45. *Solvent-modified Polymer Networks. Part IV.*[1] *Styrene–Divinylbenzene Copolymers made in the Presence of Non-solvating Diluents.*

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

The previously proposed model for copolymerisation of styrene and divinylbenzene in the presence of solvating diluents is extended to the case in which the diluent does not solvate the resulting network polymer. Ideally non-solvating systems are not realisable in practice, but the properties of copolymers formed in a poorly-solvating system, in which heptane was used as the diluent, show qualitative agreement with those predicted from the model, as does the equilibrium and kinetic behaviour of the derived cation-exchangers, in which the characteristic structure persists.

WHEN styrene and divinylbenzene are copolymerised in the presence of a diluent which, like the monomers, solvates the copolymer, the latter is formed in a swollen state and the resulting structure differs from that produced in the absence of a solvent. At divinylbenzene contents lower than 15—20%, an " expanded structure " is formed, while at higher divinylbenzene contents, comparatively highly cross-linked nuclei, joined by chains of substantially linear polymer, are present, and in extreme cases, macropores having a modal diameter of several hundred Ångstroms are formed.[2]

Where the diluents used do not solvate the copolymer,[3] there is no comparable swollen state, and the structure differs not only from materials prepared in the absence of diluent but from those where the diluent itself can swell the copolymer.

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[1] Part III, Millar, Smith, Marr, and Kressman, *J.*, 1964, 2740. The sub-captions to Figs. 9 and 10 in Part III on page 2743 have been transposed.

[2] Millar, Smith, Marr, and Kressman, *J.*, 1963, 218.

[3] Millar, B.P. 849,122/1957.

21% Divinylbenzene copolymer ($F_M = 0{\cdot}6$) × 65,000. Corresponding micrographs of linear polystyrene and of conventional 15 and 55% divinylbenzene copolymers were completely featureless.

The purpose of the work described in the present Paper was to study copolymers formed in the presence of the poorly-solvating diluent heptane and to compare them with the conventional and solvent-modified copolymers already described.

EXPERIMENTAL AND RESULTS

Materials.—All the materials used in the preparation and characterisation of the copolymers were identical with those previously described.[2,4,5] Gas–liquid chromatography of the n-heptane fraction (low in aromatics) showed the absence of both benzene and toluene, the major impurity being methylcyclohexane. All other reagents were G.P.R. grades, used as received.

Polymerisation.—This was carried out at 80 ± 1°, as previously described,[2] the n-heptane fraction being used as the diluent. The smaller-scale preparations were made in sealed bottles in Promulsin (Watford Chemical Co. Ltd.), and the larger-scale ones by conventional suspension polymerisation, poly(vinyl alcohol) being used as stabiliser, exactly as before.

Characterisation of the Hydrocarbon Copolymers.—*Regain measurements.* These were carried out as before,[1] at room temperature (*ca.* 20°). For toluene-modified copolymers, the toluene regain, U_X (in ml. per g.), of the product was shown [2] to be given by:

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

where U_N is the toluene regain (also in ml. per g.) of the corresponding conventional copolymer (made in the absence of diluent) and S is the volume of diluent present per g. of original monomer mixture. The toluene regains calculated from this relationship are plotted in Fig. 1 against the observed toluene regains for a series of copolymers of different divinylbenzene contents made in the presence of various proportions of heptane.

As before,[2] cyclohexane regains measured after 16 hrs. equilibration are used as a criterion of macroporosity. Fig. 2 maps the incidence of such macroporosity as a function of the two independent variables, F_M (the volume fraction of monomers in the polymerisation mixture) and the divinylbenzene content of the monomer mixture. The boundary between macroporous and non-macroporous materials, as indicated by the above criterion, is shown on the curve as a full line, and the corresponding boundary for the toluene-modified copolymers (taken from Fig. 6, ref. 2) as a dotted line.

Swelling times. The times to full swelling in toluene of two series of copolymers (made with heptane at $F_M = 0{\cdot}7$ and $= 0{\cdot}5$) were measured by observation between crossed polarising filters, as previously described.[2] The opacity of some of the copolymers made this method somewhat less easy to use than before, and individual observations were accordingly rather less reproducible. Fig. 3 shows the curves of swelling time *vs.* divinylbenzene content for the two series of copolymers. The range of the experimental figures is shown for each point. Also shown, for comparison, are the corresponding curves for conventional copolymers ($F_M = 1{\cdot}0$) and for toluene-modified copolymers with the intermediate value of $F_M = 0{\cdot}6$ (both taken from Fig. 3, ref. 2).

Electron microscopy. The plate shows an electron micrograph of a section, *ca.* 150 Å thick, of a copolymer containing 21% divinylbenzene and made with heptane at $F_M = 0{\cdot}6$. Pores of diameter up to 2000 Å are visible, while the modal-pore diameter appears to lie between 500 and 750 Å. This should be compared with the micrograph of a toluene-modified 55% divinylbenzene copolymer given in ref. 2. Micrographs of conventional polymers of similar divinylbenzene contents are quite featureless.

Preparation and Characterisation of the Sulphonated Copolymers.—Sulphonations,[2,4] and measurements of water regain,[4] organic-solvent regain on the dry resins,[2] and total ion-exchange capacity,[4] were carried out as before.

In Table 1, a sulphonated macroporous resin containing 21% divinylbenzene and prepared in heptane at $F_M = 0{\cdot}6$ (capacity 4·74 mequiv./g.; water regain 1·10 g./g.) is compared with a conventional sulphonated resin (capacity 5·24 mequiv./g.; water regain 1·08 g./g.) in terms of the regains of three typical solvents shown by both the hydrocarbon matrix and its sulphonated derivative. All regains in Table 1 are referred to unit weight of the original hydrocarbon copolymer, in order to provide directly comparable figures.[2]

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[4] Millar, *J.*, 1960, 1311.

[5] Millar, Smith, and Marr, *J.*, 1962, 1789.

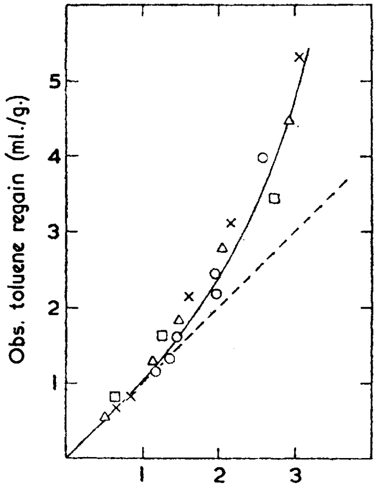

FIG. 1.

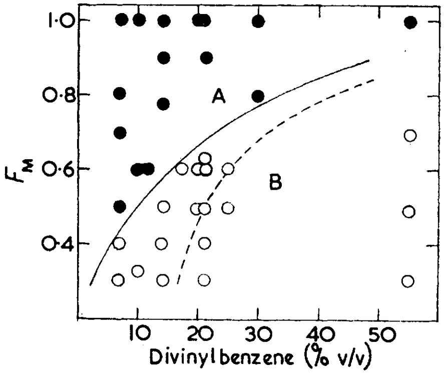

FIG. 2.

FIG. 1. Observed toluene regains compared with those calculated from eqn. 1. Divinylbenzene contents: (○) 7%; (×) 14%; (△) 21%; (□) 55%. The broken line is drawn with unit slope.

FIG. 2. Incidence of macroporosity.

(●) 16-Hr. cyclohexane regain <0·1 ml./g. (○) 16-Hr. cyclohexane regain >0·1 ml./g. (A) Non-macroporous region. (B) Region of macroporous structures. – – – – Critical curve for toluene-modified copolymers (from ref. 2).

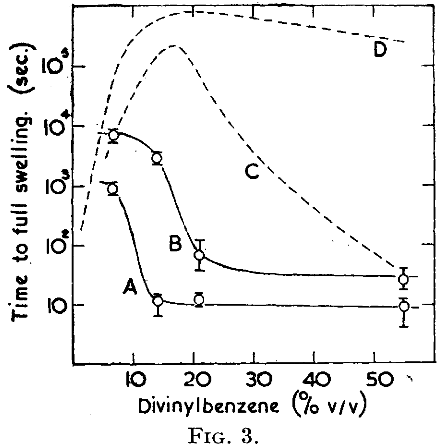

FIG. 3.

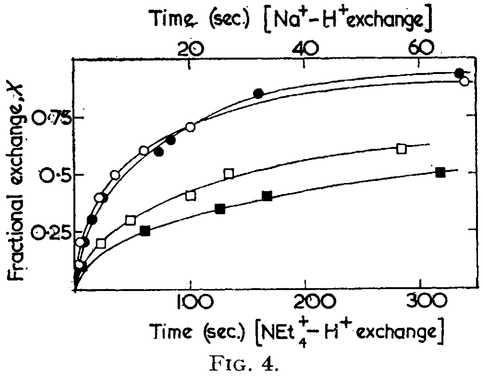

FIG. 4.

FIG. 3. Swelling times.

(A) Heptane-modified, F_M = 0·5. (B) Heptane-modified, F_M = 0·7. (C) Toluene-modified, F_M = 0·6. (D) Conventional copolymers, F_M = 1·0 (from ref. 2).

FIG. 4. Exchange kinetics at 25°.

Circles, Na^+–H^+ exchange at 2·0N. Squares, $NEt_4{}^+$–H^+ exchange at 0·02N. (●, ■) 21% Divinylbenzene (F_M = 0·62) heptane-modified resin. (○, □) 27% Divinylbenzene (F_M = 0·51) toluene-modified resin.

TABLE 1.

Regain (ml./g. of hydrocarbon copolymer matrix)

Solvent	Macroporous resin Hydrocarbon copolymer	Macroporous resin Sulphonated copolymer	Conventional resin Hydrocarbon copolymer	Conventional resin Sulphonated copolymer
Toluene	1·27	0·63	0·79	nil
Heptane	0·97	0·47	nil	nil
Nitromethane	0·93	1·26	0·18	0·26
Water	0·38	1·78	nil	1·86

TABLE 2.

	Heptane-modified	Toluene-modified
Divinylbenzene (% v/v)	21	27
F_M	0·62	0·51
Wt. capacity (mequiv./g.)	4·75	4·36
Specific water regain (g./mequiv.)	0·20	0·22
Na^+–H^+ exchange: Q_∞	1·0	1·0
Na^+–H^+ exchange: $10^6 D_i$	2·8	3·0
NEt_4^+–H^+ exchange: Q_∞	0·80	0·87
NEt_4^+–H^+ exchange: $10^6 D_i$	0·13	0·23

Q_∞ is the limiting extent of exchange in mequiv./mequiv. of total capacity. D_i is the apparent coefficient of interdiffusion in cm.^{2} sec.$^{-1}$.

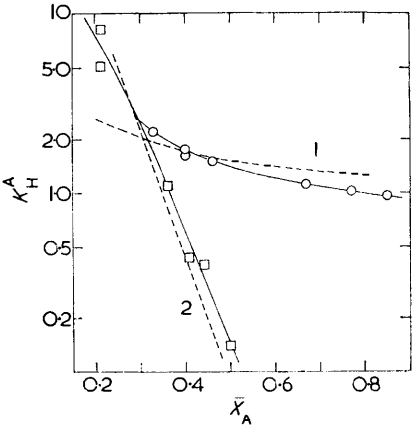

FIG. 5.

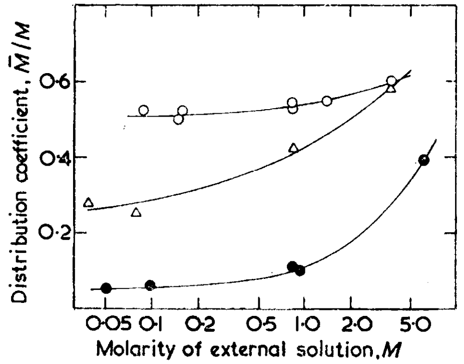

FIG. 6.

FIG. 5. Exchange equilibria at 25°. 21% Divinylbenzene ($F_M = 0·62$) heptane-modified resin: Circles, Na^+–H^+ exchange (A = Na); squares, NEt_4^+–H^+ exchange (A = NEt_4). The corresponding curves for the 27% divinylbenzene ($F_E = 0·51$) toluene-modified resin, from ref. 1, are shown as broken lines: (1) A = Na; (2) A = NEt_4.

FIG. 6. Electrolyte (HCl) invasion in a conventional exchanger and in comparable toluene- and heptane-modified exchangers (H^+-form): (○) heptane-modified, 21% divinylbenzene, $F_M = 0·62$, SWR = 0·20; (△) toluene-modified, 27% divinylbenzene, $F_M = 0·51$, SWR = 0·22; (●) conventional resin, 7% divinylbenzene, $F_m = 1·00$, SWR = 0·21.

Equilibria and Kinetics of Exchange.—These were measured, exactly as before,[1,5,6] on the H^+-form of a sulphonated heptane-modified resin (similar to that of Table 1) for the two ions Na^+ and NEt_4^+ at 25°. Rates of Na^+ exchange were measured in 2·0N-solution, and of NEt_4^+ exchange in 0·02N-solution, resulting in each case in particle-diffusion-controlled kinetics. For the organic ion, the limiting fractional extent of exchange, which was not unity, was determined as previously described.[6] The characteristics of both resin and kinetics are given, together with the corresponding figures on a comparable toluene-modified resin, in Table 2. Fig. 4 shows the

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[6] Millar, Smith, Marr, and Kressman, *J.*, 1963, 2779.

fractional extent of exchange (X) plotted as a function of time (t) for the Na^+–H^+ exchange and the $NEt_4{}^+$–H^+ exchange on the two resins.

The relative affinity coefficients for the Na^+–H^+ and the $NEt_4{}^+$–H^+ equilibria are plotted against the extent of exchange in Fig. 5.

Electrolyte Invasion.—This was measured by the method of Bauman and Eichhorn.[7] Fig. 6 shows the ratio of internal to external molarity of HCl in the H^+-form resin as a function of the external molarity for a heptane-modified, a toluene-modified, and a conventional resin, all of essentially identical specific water regain.

DISCUSSION

In the model previously put forward for the cross-linked styrene–divinylbenzene copolymer network, initial alternation of the two monomers and subsequent interaction of the pendent double bonds of the divinylbenzene units result in " nuclei " containing a high proportion of tetrafunctionally bound divinylbenzene units with " internuclear chains " of predominantly linear polymer.[2]

When the copolymerisation takes place in a system containing a solvating but otherwise inert diluent, such as toluene, the chains are at all times fully solvated, and thus during polymerisation less shrinkage occurs than in corresponding systems in the absence of a solvating agent. In consequence, the nuclei are less entangled, and with increasing dilution the growing chains attain greater lengths before mutual termination occurs. Eventual removal of diluent results in collapse of the internuclear chains of this " expanded network " to an extent depending on both the size of the nuclei and their separation. When the proportion of divinylbenzene and the dilution are sufficiently high, collapse of the chains results in contact of the nuclei before all the diluent has been removed, and true porosity (macroporosity) results on the removal of the remainder of the diluent.[2] This notwithstanding, both expanded-network and macroporous materials before the removal of the diluent, may be regarded as solvent-swollen gels.

It is not possible to realise a perfectly non-solvating system, since the monomer mixture itself can solvate the chains, but where the system contains a diluent which is non-solvating for the polymer chains, partial separation of phases may eventually occur. As the network chains form, they are no longer extended, as in the case where the diluent shows a high interaction with the polymer, and there is an increasing tendency for the growing chains to entangle inside the virtually unswollen nuclei.

The final structure, therefore, is one in which large entangled nuclei are connected by a relatively small number of coiled and crumpled internuclear chains, and the polymer and diluent phases are segregated. The diluent-filled copolymer in this case can no longer be regarded as a swollen gel; indeed, in more extreme cases where the internuclear chains are fewer and the nuclei are less firmly held together, the copolymers become friable and readily disintegrate. As with the solvent-modified materials, collapse of the system of interconnected nuclei occurs as the diluent is removed, but the larger size of the nuclei will lead to the appearance of macroporosity at considerably lower divinylbenzene contents and dilutions,* and hence for a given divinylbenzene content and dilution, the swelling rate of the copolymers will be greater than for similar copolymers prepared in the presence of solvating diluents. Further, since the internuclear chains are formed in the crumpled state, they are capable of expanding in good solvents well beyond the volume limits within which they were formed. It follows that the toluene regains of the copolymers will exceed those calculated for the case where extensibility of the final network is governed by the dilution at the time of gelation.

In practice, therefore, the situation is considerably more complex with non-solvating

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* Indeed, in the ideal case, where even the diluent–monomer solution shows zero interaction with the polymer, macroporosity should become evident at vanishingly small divinylbenzene contents, although, by the nature of our criterion for macroporosity, a finite dilution would still be required, corresponding to at least 0·1 ml. of pore-volume per g. of final product.

[7] Bauman and Eichhorn, *J. Amer. Chem. Soc.*, 1947, **69**, 2830.

diluents than with solvating ones. The degree of interaction between the monomer–diluent solution and the polymer chains is a function of the initial monomer concentration, and changes as the solvating component is converted to polymer. This is particularly marked at high F_M values, where the diluent is initially a minor component. Further, the interaction is a function of temperature, and a diluent which is virtually non-solvating at room temperature may, at the polymerisation temperature, solvate the chains appreciably. One such solvent is cyclohexane.

Nevertheless, in spite of these difficulties, the experimental results demonstrate the fundamental validity of the model. Thus, the toluene regains of several series of heptane-modified copolymers do not conform with the linear relationship previously quoted (see Fig. 1). The chain-transfer constant of the heptane is low, and deviations due to increased chain-transfer in any case merely alter the slope, and not the shape, of the line.[2] The curvature in this case is thus a reflection of the change in polymer–solvent interaction with F_M, to which reference has already been made. At high F_M values (resulting in low toluene regains), the system as a whole approximates to one in which a solvating diluent is present, and the slope tends, correspondingly, to unity. The higher the proportion of diluent, the more nearly the system approaches ideal non-solvation, and the greater is the deviation. The increased friability associated with these higher proportions of diluent becomes apparent in the case of the heptane-modified materials at F_M values less than about 0·5, when the copolymer beads became opaque and chalky. Around this value of F_M, both regain figures and swelling times became less reproducible. No such effect was observed with the toluene-modified materials, at least down to $F_M = 0{\cdot}25$.

The appearance of macroporosity at lower divinylbenzene contents and dilutions (*i.e.*, higher F_M values) in copolymers made with heptane as diluent, rather than with toluene, is illustrated in Fig. 2. The onset of macroporosity, as determined by the overnight cyclohexane regain criterion, is, as in the toluene-modified copolymer gels,[2] matched by the appearance of opalescence and a red-brown colour by transmitted light. However, whereas in the latter the colour disappears on swelling in toluene ($n_D^\alpha = 1{\cdot}497$), the more opaque heptane-modified materials became translucent, and the red-brown colour persists, unless the entering solvent has a refractive index lying within the limited range of $n_D^\alpha = 1{\cdot}590 \pm 0{\cdot}025$, corresponding roughly to the refractive index of the matrix. This is a further indication of the relative paucity of internuclear chains in these materials, since in the toluene-modified materials their numbers, although insufficient to " iron-out " the optical heterogeneity due to the macropores when the latter are filled with air of approximately unit refractive index, will be sufficient to do so when the surrounding refractive index is increased to that of toluene.

The earlier onset of macroporosity in the heptane-modified copolymers is also demonstrated in the increased rates of swelling and the shift to lower divinylbenzene contents shown by the full curves of Fig. 3.

Sulphonated Copolymers.—The characteristic structure of these hydrocarbon copolymers is retained in their sulphonated derivatives, just as it is when they are made in the presence of solvating diluents.[2] This is demonstrated in Table 1, where it can be seen that the macropores responsible for the water regain of the hydrocarbon copolymer are also responsible for the toluene and heptane regains of the sulphonated derivative. A typical hydrocarbon copolymer made conventionally shows no water regain, and the sulphonated derivative no uptake of either toluene or heptane.

The differences in structure associated with solvating and non-solvating diluents are well illustrated by comparing ion-exchange kinetics and equilibria on the resins of Table 2. Although the macroporous toluene-modified resin has a higher divinylbenzene content and lower F_M value both the specific water regains and the rates of exchange of the smaller Na^+ ion (circles Fig. 4) are substantially the same. On the other hand, the lower rate of exchange for the large organic ion (squares, Fig. 4) reflects the lower proportion of exchange sites in the macropores of the heptane-modified material.

In the equilibria, which are almost exclusively determined by the more highly cross-linked regions,[1] the relative affinity coefficients for both ions over the range of X studied are in good agreement (Fig. 5), with perhaps an indication of inversion in the Na^+–H^+ exchange at high X values for the lower cross-linked but more highly entangled heptane-modified resin. In both cases, the differences are in the direction expected from consideration of the model.

The exceptionally high electrolyte invasion of the macroporous sulphonated copolymers (Fig. 6) is a reflection of the low counterion charge-density within the macropores.[1] The macroporosity of the heptane-modified resin is, however, not only appreciably greater than that of the corresponding toluene-modified one, but the extent of invasion does not show so great a falling-off with increasing dilution. Both are in accord with the postulated structures of the two materials, and, in particular, with the attribution of much lower charge-densities to the macropores of materials made in the presence of the poorly-solvating diluent.

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