Physical characterization of suspension-crosslinked polystyrene particles and their sulphonated products:

1. Nonionic networks

F. P. Regas and G. N. Valkanas
Laboratory of Organic Chemical Technology, Department of Chemical Engineering, National Technical University of Athens 42, 28th Octobriou Street, Athens, Greece

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Suspension-crosslinked particles of polystyrene have been prepared via a novel Friedel–Crafts reaction. Their structure and physical behaviour have been investigated using mercury porosimetry and swelling studies. The crosslinking agent used was 1,4-dichloromethyl-2,5-dimethyl benzene which exhibits limited polycondensation under the crosslinking reaction conditions. The degree of polymerization of the crosslinking agent between two crosslinks has been estimated for the crosslinked systems. The average size of the network structure has been estimated also with reference to potential g.p.c. applications.

Keywords Crosslinking; post-polymerization crosslinking; molecular weight per crosslinked unit; network size; network

INTRODUCTION

Polystyrene (PS) network structures are prepared usually by copolymerization of styrene and divinylbenzene (DVB)[1]. Owing to different reactivity ratios of styrene and DVB a wide network size distribution is usually obtained. When crosslinked PS particles are used for separation methods this size distribution may affect the efficiency of such separation processes as gel permeation chromatography (g.p.c.)[2]. Recently, a technique has been reported which introduces the crosslinks after the polymerization in a solution of the polymer via a Friedel–Crafts reaction. This method seems to be preferable as it leads to uniform distribution of the crosslinks[3]. Nevertheless, the products of this method have to be crushed afterwards for the necessary particle size distribution to be obtained[4]. The irregularly shaped crosslinked particles that result have very poor hydrodynamic properties. To overcome this disadvantage, suspension crosslinking in various suspension media has been examined[5,6], where the products are obtained in a suitable spherical form.

Here, as in a study reported previously[5], a medium composed of silicone oil and 1,2-dichloroethane (DCE) is used for the suspension of polystyrene (PS) solution. By changing the reaction time and molar ratio, S, of polystyrene repeating units relative to the cross-linking agent used, it is possible to prepare crosslinked particles of low or high crosslinking density. These gels are examined mainly with respect to their structure. Thus, qualitative estimations based on swelling equilibria and quantitative calculations of the crosslinking densities are obtained using known polymer–solvent interaction parameters. The networks are examined also as potential packing materials in gel permeation chromatography (g.p.c.).

EXPERIMENTAL

Preparation of crosslinked PS

The crosslinked PS samples used were prepared from atactic (thermally polymerized) PS supplied by Dow-Chemicals Hellas and having $\bar{M}_n = 117\,500$, $\bar{M}_w = 265\,000$, and softening point $T_s = 101.5$°C. The crosslinking agent, 1,4-dichloromethyl-2,5-dimethyl benzene was prepared by the method reported by Peppas and Valkanas[7].

The procedure for the preparation of the crosslinked particles of PS has been reported previously[5]. Briefly, a solution of PS, crosslinking agent and a catalyst, $SbCl_5$, was dispersed in a suspension medium consisting of a solution of silicone oil and DCE at a volume ratio of 3:2. The system was continuously kept in suspension at 500 rev min^{-1} and at a temperature of choice until the end of the reaction. Then, the PS particles were received by filtration, rinsed with petroleum ether, purified in boiling methyl ethyl ketone and dried *in vacuo*.

The conditions of preparation of the particles with a variety of crosslinking densities are given in *Table 1*. All the particles were prepared at a constant catalyst concentration of 3.3×10^{-3} mol l^{-1}, at 50°C.

Mercury porosimetry

To obtain pore radii as a function of mercury intrusion up to ≈415 MPa, a mercury porosimeter (American Instrument Company) was used. Approximately 0.05 g of polystyrene particles were placed in a glass penetrometer and evacuated to a pressure of <3 Pa. Mercury was then allowed to enter the penetrometer and intrusion volumes determined.

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Table 1 Conditions of preparation and porosity of the dry crosslinked PS particles

Sample no.	Molar ratio, S (mol/mol)	Crosslinking time (h)	Porosity ($cm^3 g^{-1}$)
1	4	4	0.175
2	4	2	–
3	8	4	0.140
4	8	2	–
5	16	4	0.125
6	16	2	–
7	32	4	–
8	32	2	–
9	64	4	–
10	64	2	–
11	128	4	0.117
12	128	2	–
13	256	4	–
14	256	2	0.116

particles, mercury porosimetry was carried out on nonporous glass spheres (Cataphote Division of Ferro Corp.) of similar particle size distribution.

Critical point drying of the polymer particles was required for mercury porosimetry; it was carried out in a critical point drying apparatus (Polaron Model 3000).

Determination of the degree of swelling

Samples of the crosslinked PS particles ($\approx$0.2 g) were swollen in toluene in small glass filters for at least two days at 25° ± 0.5°C. Subsequently, the filters were drained via suction filtration for 2 min and immediately weighed. The filters were reweighed, after vacuum drying at 80°C up to constant weight, with and without the dry samples. Thus, the weight of the dry polymer, m_2, and that of the polymer plus solvent at equilibrium, $m_{2,\mathrm{app}}$, were obtained. The polymer volume fractions, $v_{2,\mathrm{app}}$, of the samples were calculated via equation (1):

$$v_{2,\mathrm{app}} = \frac{m_2/\rho_2}{m_2/\rho_2 + (m_{2,\mathrm{app}} - m_2)/\rho_1} \qquad (1)$$

where ρ_1 and ρ_2 are the densities of the solvent and the polymer, respectively. Special attention was taken, to remove any entrapped interparticle solvent by suction, before determining the values of $m_{2,\mathrm{app}}$.

RESULTS AND DISCUSSION

Porosity of the crosslinked particles

The results of the porosity determination of the crosslinked polystyrene beads are given in *Table 1*. The porosity of the PS particles remains at low values (<0.3 $cm^3 g^{-1}$) in all the samples. Consequently, the microbeads should be considered to be of the gel-type rather than macroporous. This consideration is enhanced by the fact that the particles examined under an optical microscope are transparent and not opaque or white. This is despite the fact that the procedure of their preparation, i.e. post-polymerization crosslinking in the presence of a diluent, may classify the products as being of the macroporous type[8].

The increase of the porosity with nominal crosslinking ratio, S, should not be attributed to different initial quantities of the diluent, because the porosity ratio of the extreme products (*1C* and *14C*) is 1.51, which is considerably higher than the ratio (1.05) of the corresponding initial polymer volume fractions. However, this increase may be attributed to the increase of the mean size of the diluent molecule, due to the presence of the crosslinking agent, and more generally to the decrease of the thermodynamic affinity of the diluent for the polymer[9].

Molecular weight per crosslinked unit

The molecular weight per crosslinked unit in a nonionic network may be calculated from the relation[10]:

$$-[\ln(1 - v_{2,s}) + v_{2,s} + \chi_1 v_{2,s}^2] = (v_1/\bar{v}\bar{M}_c)(1 - 2\bar{M}_c/\bar{M}_n)(v_{2,s}^{1/3} - v_{2,s}/2) \qquad (2)$$

where $v_{2,s}$ is the equilibrium swelling volume fraction of the polymer, χ_1 is the polymer–solvent interaction parameter, v_1 is the molecular volume of the solvent, $\bar{v}$ is the specific volume of the polymer, $\bar{M}_n$ is the number-average molecular weight of the uncrosslinked polymer, and $\bar{M}_c$ is the number-average molecular weight per crosslinked unit.

The polymer–solvent interaction parameter, χ_1, for a binary polymer–solvent system is dependent on both temperature and concentration, v_2. However, for post-polymerization crosslinking with a polyfunctional crosslinking agent, a gradual modification of the polymer structure occurs which may affect also the correlation $\chi_1 = f(T, v_2)$. Although chemical structure changes occur during the crosslinking reaction investigated here, the chemical similarity of the crosslinking agent to the PS repeating unit may allow use of previously reported values of χ_1 for pure PS solutions.

Another significant factor that may influence the accuracy of structural analysis of Friedel–Crafts-crosslinked PS is the porosity of the particles. The swelling agent fills the pores, thus changing the equilibrium swelling volume fraction of the polymer, $v_{2,s}$. Therefore, the observed (apparent) values of the equilibrium polymer volume fraction in the swollen particles, $v_{2,\mathrm{app}}$, must be corrected for porosity to obtain the true value of $v_{2,s}$. It has been established[11] that the volume fraction $v_{2,s}$ is related to the volume fraction $v_{2,\mathrm{app}}$ by equation (3):

$$\frac{1}{v_{2,s}} = \frac{1}{v_{2,\mathrm{app}}} - \rho_2 \cdot p \qquad (3)$$

where p is the porosity of the polymer, in cm^3, of pores per g of solid polymer.

In addition to porosity effects, changes of the density of the polymer due to crosslinking may influence the estimated $v_{2,s}$ as is evident in equation (3). Generally, the density of a polymer, ρ_2, increases with crosslinking density due to a better packing of the polymeric molecules. Consequently, the accuracy of estimation of $\bar{M}_c$ increases for the networks of lower degree of crosslinking, because of lower density and diminished chemical consistency deviations. However, even for loosely crosslinked networks, significant alteration of the chemical structure may occur due to homopolymerization of the crosslinking agent in the crosslinking bridges, as shown by Peppas and Staller[12] and discussed later.

The molecular weights per crosslinked unit of the crosslinked particles, $\bar{M}_c$, were calculated on the basis of equilibrium swelling in toluene. First, the values of $v_{2,\mathrm{app}}$ were calculated and then, equation (3) was used for the estimation of $v_{2,s}$. The PS density, ρ_2, was measured as 1.057 g cm^{-3}. Some values of porosity, p, which were not obtained were determined by linear interpolation of the existing values. The values of parameter χ_1, which is a function of $v_{2,s}$ at a constant temperature, were taken from Flory[13]. Finally, the molecular weight per crosslinked unit was calculated via equation (2). The results are shown in *Table 2*. It is concluded that the correction of the volume fraction $v_{2,\mathrm{app}}$ to $v_{2,s}$ is not necessary for the loosely crosslinked products.

It must be emphasized that it was possible to obtain network structures with molecular weight per crosslinked unit, $\bar{M}_c$, up to $\approx$45 000, which is very close to the theoretical limiting value (59 000). However, these gel beads adhered to each other and often were difficult to handle.

Degree of polymerization of the crosslinks

As mentioned previously, it is possible to have a low degree of crosslinking and, at the same time, a considerable presence of the crosslinking agent in the polymer, because of its homopolymerization during crosslinking. This degree of polymerization may be calculated approximately as follows.

The molecular weight per crosslinked unit is by definition:

$$\bar{M}_c = \frac{N_0 \cdot M_0}{v} \tag{4}$$

where N_0 is the number of molecules of the repeating unit, M_0 is the molecular weight of the repeating unit and v is the number of the crosslinked units. Provided a difunctional crosslinking agent is used, it follows that:

$$S_r = \frac{N_0}{N_c} = \frac{N_0}{v/2} \tag{5}$$

where S_r is the molar ratio of repeating units relative to the crosslinking agent reacted with the polymer and N_c is the number of molecules of the crosslinking agent reacted (not the added ones).

Table 2 Molecular weight per crosslinked unit

Crossl. PS Sample no.	App. polymer volume fraction, $v_{2,\mathrm{app}}$	Polymer volume fraction, $v_{2,s}$	Mol. wt per cross. unit, $\bar{M}_c$
1C	0.3760	0.4041	1120
	±0.0102	±0.0117	± 90
2C	0.3187	0.3364	1890
	±0.0092	±0.0103	±150
3C	0.2726	0.2841	2970
	—	—	—
4C	0.1861	0.1909	7890
	±0.0088	±0.0092	±760
5C	0.1605	0.1640	10 550
	—	—	—
6C	0.1223	0.1242	17 800
	±0.0039	±0.0040	±860
7C	0.2999	0.2376	4730
	±0.0145	±0.0156	±690
8C	0.1507	0.1537	11 920
	±0.0110	±0.0115	±1570
9C	0.1057	0.1071	21 940
	±0.0018	±0.0018	±500
10C	0.0875	0.0885	27 620
	±0.0045	±0.0046	±1550
11C	0.0854	0.0864	28 330
	±0.0025	±0.0026	±910
12C	0.0761	0.0769	33 270
	±0.0099	±0.0101	±3850
13C	0.0498	0.0501	44 160
	±0.0001	±0.0001	± 30
14C	0.0479	0.0482	44 960
	±0.0006	±0.0006	±270

Then, the theoretical or expected molecular weight per crosslinked unit, $\bar{M}_{c,t}$, may be derived from equations (4) and (5), provided the crosslinks are monomolecular:

$$\bar{M}_{c,t} = \frac{S_r}{2} M_0 \tag{6}$$

It is evident that, when the crosslinking agents forms chains of a mean degree of polymerization $X_{n,c}$, then N_c and v are correlated by equation (7):

$$\frac{v}{2} = \frac{N_c}{\bar{X}_{n,c}} = \frac{N_0}{S_r} \frac{1}{\bar{X}_{n,c}} \tag{7}$$

and $\bar{M}_c$ is equal to:

$$\bar{M}_c = \frac{S_r}{2} \bar{X}_{n,c} \cdot M_0 \tag{8}$$

where $\bar{M}_c$ is the (real) molecular weight per crosslinked unit determined experimentally.

The average degree of polymerization of the crosslinks, $X_{n,c}$, may be determined, by combining equations (6) and (8):

$$\bar{X}_{n,c} = \frac{\bar{M}_c}{\bar{M}_{c,t}} = \frac{2\bar{M}_c}{S_r M_0} \tag{9}$$

On the assumption that the losses result from unreacted crosslinking agent in cases of nonquantitative reactions (sample nos. 1–8), it is possible to calculate S_r on the basis of the percentage of the reacted crosslinking agent. Sample nos. 9–14 cannot be utilized in this way because of confusion between the content of crosslinking agent and the overall losses. The results are shown in *Table 3*. Using equation (9) the value of $\bar{X}_{n,c}$ was calculated as 2.5 ± 0.6. In this analysis the value $\bar{X}_{n,c}$ 10.0 was excluded as it statistically differed significantly from the others.

Table 3 Yields and molar ratios of repeating units to crosslinking agent, S_r

Crossl. PS Sample no.	Yield (%)	Molar ratio, S_r	Degree of pol., $\bar{X}_{n,c}$
1	75.8	9.9	2.2
2	74.3	12.1	3.0
3	85.6	19.6	2.9
4	82.3	53.7	2.8
5	94.7	20.2	10.0
6	90.1	113.1	3.0
7	96.2	63.0	1.4
8	95.4	108.8	2.1
9	98.0	–	–
10	96.0	–	–
11	97.3	–	–
12	96.5	–	–
13	97.4	–	–
14	98.8	–	–

Gel particles as packing materials for gel permeation chromatography (g.p.c.)

The prepared gel particles are very promising packing materials for gel permeation chromatography, especially because of their isoporous networks and ease of preparation. The analysis which follows is related to such an application.

For vinyl polymer, the number of bonds in the chain between the crosslinkages, n, is related to the molecular weight per crosslinked unit, $\bar{M}_c$, by:

$$n = 2\frac{\bar{M}_c}{M_0} \qquad (10)$$

By comparing equations (8) and (10) the number of links, n, is obtained:

$$n = S_r \cdot \bar{X}_{n,c} \qquad (11)$$

The mean square end-to-end distance of the unperturbed chain between the crosslinks, $\overline{(r^2)}_0^{1/2}$ is estimated[14] from equation (12):

$$\overline{(r^2)}_0 = C_\infty n l^2 \qquad (12)$$

where l is the bond length ($l = 0.154$ nm), and C_∞ is the characteristic ratio or rigidity factor of PS ($C_\infty = 10.8$)[15]. As the network particles are used 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 as:

$$r_c = \overline{(r^2)}_0^{1/2} q_s^{1/3} \qquad (13)$$

When using these gels for molecular weight determinations of PS with toluene as a solvent, the values of r_c are calculated from the corresponding values of the molar ratio n, and the equilibrium degree of swelling, q_s, The dependence of the average size of the network structure, r_c, on the molar weight per crosslinked unit, M_c, is given in *Figure 1* which shows that the obtained values of r_c varied from 3.1 to 40.9 nm.

Similar bead-shaped PS gels were prepared by copolymerization of styrene and DVB in suspension in the absence of a non-solvent of the polymer, thus being of the gel-type. These crosslinked particles with average sizes of the network structure, r_c, varying from 5.0 to 21.5 nm are good packing materials for g.p.c.[16]

Consequently, the gels examined here are expected to be even better g.p.c. packing materials due to higher values of r_c and narrower network size distribution. In a future publication, the feasibility of using these gel beads for such an application is experimentally demonstrated.

CONCLUSIONS

The networks produced in a silicone oil suspension possess a low porosity (<0.175 cm^3 g^{-1}), thus being gel-type particles. It is possible to obtain a series of products with a wide range of crosslinking density as judged by $\bar{M}_c$, which varies from 1100 to 45 000. The degree of polymerization of the crosslinking agent in the crosslinks is 2.5. The average size of the network structure, r_c, varies from 3.1 to 40.9 nm.

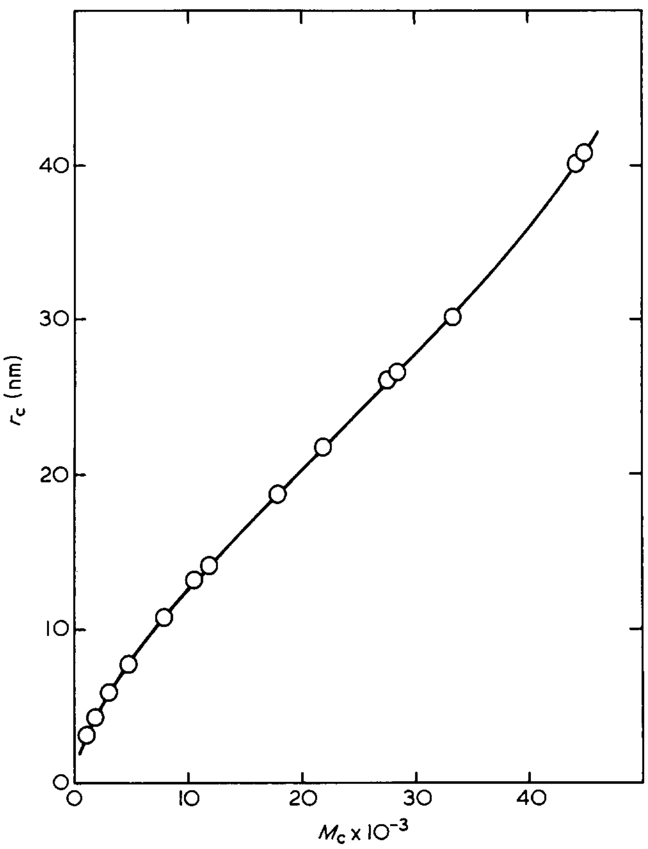

Figure 1 Effect of molecular weight per crosslinked unit, $\bar{M}_c$, on the average size of the network structure, r_c

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