263. *Interpenetrating Polymer Networks. Styrene–Divinylbenzene Copolymers with Two and Three Interpenetrating Networks, and Their Sulphonates.*

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Two series of cross-linked polymers containing two and three interpenetrating networks were prepared from styrene and divinylbenzene (DVB). Physical properties and swelling characteristics of these polymers, and of the sulphonic resins derived from them, have been compared with those of conventional cross-linked polystyrene materials and their sulphonates. The results suggest that network entanglement plays the major part in determining the properties of the copolymers here described, and may also govern some of the properties of conventional materials of medium to high cross-linking.

PEPPER[1] has used the " weight-swelling " in toluene as a measure of the degree of cross-linking of styrene–divinylbenzene copolymers, since their copolymer composition was not determinable by normal methods. A plot of weight-swelling *versus* divinylbenzene

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[1] Pepper, *J. Appl. Chem.*, 1951, **1**, 124.

content of the parent monomer mixture gave a curve of the form expected from consideration of the Flory–Rehner theory [2] of swollen networks; this theory had previously been tested by Boyer and Spencer [3] who measured the swelling volumes of very lightly cross-linked polystyrenes in various solvents, and calculated μ_G (thermodynamic polymer–solvent interaction constant) values for various solvents by using the Flory–Rehner relation. They obtained values in reasonable agreement with, although generally somewhat higher than, those obtained for the corresponding solvent–polystyrene systems by osmotic or cryoscopic methods. Their polymers contained only about one divinylbenzene unit in every 2500 monomer units, and justified assumption of the Flory–Rehner theory (which relates swelling-volume to mesh-width of the cross-linked network for cases in which the mesh-width is sufficiently great for the chain between cross-links to be treated statistically).

At the higher divinylbenzene contents used in Pepper's work, the swellings of the copolymers are not readily calculated from their divinylbenzene contents even if these were known, because the calculated average mesh width is small, reaching a figure as low as 6 monomer units at about 20% of divinylbenzene (when every divinylbenzene unit is assumed to behave as a tetrafunctional point of cross-linkage) and the chains are entangled to a considerable extent.[4] (In the Flory–Rehner theory entanglement of chains was not ruled out, but the tetrahedral cell model postulated was supposed not to be affected by such entanglement.)

We studied styrene–divinylbenzene copolymers in which the order of entanglement had been deliberately increased by the introduction of further interpenetrating networks. A series of such copolymers has been prepared by causing conventional divinylbenzene-cross-linked polystyrene resins to imbibe a calculated amount of a suitable mixture of styrene and 50% divinylbenzene solution, containing catalyst, and then polymerising the imbibed monomers within the original polymer network, following the method described by Solt.[5] In some instances this imbibition and subsequent polymerisation has been carried out again on the secondary intermeshed copolymer so produced, giving the corresponding copolymer containing three interpenetrating networks. The densities of the copolymers were measured by a flotation method, and their weight-swellings in toluene by Pepper's method; [1] the swelling process was observed between crossed polarising filters (cf. Wheaton and Harrington [6] and Abrams [7]).

Sulphonation of these secondary and tertiary intermeshed hydrocarbon copolymers yields corresponding series of intermeshed cation-exchange materials of different degrees of swelling. The cation-exchange capacities and water regains of these polymers have been compared with those of the sulphonated primary copolymers, which correspond to the series of polystyrene sulphonates described by Pepper *et al.*[1,8] and Gregor *et al.*[9] However, the water-swelling properties of the intermeshed ion-exchange materials differ from those predicted from the toluene-swelling properties of the parent copolymers; this difference can be related to the structure of the intermeshed copolymers.

EXPERIMENTAL

Materials.—Commercial styrene monomer was washed with dilute sodium hydroxide solution to remove phenolic inhibitors, water-washed, dried over sodium sulphate, and vacuum-distilled under nitrogen with powdered sulphur as inhibitor. A commercial divinylbenzene solution (nominally 50% by weight of divinylbenzene isomers, the remainder being ethylstyrene) was

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[2] (*a*) Flory and Rehner, *J. Chem. Phys.*, 1943, **11**, 521; (*b*) Flory, *ibid.*, 1950, **18**, 108.

[3] Boyer and Spencer, *J. Polymer Sci.*, 1948, **3**, 97.

[4] Blanchard and Wootton, *J. Polymer Sci.*, 1959, **34**, 627.

[5] Solt, B.P. 728,508.

[6] Wheaton and Harrington, *Ind. Eng. Chem.*, 1952, **44**, 1796.

[7] Abrams, *Ind. Eng. Chem.*, 1956, **48**, 1469.

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

[9] Gregor, Sundheim, Held, and Waxman, *J. Colloid Sci.*, 1952, **7**, 511.

treated in the same way, except that the final step was flash-distillation to avoid alteration in composition of the mixture. The toluene was reagent-grade material, free from sulphur compounds, and was re-distilled. The suspension stabiliser was " Rhodoviol HS-100," a poly-(vinyl alcohol) preparation (R. W. Greeff and Co., London), and a commercial grade of azodi-isobutyronitrile containing about 7% of moisture was used as catalyst. All other materials were laboratory-reagent grades, except where otherwise specified.

Polymerisation.—(a) *Primary cross-linked polystyrene polymers.* A conventional pearl polymerisation technique was used. The appropriate mixture of styrene and 50% divinylbenzene solution, containing 0·2% w/v of azodi-isobutyronitrile as catalyst, was suspended in about twice its volume of 0·1% " Rhodoviol " solution, and maintained in a closed vessel at 70°, with stirring at a controlled rate to yield the copolymer as spheres in the range 18—60 B.S.S. mesh. The gelation stage (about 5% conversion) occurred about 1 hr. from the start of the run. After 4—5 hr. the copolymer beads became denser than the suspension medium, and the temperature of the system was increased to 100° during about an hour. Finally, the beads were filtered off, washed free from adhering stabiliser, and dried overnight at 95°. No special precautions were taken to exclude oxygen during the polymerisation.

(b) *Intermeshed copolymers.* The (primary) products from process (a) were fully swollen in their appropriate styrene–divinylbenzene mixtures (containing 0·2% of azodi-isobutyronitrile), suspended in about twice their weight of 0·1% " Rhodoviol " solution, and maintained overnight at 70° in a closed vessel, with constant agitation to prevent aggregation. The secondary intermeshed copolymer so produced was filtered off, washed, and dried as previously described. Repetition of the process yielded the tertiary intermeshed product; in this case, the parent beads were taken from a 36—60 B.S.S. mesh fraction of the original material; otherwise, 25—36 mesh fractions were used. The final products in each case were thus roughly comparable in size with the remainder of the original material. Yields of the various copolymers were within the range 90—100%.

Since the *volumes* of good swelling agents taken up by unit weight of dry polymer were found to be very nearly constant, the volume of monomer mixture required for full swelling was conveniently calculated from the toluene regain, determined as indicated below. Separate experiments confirmed that this calculated-addition method gives the same product as does the use of an excess of monomer mixture, followed by centrifuging.

The polymerisation was carried out when the beads had imbibed all the added monomer, and the network had reached a state of balanced stress, as indicated by the disappearance of the characteristic strain patterns between crossed polarising filters.[6,7] Most of the beads of higher toluene regain reached equilibrium in 1—2 hr., while those of lower regain were left overnight. In the three tertiary intermeshed copolymer preparations, the final state was reached in each case in less than 2 hr. However, this state in the case of the 4% divinylbenzene polymer was not one of balanced stress, and this mixture, too, was left overnight before polymerisation.

Sulphonation of Copolymers.—This was carried out essentially as described by Pepper,[1] but without silver sulphate catalyst, and by using a ratio of 100 ml. of concentrated sulphuric acid to 10 g. of copolymer. The mixture was kept at 90° ± 1° for 18—64 hrs., the longer periods being used with the materials of low toluene-swelling. The product was filtered off, then washed with sulphuric acid of decreasing concentration and finally, until free from acid, with demineralised water. The resin was cycled once or twice between the sodium and the hydrogen form and finally converted into the hydrogen form with excess of 2N-hydrochloric acid. Excess chloride and acidity were lastly removed by washing the resin with demineralised water.

Characterisation of Products.—(a) *Density.* Densities of the hydrocarbon copolymers were measured by determining the concentration of sodium chloride solution in which the polymer neither floated nor sank. A solution of " AnalaR " sodium chloride of known concentration in boiled-out, demineralised water was quantitatively diluted with similar water at 25° ± 0·2° until ~10% of a sample of polymer beads sank, then further until only about 10% floated. The mean of these two concentrations was taken as that at which the solution density corresponded to the mean density of the copolymer. Reproducibility and accuracy were about ±0·1%; in most cases the polymer showed a range of densities only just within this range.

(b) *Toluene regain.* The method was substantially that of Pepper,[1] but the resins were equilibrated at room temperature (about 20°) and sintered-glass filters of porosity 2 were used, as for water-regain measurements.[8] The precision was thereby reduced to about ±3%.

Where the divinylbenzene content of the monomer mixture used for the second network was low, traces of soluble material were present in the beads. However, even with 0·5% v/v of divinylbenzene in the monomer mixture (the lowest proportion studied), the correction for this is less than the experimental error of the determination, and no correction was therefore applied.

(c) *Water regain.* The weight-swelling of the sulphonated copolymers in the hydrogen form was determined essentially as described by Pepper *et al.*[8] Variations from their procedure were: about 1·5 g. of wet resin were taken, after being kept for ~1 hr. in a 0·1% solution of Lissapol NDB (a salt-free commercial non-ionic detergent); centrifuging was carried out at room temperature for 1 hr. at ~200 **g**; the resin samples, after being weighed, were dried to constant weight at *ca.* 100° for 18—24 hr.; the corresponding average corrections for water held in the sinter and between the beads were 0·003 g. and 0·03 × wet weight of beads respectively. The accuracy of the measurement was about ±3%, *i.e.*, the same as that of the toluene-regain measurements on the original hydrocarbon polymers.

(d) *Total ion-exchange capacity.* The exchangers are unifunctional and their ion-exchange capacity is wholly associated with sulphonic groups. The total number of exchangeable hydrogen ions was determined by stirring 0·5—1 g. of H^+-resin with about 50 ml. of water containing about 1 g. of " AnalaR " sodium chloride and titrating the total acid liberated with 0·1N-sodium hydroxide to phenolphthalein. Duplicate results agreed within 0·03 milliequiv./g.

RESULTS AND DISCUSSION

In linear macromolecules, substitution of alkyl groups in the side chain normally tends to reduce the density, the less efficient packing of the polymer chains more than offsetting the increase in molecular weight of the repeating unit. On the other hand copolymerisation of increasing amounts of divinylbenzene with styrene results in a slight but progressive increase in density from 1·049 g./c.c. for linear polystyrene to 1·054 g./c.c. at 17% v/v divinylbenzene content. This discrepancy may be explained by the filling of some of the " holes " in the comparatively loosely packed[10] amorphous polystyrene structure by self-entanglement of the growing network. A necessary corollary is that the system is no longer topologically equivalent to a simple four-connected net. The deliberate introduction of (formally) independent secondary and tertiary networks intermeshed with such a primary structure should therefore produce similar but more marked effects both on the swelling and the density of the resultant copolymer.

Figs. 1 and 2 show the effect on copolymer density and toluene regain of the introduction of secondary and tertiary interpenetrating networks made from the same monomer mixture as was used in forming the primary network. Although the networks are indistinguishable qualitatively and the overall divinylbenzene content of the copolymer is unchanged, there is a progressive increase in density and decrease in toluene regain. The similarity of curves *B* and *C* to *A* suggests that the differences between the intermeshed and primary copolymers are of degree rather than fundamental.

Fig. 3 shows the relation between the toluene regain, and the v/v percentage (m_1) of divinylbenzene isomers in the imbibed monomer mixture for different primary networks. [The nominal divinylbenzene content (n) of the primary network is expressed in the same way.]

The increased entanglement is again shown by a lowering of the toluene regain of the copolymer. Where $m_1 \leqslant n$, the toluene regains of the secondary intermeshed copolymers are sensibly constant for a given primary matrix; where $m_1 > n$, the toluene regains decrease regularly with increasing m_1 in a manner similar to the decrease in regain with increasing cross-linker content described by Pepper.[1]

There appears to be no simple quantitative relation between the regain of an intermeshed copolymer and the regains of its individual networks. However, it seems that the toluene regain of the intermeshed copolymer is governed by the network which has the higher divinylbenzene content and would, by itself, have the lower regain. The other network is therefore in general less fully extended than it would otherwise be, and the

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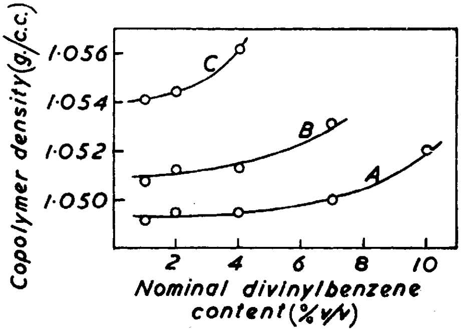
[10] Heller and Thompson, *J. Colloid Sci.*, 1951, **6**, 57.

whole system must be one in which the swelling process is more complex than in a normal copolymer.

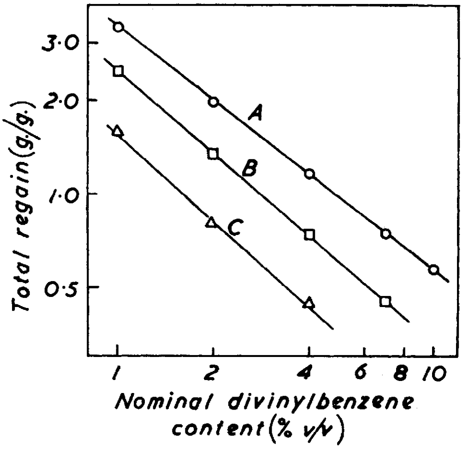
This has been confirmed by observing the swelling process in polarised light. Conventional cross-linked styrene copolymers, on swelling in toluene, show a characteristic sequence of coloured strain patterns when observed by white light between crossed polarising filters.[6,7] The average time taken to complete the sequence from the initial penetration of solvent to the uniform dark grey field (which corresponds to a state of balanced principal stresses), although not highly reproducible, gives a rough measure of the degree of entanglement of the network. All conventional materials showed the final balanced-stress pattern, although the relaxation times varied from about 4 min. for a 1%, to about 4000 min. for a 10% divinylbenzene–styrene copolymer. All the intermeshed copolymers, however, showed considerably longer relaxation times than their primary copolymers, and many never achieved the final balanced-stress state, the sequence being " frozen " at one of the stages following complete penetration of solvent, sometimes with additional dark lines particularly characteristic of the copolymers containing three interpenetrating networks.

FIG. 1. *Copolymer densities at 25°.*



A, Primary intermeshed copolymers (n% DVB). *B, Secondary intermeshed copolymers* ($m_1 = n$). *C, Tertiary intermeshed copolymers* ($m_1 = m_2 = n$).

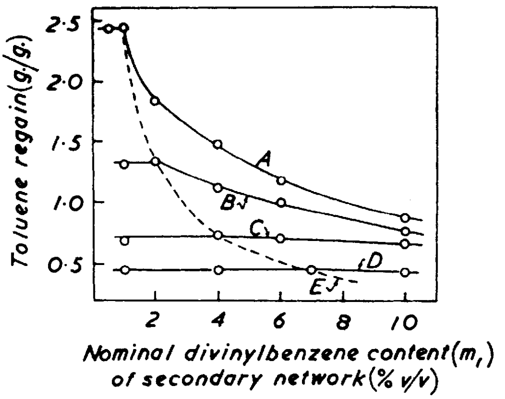
FIG. 2. *Copolymer toluene regains.*



Curves A, B, and C as for Fig. 1.

FIG. 3. *Copolymer toluene regains.*

Secondary intermeshed copolymers: A, $n = 1$% DVB; *B,* $n = 2$% DVB; *C,* $n = 4$% DVB; *D,* $n = 7\frac{1}{2}$% DVB. *E, Locus of points where* $m_1 = n$ *(Fig. 2, curve B)*



If we assume with Blanchard and Wootton [4] that the proportion of " trapped entanglements " increases with increased cross-linking, the extension to a secondary copolymer would require that the swelling be related to the divinylbenzene content of the secondary network. However, there is an overriding requirement that the total volume swelling cannot appreciably exceed that of the primary network, unless disentanglement occurs. (It should be emphasised that this disentanglement would have to be reversible, since the toluene regain figures can be reproduced on the same sample of hydrocarbon copolymer beads.) Since at least part of the volume-swelling potential of the primary network is taken up with the volume occupied by the interpenetrating secondary copolymer, this is bound to reduce the regain figure, particularly as the density of the polymer itself is increased. These considerations provide at least a qualitative explanation for the results summarised in Fig. 3.

Pepper[1] has demonstrated an almost linear relation between the water regain and ion-exchange capacity of a styrene–divinylbenzene copolymer sulphonated to various extents. It follows that the specific water regain (that is, the weight-swelling in water of the sulphonated copolymer divided by the ion-exchange capacity) is, to a first approximation, a constant for, and characteristic of, a given copolymer matrix. In the present work, the capacities of the several ion-exchange materials did not necessarily correspond to exact monosubstitution, and in consequence the specific water regain (g. of water/milliequiv.), rather than the water regain, has been taken as characteristic of the resin matrix.

Pepper[1] has further shown that there is a smooth relation between the toluene regain of the parent hydrocarbon copolymer and the water regain of the monosulphonated product. Provided, therefore, that the net cross-linking of the resin is unchanged during the sulphonation, the specific water regain of the ion-exchanger and the toluene regain of the hydrocarbon copolymer provide independent criteria of the degree of cross-linking or entanglement of the polymer matrix. That this is true has already been demonstrated[1] for the primary copolymers; it has been confirmed for the secondary and tertiary intermeshed copolymers by sulphonation of the 2% divinylbenzene materials and plotting the specific water regain as a function of time. If the net cross-linking increased (*e.g.*, by sulphone formation) the specific water regain would fall with time, whereas if it decreased the specific water regain would rise. The experimental results showed in each case merely a slight random variation (within the experimental error of the determination) about the mean value characteristic of the fully sulphonated product, and hence no net change in cross-linking, over a range of sulphonation times of 1—120 hr. and a range of capacities of 4·8—5·3 milliequiv./g.

The apparent divinylbenzene contents of the intermeshed resins were calculated by these two methods, using Pepper's figures[1,8] (see results in the Table). They show that

Hydrocarbon copolymer				Sulphonated copolymer			Apparent DVB content (% v/v)	
Nominal DVB content of network (% v/v)[a]			Toluene regain (g./g.)	Water regain (g./g.)	Exchange capacity (meq./g.)	Spec. water regain (g./meq.)	From spec. water regain	From toluene regain
n	m_1	m_2						
1	—	—	3·38	10·5	5·66	1·85	1·0	1·0
1	1	—	2·44	5·24	5·27	0·995	1·3	1·5
1	1	1	1·57	3·64	5·25	0·694	1·7	2·7
2	—	—	1·93	2·67	5·00	0·534	2·1	2·1
2	1	—	1·30	2·13	5·29	0·403	3·2	3·5
2	2	—	1·33	2·19	5·22	0·419	3·0	3·3
2	10	—	0·76	1·15	4·96	0·232	6·0	6·9
2	2	2	0·79	1·75	5·31	0·329	4·1	6·5
4	—	—	1·17	1·74	5·17	0·337	4·0	4·0
4	1	—	0·68	1·15	5·08	0·216	6·6	8·0
4	4	—	0·73	1·19	5·06	0·235	6·0	7·2
4	10	—	0·66	0·91	4·24	0·215	6·6	8·2
4	4	4	0·44	0·94	5·17	0·182	7·3	14·0
7	—	—	0·74	0·91	5·01	0·182	7·3	7·3
7	1	—	0·44	0·65	4·99	0·130	10·7	14·0
7	7	—	0·44	0·66	5·00	0·132	10·2	14·0

[a] v/v% has been used throughout for practical reasons. 1·0% v/v = 1·01% w/w = 0·82 mole %.

where swelling of the hydrocarbon matrix in toluene is restrained by additional network entanglement the water regain of the sulphonated materials is higher than would be expected from the toluene regain of the matrix; this suggests that the ionic forces involved in the water-swelling of the ion-exchanger can cause irreversible disentanglement which the van der Waals forces involved in the toluene-swelling process cannot. The discrepancy between the apparent divinylbenzene contents is thus a measure of this disentanglement; it is particularly noticeable at the higher equivalent degrees of cross-linking, but while, in part, this might be ascribed to the flattening of the curve of regain against cross-linked content, it is in general too great to be accounted for in this way.

The behaviour of the secondary intermeshed 7% divinylbenzene copolymer, which had a toluene regain equivalent to a conventional 14% v/v divinylbenzene copolymer and showed a specific water regain after sulphonation corresponding to that of a 10% v/v divinylbenzene copolymer, recalls a finding by Hale, Packham, and Pepper[11] that a conventional 15% cross-linked polystyrene monosulphonate underwent irreversible structural change, to a similar extent, on complete conversion into the tetraethylammonium form. The structural change postulated was the rupture of weak cross-links of unspecified type in order to make room for the bulky quaternary ammonium ion. However, the present work suggests an alternative mechanism, the partial but irreversible disentanglement of the complex network, under conditions of considerable osmotic stress. The actual energy required to rupture an individual C–C or O–O " weak " linkage introduced during polymerisation [12] may be considerably less than the corresponding average bond energy (59 and 35 kcal./mole, respectively [13]) but it seems likely that the polymer–polymer interaction energies of the type involved in primary network entanglement would be still less. These points of entanglement correspond to the points of adhesion in the " thermally fixed structure " of Ueberreiter and Kanig,[14] and may indeed be regarded as weak cross-links. They are probably strong enough to resist, not only toluene-swelling forces, but also the normal osmotic forces involved in hydration of the sulphonic acid groups. In interpenetrating networks, the packing of the sulphonic acid groups is tighter and the hydration forces correspondingly greater, while the concentration, along the chains, of normal tetrafunctional cross-links corresponds to that of a comparatively lightly cross-linked material. In consequence, hydration rearranges the entanglements to a degree which solvation by toluene cannot, since the ionic forces vary inversely as r^2 while the van der Waals forces vary inversely as r^7.

The results reported in this paper emphasise the importance of the entanglement concept for the physical properties of conventional cross-linked polymers, and show how it may be possible to modify physical properties by increasing the entanglement factor without necessarily increasing the concentration of covalent cross-links. With sulphonated copolymers, other properties, notably ion-exchange equilibria and kinetics, are affected by the cross-linking, and it is likely that these new sulphonic acid exchangers which differ in order of network entanglement may prove unconventional in their exchange behaviour also.

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[11] Hale, Packham, and Pepper, *J.*, 1953, 850.
[12] Grassie, *Chem. and Ind.*, 1957, 539.
[13] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, New York, 2nd edn. 1949, p. 53.
[14] Ueberreiter and Kanig, *J. Chem. Phys.*, 1950, **18**, 399.