CROSSLINKED STYRENE/DIVINYLBENZENE NETWORK SYSTEMS

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ABSTRACT

Differences in properties of pure *meta*- and pure *para*-divinylbenzene crosslinked polystyrene and their sulphonated products have been correlated with probable network structural differences. The *para*-divinylbenzene copolymerizes more slowly than does the *meta* isomer to give a crosslinked copolymer which swells less, sulphonates less rapidly, and, when sulphonated, gives an ion exchanger which has lower selectivity. It is concluded, on the basis of copolymerization data, that the *para* crosslinked network is tighter and less uniform than that of the *meta* crosslinked network.

Techniques have been developed for the synthesis, separation and purification by gas chromatography, polymerization, and copolymerization of 99·5–99·9 per cent pure *meta*- and *para*-divinylbenzenes. Kinetics of the polymerization and copolymerization have been determined by radiocarbon techniques and computer analysis of high-conversion data. The preparation and sulphonation of the bead copolymers of styrene with the pure *meta*- and *para*-divinylbenzenes have been developed in detail and the exchange isotherms of the sulphonated beads have been evaluated.

INTRODUCTION

Most ion exchange resins are prepared from styrene/divinylbenzene crosslinked copolymers in bead form by processes that are not usually specified. These processes use for divinylbenzene the commercially available mixture of the *meta*- and *para*-divinylbenzene isomers. This mixture also contains varying amounts of other ingredients—chiefly *meta*- and *para*-ethylstyrenes. This ambiguously defined process leads to a network structure that is difficult to obtain reproducibly, and problems are thus added to the usual complications involved in studies of crosslinked polymer systems.

In our studies[1–34] we have obtained data on the properties of pure *meta*- and pure *para*-divinylbenzenes[2, 3, 8, 14, 23, 30]; on the kinetics of their polymerization[12, 26] and styrene copolymerization[4, 9, 15, 20, 28, 32, 33]; on the characteristics of the copolymers[18, 19, 25, 27] and their sulphonation[11, 13, 16, 18, 21, 24]; and some data on their sulphonated products[1, 10, 31, 34]. Some related data have been obtained for *ortho*-divinylbenzene, 1,2,4- and 1,3,5-trivinylbenzenes, and a series of divinyl compounds of the type $CH_2{=}CHC_6H_4{-}X{-}C_6H_4CH{=}CH_2$[1, 6, 17, 20, 22].

The questions for which we have sought answers are: (1) what kind of data establish a difference between the *meta* and the *para* crosslinked systems and (2) what are the structural implications available from such differentiations? It is the extent to which we can provide answers to these questions that we wish to consider in this report.

DIVINYLBENZENE MONOMERS

The commercially available divinylbenzene is a complex mixture of 8–12 components. It is made by dehydrogenation of diethylbenzenes, in turn obtained by Friedel–Crafts alkylation of benzene with ethylene. The ethylbenzenes are a mixture of *ortho*, *para* and *meta* isomers. The *ortho* isomer is converted to naphthalene in the dehydrogenation and there is little to be gained in separating the ethylbenzenes prior to dehydrogenation, as the dehydrogenation catalyst re-equilibrates the isomeric mixture. One dehydrogenation process has been operated using an iodine catalyst which does not equilibrate the isomeric mixture, and during the time of its development relatively pure *meta*- and *para*-divinylbenzenes were available. Also, a process[23] for the separation of the divinyl isomers based on a Werner complex formation was at one time operated on a developmental basis. We have reported analytical gas chromatographic data for commercial divinylbenzene samples. Typical data are given in *Figure 1.* A complete listing of the components as identified by comparisons with retention times of known mixtures is given in *Table 1.*

It is essential, for the purposes of establishing possible differences in the network systems obtained on copolymerization, that the pure *meta* and *para* isomers of divinylbenzene be separated and purified. The methods we have developed for this purpose are based on preparative gas chromatography

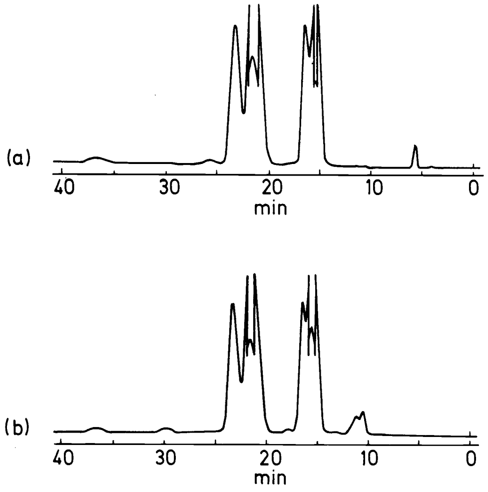

Figure 1. Chromatograms of commercial divinylbenzene: (a) sample I and (b) sample II of *Table 1*

Table 1. Net retention times and relative retention ratios for components of commercial divinylbenzene samples

		Observed net retention times, min			
Peak No.[a]	Component	Known compounds[c]	Mixture of known compounds[d]	Sample I[e]	Sample II[f]
1	Air	0	0	0	0
2	Ethylbenzene	4.7	4.1	4.0	—
3	Styrene	—	5.7	5.5	—
4	*m*-Diethylbenzene	12.7	10.4	10.2	10.1
5	*p*-Diethylbenzene	13.6	11.0	10.9	10.8
6	*m*-Ethylvinylbenzene	18.1	15.1	14.9	15.1
7	*p*-Ethylvinylbenzene	19.1	16.0	15.8	15.8
8	*o*-Divinylbenzene	21.3	17.4	17.0	17.1
9	*m*-Divinylbenzene	25.1	20.7	20.7	20.6
10	*p*-Divinylbenzene	26.5	22.3	22.3	22.3
11	Unknown	—	—	24.3	28.3
12	Naphthalene	—	35.8	34.9	34.8

		Relative retention ratios[b]			
Peak No.[a]	Component	Known compounds[c]	Mixture of known compounds[d]	Sample I[e]	Sample II[f]
1	Air	—	—	—	—
2	Ethylbenzene	0.187	0.198	0.193	—
3	Styrene	—	0.277	0.266	—
4	*m*-Diethylbenzene	0.506	0.503	0.493	0.491
5	*p*-Diethylbenzene	0.541	0.531	0.527	0.525
6	*m*-Ethylvinylbenzene	0.721	0.729	0.719	0.734
7	*p*-Ethylvinylbenzene	0.760	0.772	0.764	0.766
8	*o*-Divinylbenzene	0.849	0.841	0.822	0.830
9	*m*-Divinylbenzene	1.00	1.00	1.00	1.00
10	*p*-Divinylbenzene	1.06	1.08	1.08	1.08
11	Unknown	—	—	—	—
12	Naphthalene	1.68	1.73	1.68	1.69

[a] In *Figure 1*.
[b] *m*-Divinylbenzene as reference.
[c] Chromatographed singly, in sequence, on the same column, within 10 h.
[d] Prepared from samples used for data in 'Component' column containing about the same relative amounts.
[e] Koppers Company, Lot No. 1992.
[f] Dow Chemical Company, Lot No. 12042.

of appropriate starting materials[2, 14]. The pure (99.9 per cent) *meta* isomer is obtained by repetitive preparative gas chromatography of the commercial divinylbenzene mixture. Three passes through a 1 in × 6 m polypropyleneglycol (Ucon) on Chromosorb W column sufficed. Larger columns have been used in the initial separation. The pure (99.9 per cent) *para* isomer, being the lesser and trailing component and having a bothersome tendency to crystallize (m.pt, 35°C), cannot be readily separated from the commercial mixed divinylbenzene isomers. It can be obtained in reasonable yield and fair purity by decarboxylation of *p*-phenylenediacrylic acid, in turn prepared from terephthaldehyde and malonic acid[3]. This material must be further purified, and to do so we customarily put it through a preparative GLC column (Bentone 34/Ucon on Chromosorb W) on which the *para* isomer precedes the *meta* and then finally distil from potassium hydroxide. The isomers thus purified gave reproducible kinetic data and bead copolymerization systems. NMR and mass spectral characteristics of the two pure isomers have been recorded[8, 30]. Similar data have been obtained for 1,2,4- and 1,3,5-trivinylbenzenes[17].

KINETICS OF THE POLYMERIZATION AND COPOLYMERIZATION OF META- AND PARA-DIVINYLBENZENES

The kinetic data for the polymerization of pure *meta*- and pure *para*-divinylbenzenes up to the gelation point show that the conversion to polymer is directly proportional to time and to the square root of the initiator concentration. Data have been obtained for viscometric measurements in toluene[9] and t-butylbenzene[12] at 65 and 80°C. Typical data are given in *Figure 2* for the 65°C, t-butylbenzene experiments. Activation energies calculated from initial linear data are given in *Table 2*. Typical values are 23.3 kcal/mol (*meta*) and 27.1 kcal/mol (*para*). The data from the dilatometric measurements[26] are shown in *Figure 3*, and can be seen to be linear up to the gel point. Both data sets show that the *meta* isomer polymerizes more rapidly than does the *para* isomer. Gelation occurs at 90 min and 19.3 per cent conversion for the *meta* isomer; at 126 min and 16 per cent conversion for the *para* isomer. In other experiments it has been shown that the gel time is a linear function of the square root of the reciprocal of the initiator concentration and conversion at gel point is a linear function of the square root of

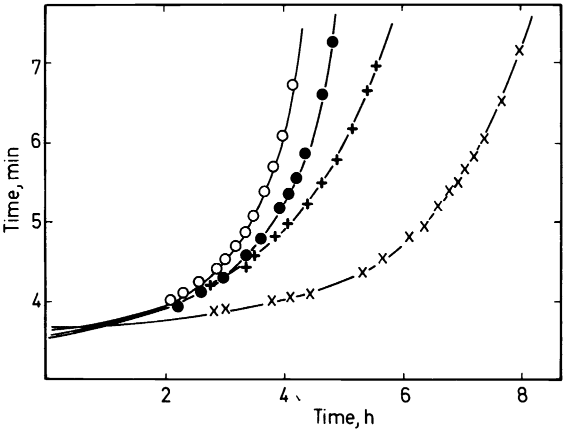

Figure 2. Rate of polymerization of divinyl isomers in t-butylbenzene at 65°C: ○, *m*-divinylbenzene; ●, 2:1 *m*:*p*-divinylbenzene; ×, *p*-divinylbenzene; +, commercial divinylbenzene. Abscissa, time of polymerization in hours; ordinate, efflux time in minutes

the initiator concentration. The activation energies are normal for vinyl polymerizations and, up to the gel point, these divinyl monomers are behaving as typical monovinyl types with the *para* isomer the less rapidly polymerizing. It may be noted that the second vinyl group, whose reaction is required for crosslinking, should react as an alkyl-substituted styrene—

Table 2. Ratios of rate constants and activation energies for polymerization of divinylbenzene (DVB) isomers at 65 and 80°C

	Commercial DVB[a]		*m*-DVB		2:1/*m*:*p*-DVB		*p*-DVB	
Efflux time, min	Rate ratio[b]	E_A, kcal/mol[c]	Rate ratio[b]	E_A, kcal/mol[c]	Rate ratio[b]	E_A, kcal/mol[c]	Rate ratio[b]	E_A, kcal/mol[c]
4	2.57	14.9	3.09	17.8	3.09	17.8	3.72	20.8
5	3.81	21.1	4.04	22.1	4.09	22.3	5.04	25.6
6	4.23	22.8	4.29	23.0	4.36	23.3	5.29	26.3
7	4.42	23.5	4.34	23.2	4.47	23.7	5.47	26.9
Limiting value[d]	4.52	23.8	4.35	23.3	4.48	23.7	5.54	27.1

[a] Commercial divinylbenzene (Koppers).

[b] Ratio of polymerization times $t_{65°}/t_{80°}$ at stated efflux time.

[c] Activation energy calculated as $E_A = [RT_1T_2/(T_2 - T_1)] \ln(t_1/t_2)$.

[d] Constant value that the ratios t_1/t_2 reach at gelation time, calculated by extrapolation.

Ratios of rate constants and activation energies for copolymerization of styrene–divinylbeznene isomers at 65 and 80°C

	Commercial DVB		*m*-DVB		2:1/*m*:*p*-DVB		*p*-DVB	
Efflux time, min	Rate ratio	E_A, kcal/mol	Rate ratio	E_A, kcal/mol	Rate ratio	E_A, kcal/mol	Rate ratio	E_A, kcal/mol
4	1.77	9.0	2.57	14.9	1.91	10.2	2.15	12.1
5	2.16	12.2	2.58	15.0	2.45	14.2	2.75	16.0
6	2.23	12.7	2.58	15.0	2.61	15.2	2.96	17.1
7	2.27	13.0	2.59	15.0	2.67	15.5	3.05	17.6
Limiting value	2.27	13.0	2.60	15.1	2.68	15.6	3.07	17.7

corresponding roughly to an isopropylstyrene. We have shown that *para*-isopropylstyrene is a less reactive monomer than is styrene in copolymerization with styrene[29].

The gelation characteristics of the two divinylbenzene isomers show distinctions which are apparently related to different crosslinking processes and network structures. Gelation time is a linear function of rate: i.e. the lower the rate, the longer the time to gelation, for both isomers. The rate is different for the two isomers. Significantly, however, the conversion at gelation also varies for the two isomers. At every rate level the more slowly polymerizing *para* isomer shows a lower conversion at gelation. This requires that less

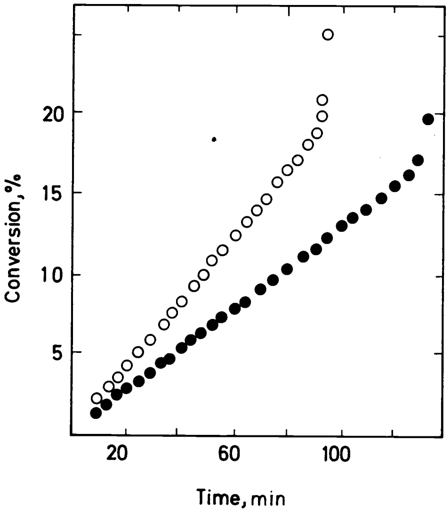

Figure 3. Polymerization of *m*-(○) and *p*-(+) divinylbenzenes in toluene at 70°C. Concentration of divinylbenzene 2.28 mol/l; of dibenzoyl peroxide 7.29×10^{-3} mol/l. Conversion versus polymerization time. Dilatometric data

monomer be incorporated into the *para* crosslinked structure at gelation and suggests that there is a greater build-up of molecular weight prior to crosslinking in the *meta* derived network. Alternatively, if the *para* derived structure is inherently less soluble (has a different solvent interaction relation), its structure must be inherently different.

The viscometric copolymerization kinetic rate data[9, 12] for the styrene/*meta* and *para* systems show similar, but less pronounced, differences. The styrene/*meta* copolymerization is more rapid and has a lower activation energy

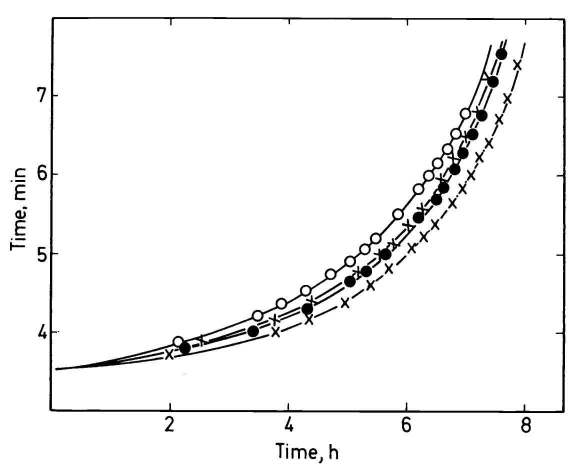

Figure 4. Rate of copolymerization of divinylbenzene isomers with styrene in t-butylbenzene at 65°C; ○ styrene/*m*-divinylbenzene; ● styrene/2:1-*m*:*p*-divinylbenzene; × styrene/*p*-divinylbenzene; + styrene/commercial divinylbenzene. Coordinates as in *Figure 2*

(15.1 kcal/mol) than does the styrene/*para* copolymerization (17.7 kcal/mol). It is to be noted that the pronounced Trommsdorf ('gel') effects shown in the non-linear increase in rate with time is not customarily observed in styrene polymerizations. Data are shown in *Figure 4*.

COPOLYMERIZATION REACTIVITY RATIO DATA FOR THE STYRENE/DIVINYLBENZENE SYSTEMS

It is in the kinetic data for the copolymerization reactivity ratios that the most striking differences in the characteristics of the *meta*- and *para*-divinylbenzenes are observed. Using ^{14}C-labelled styrene and radioactivity assay for the copolymer analysis[4, 5, 15], we have determined the concentration of styrene in the instantaneous (actually low-yield) copolymers for each of the styrene/*meta*- and *para*-divinylbenzene pairs. The reactivity ratios have been evaluated in the usual fashion from the differential equation. The technique is reliable and has given some of the best data available for conventional monomer types[5]. Data for the styrene/glycol dimethacrylate pair[4] ($r_1 = 0.4$; $r_2 = 0.64$: *Figure 5*) compare favourably with those for styrene/methyl methacrylate and are definitive. The 'instantaneous' (low-yield) copolymer would be expected to have involved no significant amount of the second vinyl group in a crosslinking reaction. The data for the styrene/*meta*-divinylbenzene pair show intersects[15] which, as required by theory, give unique solutions. There is, however, considerable variation in the values depending apparently on the extent of the 'low' yield actually taken and possibly the temperature of copolymerization. Thus: r_1 (styrene) = 0.6; r_2 (*m*-DVB) = 0.88 at 80°C and 1.8–3.7 per cent conversion (*Figure 6*); $r_1 = 1.27$; $r_2 = 1.08$ at 2.7–5 per cent conversion (*Figure 7*); and $r_1 = 0.65$; $r_2 = 0.60$ at 60°C (*Figure 8*). The methyl methacrylate/*meta*-divinylbenzene pair shows values of $r_1 = 0.41$, $r_2 = 0.61$ (*Figure 9*)[28] very close to the values for styrene/methyl methacrylate and styrene/glycol dimethacrylate. In all of these experiments *meta*-divinylbenzene behaves more or less normally as a substituted styrene with no apparently inexplicable interference from the

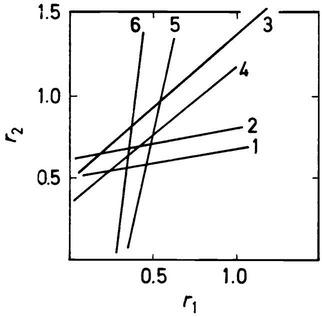

Figure 5. Graphical solution of the copolymerization equation for the styrene ($r_1 = 0.40$) – ethylene glycol dimethacrylate ($r_2 = 0.64$) copolymerization.

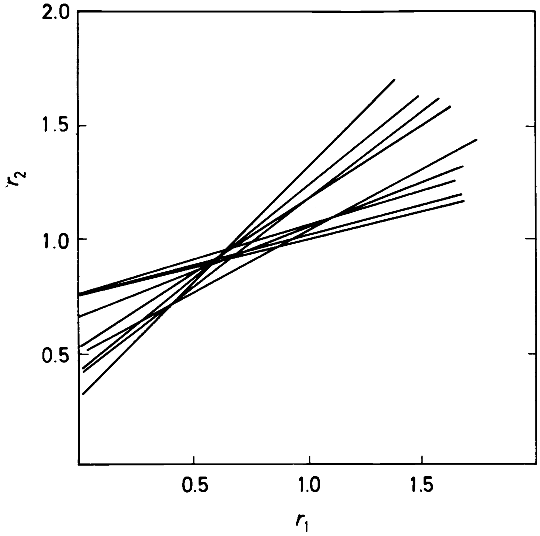

Figure 6. Intersect plot for the copolymerization of styrene (r_1 = 0.6) with *m*-divinylbenzene (r_2 = 0.88) at 80°C with benzoyl peroxide initiator. Conversion, 1.8–3.7%

second vinyl substituent. The *Q*- and *e*-values calculated for the styrene/ and the methyl methacrylate/*meta*-divinylbenzene pairs are comparable to those for related monomers[15, 28].

The monomer reactivity ratio data for the styrene/*para*-divinylbenzene pair cannot be so obviously correlated with the data for monovinyl pairs. The theoretically required intersect is not observed in plots of the differential data. Such data, based on low-yield copolymer analyses, show three or more intersects from copolymerizations at three different comonomer ratios (*Figure 10*)[4, 15]. Approximations of the r_1- and r_2-values can be obtained by eliminating the high *para*-divinyl copolymerization pairs (as the more likely to involve participation of the second vinyl group) or by a least squares

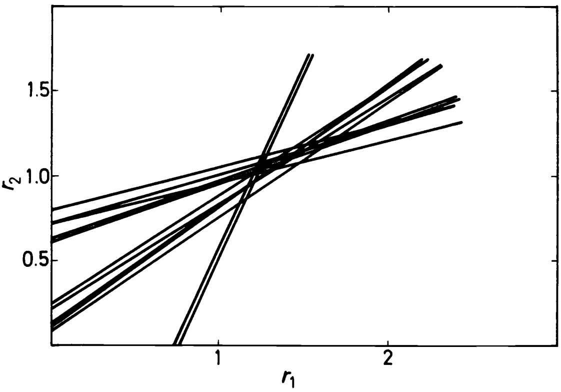

Figure 7. Intersect plot for the copolymerization of styrene (r_1 = 1.27) and *m*-divinylbenzene (r_2 = 1.08) at 80°C with benzoyl peroxide initiator. Conversion, 2.7–4.96%

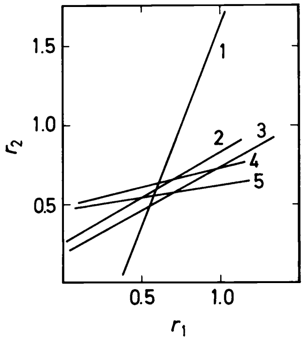

Figure 8. Intersect plot for the copolymerization of styrene ($r_1 = 0.65$) with *m*-divinylbenzene ($r_2 = 0.60$) at 60°C with benzoyl peroxide initiator. Direct counting assay.

analysis of the linear plot of the data. There is not very persuasive reasoning to support either approximation, but both give values (0.15/0.5 and 0.77/2.08) of the same relative magnitude; i.e. r_1 much lower than r_2. An $r_1 r_2$ product greater than 1 argues against the validity of the linear least squares approximation. A similar situation is met in the methyl methacrylate/*para*-divinylbenzene data (*Figure 11*)[28]. Least squares analysis of the linear plot gives values of 0.1/0.93 if all points are used or, if two highly erratic sets of data are discarded, 0.62/1.30. This approach being somewhat less than satisfactory, attention was directed to use of the integral form of the copolymerization.

Using the integral form of the copolymerization equation and a Fortran II program developed by others[37], high-conversion data for the styrene/*para*-divinylbenzene pair were analysed and compared with similar data for the styrene/*meta*-divinylbenzene pair[32]. The latter gave values of $r_1 = 0.95$–1.31 and $r_2 = 1.00$ for the *meta* isomer (*Tables 3, 4*). For the *para* isomer the values are $r_1 = 0.15$–0.25 and $r_2 = 1.00$. The integral *meta* values are thus in fairly reasonable accord with the differential values. Both sets of data indicate

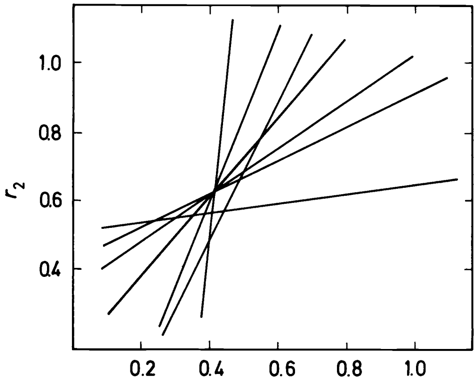

Figure 9. Intersect plot for the copolymerization of methyl methacrylate ($r_1 = 0.41$) with *m*-divinylbenzene ($r_2 = 0.61$) at 70°C with benzoyl peroxide initiator

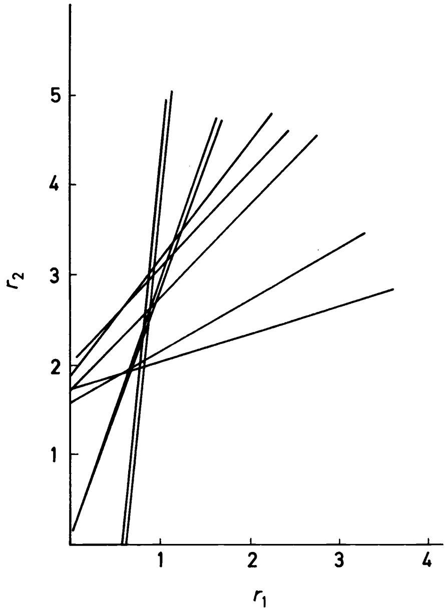

Figure 10. Intersect plot for the copolymerization of styrene (r_1 = 0.77) and *p*-divinylbenzene (r_2 = 2.08) at 80°C with benzoyl peroxide initiator

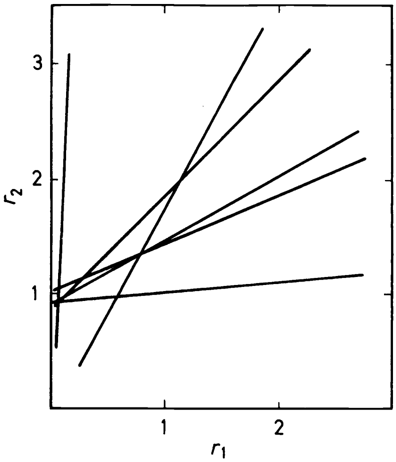

Figure 11. Intersect plot for the copolymerization of methyl methacrylate (r_1 = 0.62) with *p*-divinylbenzene (r_2 = 1.3) at 70°C and with benzoyl peroxide initiator. Values of r_1 and r_2 from least squares analysis of linear plot omitting the two extreme divergencies

Table 3. Monomer reactivity ratios (r_1 and r_2) for the styrene/*m*-divinylbenzene copolymerization

Pairs[a, b]	Av. conversion, %	r_1[c]	r_2[d]
1(4.7), 3(6.7)	5.7	0.95	1.00
1(4.7), 2(18.2)	11.4	0.92	1.00
3(6.7), 2(18.2)	12.4	1.08	1.00
1(4.7), 4(24.4)	14.5	1.16	1.00
3(6.7), 4(24.4)	15.5	1.31	1.00
2(18.2), 4(24.4)	21.3	1.29	1.00

[a] Pairs of data points used, identified as experiment numbers in ref. 32 with the conversion in parentheses.

[b] Variation of these values by ±10% gave r_1 values (top to bottom) of 0.912, 0.920, 1.077, 1.157, 1.314, 1.292, and r_2 values of 1.00.

[c] Average, $r_1 = 1.11$.

[d] Average, $r_2 = 1.00$.

that for the styrene/*meta* pair the two monomers are essentially equivalent in reactivity towards the other radical with perhaps a slight alternating tendency. The data for the *para* isomer, although much less consistent, show a marked preference of styrene radical for *para*-divinylbenzene (r_1 always significantly lower than r_2) and of *para*-divinylbenzene for itself (r_2 above 1.0 and significantly greater than r_1).

Table 4. Monomer reactivity ratios (r_1 and r_2) for the styrene/*p*-divinylbenzene copolymerization

Pairs[a, b]	Av. conversion, %	r_1[c]	r_2[d]
6(1.93), 9(9.04)	5.48	0.15	1.00
6(1.93), 8(14.89)	8.41	0.25	1.01
6(1.93), 7(14.95)	8.44	0.25	1.01
7(14.95), 9(9.04)	11.99	0.18	1.00
7(14.95), 8(14.89)	14.92	0.21	1.00

[a] Pairs of data points used, identified as experiment numbers in ref. 32 with the conversion in parentheses.

[b] Variation of these values by ±10% gave r_1 values (top to bottom) of 0.149, 0.182, 0.268, 0.178, 0.209, and r_2 values of 1.00.

[c] Average, $r_1 = 0.20$.

[d] Average, $r_2 = 1.00$.

A structural implication is rather clearly established by these kinetic data. The *para* isomer polymerizes and copolymerizes more slowly than does the *meta* isomer. It is a monomer distinctly different from styrene. In copolymerization systems styrene and probably *para*-divinylbenzene prefer *para*-divinylbenzene, so that the *para*-divinylbenzene monomer will be rapidly exhausted from the polymerizing mixture. This suggests that, when the crosslinking stage is reached, the crosslinkages will be formed in bunches and probably some of the second vinyl groups will be buried and unavailable for crosslinkages. The picture is one of heterogeneities. The *meta* isomer, however, presents a picture of a more uniformly distributed divinyl unit with, ultimately, evenly spaced crosslinkages and a homogeneous network.

The question is now whether these widely different copolymerization characteristics will be reflected in differences in copolymer properties associated with presumably different networks.

CHARACTERISTICS OF THE STYRENE/META- AND PARA-DIVINYLBENZENE BEAD COPOLYMERS

Bead copolymers of styrene and pure *meta*- or pure *para*-divinylbenzene were prepared by suspension copolymerization. Beads of 0.65–0.85 mm (20–30 mesh) and 125–250 μm size were separated for the experiments. The larger beads were prepared with carboxymethylcellulose as the suspending agent. The smaller beads were prepared with a sulphated polyvinyl alcohol as suspending agent. Details of the copolymerization techniques and preparation of the sulphonated polyvinyl alcohol are given in the published reports[1, 23]. The over-all size distribution observed in preparations of the smaller size beads is given in *Figure 12*. Yields of 70–90 per cent of beads of 125–250 μm size were typical.

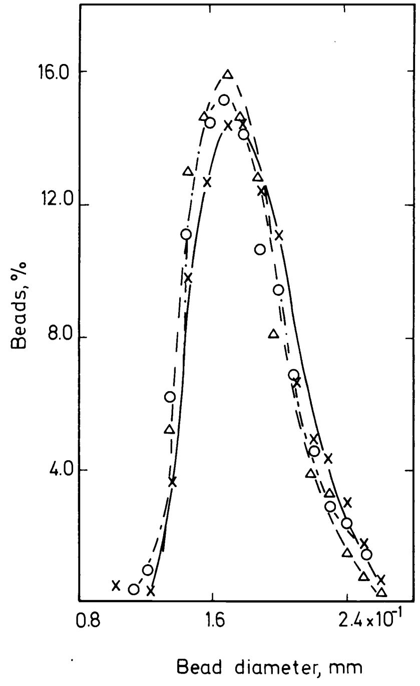

Figure 12. Size distribution curve of crosslinked bead copolymers of styrene with 4 mol % of × commercial divinylbenzene, △ *m*-divinylbenzene and ○ *p*-divinylbenzene.

Rates of sulphonation were measured by titrating the increase in exchange capacity—for both size beads and with beads swollen in ethylene dichloride or dimethyl sulphoxide[11, 13, 21, 24]. The latter solvent gives a homogeneous medium for the sulphonation. Data for the rates are given in *Figure 13*. The rate is higher for the *paja* crosslinked structures and in dimethyl sulphoxide. It has also been noted that the rate of sulphonation for the copolymer crosslinked with a 2/1 *meta*/*para* mixture of divinylbenzenes is more rapid than that of pure isomer crosslinked copolymer (*Figure 14*).

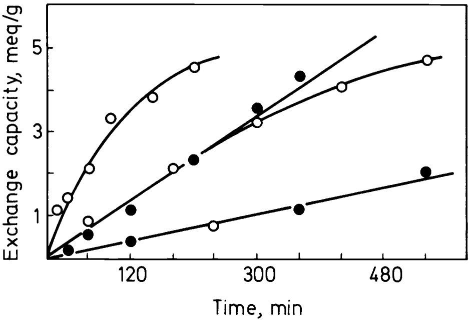

Figure 13. Sulphonation of bead copolymers of styrene with 8% pure *m*- and pure *p*-divinylbenzene: ○ in dimethyl sulphoxide; ● in ethylene dichloride. The upper pair of curves is for the *para*, the lower pair for the *meta* isomer

The structural conclusion consistent with these observations is that the sulphonating species, presumably sulphur trioxide (SO_3), is too large to penetrate the more uniformly crosslinked *meta* structure easily but has ready access to the long segments of polystyrene in the heterogeneously crosslinked *para* structure. In the early stages of the reaction in which the kinetic data are obtained, this distinction will be most pronounced.

Pyrolysis data for the *meta*- and *para*-divinylbenzene crosslinked copolymers of both styrene (*Figure 15*)[7] and methyl methacrylate (*Figure 16*)[18]

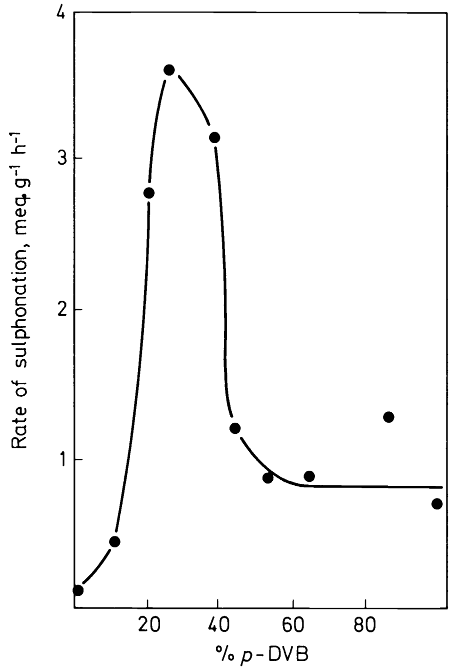

Figure 14. Rates of sulphonation, meq. g^{-1} h^{-1}, of polystyrene crosslinked with 8% of varying mixture of *meta*- and *para*-divinylbenzene

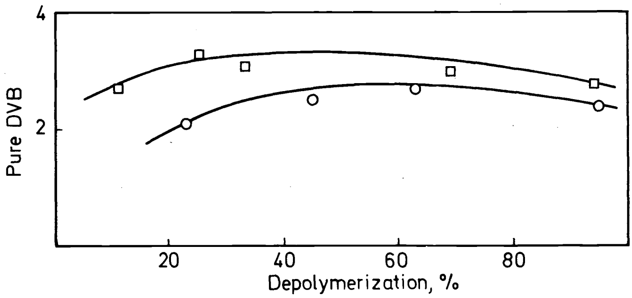

Figure 15. Rate of formation of pure divinylbenzene at 560°C from □ 8 % *m*-divinylbenzene and from ○ 8 % *p*-divinylbenzene styrene bead copolymers

show that the rate of appearance of *meta*-divinylbenzene, and the *meta* substituted products related to it, is higher than that for the *para*-divinylbenzene. This, also, is to be correlated with the presumed bunching of the *para* units in, in this case, less heat vulnerable positions. The data for the methyl methacrylate copolymers provide a more definitive picture presumably because the principal degradative process for the methacrylate structure

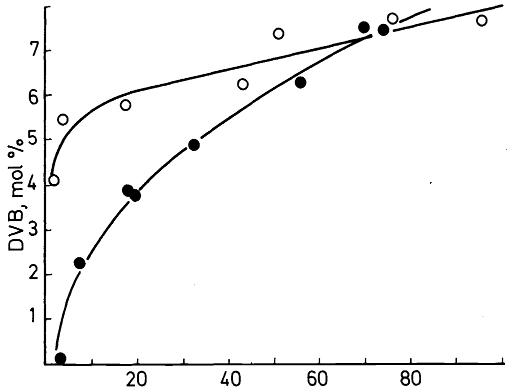

Figure 16. Rate of appearance of divinylbenzene-derived products in the pyrolysis at 552°C of 8 % bead copolymers of ○ *m*-divinyl copolymers and of ● *p*-divinyl copolymers

is almost exclusively depolymerization. These data should correlate better with mass spectral data[25] than has up to now been observed. There is a need for GLC/MS and TGA/MS data to provide additional information about these structural distinctions.

CHARACTERISTICS OF THE SULPHONATED COPOLYMERS OF STYRENE/META- AND PARA-DIVINYLBENZENE

Swelling ratios have been determined for the bead copolymers and the sulphonated copolymers[1, 19]. These data are admittedly difficult to obtain with precision[35], and the differences we have observed for the *meta* and *para* crosslinked types are not great. The maximum difference is about ten per cent for the one per cent crosslinked polymers (4.70 *meta* and 4.28 *para*) and sulphonated products (16.79 *meta* and 15.14 *para*). In all instances, however, the *para* crosslinked structures swell less than do the *meta* types. For the eight per cent divinyl copolymer beads, the ratios are 1.53 (*para*), 1.77 (*meta*) and 1.82 (2/1 *meta*/*para*). The data correlate with the rates of sulphonation: i.e. are in the same relative increasing order. Thus the *para* structure swells least and sulphonates least rapidly. The structural implications from these data are that the bunched *para* crosslinkages give a tighter, less solvent expandable network than does the uniformly distributed *meta* crosslinkage.

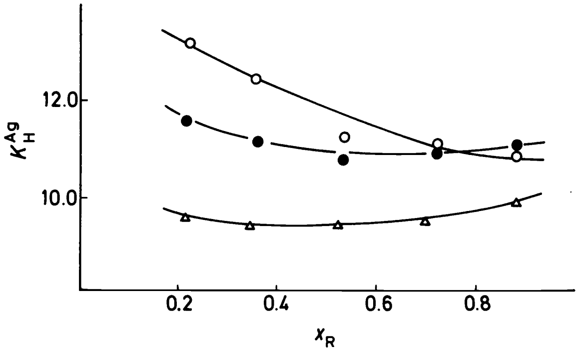

Figure 17. Silver–hydrogen exchange on 8% divinylbenzene crosslinked, sulphonated styrene bead copolymers: ○ commercial divinylbenzene; ● *p*-divinylbenzene; and △ *m*-divinylbenzene crosslinking

Equilibrium isotherms (selectivity coefficients) have been determined for the sulphonated copolymers[34]. The data for the sodium–, potassium–, rubidium–, caesium– and silver–hydrogen systems have been measured. Data for the other ions are similar—with lower values for K and with less pronounced differences in the plots. There are significant affinity differences between the sulphonated eight per cent *meta*- and *para*-divinylbenzene crosslinked materials to be seen in these data. The value of K_H^M for a given ion pair is clearly higher for the eight per cent *para* than for the eight per cent *meta* resin when the resins are predominantly in the hydrogen form—but an intersection of the *meta* and *para* curves occurs at $X_R = 0.65–0.8$ for all of the alkali metal (but not silver) systems. This *meta–para* difference in K_H^M increases with increasing hydrated ionic radius of the metal ions. These differences are also seen to vary with the cationic composition (X_H^R) of the resin, with a greater variation of K_H^M for the *para* network. These effects are consistent with the concept that the *para* crosslinked network is the more heterogeneous (i.e. these effects are directly related to heterogeneity of exchange site) and with the greater impermeability of the *meta* crosslinked network to the larger of the reacting species—an effect observed in sulphonation reactions also.

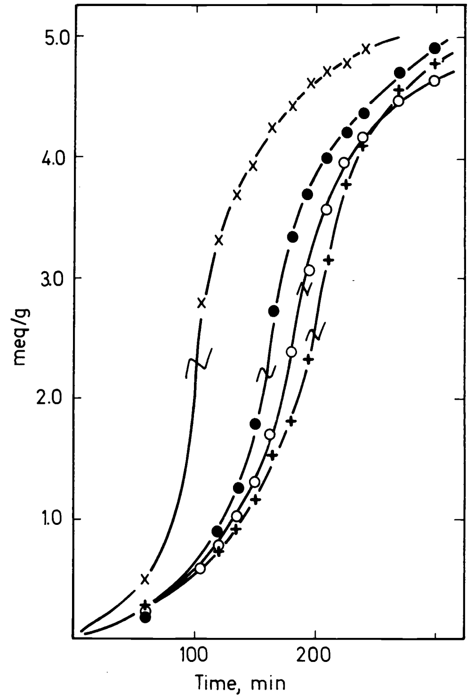

Figure 18. Rate of formation of acid in the peroxide-induced degradation of sulphonated styrene–divinylbenzene bead copolymers. Meq. of acid liberated per g of copolymer versus time. Inflection points indicated by break are taken from differential plots. + *meta*, ● *para*, ○ commercial divinylbenzene crosslinkage; ẋ Resin-50W–8X

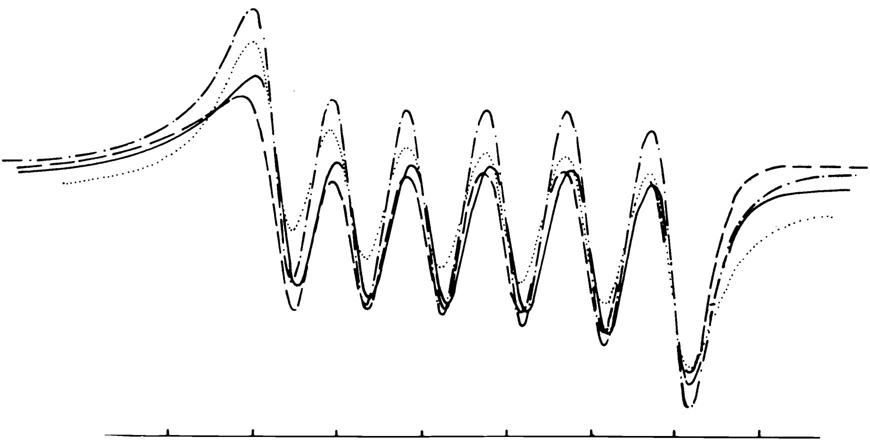

Figure 19. EPR spectra of Mn(II) on various ion exchange resins: sulphonated polystyrene crosslinked with 8% *m*-divinylbenzene (— —); with 8% *p*-divinylbenzene (——); and with 8% commercial (55%) divinylbenzene (—·—); and for a commercial resin (50W–8X) (····). Scale divisions are 100 G. Readings of line widths and peak separations are given in ref. 31. These samples were prepared by exchange of excess Mn(II) sulphate with the acid form of the resin

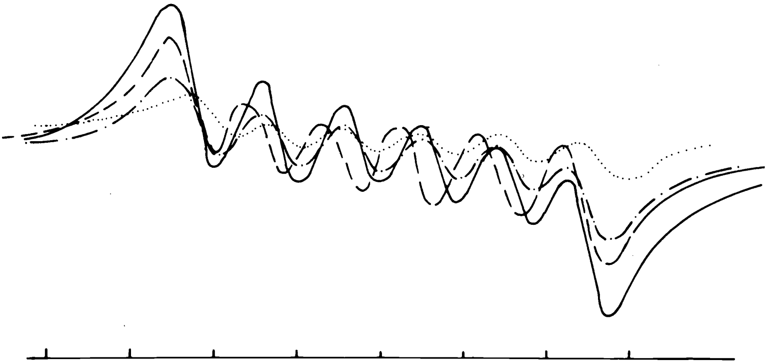

Figure 20. EPR spectra of Mn(II) on various ion exchange resins. The legend is the same as that for *Figure 19.* These samples were prepared by exchange of *ca.* one-half the equivalent amount of Mn(II) sulphate with the sodium form of the resins

The rate of degradation on treatment of the sulphonated copolymers with hydrogen peroxide is shown in *Figure 18.* The reaction is followed in terms of acid formation[27]. This reaction is thought to involve depolymerization because the beads dissolve during the course of the reaction; because the reaction is not induced by acid alone and is probably, therefore, not a simple desulphonation; and because the unsulphonated copolymers are not degraded by peroxide under comparable conditions. The *para* crosslinked structure degrades the more rapidly. From these data it is concluded that the acid is formed in a depolymerization which proceeds rapidly until a crosslinkage is reached—sooner with the *meta* than with the *para* network structure.

The electron paramagnetic resonance spectra have been observed[31] (*Figures 19–21*) for the exchange of manganese(II) with sodium and hydro-

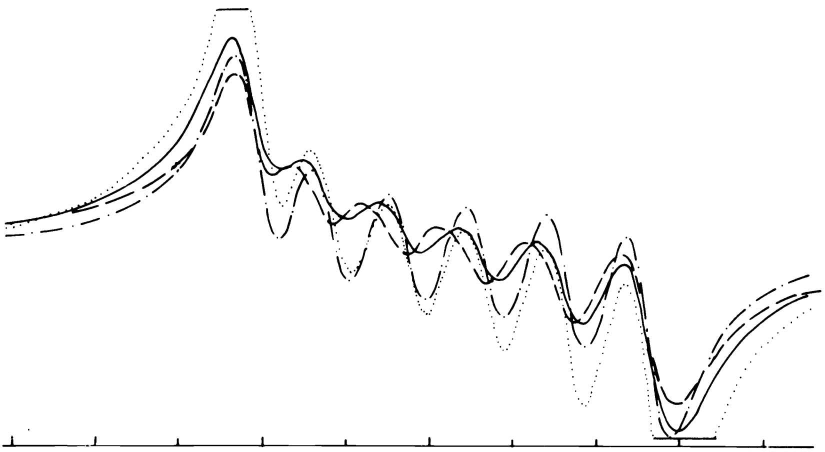

Figure 21. EPR spectra of Mn(II) on various ion exchange resins. The legend is the same as that for *Figure 19.* These samples were prepared by exchange of excess Mn(II) sulphate with the sodium form of the resins

gen ions. The data show variations in hyperfine structure (HFS) intervals and line widths which distinguish the *meta* and *para* crosslinked networks. Line width broadening effects have been attributed to differences in ionic environments[36]. Ionic environemnts of different symmetry would be predicted for the differences in heterogeneity attributed to the resins. And, again, it is the *para* crosslinked network which shows the greater line broadening and, hence, greater heterogeneity of site. These site differences can be associated with inherent structural heterogeneities or with variable, and therefore also more heterogeneous, exchange of the large manganese(II) ion.

CONCLUSIONS

Network structural variations can be produced by selected synthetic procedures, and these can be related to controlled variations in properties of the network. These conclusions are based on studies with copolymers of styrene with pure *meta*- and pure *para*-divinylbenzene in which the differences arise from differences in copolymerization characteristics. For these systems the differences are often subtle. Other networks[1,6] with enhanced structural differences can be envisaged.

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