

THE THEORY
AND PRACTICE
OF
ION EXCHANGE

The Theory and Practice of Ion Exchange

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FOREWORD

The Society of Chemical Industry last organised an International Conference on Ion Exchange in July 1969. At that time the scope of the meeting was broad and aimed at a wide range of applications and techniques. Sessions were devoted to ion exchanger developments, both organic and inorganic, ion exchange plant and equipment design, processes ranging from water treatment to the handling of radioactive wastes. On this occasion, the subject matter is narrowed and some emphasis is placed on the theory of ion exchange operations in an attempt to bridge the gap between academic endeavour and industrial practice. Regrettably, some papers have fallen by the wayside and others were not available at the time of printing. Nevertheless, the Organisers hope that these Proceedings will prove useful to practitioners in the field and record another landmark in the progress of ion exchange technology.

ACKNOWLEDGEMENT

I would like to express my gratitude to all the willing helpers who assisted in the preparation of this book. In particular, I wish to thank Miss S. Box for her undaunted typing, correcting and re-typing of numerous manuscripts.

M. Streat

THE MECHANISM OF NETWORK FORMATION IN STYRENE-DIVINYLBENZENE COPOLYMERS

L. ROUBINEK and D.G. SMITH*

The relative rates of disappearance of various monomers as function of time and conversion during network formation in styrene-divinylbenzene copolymers have been investigated. Also the formation and disappearance of the divinylbenzene pendant double bond was followed and interesting conclusions were made about its reactivity. The swelling properties of intermittent copolymer samples were measured and it has been found that the previously derived equation valid for the preparation of resins in the presence of swelling solvent was also valid for these samples in which the monomer was the swelling solvent. The formation of resin network was followed through the whole polymerisation period up to 100% conversion.

INTRODUCTION

The copolymers of styrene with divinylbenzene have a three-dimensional cross-linked structure resulting from the polyfunctionality of divinylbenzene. The degree of crosslinking is determined by the fraction of divinylbenzene in the copolymer. In early days of ion-exchange, the picture of an ion-exchanger has been referred to as a homogeneous gel model and until recently the properties and behaviour of synthetic resins based on these monomers were usually explained on this basis.

The early thinking on resins was confused by the method of imagining the structure of a copolymer of styrene with divinylbenzene as a simple open network with parallel chains and uniform crosslinks. In practice, this is very far from the truth. When the original styrene-divinylbenzene mixture starts to polymerise under the influence of the catalyst, a very large number of different crosslinked chains starts to form simultaneously. As they grow, they intermingle with each other and grow through each other with the result of an entangled structure. The measured crosslinking of every resin is in fact the total of the two effects, of divinylbenzene crosslinks together with entanglement.

In the copolymerisation of the pure isomers of divinylbenzene with styrene, the first polymer to form has an excessively high divinylbenzene content. As the reaction proceeds during a period of hours, the later polymer is less and less crosslinked, until the final chains are almost linear.

For a commercial system in which a mixture of m- and p-divinylbenzene are used, this has never been established quantitatively, however, the final copolymer, and the resins made from it, are heterogeneous, with highly crosslinked regions, surrounded by more loosely crosslinked areas.

This differential crosslinking has two disadvantages:

- (a) As the resin has a different swelling in different parts of its structure, strains are introduced which can lead to mechanical weakness.

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- (b) In the case of anion-exchange resins, organic matter from the water becomes locked in the highly crosslinked areas and cannot be removed.

The heterogeneity of styrene-divinylbenzene structures has its origin in the mechanism of copolymerisation which has been studied in detail in the past thirty years. Mayo and Lewis (1) found that the polymerisation of two monomers gives a polymer in which the ratio of the two monomers being incorporated into a polymer is a function of the fraction of monomer which has already polymerised.

In recent years it was Wiley and his co-workers who studied the copolymerisation of styrene with divinylbenzene in detail. In their first paper (2) they found, using a tracer technique, a good intersect plot for the system styrene/*m*-divinylbenzene by modifying the usual two component copolymerisation equation by the use of $2M_2$ for the M_2 term. They concluded that in styrene/*m*-divinylbenzene mixtures the two vinyl groups copolymerise independently and are equivalent in their reactivity.

The data for the styrene/*p*-divinylbenzene did not give plots which intersected and the authors concluded that this monomer pair cannot be regarded as a two component system because of a different reactivity of the second double bond of the DVB molecule before and after the reactivity of the first one.

However, in their later paper (3), Wiley and his co-workers re-measured these ratios using better polymerisation and detection methods and they were able to establish the reactivity ratios for both DVB isomers. They also found that these ratios - at least in the case of styrene/*m*-divinylbenzene copolymerisation changed with conversion because of an increased participation of the second of the divinyl units in the propagation step.

Malinsky et al also studied the reactivity ratios of styrene/divinylbenzene mixtures. In their first paper (4) they investigated the copolymerisation composition before the gelation point using infra-red spectrometry and found a substantially higher reactivity of vinyl group of *p*-divinylbenzene, when compared with *m*-divinylbenzene. In their subsequent paper (5) again using the infra-red spectrometry technique, they compared the experimental results with the values derived previously calculated on the assumption that the reactivities both of the vinyl groups in the monomers and of the pendant vinyl groups were independent of conversion.

In our investigation we followed the copolymerisation through the whole polymerisation period up to 100% conversion. We did not study the copolymerisation behaviour of pure *m*- and *p*-divinylbenzene toward styrene, but we concentrated our attention to imitate the copolymerisation conditions as they exist in the industrial production of styrene-divinylbenzene copolymers used in the manufacture of ion-exchange resins.

The copolymerisation was carried out in aqueous dispersion and technical monomers without further purification were used throughout. The commercial divinylbenzene used as crosslinker was a mixture containing the two divinyl isomers, together with substantial content of substituted styrenes. Under these conditions it was impossible - and it was actually not intended - to measure the reactivity ratios of this multi-component system.

Nevertheless, we were able to follow the conversion of monomers to cross-linked and linear polymers at different divinylbenzene concentration. We also followed the disappearance of divinylbenzene isomers from the monomer mixture and their build-up in the polymer as well as the formation and subsequent disappearance of the pendant double bond during polymerisation. We compared the equilibrium swelling capacities in toluene of the three-dimensional intermittent copolymer samples with theoretical values using the equation derived by Millar et al (6).

EXPERIMENTAL

The polymerisation was carried out in a conventional 2-litre reaction vessel. The monomers, with the inhibitors removed and dissolved catalyst (benzoyl peroxide), were stirred in water containing a commercial dispersion

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stabilizer Rhodoviol 25/100M to produce droplets of 0.3-1.0 mm in diameter. The polymerisation temperature was 80°C. The commercial divinylbenzene mixture was supplied by the Dow Chemical Company, of the following composition

m-divinylbenzene	:	34.12%	w/w
p-divinylbenzene	:	16.47	w/w
m-ethylstyrene	:	30.40	w/w
p-ethylstyrene	:	14.10	w/w
Saturates	:	4.91	w/w

Styrene monomer was a commercial product, used without further purification.

Samples were taken at intervals by transferring them into large amounts of cold water which effectively halted the polymerisation. The partially polymerised monomer swollen gels were washed with water and dried over anhydrous CaCl₂ to constant weight. The weight of dried sample was usually 20-30g. Experiments carried out, using monomer samples of known composition showed that anhydrous CaCl₂ does not interact with or absorb monomers.

The dried sample was weighed into a sintered glass-bottomed Soxhlet extraction thimble and extracted for 4-6 hours with acetone containing about 0.03% w/v of hydroquinone. The polymer obtained was dried to constant weight in a vacuum desiccator at room temperature over phosphorous pentoxide. The acetone extract was fractionated in a Dufton column up to a maximum distillation temperature of 70°C, and the weight of residual extract noted. Analysis of this extract by G.L.C. gave the relative proportions of the monomers present. G.L.C. analyses were carried out in Perkin Elmer F11 Gas Chromatograph (Flame Ionisation) using a 4m Apiezon L column at 200°C. Calibration of the detector using known styrene-divinylbenzene mixtures showed the percentage of component to be proportional to percentage of peak area within an experimental error of ±5%. The residual acetone extract was also used for the determination of the linear polymer in the extracted monomers by evaporation of a weighed sample to dryness. Knowing the weight of this residue, and the weight of monomers, the linear polymer content of the monomers is readily calculated. To determine the unsaturation in the dried extracted polymers, a weighed quantity of the material (0.2-0.4g) was allowed to swell in an iodine flask for about a week in CCl₄ to equilibrate fully. N/10 bromine solution in CCl₄ was then added and the flask kept in the dark for 6-24 hours, according to the amount of crosslinker present, before back-titration. This was carried out in the usual manner by adding excess KI and water to liberate an equivalent quantity of iodine and titrating the excess with N/10 Na₂S₂O₃. When the endpoint was reached, KIO₃ was added and the titration continued to determine substituted bromine.

RESULTS

Three series of experiments were carried out using monomer mixtures containing 8.6, 17.2 and 34.4% w/w divinylbenzene respectively. The polymerisations were carried out under essentially identical conditions. The composition of the intermittent samples was calculated from the peak areas of the gas chromatography charts, using a planimeter, and the results were expressed as weight percentages. The composition of the unreacted monomer mixture at different degrees of conversion is shown in Table 1, and the concentration of each monomer is compared to that of styrene, the major component. Table 2 lists the cumulative percentages of divinylbenzene (m- and p- derivatives are added together) in the intermittent samples of the crosslinked polymer. In the same Table are also given the concentration of divinylbenzene with pendant double bonds and the calculated values of divinylbenzene concentration incorporated into the polymer network by both vinyl groups.

The percentage of divinylbenzene in the polymer was calculated as follows:-

$$XY + (100-X)Z = 100S \dots\dots\dots (1)$$

- where
- X = % conversion
 - Y = % divinylbenzene (m + p) in polymer
 - Z = % divinylbenzene (m + p) in extracted monomers
 - S = % divinylbenzene (m + p) in the original monomer mixture

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TABLE 1 - Composition of Monomer Mixture during Polymerisation

Con- version Total *	Styrene	Monomer Contents %				Monomer Ratios			
		m-ES	p-ES	m-DVB	p-DVB	<u>Styrene</u> m-ES	<u>Styrene</u> p-ES	<u>Styrene</u> m-DVB	<u>Styrene</u> p-DVB
8.6% DVB/Styrene									
0	83.00	5.17	2.80	5.80	2.80	16.05	34.60	14.31	40.10
9.46	84.85	4.95	2.22	5.10	2.02	17.15	38.21	16.64	42.00
19.80	85.75	5.08	2.29	4.53	1.49	16.88	37.42	18.92	57.51
29.50	86.75	5.10	2.29	3.81	1.14	17.00	37.86	22.76	76.10
79.90	86.10	5.87	3.10	1.31	0.31	14.67	27.76	65.65	278.80
88.00	87.10	4.45	2.67	0.86	0.27	19.58	32.06	101.04	322.50
17.2% DVB/Styrene									
0	66.00	10.33	4.80	11.60	5.60	6.38	13.75	5.68	11.78
8.45	69.40	9.87	10.56	10.30	4.30	7.03	15.22	6.73	16.12
22.90	71.70	9.99	4.67	8.70	3.17	7.17	15.36	8.24	22.60
39.80	72.70	10.29	4.81	7.77	2.46	7.07	15.12	9.35	29.55
61.80	76.00	10.10	5.26	4.48	1.08	7.53	14.44	16.95	70.32
79.00	74.25	10.97	5.84	2.55	0.79	6.77	12.72	29.05	94.00
82.90	74.25	10.86	5.71	2.16	0.69	6.84	13.00	34.36	107.60
34.4% DVB/Styrene									
0	32.07	20.62	9.58	23.30	11.20	1.56	3.35	1.38	2.86
13.02	39.92	19.50	9.02	20.28	8.50	2.05	4.43	1.97	4.70
27.20	41.85	20.25	9.56	18.50	6.40	2.06	4.38	2.26	7.52
48.20	43.05	21.80	11.21	14.75	4.40	1.97	3.84	2.92	9.78
65.50	44.30	23.02	11.64	10.45	2.40	1.92	3.81	4.24	18.45
76.00	44.50	23.73	12.39	7.60	1.75	1.88	3.59	5.85	25.42
78.40	45.85	21.93	12.79	6.10	1.66	2.09	3.58	7.51	27.63

ES = Ethylstyrene DVB = Divinylbenzene
 % = Weight Percentage
 * = Crosslinked and Linear Polymers

The swelling of the intermittent and of the final polymer samples in toluene was determined after equilibration at room temperature and it was expressed as "toluene regain" (g of toluene per g dry resin). These values are listed in the last column of Table 2. Finally, in Table 3 are given the percentages for solvent soluble linear polymer as function of conversion.

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TABLE 2 - Composition of Intermittent Crosslinked Polymer Samples and their Swelling Properties - Found and Calculated

% Conversion Total*	% m + p DVB Total in Polymer	% m + p DVB with Pendant Double Bond	% m + p DVB as Cross-linker in Polymer	Toluene Regain g/g corres. to Cross-linking	0.954S from Equation 1	Calc. Toluene Regain g/g accord. to Equation 1	Measured Toluene Regain g/g
8.6% DVB							
9.46	24.60	68.94	7.64	0.71	14.88	15.59	13.30
19.80	20.80	78.73	4.42	1.07	4.50	5.57	6.34
29.50	18.00	76.53	4.23	1.11	2.49	3.60	4.22
79.90	10.30	43.85	5.78	0.88	0.23	1.13	1.12
88.00	9.60	29.79	6.74	0.78	0.13	0.91	0.82
17.2% DVB							
8.45	44.40	65.71	15.23	0.42	21.00	21.42	22.60
22.90	36.40	71.06	10.53	0.56	3.66	4.22	4.55
39.80	30.20	75.33	7.45	0.72	1.52	2.24	2.45
61.80	24.20	60.44	9.57	0.60	0.60	1.20	1.15
79.00	20.60	42.28	11.89	0.51	0.26	0.77	0.65
82.90	20.00	38.66	12.27	0.49	0.20	0.69	0.60
34.4% DVB							
13.02	71.00	64.53	25.19	0.29	10.97	11.26	11.30
27.20	61.00	68.39	19.28	0.35	2.94	3.29	3.04
48.20	51.30	71.33	14.71	0.43	1.06	1.49	1.35
65.50	45.30	53.09	21.26	0.33	0.51	0.84	0.77
76.00	41.60	43.90	23.34	0.30	0.31	0.61	0.52
78.40	40.80	38.54	25.08	0.29	0.27	0.56	0.48

DVB = Divinylbenzene
 % = Weight Percentage
 * = Crosslinked + Linear Polymers

TABLE 3 - Percentages of Crosslinked and Linear Polymers in Intermittent Samples

% Total Conversion	% Crosslinked Polymer	% Linear Polymer
8.6% DVB		
9.46	6.06	3.40
19.80	17.50	2.30
29.50	27.80	1.70
39.20	37.80	1.40
17.2% DVB		
8.45	4.35	4.10
22.90	20.70	2.20
39.80	38.60	1.20
61.80	61.20	0.60
34.4% DVB		
13.02	8.02	5.00
27.20	24.50	2.70
48.20	47.30	0.90
65.50	65.20	0.30

In Figure 1 the percentage conversion as a function of time of reaction is plotted for each of the three experiments carried out. It can be seen that as the percentage of divinylbenzene in the starting mixture increases, so does the rate of reaction. The shape of the curves is that to be expected for systems which show progressively reduced termination rates due to reduced rate of polymer radical diffusion (7). However, the S type curve may also indicate retardation by atmospheric oxygen of the reaction rate during the early stages of polymerisation.

In Figure 2, 3, and 4 are plotted percentage conversion against percentage divinylbenzene in the polymer for the runs with 8.6, 17.2, and 34.4% w/w divinylbenzene respectively. Each Figure shows the total amount of divinylbenzene incorporated into the polymer network and also the content of divinylbenzene with pendant double bond and divinylbenzene incorporated into the polymer by both vinyl groups. The unsaturation in the intermittent samples is also expressed usefully as the percentage of total divinylbenzene (m and p isomers taken together) against percentage conversion. This is shown in Figure 5 for all three divinylbenzene concentrations. In this Figure the unsaturation is corrected at the early stages of conversion by including the linear polymer which is assumed to contain 100% unsaturation.

The intermittent samples can be considered as solvent modified styrene-divinylbenzene copolymers, the unreacted monomer being the solvent. A simple relation has been found by Millar et al (6) between the swelling of a given copolymer in toluene ("toluene regain") and the amount of a solvating diluent added to the monomer mixture. As the true concentration of chemical crosslinker and the ratio of monomer to copolymer for each intermittent sample are known, this equation can be used to predict the toluene regain of any intermittent sample and its validity checked by comparing them with values found experimentally. The original equation (6) was modified in such a way that the swelling parameters and the amount of diluent present could be expressed in weight instead of volume units and regard was given also to the difference in densities of monomer mixture and toluene:

$$U_X^1 = U_N^1 + 0.954 S \dots\dots\dots(2)$$

where U_X^1 is toluene regain (g/g) of the intermittent polymer, U_N^1 is toluene regain (g/g) of a polymer of the same DVB content but at 100% conversion (8) and S is the ratio (by weight) of monomer to polymer in the intermittent samples. The factor 0.954 is the density ratio toluene/monomer. The toluene regains calculated and found are shown in Table 2 and also in Figure 6 for intermittent samples containing 8.6, 17.2, and 34.4% w/w divinylbenzene in the starting monomer mixture.

For calculations involving the percentage conversion, the percentage crosslinked polymer obtained from the quantitative extraction of the intermittent samples must be corrected for the percentage linear polymer formed. The conversion figures in Table 1 and 2 include linear polymer. Although at high conversions the figures are insignificant (< 1%), at low conversions it can be almost as much as the crosslinked polymers as shown in Table 3.

So far little has been said about the individual monomers included in the polymerisation from the G.L.C. results, shown in Table 1, it seems that there is some difference in the reactivity of the m and p-divinylbenzene but little difference in the reactivity of m- and p-ethyl styrene, both of which have the same order of reactivity as styrene.

DISCUSSION

The reaction rate curves of the three copolymerisation experiments are shown in Figure 1. At relatively low conversion, the rate is highest for the mixture containing the higher proportion of the more reactive divinylbenzene. At high conversion the curves cross over and the system with lowest content of divinylbenzene, 8.6% w/w is fastest. Also at high conversion the three dimensional network takes its final shape, the number of pendant double bond decreases and the amount of actual crosslinks attains its final density. The reaction becomes diffusion-controlled - i.e. the diffusion of unreacted monomer molecules towards the free radicals on the propagating chains becomes rate controlling, and the decrease in polymerisation rate is most noticeable for copolymers of highest crosslinking density. Figure 1 does not show the curves up to 100% conversion but it can be easily imagined, from the shape of the curves at high conversion, that to remove the monomer from the reaction mixture completely is very difficult indeed.

These copolymerisation experiments confirmed the initial faster consumption of divinylbenzene as predicted by the reactivity ratios for the system. Thus the polymer molecules formed initially are enriched with DVB. Figures 2, 3, and 4 show that the difference in divinylbenzene content in the polymer at the beginning and at the end of polymerisation is enormous. Moreover, these curves show the cumulative concentrations, not instantaneous ones which would show still larger differences in divinylbenzene content.

The proportion of crosslinks, i.e. of doubly reacted DVB at any time in the polymer network is actually less than indicated by the curves showing the total amount of divinylbenzene incorporated into the polymer by the first double bond.

The same Figures 2, 3, and 4 also show - again as a function of conversion - the percentage of divinylbenzene reacted by both vinyl groups - i.e. the actual amount of crosslinker bridges incorporated into the polymer at any instance of conversion. This curve is much more shallow with a minimum of about 50% conversion.

The reactivity of the second vinyl group of divinylbenzene unit was considered already in the papers by Wiley et al (2,3) and later in a paper by Malinsky et al (5), who actually plotted the fractions of divinylbenzene units with pendant vinyl group as function of conversion. However, their experimental values do not fit well to the theoretical values calculated from the reactivity ratios of a ternary system; styrene-divinylbenzene - pendant double bond. Their conclusion clearly indicates that the pendant double bond of divinylbenzene was similar in reactivity to styrene, and at least their theoretical values for the pendant double bond showed its complete disappearance at 100% conversion. It is improbable that its reactivity is in any way lowered because it is an integral part of the polymer structure. In our system we also found the percentage of pendant double bond was surprisingly high and it fell off first towards the end of the reaction. This is shown in Figure 5 in which it is expressed as a plot of percentage of total divinylbenzene incorporated into the polymer chains against conversion. This Figure, as well as Figures 2, 3, and 4, show that the pendant double bond disappears completely from the polymer structure at 100% conversion. This is not accidental but it indicates that the reactivity of the pendant double bond is identical to that of styrene monomer. If the reactivity of the pendant double bond were faster than the reactivity of styrene, it would disappear prior to 100% conversion and there would be very probably linear polystyrene present in the final resin because of the low concentration of divinylbenzene monomer in the unreacted mixture towards the end of polymerisation. If, on the other hand, the reactivity of pendant double bond should be lower than the reactivity of vinyl group in styrene, the final copolymer would contain unsaturation. Neither of this is true and the final resin is a well and fully copolymerised three-dimensional network.

These results also show that the ternary system - styrene/m-DVB/p-DVB behaves very similarly to the binary systems used by Malinsky (5). We, therefore, tried to calculate the copolymer composition by applying the simple equation for a two component copolymerisation to the two systems, styrene/m-divinylbenzene and styrene/p-divinylbenzene. In the absence of reactivity ratios for the copolymerisation of m-DVB/p-DVB, we were forced to make the assumption that we could consider our system as a mixture of two binary systems polymerising simultaneously. This simplified approach gives a reasonable prediction of copolymer composition (in terms of styrene and divinylbenzene) for monomer systems of 7 mole % DVB or less - (e.g. calculated DVB content in initial copolymer 25.1 mole %, observed 29.2 mole %). As the DVB content of the monomer increased the validity of our assumption is poorer, and the agreement between calculated and observed copolymer DVB content decreased. (At 14 mole % DVB monomer, calculated DVB in initial copolymer was 37 mole %, observed 43.5 mole %, whilst at 29.6 mole % DVB monomer, calculated DVB content was 52.7 mole %, observed 82.0 mole %).

The agreement between the measured and calculated degree of crosslinking (Table 2) indicates that very little cyclisation occurs over the range of conversion and DVB contents studied. Cyclisation occurs when a growing chain radical reacts with a double bond pendant to the same backbone rather than adding a monomer molecule. Chain growth then continues as normal with further monomer addition. This phenomenon has been postulated previously (5). Equation 1 shows that the extra volume swelling of the intermittent samples is due solely to the presence of the solvent, in this case the monomer. [We consider the monomer mixture to be as good a solvent for the polymer as toluene; the solvent used when the original relationship was established]. If cyclisation occurred the resultant toluene uptake after allowing for the volume of "solvent" would be more than that calculated from the measured crosslinking using Pepper's relationship (8).

The variation of the latter with conversion is particularly interesting. In spite of the more rapid incorporation of divinylbenzene into polymer at low conversion, the measured percent crosslinking is lower even than that expected from the monomer mixture. The change in total volume on proceeding from

monomer droplets to 100% copolymer at all times parallels the increase in particle density. This means that polymer formed later in time is incorporated within the primary network formed at gelation. Up to about 60% conversion this process occurs with little entanglement. Above this conversion further extra crosslinking in the form of entanglement takes place. As a result, the measured toluene regain becomes progressively less than that calculated giving rise to the deviation shown in Figure 6 at low regains - (i.e. higher conversions).

The amount of divinylbenzene units incorporated in unit time into the polymer during reaction decreases fast with conversion. Thus the final polymer network seems to be a composite of a large number of structures of widely different divinylbenzene content. In reality, however, all these individual structures are interconnected by polymer chains which reacted through the pendant double bonds of the divinylbenzene units making the final copolymer into a quite compact structure.

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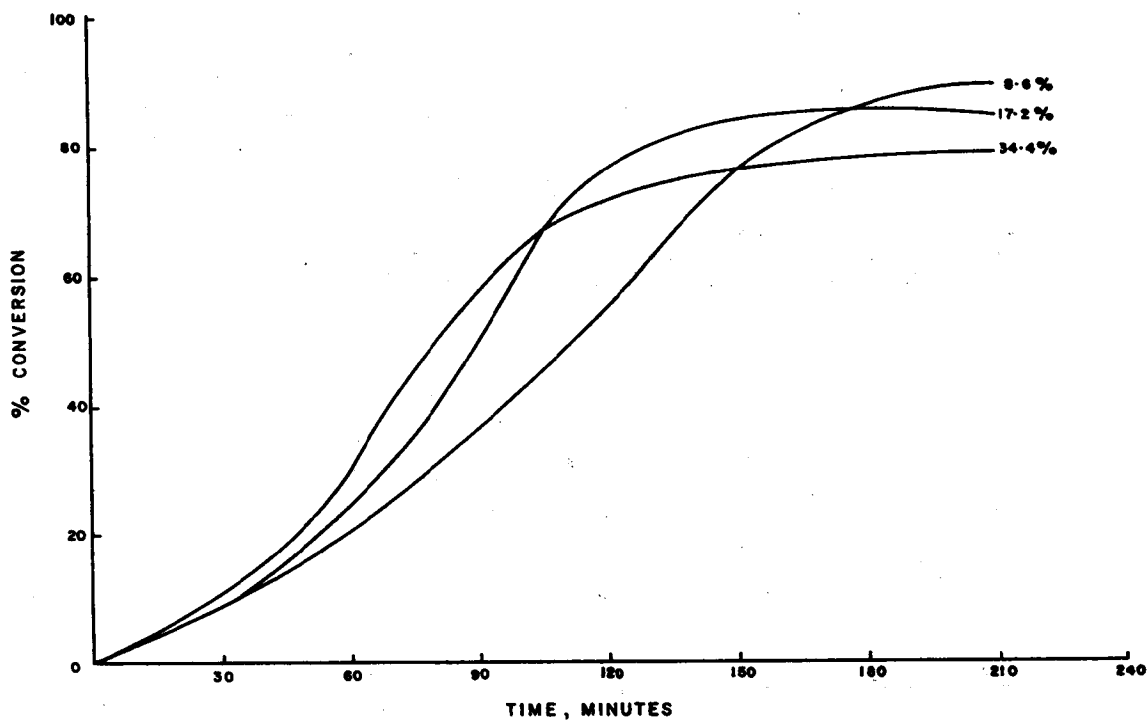


Figure 1 Rate of polymerisation of styrene/divinylbenzene mixtures at 80 C. 8.6, 17.2, and 34.4% w/w DVB.

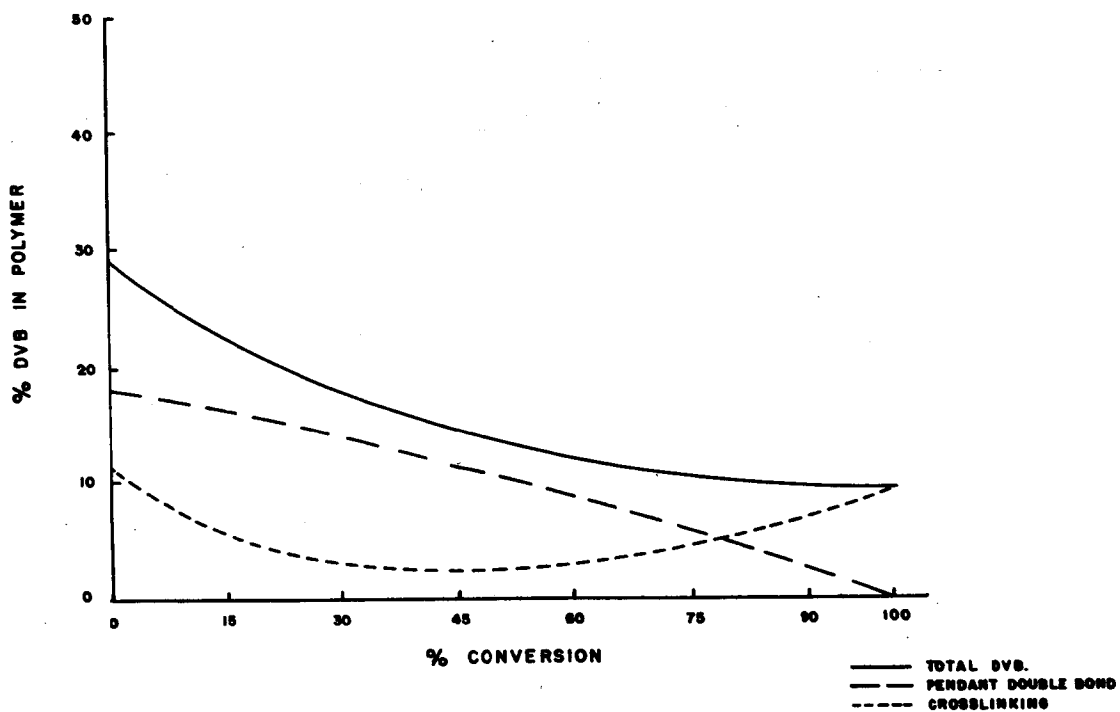


Figure 2 Percentage conversion versus percentage DVB 8.6% DVB in the starting monomer mixture.

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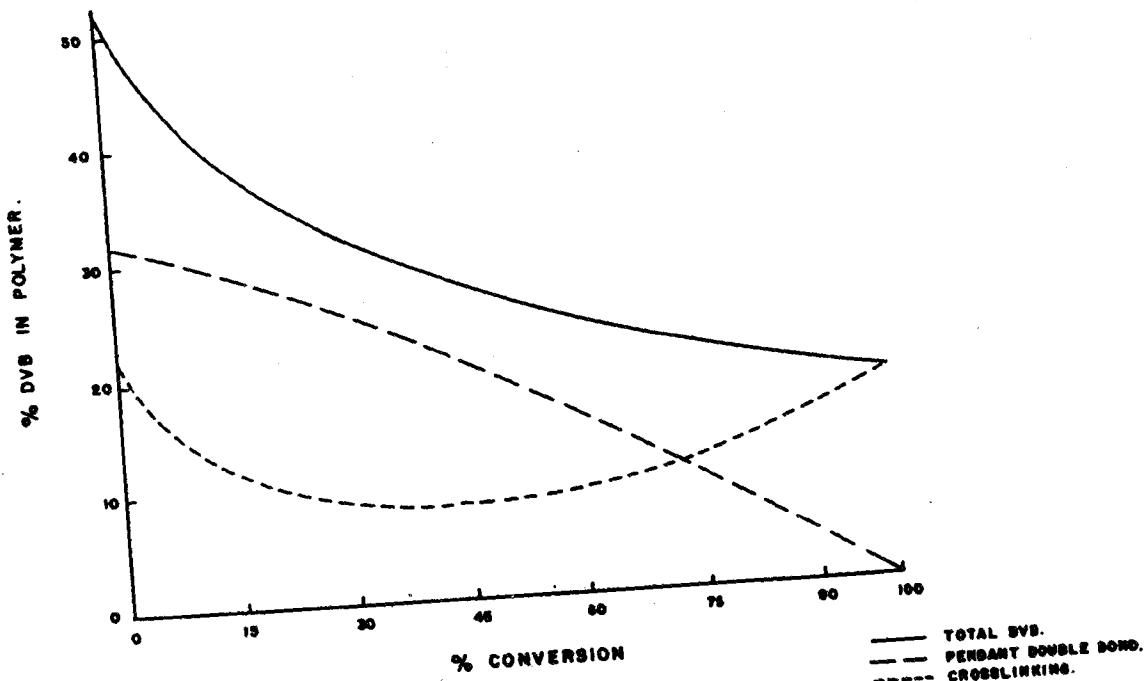


Figure 3 Percentage conversion versus percentage DVB
17.2% DVB in the starting monomer mixture.

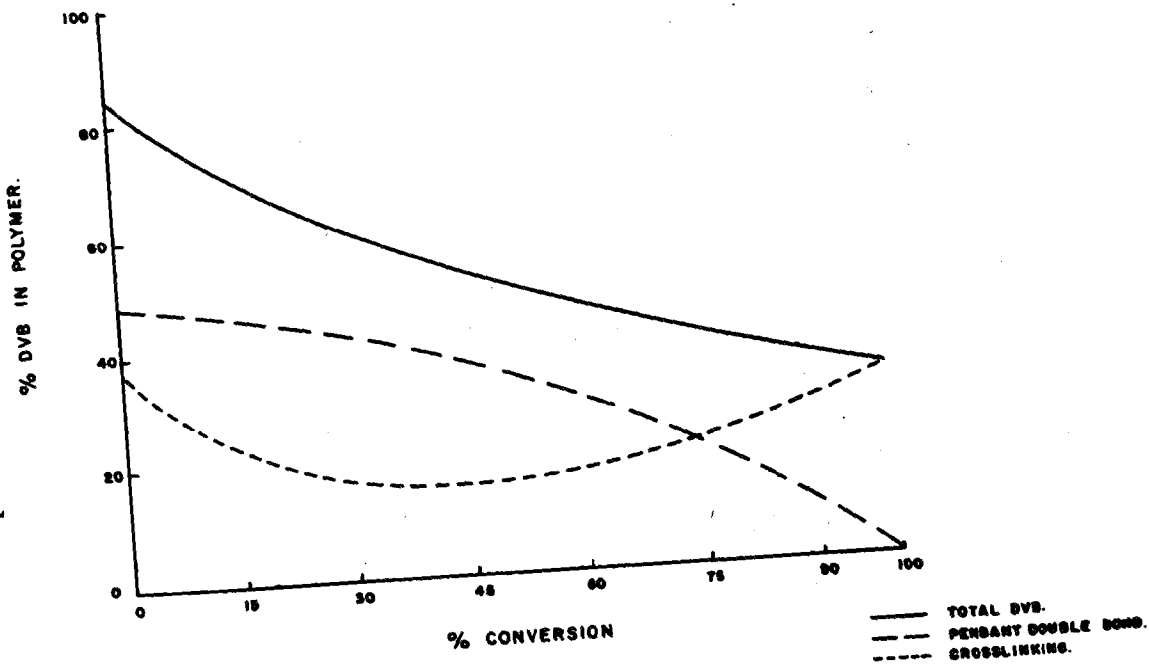


Figure 4 Percentage conversion versus percentage DVB
34.4% DVB in the starting monomer mixture.

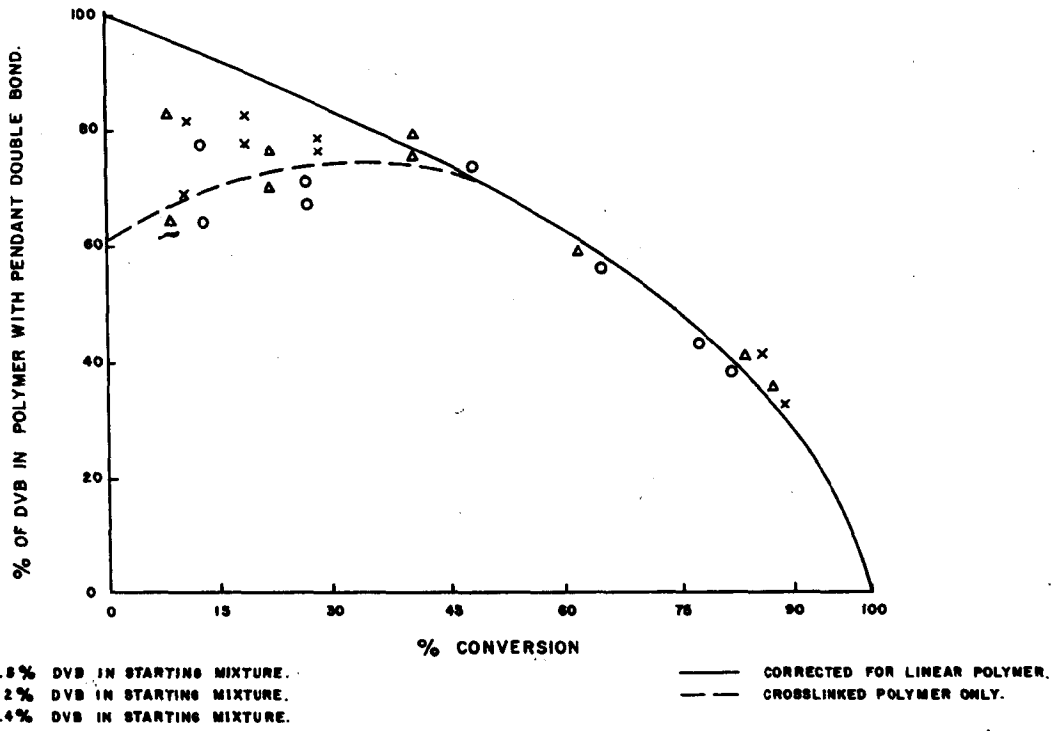


Figure 5 Unsaturation in intermediate samples

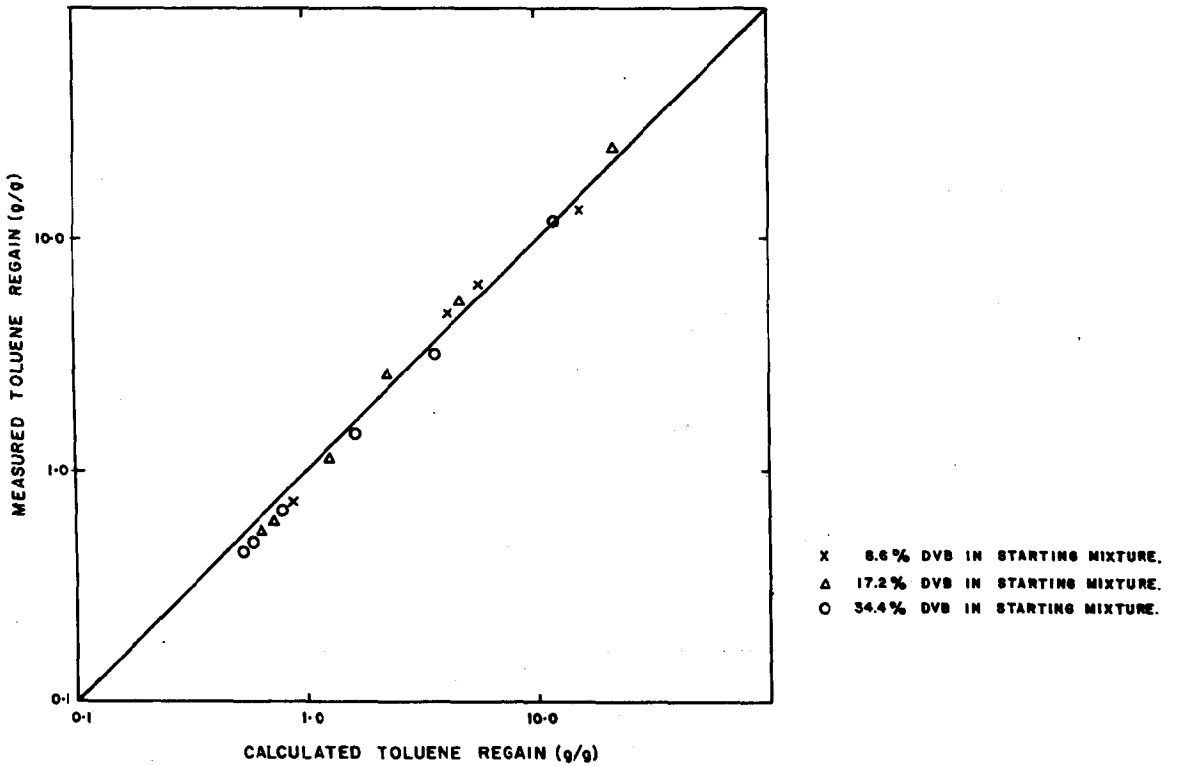


Figure 6 Toluene regains - measured versus calculated.

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INVESTIGATION OF STRUCTURE OF SOME COPOLYMERS USED FOR PREPARATION OF ION EXCHANGE RESINS BY GAS PERMEABILITY

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The gas permeability method for investigating of the structure of cross-linked polymers is useful because it gives new information. The method is mostly effective if the size of the molecules of the test-gas is close to the size of cavities in the polymer structure. Copolymers of styrene and MMA with p- and m-DVB show many deviations from what has been considered as a normal behavior. The data obtained may simply be explained by microheterogeneities in the copolymers leading to the appearance of different diffusion zones. Redistribution of low- and high permeable parts in the polymer networks takes place under the influence of temperature.

INTRODUCTION

Gas permeability can be a new source of information about the structure of three dimensional copolymers used as basis for preparation of ion exchange resins. As far as we know this method has not been used before for this purpose.

EXPERIMENTAL

p- and m-isomers of divinylbenzene (DVB) containing not less than 98% of the main substance and commercial DVB containing 55% of these isomers were used for the preparation of the samples. They were prepared as membranes of 20-200 μ (microns) thickness. The polymerization was carried out according to method described by Zundel(1). The measurements of the gas permeability were carried out in a device analogous to that described by Barrer(2). Density was determined by the immersion method having water solutions of salts as immersion liquids. The permeability (P) and diffusion (D) coefficients were calculated as described in the reference (2).

PRECISION AND REPRODUCIBILITY

The following sources of experimental errors were taken into account in the evaluation of the precision and reproducibility of our results:

1. Differences in properties of different pieces of membranes prepared at different times and of different parts of the same sample.
2. Errors in the measurements of the leaking curves.
3. Errors in the determination of the thickness and area of the samples.
4. Changes in the properties of the samples with time.

We came to the conclusion that when studying P and D as functions of the cross-linkage the deviations are due to the effects mentioned under 1 above. The time effect is also important but it can be avoided by only working with fresh samples. The average error in P and D was about 30%. The errors under point 2 above are only important when calculating the effective activation energies (E_p) of the permeability and that of diffusion (E_D) because the samples were not removed from the cell before the measurements of temperature dependence of permeability had been completed. We evaluated the average error in E_p and E_D as 2 kcal/mole.

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