/Accepted: 5 February 2000

SUMMARY:

Highly crosslinked poly(styrene/DVB) beads have been synthesised by suspension polymerisation using different porogens and porogens mixtures. The porosity of the resulting resins was analysed by the nitrogen and mercury intrusion porosimetry techniques.

INTRODUCTION:

The diverse applications of polymer supports in heterogeneous catalysis and solid phase synthesis require careful design and control of the porous structure of the support (1). Polymer beads with a permanent porous structure in the dry state can be obtained by suspension polymerisation of an organic phase containing the monomers, a crosslinker, an initiator and a diluent (also called "porogen"). The porosity of these supports depends mainly on the amount of crosslinker and on the type and quantity of the porogen used (2).

Nitrogen sorption and mercury intrusion porosimetry are accurate tools commonly used to determine the structure of porous solids (3) (i.e specific surface area, pore size distribution, pore volume...). With this in mind, we decided to study the porosity of some poly(styrene/divinylbenzene) resins obtained by suspension polymerisation in the presence of different porogens.

EXPERIMENTAL:

Suspension Polymerisation :

Styrene, divinylbenzene (DVB) (80% tech. grade, mixture of m,p divinylbenzene and ethylstyrene) and the porogens were used as received. In a typical experiment, styrene (3.12g,

---

[*] Corresponding author

30mmol), DVB (9.11g, 70mmol) and AIBN (0.61g, 3.7mmol) were mixed with 2-ethylhexanol (13.4ml). The aqueous phase used in the polymerisation was composed of a suspension stabiliser (a mixture of gelatin and poly(diallyldimethylammonium chloride), high molecular weight) in water. The organic phase was injected into the aqueous phase (260 ml) in a parallel-sided glass reactor at 60°C under mechanical stirring (700 rpm). The temperature was then raised at 80°C for 8 hours after which the resulting spherical particles were washed with water, ethanol and extracted with acetone in a soxhlet apparatus for 48hours. The resins beads were finally dried under vacuum. The particle size distribution was estimated by manual sieving.

Porosity analysis:

The surface area (SA) of the samples was determined by the nitrogen adsorption BET technique.(4) The instrument employed was a Micromeritics Accusorb 1100E. Computer calculations were made using the Micromeritics 2100 SA programme. The pore size distribution (PSD) was determined using the BJH model assuming a cylindrical pore geometry (5).

Before each experiment, the samples were degassed at 100°C under a pressure of 2.10^{-5} bar during 24 hours.

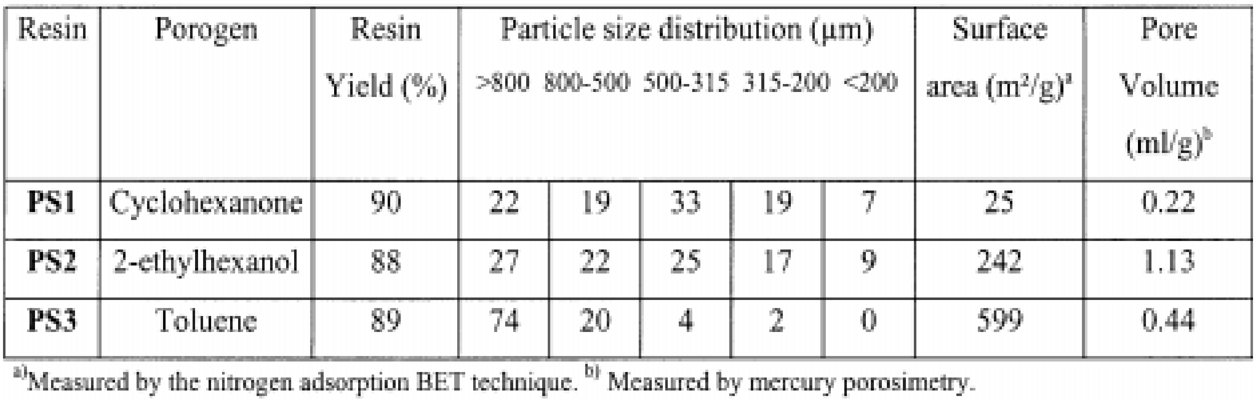
The pore volume of the samples was deduced from the maximal volume of mercury intrusion measured with a Micromeritics 414 MPa apparatus.

RESULTS AND DISCUSSION

1. Influence of the porogen on the structure of the polymer :

Three poly(styrene/DVB) resins with a high nominal crosslink level (70mol% DVB) have been synthesised by suspension polymerisation using three different porogens : cyclohexanone (**PS1**), 2-ethylhexanol (**PS2**) and toluene (**PS3**). Throughout this work, the volume ratio of porogen to monomers in the organic phase was kept at 1. The surface area of the polymers thus obtained was analysed by the nitrogen sorption technique while the pore volume was determined by mercury porosimetry. As can be seen from the results reported in Table 1, the porogen has a strong influence on the structure of the porous beads. The specific surface area is quite low (25 m^2g^{-1}) when cyclohexanone is used as porogen whereas a high surface area (600 m^2/g) results when using toluene. An intermediate value is obtained with 2-ethylhexanol. The effect of the porogen can be explained in terms of solubility parameters (6)

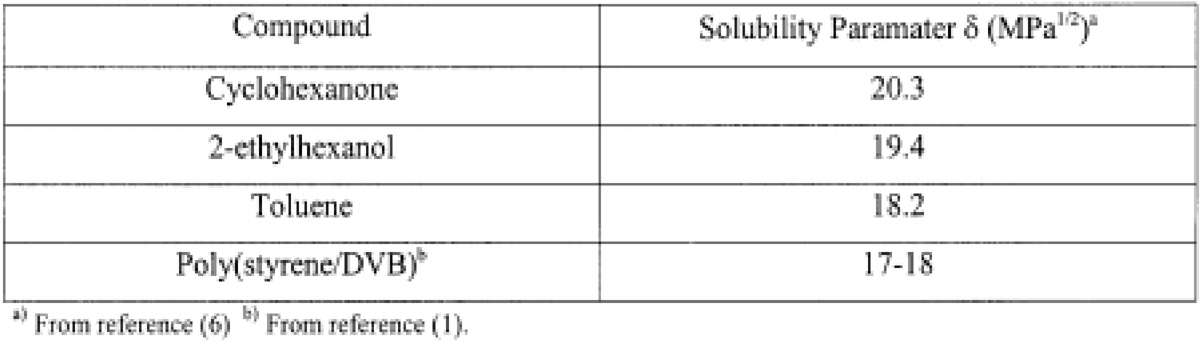
(Table 2). The lower the difference between the solubility parameters of the resin and the porogen, the higher the affinity between these two compounds (7). The solubility parameter for styrene-divinylbenzene copolymers (1) ranges from 17 to 18 MPa$^{1/2}$. Therefore the affinity between the polymer chain and the diluents used in this work increases in the order : cyclohexanone < 2-ethylhexanol < toluene.



Resin	Porogen	Resin Yield (%)	Particle size distribution (µm)					Surface area (m^2/g)^a	Pore Volume (ml/g)^b
			>800	800-500	500-315	315-200	<200		
PS1	Cyclohexanone	90	22	19	33	19	7	25	0.22
PS2	2-ethylhexanol	88	27	22	25	17	9	242	1.13
PS3	Toluene	89	74	20	4	2	0	599	0.44

[a] Measured by the nitrogen adsorption BET technique. [b] Measured by mercury porosimetry.

Table 1 - Characteristics of porous poly(styrene/DVB) beads obtained with pure solvents as porogen.



Compound	Solubility Paramater δ (MPa$^{1/2}$)^a
Cyclohexanone	20.3
2-ethylhexanol	19.4
Toluene	18.2
Poly(styrene/DVB)^b	17-18

[a] From reference (6) [b] From reference (1).

Table 2- Solubility parameters of the porogens and of the poly(styrene/DVB) copolymers.

During the polymerisation, a phase separation between the porogen and the growing polymer chains takes place. When a porogen having a good compatibility with the polymer is used (such as toluene), this phase separation occurs at high monomer conversion. On the other hand, when a precipitating porogen is used (i.e. when the difference between the solubility parameters is above 1,7 MPa$^{1/2}$ (8)), the phase separation occurs a low conversion. According to the model proposed by Albright (9), the macroporous polymers are composed of clusters of microgel particles that are glued together at their interface. The meso and macroporosity porosity arises from the voids within the clusters and the spaces between the microgel from which the clusters are constructed. Therefore, the specific surface area observed will be directly related with the size of the microgel particles and their degree of fusion. A phase separation occuring rapidly in the course of the polymerisation will give access to more connected microgels, and , therefore, to lower specific surface areas than a phase separation ocurring latter. As a consequence, the surface area of our resins increases in the order : **PS1** < **PS2** < **PS3**, the solubility parameters of the porogen used becoming progressively closer from the one of the polymer The structural differences between resin **PS3** (porogen : toluene) and **PS2** (porogen : 2-ethylhexanol) are well illustrated by their nitrogen adsorption-desorption isotherms reported in Figure 1.

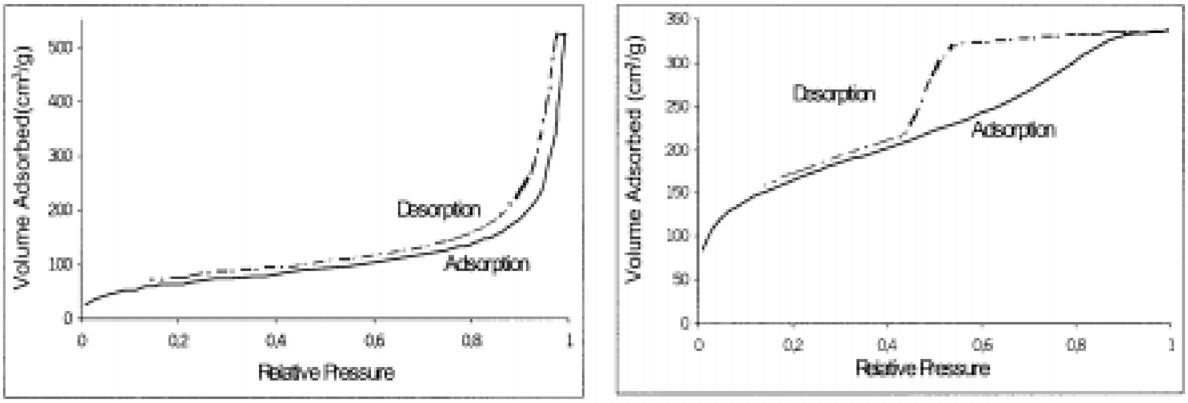


Figure 1 - Nitrogen adsorption-desorption isotherm of resin **PS2 and PS3**.

Resin **PS2** exhibits a type II isotherm characteristic of non-porous or macroporous solids while resin **PS3** displays a type IV isotherm with an initial sharp rise at low relative pressure indicative of the presence of micropores with a wide hysteresis loop at higher relative pressures which is usually associated with capillary condensation in mesopores (10). Indeed, the shape of this hysteresis loop is typical of porous solids with a low pore connectivity (11). These observations are in agreement with the pore size distributions of the two resins calculated by the BJH method (5) (Figure 2).

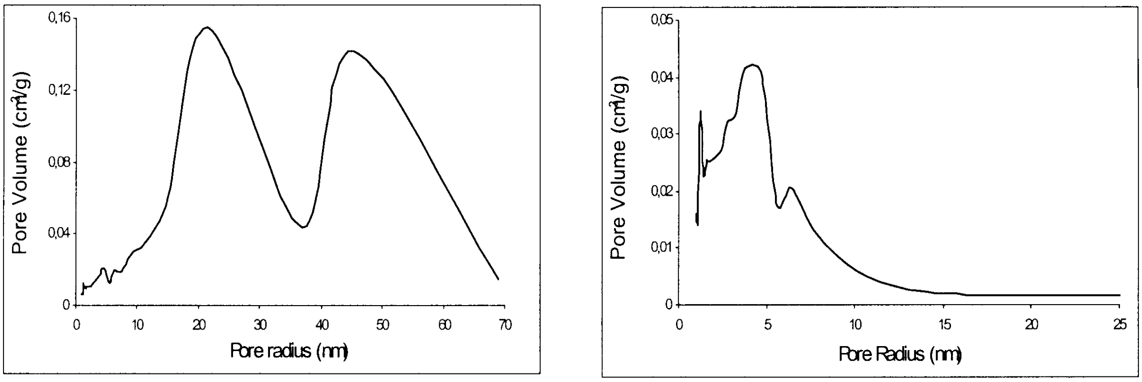


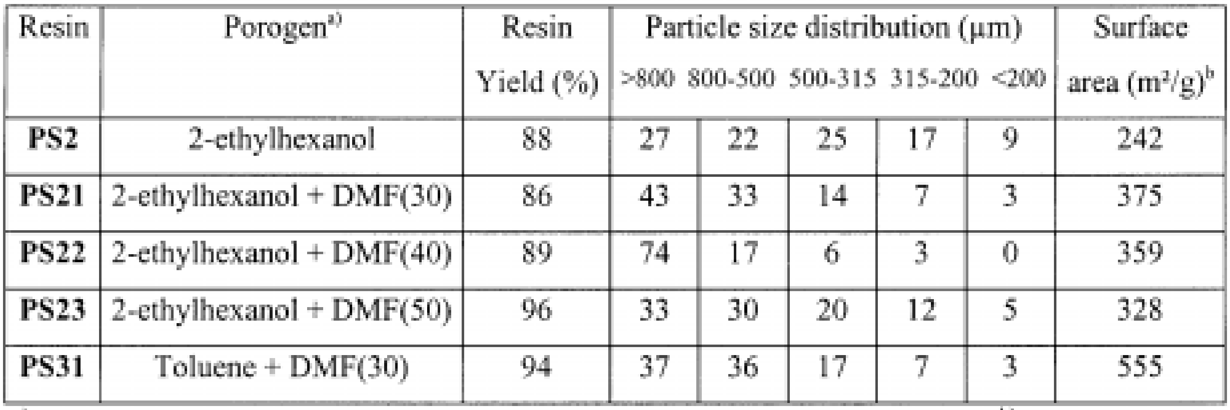
Figure 2 - Pore size distribution of resin **PS2** and **PS3** obtained by the nitrogen sorption technique using the BJH method .

Resin **PS2** displays a bimodal distribution in pore size around 20 and 45nm while resin **PS3** exhibits a unimodal distribution centered around 4nm. (note : a full micropore isotherm at low relative pressure was not recorded so that data below 4 nm are only approximate.) The smaller pore size of resin **PS3** and its low pore connectivity result from the good affinity between toluene and styrene-divinylbenzene copolymers. This might also explain why the pore volume of this resin (measured by mercury porosimetry) is lower than for resin **PS2** although the same amount of porogen has been used in both cases : the low pore size and connectivity hinder the mercury intrusion. Furthermore, under the pressure of the mercury intrusion (310 MPa), a pore collapse phenomenon is quite plausible.

2. Mixture of solvents as porogen :

2.1 Mixture of 2-ethylhexanol/DMF :

Suspension polymerisation needs to start with a liquid monomer mixture. Therefore, the solubilisation of polar solid comonomers (such as maleimides) can require the use of polar solvents (such as DMF). With this in mind, we studied the influence of adding DMF to 2-ethylhexanol as porogen. Three resins with increasing DMF content in the porogen were thus synthesised (resins **PS21**, **PS22** and **PS23**). The particle size distribution and the surface areas of these polymers are reported in Table 3.



Resin	Porogen[a)]	Resin Yield (%)	Particle size distribution (μm) >800	800-500	500-315	315-200	<200	Surface area (m²/g)[b]
PS2	2-ethylhexanol	88	27	22	25	17	9	242
PS21	2-ethylhexanol + DMF(30)	86	43	33	14	7	3	375
PS22	2-ethylhexanol + DMF(40)	89	74	17	6	3	0	359
PS23	2-ethylhexanol + DMF(50)	96	33	30	20	12	5	328
PS31	Toluene + DMF(30)	94	37	36	17	7	3	555

[a)] The number in brackets represent the volume percent of DMF in the porogen mixture [b)]Measured by the nitrogen adsorption BET technique.

Table 3 Synthesis of poly(styrene/DVB) supports with of 2-ethylhexanol/DMF as porogen.

The adsorption-desorption isotherm and the pore size distribution of resin **PS21** are displayed in Figure 3. When 30vol% of DMF is introduced in the porogen mixture (resin **PS21**), the same type of isotherm as for resin **PS2** is obtained. Nevertheless, an increase of the resin surface area is observed and the pore size distribution becomes unimodal (maximum 20nm).

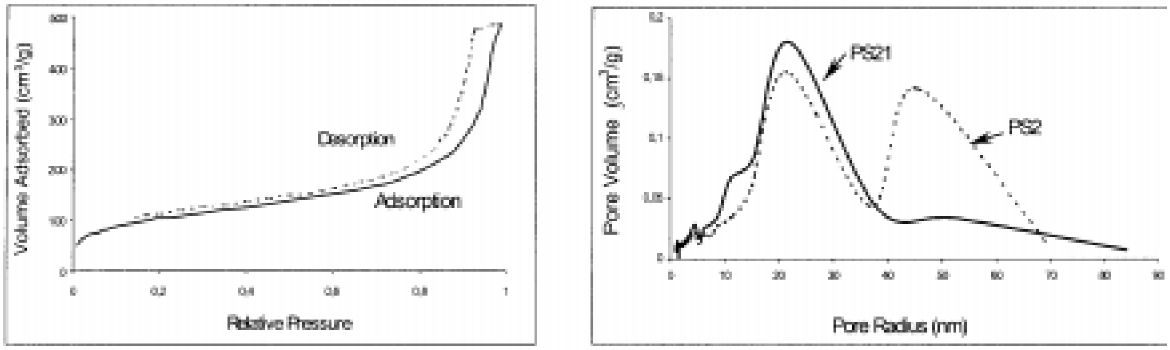


Figure 3 - Nitrogen adsorption-desorption isotherm of resin **PS21**.and pore size distribution of resin **PS21** obtained by the nitrogen sorption technique using the BJH method (with comparison with **PS2**).

These results come as a surprise, considering that the solubility parameter of DMF is 24.8 MPa$^{1/2}$ i.e. this compound is a poorer solvent for poly(styrene/DVB) copolymers than 2-ethylhexanol. It seems, therfore that with 30% DMF in 2-ethylhexanol the mutual interaction of these solvents results in an overall enhancement of interaction with the polymer matrix i.e. the solvation power of the mixture increases relative to that of 2-ethylhexanol. As a result phase separation is delayed in the polymerisation eventually leading to less fused microgel particles and an increase in surface area. The situation is, however, very complex because when more DMF is added to the porogen mixture, the surface area of the resulting beads slowly decreases. This might arise because some of the DMF will migrate into the aqueous phase due to the solubility of this solvent in water. Hence, the actual porogen to monomer ratio may decrease as the proportion of DMF in the porogen mixture increases. Likewise increasing levels of DMF will solubilise more water in the the porogen mixture. Overall the effect is to lower the surface area of resins **PS22** and **PS23** relative to **PS21**.

2.2 Mixture of toluene and DMF.

In this case, the introduction of 30 vol% of DMF in the porogen mixture results in a decrease of the surface area of the polymer **PS31** (table 3). Toluene and DMF are both poor H-bonding diluents. Therefore, since DMF is a poorer solvent for poly(styrene/DVB) copolymers than toluene, the toluene/DMF mixture has a lower affinity for the polymer than toluene alone . it induces earlier phase separation accounting for the slightly lower surface area of the resulting beads. Solubilisation of water in this porogen mixture would also have a similar effect.

CONCLUSION:

The use of the nitrogen sorption technique and of mercury intrusion porosimetry has enabled us to study the porosity of some highly crosslinked poly(styrene/DVB) beads synthesised using different porogens. When cyclohexanone is used as porogen, a low surface area macroporous resin is obtained. The use of 2-ethylhexanol generates a structure with large pores and a modest surface area compared to toluene which generates a structure with small pores and a low pore connectivity. When a 2-ethylhexanol/DMF (70/30 vol) mixture is used, a resin with a larger surface area than that produced with pure 2-ethylhexanol is obtained due to the decrease of the H-bonding interactions between the solvent molecules. This phenomenon can not be reproduced when another poor H-bonding solvent such as toluene is used. In that case, the surface area obtained with a toluene/DMF mixture is lower than with toluene alone. It seems therefore that mutual interactions within this porogen mixture result in overall better compatibility with the resin matrix. A similar mixture of toluene/DMF (70/30 vol) shows reduced compatibility with the polymer network in keeping with the solubility parametres and a small reduction in surface area in the resin formed relative to that with pure toluene. The use of DMF in the porogen mixture gives access to the suspension polymerisation of polar, solid monomers such as maleimides (12).

REFERENCES:

1. Sherrington D.C., (1998) Chem. Commun. 2275.
2. Guyot A.,(1988) Synthesis and Structure of Polymer Supports. In Sherrington D.C. and Hodge P., (ed) Synthesis and Separations using Functionnal. Polymers, J. Wiley and Sons, Chichester, UK,Chap 1, p1.
3. Webb P.A. and Orr C., (1997) Analytical Methods in Fine Particle Technology, Micromeritics Instrument Corp., Chap: 3 and 4.
4. Brunauer S., Emmett P.H. and Teller E., (1938), J. Am. Chem. Soc., 60 : 309.
5. Barret E.P., Joyner L.G. and Halenda P.P., (1951) J. Am. Chem. Soc. 73 : 373.
6. Grulke E.A.,(1989) Polymer Handbook, 3rd Ed., 7 : 519.
7. Coutinho F.M.B. and Cid R.C.A., (1990) Eur. Polym. J. 26,11 : 1185.

8. D. Rabelo D. and Coutinho F.M.B., (1993) Polym. Bull. 31 : 585.

9. Albright R.B., (1986), React. and. Funct. Polym. 4 : 155-174.

10. Sing K.S.V., Everett D.H., Haul R.A.W., Moscou L., Pierotti R.A., Rouquérol J. and Siemieniewska T., (1985) Pure & Appl. Chem. 57, 4: 603.

11. Zgrablich G., Mendioroz S., Daza L., Pajares J., Mayagoitia V., Rojas F. and Conner W.C., (1991) Langmuir 7: 779.

12. Deleuze. H., Schultze X., Sherrington D. C., J. Polym. Sci. Polym. Chem. submitted.