Physical characterization of suspension-crosslinked polystyrene particles and their sulphonated products:
2. Ionic networks

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Strong cationic resins have been prepared from isoporous polystyrene networks in bead form with H_2SO_4 and HSO_3Cl as sulphonating agents. The effect of the reaction time of H_2SO_4 sulphonation on ion exchange capacity has been examined. The polymer–solvent interaction parameter, χ, with aqueous electrolyte solutions has been calculated after minimization of electrostatic repulsions. The average molecular weight per crosslinked unit, $\bar{M}_c$ has been measured after sulphonation and an estimation of formation of sulphone-type crosslinks has been attempted. The average size of the network structure, r_c, has been calculated as a function of the ionic strength of aqueous electrolyte solutions for networks of different molecular weight per crosslinked unit, $\bar{M}_c$. The ion exchange capacity of the prepared resins has been measured.

INTRODUCTION

Sulphonation of polystyrene (PS) matrices may be obtained by various sulphonating agents, e.g. H_2SO_4, HSO_3Cl or sulphur trioxide. The quality of the sulphonated products is very difficult to control because of the formation of crosslinks between the pendant sulphonate groups in the polymer chains[1]. To avoid these sulphone crosslinks some procedures have been developed for sulphonation of either crosslinked[2] or uncrosslinked PS[3]. No information is available on the quantitative correlation of these crosslinks to the physical characteristics of the resins.

the preparation of water-soluble sulphonated PS and in the preparation of crosslinked sulphonated PS with large network size, due to the associated decrease of the average size of the network structure, r_c. The increased size of the network is indispensable for the accessibility of the exchange sites by such high molecular weight molecules as peptide fragments obtained from proteins after treatment with proteolytic enzymes or cyanogen bromide[4]. This accessibility is also very important in using sulphonated PS gel particles as catalysts in various organic syntheses, e.g. alkylations[5].

There is a variety of catalysts suggested for sulphonation with H_2SO_4, including Ag_2SO_4[6] or even phase transfer catalysts such as quaternary ammonium salts[2]. The conditions suggested are temperature $\approx 80°C$ and a few hours reaction time.

Davankov and his co-workers[7] were the first to note the significance of the type of polymeric matrix on the physical properties of the resins produced. Thus, isoporous PS networks prepared via Friedel–Crafts post-polymerization crosslinking were shown to exhibit unusual physical characteristics compared with the standard styrene–divinylbenzene (DVB) copolymers which possess an extremely inhomogeneous structure. Upon sulphonation, the ability of swelling in organic solvents of the isoporous PS networks and the availability of the exchange sites to bulky groups were also unexpected[8]. No attempt has been reported previously for the estimation of the average size of the network structure, r_c.

EXPERIMENTAL

Preparation of isoporous PS gel particles

The procedure for preparation of isoporous PS matrices in a silicone oil–dichloroethane suspension medium with $SbCl_5$ as a catalyst has been reported previously[9] and the conditions of preparation of particles with a variety of crosslinking densities have been given elsewhere[10]. The porosity, p, and the molecular weight per crosslinked unit, $\bar{M}_c$, of the particles used for the sulphonation reactions are shown in *Table 1*.

Procedure for sulphonation of PS networks

In a glass reactor (250 ml) equipped with mechanical agitation, vertical condenser and thermometer, 150 ml H_2SO_4 (95–97%) and 10–20 g crosslinked PS beads swollen in DCE were added at 80°c and stirred. After 10 min the sulphonated networks were obtained by suction filtration and washed thoroughly with de-ionized water until no H_2SO_4 was detected by $BaCl_2$. The product was washed for 24 h in a large volume of de-ionized water (500–1000 ml) which was checked

Table 1 Porosity, *p*, and molecular weight per crosslinked unit, $\bar{M}_c$, of PS particles for sulphonation

Sample no.	Porosity (cm^3 g^{-1})	Mol. wt. $\bar{M}_c$
1	0.175	1120
2	0.134	4730
3	0.125	10550
4	0.124	11920
5	0.119	21940
6	0.117	27620
7	0.117	28330
8	0.117	33270
9	0.116	44160
10	0.116	44960

Table 2 Ion-exchange capacity of sulphonated PS particles in meqs g^{-1} as a function of the sulphonation time

Sulphonation time (min)	Sample no.		
	1	2	3
5	1.7	1.2	1.6
10	3.0	4.3	3.2
30	3.1	4.3	3.3

periodically for H_2SO_4. Upon complete purification the product was dried *in vacuo* at 80°C for 24 h.

In some cases, chlorosulphonic acid was used as a sulphonating agent in small quantities (1.25, 2.5 and 5 ml g^{-1} (PS)) upon dilution in 150 ml DCE. The reaction time was the same and the temperature was 0°C, due to the high reactivity of HSO_3Cl. Only the particles with molecular weight per crosslinked unit, $\bar{M}_c$, equal to 28330 were sulphonated by both techniques.

Determination of the degree of swelling

The degree of swelling of the particles in various aqueous solutions was determined gravimetrically using the method described previously[10].

Ion-exchange capacity

The ion-exchange capacity of the resins was determined by the following batch procedure.

In a conical bottle containing a solution of known volume and concentration of an ion A^{n+}, a preweighed quantity of a sulphonated resin in the PS–B^{m+} form was added and the remaining concentration of the ion A^{n+} was determined after 24 h. From the difference of concentrations, the ion-exchange capacity of the resin expressed in meqs g^{-1}, was obtained for the exchange PS–B^{m+}→PS–A^{n+}.

RESULTS AND DISCUSSION

Effect of the reaction time on sulphonation

Some sulphonations with H_2SO_4 were carried out on particles with sample nos. 1, 2 and 9 for the determination of the effect of reaction time. The samples were sulphonated for 5, 10 and 30 min and their ion-exchange capacity for the exchange HPSS→NaPSS was chosen as a control parameter. The results are given in *Table 2* which shows that sulphonation times > 10 min cannot improve the capacity significantly. On the contrary, longer times enhance undesirable reactions, producing sulphone-type crosslinks; this effect is discussed later.

Minimization of electrostatic repulsions in ionic networks

When ionic groups are introduced in the polymer network, electrostatic repulsions become important in addition to elastic and osmotic forces. In this case equation (1) describes the behaviour of the swollen networks at equilibrium[11]:

$$(i \cdot v_{2,s}/V_u)^2/4S^*$$
$$\simeq (1/V_1)[\ln (1-v_{2,s}) + v_{2,s} + \chi_1 \cdot v_{2,s}{}^2]$$

$$+ \frac{(1-2\bar{M}_c/\bar{M}_n)}{\bar{v}\bar{M}_c}(v_{2,s}^{1/3} - v_{2,s}/2) \tag{1}$$

where *i* is the degree of ionization multiplied by the valency of the ionic group attached to the polymer chain, $v_{2,s}$ is the equilibrium swelling volume fraction of the polymer, V_u is the molar volume of a structural unit, S^* is the ionic strength of the aqueous solution in which the network is swollen, V_1 is the molecular volume of the solvent, χ_1 is the polymer–solvent interaction parameter, $\bar{M}_n$ is the number average molecular weight of the uncrosslinked polymer, and $\bar{v}$ is the specific volume of the polymer.

The ionic term $(i \cdot v_{2,s}/V_u)^2/4S^*$ in equation (1) may be eliminated by the efficient shielding of the fixed charges provided by mobile electrolyte ions. The determination of the minimum electrolyte concentration needed for the elimination of the ionic contribution may be obtained by plotting equilibrium swelling *versus* concentration of the electrolyte. The point where $v_{2,s}$ (or $v_{2,app}$ which is the apparent equilibrium swelling volume fraction of the polymer) approaches asymptotically a maximum value, i.e. swelling is minimized, is the desired electrolyte concentration.

The obtained curves of the apparent equilibrium swelling of some sulphonated samples *versus* concentration of NaCl solution are shown in *Figure 1*.

It is noteworthy that at very high degrees of swelling in de-ionized water $(v_{2,app} < 0.01$ or $q_s > 100)$ the internal pressure in the ionic networks due to electrostatic repulsions was excessive, especially, in the absence of the protective action of an electrolyte. As a result these loosely crosslinked products disintegrated, if they were left for a few days in pure water, being transformed to fully water-soluble PS products, because of carbon–carbon bonds rupture. A similar observation was made by Breitenbach and Karlinger[12] with poly(methacrylic acid), loosly crosslinked by divinylbenzene.

Figure 1 shows that at NaCl concentrations $\geqslant 2$ N the value of $v_{2,app}$ approaches a limiting value; thus the ionic contribution is essentially eliminated.

It is now possible to calculate the degree of crosslinking by measuring the equilibrium swelling of the sulphonated products in the form NaPSS in 2 N aqueous NaCl solutions, provided that the interaction parameter, χ, of the system 'sulphonated crosslinked PS–aqueous NaCl solution' is known.

Polymer–solvent interaction parameter for sulphonated PS–aqueous NaCl solutions

Estimation of the parameter χ_1 may be obtained from the second virial coefficient A_2 of the particular polymer–solvent system[13] as given by equation (2), when direct experimental results are not available in the
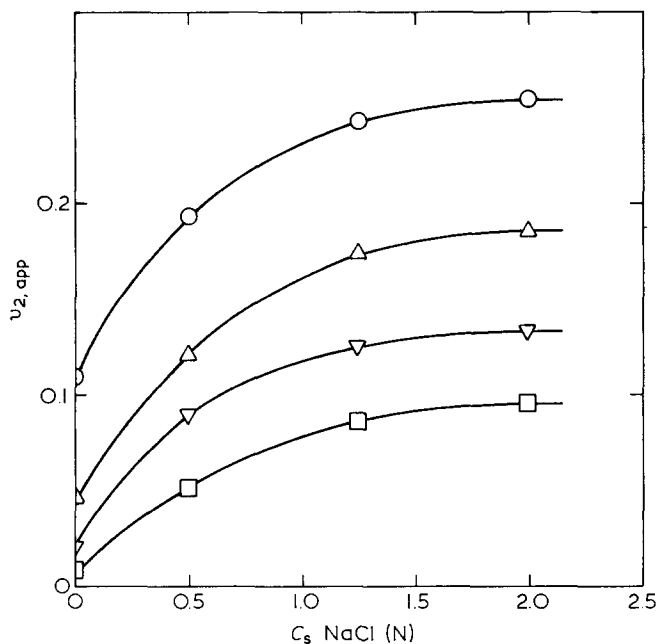
Figure 1 Apparent equilibrium swelling of some sulphonated samples *versus* concentration of NaCl solution. The samples nos. are: ○, 2; △, 5; ▽, 7; □, 9

Table 3 Molecular weight per crosslinked unit in sulphonated crosslinked PS

Crossl. PS Sample no.	App. polymer volume fraction, $v_{2,app.}$	Polymer volume fraction, $v_{2,s}$	Mol. wt. per crossl. unit $\bar{M}_c$
1	0.3554	0.3804	410
	±0.0204	±0.0235	± 80
2	0.2546	0.2641	1300
	±0.0091	±0.0098	±140
3	0.2567	0.2656	1270
	±0.0019	±0.0021	± 30
4	0.2367	0.2441	1640
	±0.0036	±0.0037	± 80
5	0.1846	0.1890	3420
	±0.0001	±0.0001	± 10
6	0.1506	0.1535	6020
	±0.0016	±0.0016	±170
7	0.1335	0.1356	8250
	±0.0039	±0.0040	±610
7a	0.1666	0.1701	4600
	±0.0076	±0.0079	±580
7b	0.2551	0.2634	1300
	±0.0037	±0.0040	± 60
7c	0.3688	0.3864	390
	±0.0052	±0.0057	± 20
8	0.1028	0.1041	15160
	–	–	–
9	0.0949	0.0960	17870
	–	–	–
10	0.0879	0.0889	20700
	±0.0016	±0.0016	±690

literature:

$$\chi_1 = 0.5 - A_2\rho_2^2\bar{V}_1 \tag{2}$$

where ρ_2 is the density of the polymer and $\bar{V}_1$ is the partial molar volume of the solvent.

The second virial coefficient A_2 of the system aqueous NaCl solution $(C_s^0 = 2 \text{ mol l}^{-1})$–NaPSS $(\bar{M}_w = 223\,000)$ was measured at $25° \pm 0.1°C$ by Takahashi *et al.*[14], using a light-scattering technique, as $A_2 = 0.56 \times 10^{-4}$.

As this value of A_2 only depends slightly on $\bar{M}_w$ and the polymers under investigation (crosslinked NaPSS) possess a structure very similar to the one of the corresponding linear products, it is assumed that the same value of A_2 is also valid for the crosslinked polymer.

As the value $\bar{V}_1$ is $\approx 19 \text{ l mol}^{-1}$ for aqueous 2N NaCl, the term $A_2\rho_2^2\bar{V}_1$ of equation (2) is of the order of 10^{-3}. Consequently, it can be neglected compared to the constant term 0.5. Thus, χ_1 comes very close to 0.5 at 25°C.

Molecular weight per crosslinked unit in sulphonated crosslinked PS.

The molecular weight per crosslinked unit of the sulphonated products can be calculated using the already calculated value of χ_1 and the equilibrium swelling of the products in NaPSS form in aq. 2N NaCl at $25° \pm 0.5°C$. The results of these swellings and the calculated values of $\bar{M}_c$ are given in *Table 3*, assuming a constant $\rho_2 = 1.057$ g cm^{-3} and χ_1 independent of $v_{2,s}$.

The values of $v_{2,app}$ were corrected to $v_{2,s}$ taking into account the porosity of the particles from *Table 1*[10,15].

It is noteworthy that the values of $\bar{M}_c$ obtained are considerably lower than those of the corresponding sulphonated PS-crosslinked particles. This increase of the crosslinking density is due to additional crosslinking of the sulphone-type.

Sulphone crosslinking

Sulphonation of crosslinked PS with various sulphonating agents results in crosslinks of the sulphone-type $(-SO_2-)$. Such crosslinks are in general undesirable, mainly because they deactivate the functional sulphonic groups and decrease the average size of the network structure, r_c.

To determine the extent of this reaction, let m be the ratio of the crosslinking densities before (ρ) snd after sulphonation (ρ_s). Then, taking into account equation (3), equation (4) is derived where the suffix s comes from sulphonation:

$$\bar{M}_c = \frac{N_0 M_0}{v} \tag{3}$$

$$m = \frac{\rho_s}{\rho} = \frac{v_s/N_0}{v/N_0} = \frac{M_0/\bar{M}_{c,s}}{M_0/\bar{M}_c} = \frac{\bar{M}_c}{\bar{M}_{c,s}} \tag{4}$$

Thus, it is now possible to determine the increase in network density due to sulphone-type crosslinks for the various sulphonation agents used, if the molecular weights per crosslinked unit before, $\bar{M}_c$, and after sulphonation, $\bar{M}_{c,s}$, are known.

Table 4 was prepared by comparison via equation (4) of the loosely crosslinked networks, for which the values of $\bar{M}_c$ are more reliable for reasons explained elsewhere[10]. There is a possibility of comparing the crosslinking function of both H_2SO_4 and HSO_3Cl. Thus, sample nos. 7a, 7b and 7c were the only ones sulphonated with HSO_3Cl in a proportion 1.25, 2.5 and 5 ml g^{-1}, respectively.

From these results it is concluded that sulphonation with H_2SO_4 results in networks which are 2.6 ± 0.6 times denser, while sulphonation with HSO_3Cl produces networks which are 2.4 to 27.9 times denser than those produced with H_2SO_4.

Table 4 Crosslinking density ratios, m, of crosslinked and sulphonated particles

Sample no.	Mol. wt., $\bar{M}_c$	Mol. wt., $\bar{M}_{c,s}$	Ratio, m
7	28 330	8250	3.4
8	33 270	15 160	2.2
9	44 160	17 870	2.5
10	44 960	20 700	2.2
7a	28 330	4600	6.2
7b	28 330	1300	21.8
7c	28 330	390	72.6

Average size of the network structure

It was mentioned previously that the availability of the exchange sites to extremely bulky groups is indispensable in certain applications such as fractionation of bio-polymers. Consequently, an estimation of the average size of the network structure, r_c, as a function of the ionic strength of the electrolyte solution, S^*, for networks of different values of molecular weight per crosslinked unit, $\bar{M}_c$, is very useful, especially if correlated to the molecular weight at the exclusion limit, M_{lim}. In this respect, the observation of Hirayama et al.[16] for the occurrence of rectilinearity between the size of the network, r_c, and the root-mean-square end-to-end distance, $(\overline{r^2})^{1/2}$, calculated from physical characteristics of an homologous polymeric series, i.e. from the values of K and η of the equation of Mark–Houwink–Sakurada $[\eta] = KM^\alpha$, seems to be valuable for the design of proper packing materials for various chromatographic techniques.

For the estimation of the average size of the network structure, r_c, the number of bonds in the chain between the crosslinkages, n, is needed. For vinyl polymers this may be calculated from equation (5) provided the value of $\bar{M}_c$ is known:

$$n = 2\frac{\bar{M}_c}{M_0} \tag{5}$$

The mean square end-to-end distance of the unperturbed chain between the crosslinks, is calculated[17] from equation (6)

$$(\overline{r^2})_0 = C_\infty n l^2 \tag{6}$$

where l is the bond length (0.154 nm for vinyl polymers), and C_∞ is characteristic ratio equal to 10.8 for PS[13]. As the network particles are in the swollen state up to a degree of swelling, $q_s = 1/v_{2,s}$, the average size of the network structure, r_c, is expressed by:

$$r_c = (\overline{r^2})_0^{1/2} q_s^{1/3} \tag{7}$$

When using the prepared gels in electrolyte solutions of various ionic strengths, the values of $v_{2,s}$ from *Figure 1* may be used, together with the values of M_c from *Table 3*. The calculated values of r_c are plotted in *Figure 2* against ionic strength S^* for different values of $\bar{M}_c$.

As seen from the Figure the average size of the network structure, r_c, decreases with increase in ionic strength. Thus, the larger molecules among those permeating the network are first squeezed out upon increase of the ionic strength in elution, based on an ionic strength gradient.
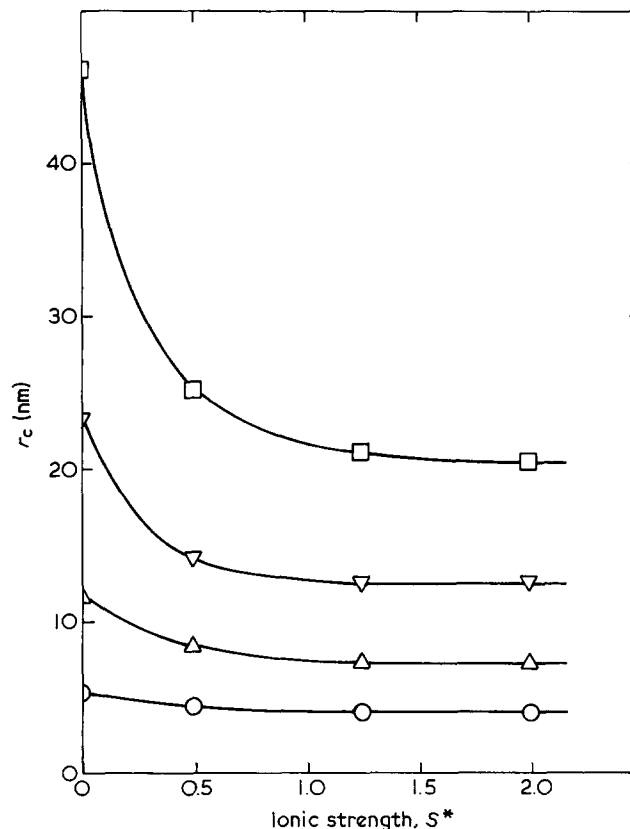

Figure 2 Average size of the network structure, r_c, as a function of the ionic strength of the electrolyte solution, S^*. The values of $\bar{M}_c$ of the samples are: $\bigcirc$, 1300; $\triangle$, 3420; $\triangledown$, 8250; $\square$, 17870

Table 5 Ion-exchange capacity of sulphonated networks compared to commercial products

Sample no.	Mol. wt., $\bar{M}_c$	Capacity for exchange of	
		$H^+ \rightarrow Na^+$	$Na^+ \rightarrow Ca^{2+}$
1	410	3.0	2.9
2	1300	4.3	3.6
3	1270	4.3	3.7
6	6020	5.0	3.4
10	20 700	3.1	3.2
7a	4600	3.1	1.9
7b	1300	3.5	2.5
7c	390	4.8	2.8
Relite® CF		4.3	2.9
Relite® CFS		4.3	--

Ion-exchange capacity measurements

The capacity of the resins was measured for exchange of H^+ by Na^+ and Na^+ by Ca^{2+}. The results of the measurements are shown at *Table 5*. The capacity of two commercial products of CYBRON/Resindion measured under identical conditions, is also given for comparison. Relite® CF is a gel-type resin, while Relite® CFS is macroporous. Both of these come from a sulphonated styrene–DVB matrix.

It can be seen from the Table that the capacity of the resins produced is similar to that of the commercial products. In particular, the resins produced with H_2SO_4 possess a greater capacity than those produced with HSO_3Cl. Moreover, the large size of their networks is

beneficial for the chromatographic fractionation of charged biopolymers of a large molecular weight, provided these are not denatured by the hydrophobic PS matrix.

CONCLUSIONS

A reaction time of ≈ 10 min is adequate for the sulphonation of isoporous crosslinked PS particles. The polymer–solvent interaction parameter for the system aqueous 2N NaCl–NaPSS is calculated to be 0.5. Due to sulphone crosslinking, sulphonation with H_2SO_4 results in 2.6 times denser networks compared to the initial non-ionic ones, while HSO_3Cl makes them 6.2–72.6 times denser. The average size of the network structure, r_c, and the ionic strength of the electrolyte solution, S^*, varies from 5.2 to 20.5 nm. The ion-exchange capacity of the resins prepared by H_2SO_4 is higher than that of the resins prepared by HSO_3Cl.

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