# **33.** *Solvent-modified Polymer Networks. Part I. The Preparation and Characterisation of Expanded-network and Macroporous Styrene–Divinylbenzene Copolymers and their Sulphonates.*

By J. R. MILLAR, D. G. SMITH, W. E. MARR, and T. R. E. KRESSMAN.

Polymerisation of styrene–divinylbenzene–solvent mixtures in suspension yields bead copolymers with modified properties. Depending on the proportion of solvent and of cross-linking agent, a gradation in properties from those of an expanded network to those of a macroporous material is obtained, with swelling properties which can be predicted from the starting conditions. Some properties of these disentangled copolymers are compared with those of corresponding conventional copolymers. Their structure is discussed and shown to persist in the derived ion-exchange resins.

IT is known that the gel properties of three-dimensional polymer networks may be modified by carrying out the polymerisation in the presence of diluents. From such polymers, ion-exchange materials have been made whose mechanical properties,[1] exchange kinetics,[2] and equilibria [3] differed from those of corresponding materials prepared in absence of the diluent. Most of this work, however, has been empirical, only Mikes [3] having attempted a systematic study.

In the present work the effect of solvating diluents on the properties of cross-linked suspension copolymers of styrene and divinylbenzene and their sulphonated derivatives has been systematically studied. The several products have been characterised by their swelling properties: in toluene for the hydrocarbon copolymers, and in water for the sulphonated derivatives.

Some physical characteristics of a number of these materials have been measured, as well as some abnormal swelling properties in liquids other than the characterising solvents. The presence of macroporosity in certain of the products (especially those of higher divinylbenzene content and higher dilution) has been demonstrated both by their physical properties and, directly, in electron micrographs of the polymer structure.

## EXPERIMENTAL

*Materials.*—Styrene, divinylbenzene, and toluene were purified as previously described.[4] Various batches of commercial divinylbenzene solution were used, each with a known content of divinylbenzene isomers. Batch analyses ranged between 50% and 60% v/v, the usual figure being about 55%. A concentrated sample, assaying 86% v/v, was obtained by fractional distillation. Xylene (low in sulphur compounds), heptane (low in aromatic compounds), and all other materials, unless otherwise specified, were G.P.R. grades, used without further purification. The catalyst was a commercial grade of azoisobutyronitrile containing about 7% of moisture. Depending on the polymerisation system used, the stabiliser was either "Promulsin" (Watford Chemical Co. Ltd.) or "Rhodoviol HS. 100" (R. W. Greeff & Co.).

*Polymerisation.*—The method used for the smaller-scale preparations was essentially that of Pepper,[5] the catalyst (0·2% w/v on the total solution volume) being dissolved in the appropriate mixture of solvent and monomers. In these preparations the volume fraction, $F_M$, of monomers ranged from 0·25 to 1·0, and the divinylbenzene contents from 7 to 86% v/v. [$F_M$ is the factor, (volume of monomer mixture)/(total volume of monomers and diluent).]

Polymerisation was substantially complete after 250—300 hours at 80° ± 1°. The resulting copolymer spheres were boiled with 2N-hydrochloric acid to hydrolyse any adhering

---

[1] Clarke, U.S.P. 2,730,768, 2,731,408, 2,731,411, and 2,732,351.
[2] Wiley and Schmitt, *J. Polymer Sci.*, 1958, **27**, 587.
[3] Mikes, *J. Polymer Sci.*, 1958, **30**, 615.
[4] Millar, *J.*, 1960, 1311.
[5] (*a*) Pepper, *J. Appl. Chem.*, 1951, **1**, 124; (*b*) Pepper and Reichenberg, *Z. Elektrochem.*, 1953, **57**, 183.

" Promulsin," and washed with water, and finally with acetone to remove any traces of solvent. (When diphenylmethane was used as solvent, extraction of the copolymer by hot acetone for about 2 hr. was necessary to remove all the diphenylmethane.) The maximum amount of soluble polymer, obtained by Soxhlet extraction with boiling toluene, was 4·5%, which has a negligible effect on the measured solvent regains.

For larger-scale preparations used as intermediates for the ion-exchange resins, polymerisations were performed in suspension essentially by the method previously described,[4] a reflux condenser loosely plugged at the top being used to avoid loss of solvent. The catalyst concentration was increased to 0·4% w/v, based on the total solution volume, to maintain a reasonable polymerisation rate and give essentially complete conversion into polymer in 24 hr. at 75—80°.

When the system was short-stopped by the addition of a small amount of 4-t-butyl catechol, the two preparative methods gave essentially identical products. The t-butylcatechol, ~0·05% w/v on the initial monomer–solvent mixture, was dissolved in a small quantity of toluene and added to the system at the end of the polymerisation period. After a further hour at polymerisation temperature, the copolymer spheres were filtered off, washed with acetone to remove solvent, and dried to constant weight at 95°.

*Sulphonation of Copolymers.*—This was carried out essentially as described by Pepper [5b] with the minor modifications previously indicated.[4] The total ion-exchange capacity of the resultant materials was determined by the usual method.[4]

*Organic Solvent Regains.*—Toluene regains were measured as previously described.[4] Regains in several other solvents were similarly measured (with appropriate correction for solvent retained between the beads and in the sinter) on both the hydrocarbon and the sulphonated copolymers. In the latter case dry samples of resin, in the appropriate ionic form, were immersed in the solvent and allowed to come to equilibrium at room temperature before the final centrifuging and weighing. In some systems the time to reach equilibrium was as much as 2—3 weeks.

Regains are expressed more appropriately as ml. of solvent/g. of polymer than as " weight swellings," where comparison is made with regains of other solvents. The implicit assumption that the liquid shows its normal density inside the polymer is justified by the agreement found between the " volume-swellings " of one polymer in a number of different " good " swelling agents, and analogy with the work of Pepper *et al.*[6]

*Water Regains.*—On the sulphonated copolymers these were measured as previously described.[4] For comparison with other regains on the parent hydrocarbon copolymers they are best expressed as ml. of water per g. of original hydrocarbon copolymer. This can be calculated from the ion-exchange capacity and the observed water regain per g. of the sulphonated copolymer. On the hydrocarbon copolymers they were measured by immersing the copolymer in methanol for 16 hr. and subsequently washing a column of the methanol-treated copolymer with demineralised water until methanol was no longer detectable. The water-containing copolymer was then centrifuged and dried in the normal manner.

*Swelling Times.*—These were determined for the hydrocarbon copolymers by immersing a few beads of identical size, taken from the interstices of a 36 B.S.S. mesh sieve, in toluene at room temperature and observing them under polarised light. A uniform grey pattern, corresponding to a state of balanced stress in the network,[4] was taken to indicate complete swelling and the time to reach this state was measured.

*Density.*—The apparent densities of the conventional hydrocarbon copolymers ($F_M = 1{\cdot}0$) were determined by a flotation method.[4] The apparent densities in air of a series of solvent-modified copolymers ($F_M = 0{\cdot}33$) were calculated [7] from their water regains and the observed matrix density of 1·11 ± 0·02. The apparent densities of the sulphonated products were measured pyknometrically in heptane, with a correction for the heptane uptake.[7]

## RESULTS

Fig. 1 shows the observed toluene regains for two series of copolymers containing 7% v/v and 55% v/v of divinylbenzene, plotted against the quantity of diluent (here toluene itself) present at the polymerisation stage. Other series of copolymers, prepared with 9%, 14%, 27%, and 86% v/v of divinylbenzene, showed parallel relationships, and in Fig. 2 the observed

---

[6] Pepper, Reichenberg, and Hale, *J.*, 1952, 3129.

[7] Reilly and Rae, " Physico-Chemical Methods," Methuen, London, 5th edn., 1954, Vol. I, 604.

regains are plotted against those calculated from the corresponding divinylbenzene contents and dilutions (see Discussion).

Fig. 3 shows the swelling times in toluene for polymers containing up to 6% of divinylbenzene prepared at different values of $F_M$. The apparent densities of the series at $F_M$ 0·33 are compared in Fig. 4 with those of conventional copolymers.

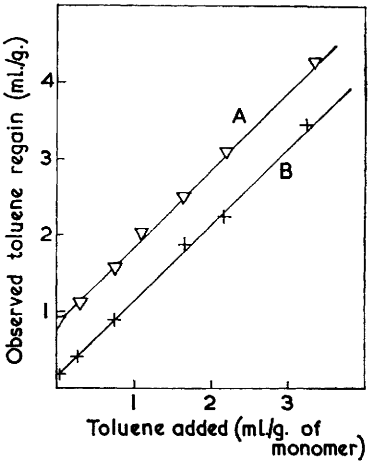


FIG. 1. Toluene regains.
Divinylbenzene contents: (A) 7%, (B) 55% v/v.

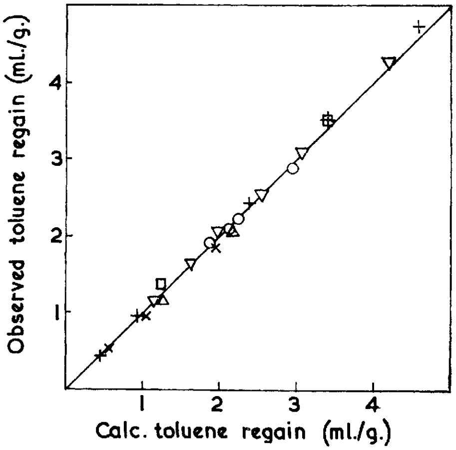


FIG. 2. Proof of general linear relation.
Divinylbenzene contents: ▽ 7%, ○ 9%, Δ 14%, ×27%, +55%, □ 88%. Regains are calculated from equation (1). The line is drawn with unit slope.

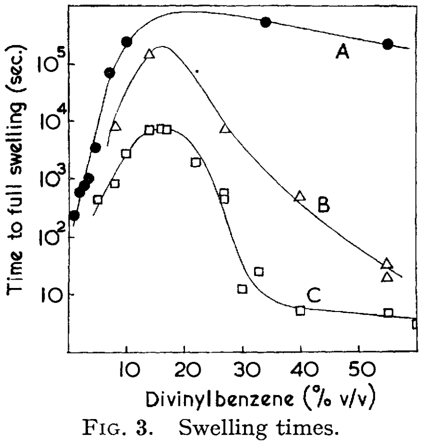


FIG. 3. Swelling times.
$F_M$ (A) 1·0, (B) 0·60, (C) 0·33.

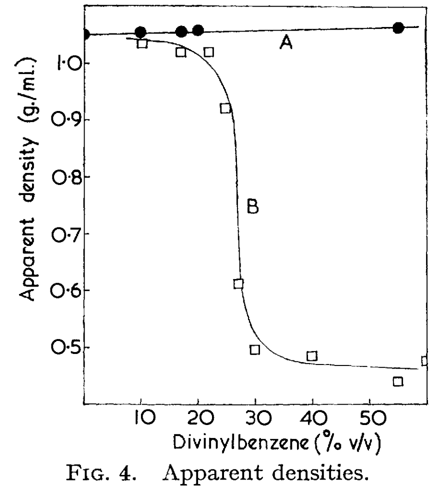


FIG. 4. Apparent densities.
$F_M$ (A) 1·0, (B) 0·33.

The cyclohexane regains shown in Fig. 5 of conventional styrene–divinylbenzene copolymers and those of two series of solvent-modified copolymers at different $F_M$ values were measured after 16 hr. only. In these conditions the conventional materials show extremely small cyclohexane regains. In Fig. 6 these and further results are mapped, by using the independent co-ordinates $F_M$ and divinylbenzene content, to illustrate the incidence of abnormally high cyclohexane regains in the solvent-modified copolymers.

In Table 1 are compared a macroporous ion-exchange resin made from a copolymer containing 55% v/v of divinylbenzene and prepared in toluene at $F_M$ 0·33, and a conventional

TABLE 1.

Comparison of a macroporous with a conventional resin.

| | Regain (ml./g. of hydrocarbon copolymer matrix) | | | |
|---|---|---|---|---|
| | Macroporous resin | | Conventional resin | |
| Solvent | Hydrocarbon copolymer | Sulphonated copolymer * | Hydrocarbon copolymer | Sulphonated copolymer * |
| Toluene | 2·21 | 1·34 | 0·79 | nil |
| Cyclohexane | 2·10 | 0·92 | nil | nil |
| n-Heptane | 2·09 | 0·96 | nil | nil |
| Nitromethane | 2·01 | 2·09 | 0·18 | 0·26 |
| Water | 1·10 | 2·24 | nil | 1·86 |
| Water on $H^+$-form | — | 2·24 | — | 1·86 |
| Water on $Li^+$-form | — | 2·18 | — | 1·82 |
| Water on $Na^+$-form | — | 2·19 | — | 1·64 |
| Water on $K^+$-form | — | 2·23 | — | 1·37 |

* Measured on the dry $H^+$-form, unless otherwise stated.

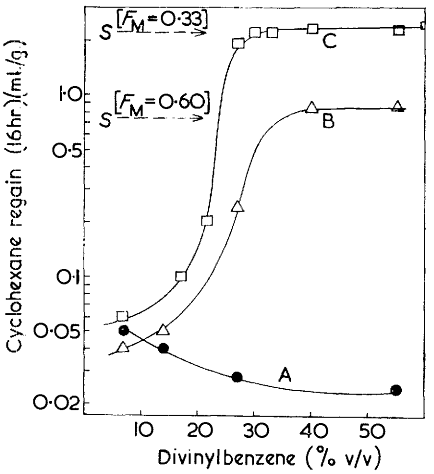


FIG. 5. Cyclohexane regains. $F_{\mathrm{M}}$ (A) 1·0, (B) 0·60, (C) 0·33.

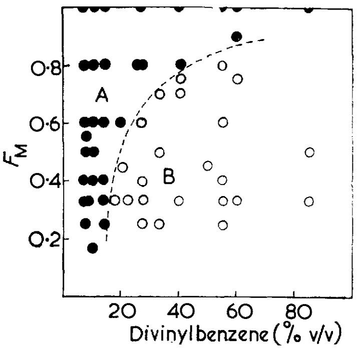


FIG. 6. Incidence of macroporosity.

(●) 16 hr. cyclohexane regain <0·1 ml./g. (○) 16 hr. cyclohexane regain >0·1 ml./g. (A) Region of expanded-network structures. (B) Region of macroporous structures.

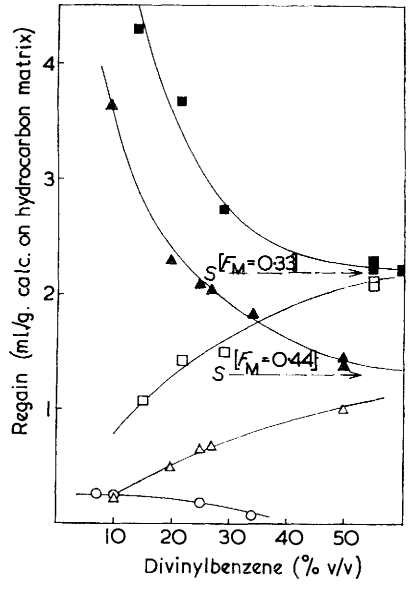


FIG. 7. Regains on sulphonated copolymers. (○) $F_{\mathrm{M}} = 1{\cdot}0$. (△) $F_{\mathrm{M}} = 0{\cdot}44$. (□) $F_{\mathrm{M}} = 0{\cdot}33$. Open symbols, nitromethane. Solid symbols, water.

sulphonic acid resin containing 7% v/v of divinylbenzene. The sulphonated products had capacities of 3·52 and 5·24 mequiv./g. and water regains, referred to the dry $H^+$-form, of 1·61 and 1·08 ml./g., respectively. In the Table, however, the regains are all expressed as ml./g. of the hydrocarbon copolymer. This provides comparable figures for the sulphonated material and the parent hydrocarbon, uncomplicated by the " dilution " brought about by the $SO_3H$ group.

The apparent densities of the two resins and their hydrocarbon precursors are given in Table 2.

TABLE 2.

Apparent densities.

| Resin | Apparent dry density (g./ml.) of: hydrocarbon matrix | $H^+$-form of sulphonated copolymer |
|---|---|---|
| Conventional ........................ | 1·05 | 1·44 |
| Macroporous ........................ | 0·44 | 0·70 |

Fig. 7 compares the water and nitromethane regains of two series of sulphonated solvent-modified copolymers prepared at $F_M$ 0·33 and $F_M$ 0·44, and the nitromethane regains of conventional materials.

## DISCUSSION

*Hydrocarbon Copolymers.*—At least up to a dilution of 3 ml. of toluene per ml. of monomers ($F_M = 0{\cdot}25$) the toluene regain (see Fig. 1) is given by

$$U_X = U_N + S, \qquad (1)$$

where $U_X$ is the regain of the product (in ml./g.), $U_N$ is the regain (in ml./g.) of the polymer produced conventionally, *i.e.*, in the absence of solvent, from the same monomer mixture, and $S$ is the volume of toluene per unit weight of monomers. That this relation holds for all divinylbenzene contents, at least up to 86%, is shown in Fig. 2 where the observed toluene regains of the polymers are plotted against those calculated from equation (1). The line is drawn with unit slope.

A similar relation is found when a solvent of somewhat higher chain-transfer constant (*e.g.*, xylene, diphenylmethane) is used, except that, as a secondary effect, chain transfer to solvent causes the slope to be slightly greater than unity (1·1 and 1·3, respectively), *i.e.*, it produces a progressively lower efficiency of cross-linking with increasing dilution. The deviation is greater the higher the chain-transfer constant and the higher the proportion of divinylbenzene.

The form of the relation suggests that for a given divinylbenzene content both the degree of entanglement and the extensibility of the final network are determined by the dilution of the polymerising system when the primary network is formed, *i.e.*, at the time of gelation. Thereafter, the polymer network continues to be formed within the ambit of the primary network, with little or no shrinkage during polymerisation, and with the polymer chains fully solvated. When the polymerisation is complete and the solvent is removed, the expanded network collapses, but reversibly, so that on the addition of a good solvating agent such as toluene it re-expands to its earlier state. A copolymer produced in the absence of added solvent, *i.e.*, at $F_M$ 1·0, is formed, effectively, in the presence of a continuously decreasing volume-fraction of solvent, the monomer acting as its own diluent and being progressively removed as it becomes converted into polymer. This results in the entanglement of the growing chains in a continuously collapsing network, until at completion of polymerisation the complex structure, which is no longer solvated, cannot regain its initial extended state when swollen with toluene. The presence of the solvent thus results in a copolymer of apparently lower cross-linking than that of a conventional copolymer of the same divinylbenzene content.

The effect of this reduced entanglement on the time of swelling in toluene is quite striking (Fig. 3). With all proportions of solvent the time to complete swelling increases steadily with increasing divinylbenzene content, reaches a maximum at 15—20% of divinylbenzene and thereafter decreases again. Everywhere the time required to achieve full swelling is lower the greater the proportion of solvent (decreasing $F_M$). This is consistent with a lower degree of entanglement at lower values of $F_M$ for a given degree of chemical cross-linking; however, there is no correlation of swelling time with apparent cross-linking. Further, the curves for both $F_M = 0{\cdot}6$ and $F_M = 0{\cdot}33$ show an inflection, which in the latter case occurs at about 27% of divinylbenzene, followed by a marked break at about 35% of divinylbenzene. Beyond this point swelling times are a matter of seconds, corresponding to a rate considerably faster even than that of a 1% divinylbenzene copolymer made in the absence of solvent, which has a higher toluene regain than any of the $F_M$ 0·33 copolymers investigated. The copolymers containing more than about 27% of divinylbenzene are opalescent and appear red-brown by transmitted light, a phenomenon characteristic of light-scattering by very small discontinuities in an optical medium.[8] These polymers quite rapidly take up, with evolution of air bubbles, liquids such as cyclohexane and heptane which are taken up by other copolymers to a negligible extent only; and at higher divinylbenzene contents the amount of organic solvent taken up approximates to the amount of inert diluent originally used, *i.e.*, to the term $S$ in equation (1). This is demonstrated for cyclohexane in Fig. 5, while the virtual identity of the cyclohexane, heptane and nitromethane regains is illustrated in Table 1. These materials, in contrast to conventional hydrocarbon copolymers, can even accommodate, without observable change in volume, appreciable quantities of water.

The apparent densities of the materials made at $F_M$ 0·33 likewise show a rapid change at about 20% of divinylbenzene, an inflection again occurs at about 27% of divinylbenzene and they become essentially constant above about 35% of divinylbenzene (Fig. 4). Comparatively little change occurs at $F_M$ 1·0.

We ascribe these phenomena to the existence of macropores in the copolymers in the region beyond the inflection, this description being used to distinguish the air-filled pores from those present in the copolymers of lower divinylbenzene content, which have a purely expanded-network structure, and in conventional cross-linked polymers prepared in the absence of added solvent. In the last two types of material, porosity is manifest only on uptake of a swelling solvent such as toluene. On removal of the toluene the structure shrinks and the pores disappear. In macroporous materials, some of the pores exist as such even in the solvent-free polymer, leading to a low apparent density.

In solvent-modified copolymers of given divinylbenzene content, macroporosity exists at all values of $F_M$ less than a critical value, whose dependence on divinylbenzene content is indicated by the diagram in Fig. 6. No truly macroporous materials of less than 18% divinylbenzene content have been prepared; on the other hand, at very high divinylbenzene content, $F_M$ values of 0·8 or higher can lead to macroporous materials. The criterion of macroporosity used in Fig. 6 is that the uptake of cyclohexane in 16 hr. should not be less than 0·1 ml. per g. of dry copolymer, a criterion that is matched by the onset of opalescence in the copolymers.

The structure of the solvent-modified materials can be deduced from a consideration of the normal mode of copolymerisation of styrene and divinylbenzene. The reactivity ratios for copolymerisation of styrene and *m*-divinylbenzene (the major constituent of commercial divinylbenzene solutions) are similar but somewhat lower than unity.[9] This means that, where the tetrafunctional monomer is the minor constituent, the polymer formed initially in a growing chain is richer, and that formed later is poorer, in divinylbenzene than the original monomer mixture.

[8] Rayleigh, *Phil. Mag.*, 1871, **12**, 447.

[9] Wiley and Sale, *J. Polymer Sci.*, 1960, **42**, 291.

Initiation occurs evenly throughout the droplets of monomer solution, and the chains grow by addition of monomer units: when a divinylbenzene unit is incorporated, the chain carries a pendent double bond, which may be incorporated in another growing chain. Combination of chains will occur more frequently at the divinylbenzene-rich end, resulting in " nuclei " whose central portion is of high divinylbenzene content and which possess a number of outward-growing chains with free-radical ends. The nuclei are swollen with the surrounding medium to an extent governed by their effective cross-linking and the nature of the medium: if the surrounding medium is a good solvent for polystyrene, the growing chains will be appreciably extended and will not tend to become entangled inside the nucleus. The monomer mixture is such a solvent, but as polymerisation proceeds in the absence of added diluent and the monomer is used up, the droplets shrink, the growing chains become less solvated, and the nuclei approach progressively closer to each other, with increased opportunities of penetration of a second nucleus by a growing chain of the first.

The effect on such a structure of increased divinylbenzene content in the monomer mixture is thus to increase the size of the nucleus at the expense of the growing chains. This encourages intranuclear entanglement, reducing also the number of outward growing chains. The final product at high conversion of a monomer mixture of high divinylbenzene content is, therefore, a compact and rigid structure with marked network entanglement in the nuclei.

In the presence of a solvating diluent which is inert, *e.g.*, toluene, there is considerably less shrinkage during polymerisation and the chains are at all times fully solvated. In consequence the nuclei are less entangled, and with increasing dilution the growing chains reach greater lengths before mutual termination occurs. Eventual removal of diluent causes collapse of the internuclear chains to an extent which depends on both the size of the nuclei (a function of divinylbenzene content) and their separation (a function of dilution).

Where the collapse of the internuclear chains results in contact of the nuclei before all the diluent has been removed, true porosity results on removal of the rest of the diluent. The macroporous materials are thus merely a special case of the general solvent-modified polymer structures, and do not differ fundamentally from them in any way.

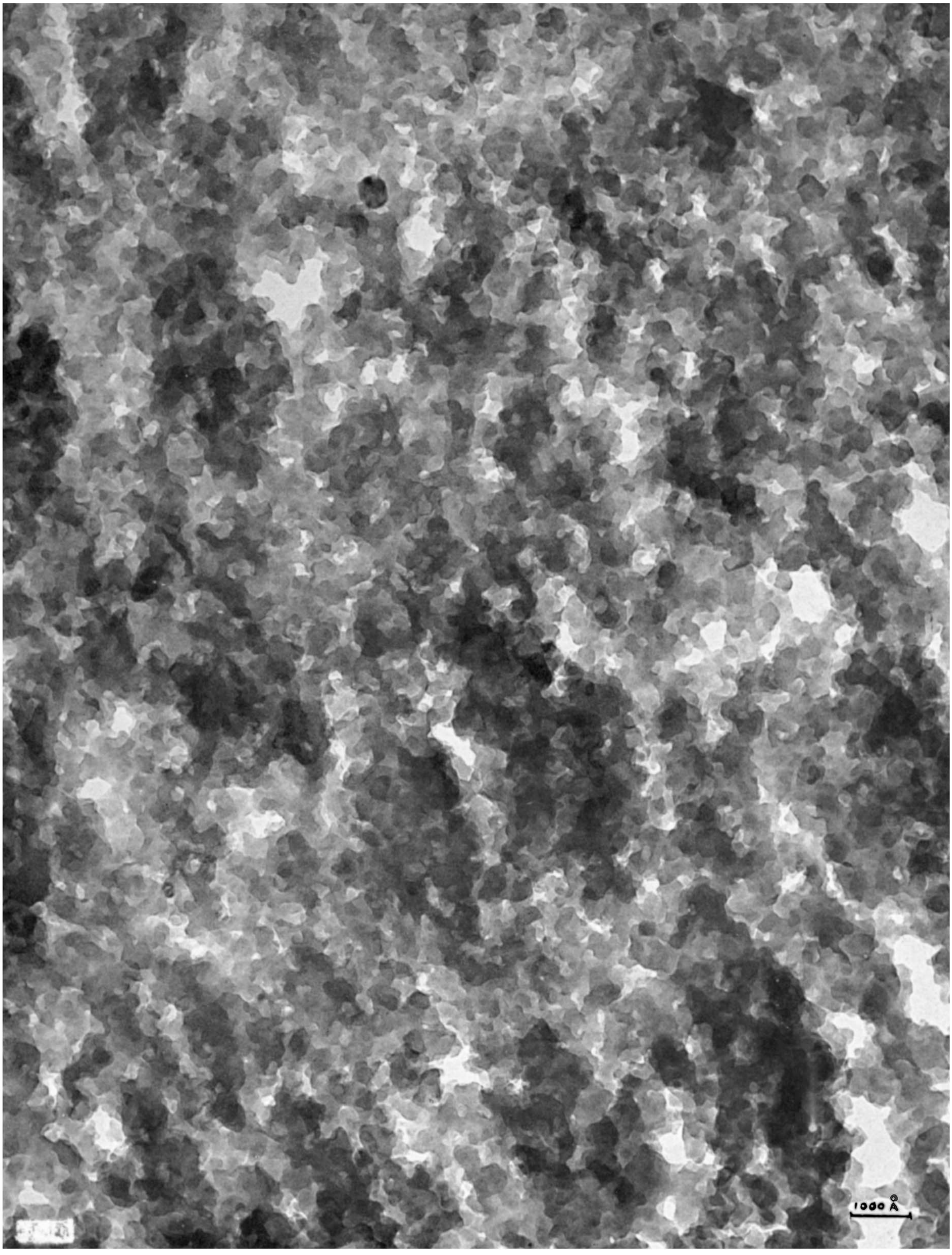
The uptake of solvents which do not normally swell cross-linked polystyrene and of water, already referred to, is readily explained on this model. The water is accommodated in the already existing air-filled pores (the true pores) but cannot solvate or swell the hydrocarbon network. Cyclohexane, heptane, and nitromethane also enter these pores and, in addition, bring about some solvation and consequent uncoiling of the internuclear chains. This uncoiling increases the accessible pore volume and the uptake of these solvents is greater than that of water by this amount. Toluene, with its much greater solvation energy, is capable additionally of swelling the nuclei. The magnitude of this effect is given by the difference between the toluene regain and those of cyclohexane, heptane, and nitromethane.

On this model, the increase in volume of the dry copolymer on taking up water should be zero; that on taking up, say, heptane should be equal to the difference between the heptane and the water regain, and that on taking up toluene to the difference between the toluene and the water regain. Within the experimental error of the determination, this has been found to be so.

The existence of macroporosity implies a large internal surface in the solvent-free copolymers. Heats of wetting in benzene measured on materials at $F_M$ 0·33 containing between 30% and 60% of divinylbenzene lay between 5 and 10 cal./g., corresponding [10]

---

[10] Bangham and Razouk, *Proc. Roy. Soc.*, 1938, *A*, **166**, 572; Maggs, in Proceedings of a Conference on the Ultrafine Structure of Coals & Cokes, B.C.U.R.A., London, 1944, p. 95; Griffith and Hirst, *ibid.*, p. 80; Bond and Spencer in Conference on Industrial Carbon and Graphite 1957, Soc. Chem. Ind., London, 1958, p. 231.



55% Divinylbenzene copolymer ($F_M = 0{\cdot}33$) × 99,000. Corresponding micrographs of linear polystyrene and of conventional 15% and 55% divinylbenzene copolymers were completely featureless.

[*To face p.* 221

to internal surfaces of between 50 and 200 sq.m./g. The corresponding figure for a conventional copolymer containing 1% of divinylbenzene, which has been calculated[11] to have an average pore diameter of ~350 Å was also ~5 cal./g. This suggests that pores of this order of magnitude are present in these macroporous materials, and electron micrographs of a number of the copolymers confirm this (see Plate).

*Sulphonated Copolymers.*—The enhanced porosity and the ability to take up liquids that do not normally swell the polymer matrix persist after sulphonation of the hydrocarbon copolymers. It will be seen in Table 1 that the conventional sulphonic acid resin has a water regain considerably greater than the toluene regain of its parent hydrocarbon copolymer. In the macroporous resin, however, the two regains are virtually identical, *i.e.*, the total pore volume and, therefore, the extension of the internuclear chains are the same whether caused by ionic or by van der Waals forces. This suggests that the entanglement occurring in the conventional resin[4] is virtually absent in the internuclear chains of the macroporous material. The total pore volume as measured by the water regain is also virtually the same whether the exchanger is in the $H^+$, $Li^+$, $Na^+$, or $K^+$ form. This is in direct contrast to the conventional material, where the water regains decrease in the order given, and (except for about one mole of water per mole of sulphonate groups[12]) represent water of hydration of the counterions.

The sulphonated macroporous product, like its parent hydrocarbon copolymer, also takes up normally incompatible solvents. Here, toluene, cyclohexane, and heptane are the counterparts of the water in the hydrocarbon copolymer and the close similarity of their regains in the sulphonated material to the water regain of the hydrocarbon, expressed in comparable units, shows that the macropores have largely survived the sulphonation.

The low apparent density shown by the macroporous hydrocarbon copolymer is also reflected in the sulphonated derivative (Table 2). The figure of 0·70 corresponds to a calculated macropore volume of 0·74 ml./g. of the sulphonate, or 1·03 ml./g. calculated on the hydrocarbon matrix. This compares with the figure of 1·13 ± 0·21 ml./g. calculated from the toluene, cyclohexane, and heptane regains of the sulphonate, and the water regain of the parent hydrocarbon copolymer, given in Table 1.

Finally, certain solvents, *e.g.*, nitromethane, are sufficiently polar to show an intermediate behaviour on the sulphonated copolymer. In sulphonated solvent-modified copolymers prepared at a given dilution, water regains decrease but nitromethane regains increase with increasing divinylbenzene content, until at very high divinylbenzene contents both (expressed as ml./g. of hydrocarbon matrix) approximate to the amount of inert diluent present at the polymerisation stage (see Fig. 7). This behaviour is analogous to that shown by the hydrocarbon materials in Fig. 5 with cyclohexane.

Thus, for both hydrocarbon and sulphonated copolymers, these " abnormal " regains decrease with increasing cross-linker content in conventional materials, while the reverse is true of the solvent-modified materials. This confirms the view that the disentangled structure characteristic of solvent-modification is a feature of the new range of ion-exchange resins made by this method. These resins show marked differences from normal materials in their ion-exchange kinetics and equilibria, which are to be the subjects of subsequent papers in this series.

RESEARCH LABORATORY, THE PERMUTIT CO. LTD.,
PONTYCLUN, GLAMORGAN.

[*Received, May 16th,* 1962.]

---

[11] Grubhofer, *Makromol. Chem.*, 1959, **30**, 96.

[12] Glueckauf and Kitt, *Proc. Roy. Soc.*, 1955, *A*, **228**, 322.