

## INFLUENCE OF THE STRUCTURE OF THE MATRIX ON THE PROPERTIES OF ION EXCHANGERS

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**Abstract** - First, a possibility for structural determination of radical polymerized styrene-divinylbenzene-copolymers by means of kinetic data of this system is reported. The addition of further suitable monomers leads to improvement of the homogeneity of the matrix which influences the properties of ion exchangers derived from it. In the same connection the statistic anionic copolymerization of styrene with divinylbenzene is discussed. Further, heterogeneous styrene polymers were produced by a special procedure of anionic polymerization. On the other hand, also homogeneous styrene-divinylbenzene blockpolymers were prepared. The comparative test of ion exchange resins thus obtained allows the conclusion that the homogeneity of the network has a great influence on the properties of ion exchangers.

### INTRODUCTION

The predominant part of commercial ion exchange resins which have found broad fields of application in science and technology are produced on the basis of styrene. These are copolymers of styrene with only small amounts of divinylbenzene (DVB) being functionalized in the subsequent reactions. The structure of the copolymers thus formed is possibly in relation with the properties of ion exchangers made out of them. The present discussion is primarily concerned with

1. a structure determination of copolymers in order to relate it to their properties and with
2. finding out methods for obtaining cross-linked polystyrenes with a known structure suitable for ion exchangers.

Relations to the properties of the final products are to be expected also in this case.

In both cases, however, the point of significance is to what extent the properties of ion exchangers are influenced by the structure of the matrix.

## RADICAL STYRENE-DIVINYLBENZENE-COPOLYMERS

Since the direct polymer-analytical methods for structure determination often fail in the case of the cross-linked insoluble polymers an attempt was made by us to draw conclusions regarding the structure from kinetics of the styrene-divinylbenzene copolymerization. The speculations about the structure of the styrene-divinylbenzene copolymers prepared radically were hitherto based essentially on the results of the investigation of the copolymerization behaviour of the divinylbenzene isomers with styrene carried out by the team of Wiley in the USA (Ref. 1). Our investigations also rested initially upon these results (Ref. 2 & 3). Between 1960 and 1971 Wiley and co-workers measured and published the copolymerization parameters of divinylbenzene isomers with styrene using various methods of determination and evaluation (Ref. 4-8). The  $r$ -values they obtained showed a more or less significant deviation from the ideal straight lines in the binary copolymerization diagram (Fig. 1).

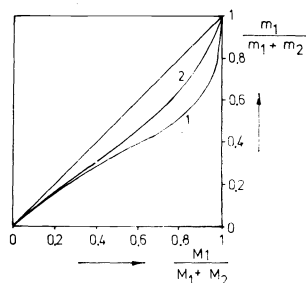


Fig. 1. Binary copolymerization diagrams of the divinylbenzene isomers with styrene.

1 = styrene and p-DVB ( $r_{12} = 0.14$ ;  $r_{21} = 0.50$ );

2 = styrene and m-DVB ( $r_{12} = 0.65$ ;  $r_{21} = 0.60$ );

$M$  = monomers in moles;  $m$  = polymers in moles;

$M_1$  = styrene;  $M_2$  = p- or m-DVB

At the beginning of the copolymerization much more DVB is incorporated in the copolymers than it corresponds to the original composition of the monomer mixture. Thus, the DVB molecules cause the formation of compact regions with a higher cross link density. Long chain, less cross-linked sections are located between them, being formed in the later stage of polymerization when the greatest part of the DVB is already exhausted. In our investigations of the diverse influence of both DVB-isomers in the ternary copolymerization system styrene/p-DVB/m-DVB, it was necessary to calculate the  $r$ -values wanted between p- and m-DVB by means of the copolymerization parameters according to Schwan and Price (Ref. 10). It was shown herein (Ref. 3) that the  $r$ -values measured by Wiley and co-workers at different times do not provide in all cases proper solutions of

Schwan and Price equation. Table 1 shows the results of the Q- and e-computation for p-DVB and m-DVB using the equations of Alfrey and Price (Ref. 10a).

TABLE 1. The r-values of the system styrene ( $M_1$ )/p-DVB ( $M_2$ ) (No. 1-5) and styrene ( $M_1$ )/m-DVB ( $M_2$ ) (No. 6-10) and Q-e-values computed from them using the equations of Alfrey/Price (Ref. 10a)

$$r_1 = (Q_1/Q_2) \exp [-e_1(e_1 - e_2)] ;$$

$$r_2 = (Q_2/Q_1) \exp [-e_2(e_2 - e_1)]$$

| No. | $r_1$ | $r_2$ | Literature reference               | $e_2$ | $Q_2$        |                  |      |
|-----|-------|-------|------------------------------------|-------|--------------|------------------|------|
| 1   | 0.14  | 0.50  | Wiley/Davis 1963 (Ref. 5)          | 0.83  | -2.4         | 1.9              | 26.3 |
| 2   | 0.77  | 2.08  | Wiley/Mathews et al. 1967 (Ref. 8) | -0.83 | $\pm$ 0.687i | no real solution |      |
| 3   | 0.77  | 1.46  | Wiley/Ahn 1968 (Ref. 6)            | -0.8  | $\pm$ 0.342i | no real solution |      |
| 4   | 0.20  | 1.00  | Wiley/Rao 1970 (Ref. 7)            | 0.47  | -2.1         | 1.4              | 17.8 |
| 5   | 0.15  | 1.22  | Malinsky/Klaban 1969 (Ref. 9)      | 0.50  | -2.1         | 2.35             | 18.9 |
| 6   | 0.65  | 0.60  | Wiley/Sale 1960 (Ref. 4)           | 0.17  | 1.77         | 0.71             | 3.34 |
| 7   | 0.605 | 0.88  | Wiley/Mathews 1967 (Ref. 8)        | -0.04 | -1.56        | 0.9              | 3.04 |
| 8   | 1.27  | 1.08  | Wiley/Mathews 1967 (Ref. 8)        | -0.8  | $\pm$ 5.6 i  | no real solution |      |
| 9   | 1.11  | 1.00  | Wiley/Rao 1970 (Ref. 7)            | -0.8  | $\pm$ 4.5 i  | no real solution |      |
| 10  | 0.54  | 0.58  | Malinsky/Klaban 1969 (Ref. 9)      | 0.28  | -1.88        | 0.8              | 4.50 |

Only the oldest values of Wiley estimated between 1961 and 1963 seem to provide for a rational calculation (Ref. 3). Since no satisfactory result was achieved, we decided to make attempts of our own for determining the r-values of styrene and divinylbenzene isomers. The gas chromatographic determination of the monomer concentration before and after the copolymerization was chosen due to our good experience in the field of the gas chromatographic analytics of divinylbenzene over many years (Ref. 11-14). The utilization of gas chromatography for determining the copolymerization parameters has been thoroughly investigated (Ref. 15) and repeatedly used lately (Ref. 16-18).

The relative small experimental expenditure of gas chromatographic determinations makes possible to repeat the same experiment many times, so that on averaging the results, reliable values can be obtained.

An important prerequisite for a successful investigation was the presence of pure DVB-isomers. The method for separating p-DVB from technical divinylbenzene using Werner's complexes with cupric chloride proposed by Rubinstein and Snyder (Ref. 19) was modified via proper selection of complexing temperature so that we succeeded in preparatory isolating both the p- and the

m-DVB with a purity of the isomers of 98 - 99 % (Ref. 20).

The monomer mixture used for the polymerization contained styrene, a DVB-isomer, azo-bis-isobutyronitrile as an initiator and ethylbenzene in a quantity below 10 % as an inner standard. It was polymerized in bulk at 60°C and 40 - 70 min later, according to the DVB-content, short before the gel point was reached, the polymerization was interrupted. The monomer mixtures were analysed by gas chromatography using a method for quick analysis (Ref. 21) before and after the polymerization. Fig. 2 shows an example of a styrene/m-DVB copolymerization.

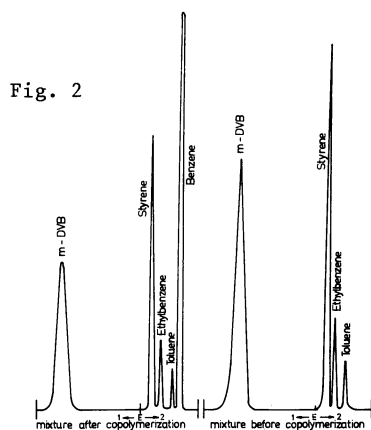


Fig. 2. Investigation of the copolymerization of styrene and m-DVB by gas chromatographic measurements

Fig. 3

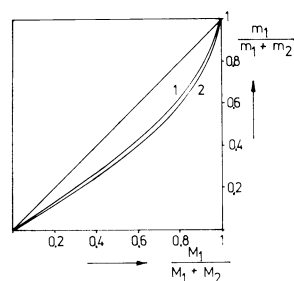


Fig. 3. Copolymerization diagrams of the divinylbenzene isomers with styrene computed with our  $r$ -values; 1 styrene/p-DVB; 2 styrene/m-DVB

Table 2 shows the results of gas chromatographic copolymerization investigations in the system styrene/m-DVB. A broad  $M_1/M_2$  interval and high conversion were used in order to get clear differences between both samples being analysed by gas chromatography before and after the polymerization. Thus, the error of the analysis was reduced. This method requires an integral technique for evaluation of the copolymerization parameters from the primary data of the gas chromatographic analysis.

Table 2. Results of the gas chromatographic measurements in the copolymerization system of styrene ( $M_1$ ) and m-DVB ( $M_2$ );  $M^0$  = monomers in the starting solution (mol);  $M$  = monomers in the reaction product (mol);  $m_2/m_1$  = copolymer composition computed;  $C$  = degree of conversion computed

| No. | $M_1^0$ | $M_2^0$ | $M_1$  | $M_2$               | $m_2/m_1$         | $C$ (%) |
|-----|---------|---------|--------|---------------------|-------------------|---------|
| 1   | 0.2744  | 0.5333  | 0.2340 | 0.3747              | 3.90              | 24.6    |
| 2   | 0.3113  | 0.5202  | 0.251  | 0.3385              | 3.01              | 29.1    |
| 3   | 0.3541  | 0.4312  | 0.3008 | 0.3086              | 2.77              | 21.3    |
| 4   | 0.4750  | 0.3892  | 0.4270 | 0.2910              | 2.05              | 16.9    |
| 5   | 0.7782  | 0.1906  | 0.6070 | 1.0000              | 0.53              | 27.0    |
| 6   | 0.8687  | 0.0742  | 0.7263 | 0.0455 <sub>4</sub> | 0.20              | 18.1    |
| 7   | 0.9181  | 0.0347  | 0.7833 | 0.0195 <sub>8</sub> | 0.11 <sub>2</sub> | 15.7    |

Therefore, we tested the method after Skeist (Ref. 22-24) and compared it with the integral method according to Mayo (Ref. 25-26). Both yield practically the same result, but the method after Mayo is easier to handle and requires less computing expenditure (Ref. 27 & 28).

The intersection point of the straight lines was determined mathematically (Ref. 29). The following  $r$ -values were obtained: styrene ( $M_1$ )/p-DVB ( $M_2$ )  $r_{12} = 0.65$ ;  $r_{21} = 1.10$  and styrene ( $M_1$ )/m-DVB ( $M_2$ )  $r_{12} = 0.54$ ;  $r_{21} = 0.88$ .

Figure 3 shows the copolymerization diagram computed using these values. As already obvious from the  $r$ -values, the curves for styrene/p-DVB and styrene/m-DVB are nearly identical. Especially the styrene/m-DVB-curve has moved away from the ideal straight line as compared with the  $r$ -values of Wiley. According to our  $r$ -values, the expected inhomogeneities of both systems styrene/p-DVB and styrene/m-DVB do not differ so significantly as presumed by the earlier  $r$ -values of Wiley.

In our former investigations we were able to show that the addition of a further monomer to the system of styrene/m- or p-DVB as well as to the system of styrene/m-DVB/p-DVB influences approximation of the copolymer composition to the ideal straight line (Ref. 30 & 31), when using the values measured by Wiley. Again, we investigated the influence of the monomer acrylonitrile on these systems using the copolymerization parameters determined and computed by us.

Figures 4 and 5 show the results in cut-out from the copolymerization diagram with acrylonitrile (Ref. 32).

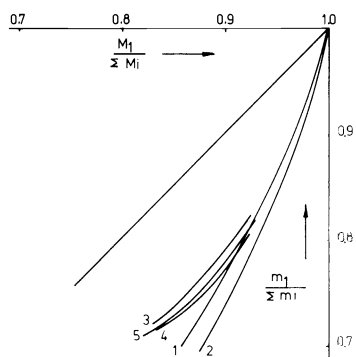


Fig. 4

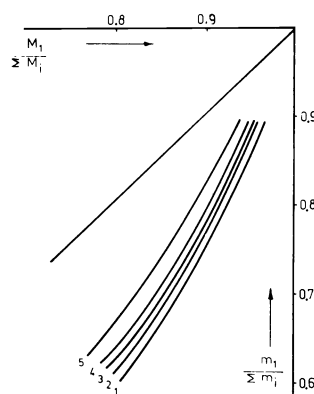


Fig. 5

Fig. 4. Section of the copolymerization diagrams of the systems

- 1 = styrene ( $M_1$ )/p-DVB ( $M_2$ )
  - 2 = styrene ( $M_1$ )/m-DVB ( $M_2$ )
  - 3 = styrene ( $M_1$ )/p-DVB ( $M_2$ )/acrylonitrile ( $M_3 = 2-10$  mol-%)
  - 4 = styrene ( $M_1$ )/m-DVB ( $M_2$ )/acrylonitrile ( $M_3 = 2-10$  mol-%)
  - 5 = styrene ( $M_1$ )/p-DVB ( $M_2$ )/m-DVB ( $M_3$ )/acrylonitrile ( $M_4$ )
- $M_2 : M_3 = 1 : 4$ ;  $M_2 + M_3 = 6$  mol-%;  $M_4 = 2-10$  mol-%

Fig. 5. Section of the copolymerization diagrams of the systems styrene ( $M_1$ )/p-DVB ( $M_2$ )/m-DVB ( $M_3$ )/acrylonitrile ( $M_4$ );  $M_2 : M_3 = 1 : 4$ ;  $M_2 + M_3 = 6$  mol-%; 1  $M_4 = 0$  mol-%; 2  $M_4 = 2$  mol-%; 3  $M_4 = 4$  mol-%; 4  $M_4 = 6$  mol-%; 5  $M_4 = 10$  mol-%

A shift of copolymer composition in direction of the ideal straight line is in turn well established, which is more obvious in the system styrene/m-DVB/acrylonitrile than by applying the  $r$ -values of Wiley.

The  $r$ -values of the systems m-DVB/p-DVB and acrylonitrile/m-DVB and acrylonitrile/p-DVB respectively, which were not measured, were calculated by us with the help of the Schwan and Price equations (Ref. 10).

Altogether these results testifying the improvement of the inner homogeneity of the cross-linked system correlate with the qualitatively improved influence of acrylonitrile in the synthesis of strongly acidic ion exchange resins through addition of a further suitable monomer (Ref. 2 & 31).

Our hitherto existing knowledge of the cross-linked system styrene/divinylbenzene has confirmed the cross-linking component being decisive for the formation of inhomogeneous polymer structures due to its polymerization behaviour deviating from styrene. Especially, the first stage of the copolymerization is decisive since at this time a large amount of the cross-linking agent is incorporated in the polymer. This is clearly expressed in the combined curve remote from the ideal straight line (Figs. 3, 4, 5). Since at these points the largest cross-link densities arise true to nature, simultaneously or at a later moment (contrary to loose ranges formed by further polymerization), we tend to speak of inhomogeneous networks. Similar conclusions were drawn by Okasha and others (Ref. 32) in a recent publication using another method of investigation.

#### STATISTIC ANIONIC STYRENE-DIVINYLBENZENE COPOLYMERS

Proceeding, on the one hand, from the knowledge that the copolymerization parameters play a decisive role in the distribution of cross-linked molecules within the polymer chain and by it within the network points and, on the other hand, from the assumption that a homogeneous distribution of the network points results in better polymer properties, we investigated the statistic copolymerization of the system styrene/DVB by the anionic mechanism. The change of the polymerization mechanism leads inevitably to alternated copolymerization parameters of the system. Butyllithium was used as initiator. The polymerization occurred in bulk. The network does not differ in principle from a network obtained by statistical radical copolymerization. Merely the active centre is not a radical, but a carbanion (Ref. 34). The  $r$ -values were determined similarly to the radical copolymerization by means of gas chromatography (Ref. 35). The following values were obtained experimentally:

|                                   |              |              |
|-----------------------------------|--------------|--------------|
| styrene ( $M_1$ )/p-DVB ( $M_2$ ) | $r_1 = 1.58$ | $r_2 = 0.32$ |
| styrene ( $M_1$ )/m-DVB ( $M_2$ ) | $r_1 = 0.65$ | $r_2 = 1.20$ |

The  $r$ -values m-DVB/p-DVB were computed (Ref. 35):

|   |                 |                 |
|---|-----------------|-----------------|
| styrene ( $M_1$ )/p-DVB ( $M_2$ )/m-DVB ( $M_3$ ) | $r_{23} = 0.25$ | $r_{32} = 3.89$ |
|---|-----------------|-----------------|

From the  $r$ -values the binary (Fig. 6) as well as the ternary copolymerization diagram (Fig. 7) may be plotted.

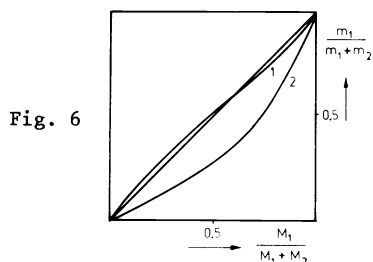


Fig. 6

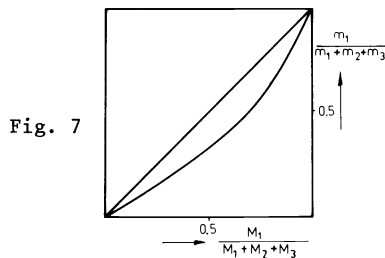


Fig. 7

Fig. 6. Copolymerization diagrams of the divinylbenzene iso- mers with styrene computed with the  $r$ -values determined by us; 1 = styrene/p-DVB; 2 = styrene/m-DVB

Fig. 7. Copolymerization diagram of the system styrene ( $M_1$ )/p-DVB ( $M_2$ )/m-DVB ( $M_3$ )

The ternary copolymerization diagram indicates that the distribution of the DVB-units in the network is somewhat more homogeneous than in radical copolymers. Speculations on the structure of such polymers have already been discussed (Ref. 36).

Concerning the influence of the structure on the subsequent products, we have a real opportunity to make a statement by their functionalizing to ion exchangers and their testing (Ref. 37). For the examination weak basic ion exchangers were produced and their osmotic stability tested. When an ex- changer is alternately charged with various ions, the degree of its swell- ing changes, the exchanger "breathes". It is loaded osmotically and under- goes a decay parallel to the increasing number of recharging cycles. More- over, the exchanger can be loaded osmotically by repeated complete drying and swelling. On swelling up the grain is unevenly expanded from outside to the centre and decomposes. The scope of the decay in both cases can be established by a sieve analysis before and after the treatment. It can be assumed that the more evenly a network is built up, the smaller the osmoti- cally induced decay should be. In Fig. 8 such a decay is illustrated.

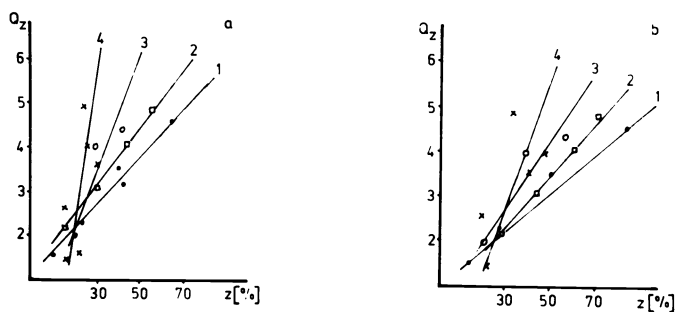


Fig. 8. Dependence of the decay (%) of weak basic ion ex- change resins on the degree of swelling  $Q_z$  of the matrix  
a) after 50 recharging cycles and  
b) after 5 additional cycles of drying-washing for  
1. Radical copolymers with technical divinylbenzene;  
2. Anionic copolymers with m-DVB;  
3. Anionic copolymers with p-DVB and  
4. anionic copolymers with technical DVB

From Fig. 8 is evident that the exchangers on the base of anionic products exhibit better osmotic stabilities.

Another possibility for testing the produced ion exchangers is to correlate their kinetic behaviour (Ref. 37). The half-life period of the load,  $t_H$ , determines in which time the half of the ions present in the solid phase from  $\text{OH}^-$  to  $\text{Cl}^-$  are exchanged. The half-lives for anionic and radical copolymers are related to the degree of swelling (Fig. 9).

The ion exchangers on the base of anionic resins show 2 - 4 times shorter exchange time than radical resins. We found therefore that a connection between structure and property of the network should exist when these preparative methods were used.

Till now cross-linked polymers have been prepared whose structure was hardly opened to influence by the process of synthesis.

For an unequivocal clarification of connections between structure and properties, resins with a known network structure are necessary. For this reason the interest in fundamental works on this problem has increased in recent years. The cross-linking of preformed very reactive polymers should result in defined matrices. Such reactive molecules may be produced from carbanionic reactions. Two methods may be used, either leading to a very heterogeneous network or to a homogeneous one.

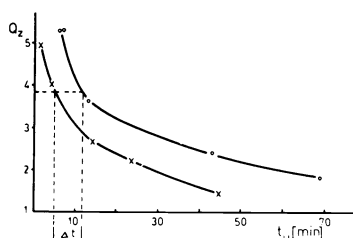


Fig. 9

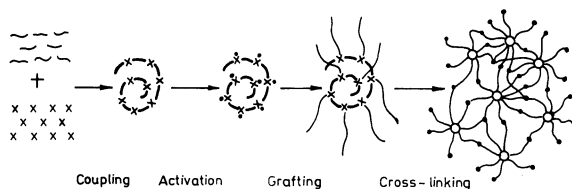


Fig. 10

Fig. 9. Dependence of half-life period of the load,  $t_H$ , of weak basic ion exchangers on the degree of swelling  $Q_2$ ; o ion exchanger on the base of radical copolymers; x ion exchanger on the base of anionic copolymers

Fig. 10. Synthesis of networks via quasi-star-shaped branched polymers

#### INHOMOGENEOUS ANIONIC MATRICES

The first method consists of four steps. Living tetramers of the methylstyrene are connected with aromatics containing halogen. A linear polymer develops that is activated and grafted with styrene (Fig. 10). Living star-shaped branched molecules later cross-linked with one another are formed (Ref. 38).

In the first step tetrameric  $\alpha$ -methylstyrene-dianions are connected with 1-chloro-2,5-bis-(chloromethyl)benzene. Under certain conditions, only the loosely bound chlorine atoms of the chloromethyl groups react at  $-78^\circ\text{C}$ . A linear chain develops carrying aromatic chlorine at a distance of four monomer units. The number of the additional steps called "coupling degree" is an important quantity which determines the functionality of the star. The



coupling degree can be controlled by changing the concentration: the higher the concentration, the larger the coupling degree (Ref. 39).

In the second step of the synthesis the coupling product is metallized with sodium naphthalene (Fig. 11). The chlorine atom is replaced by sodium. The polymer organometallic compound thus created can in analogy to phenyl sodium initiate an anionic graft polymerization. The polymer organometallic compound from the second step is used in the third step as initiator for the styrene polymerization. A graft polymer is formed which in the absence of breaking-off reactions "lives" and polymerizes the entire monomers up to the 100 % conversion (Fig. 12). The quantity of styrene determines the length of the side branches and the molecular weight of the star-shaped branched molecules can be calculated provided that the coupling degree is known (Ref. 38).

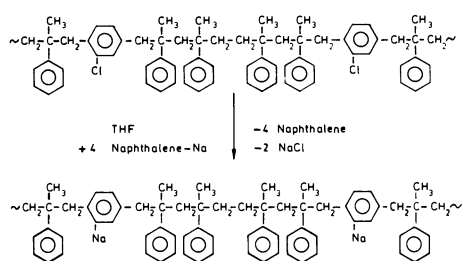


Fig. 11. Metallizing reaction

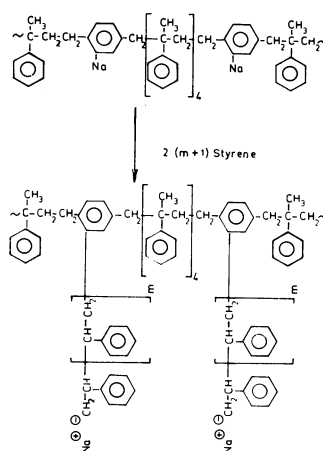


Fig. 12. Graft reaction

We succeeded in proving the structure of the star-shaped polystyrenes by means of pyrolysis gas chromatography (Ref. 40). These living stars can be cross-linked with each other, e.g. with divinylbenzene. Small amounts are used, for instance 2 - 3 molecules DVB per polymer chain end. The DVB polymerizes and forms small knots and connects the chain ends. Networks develop which are very inhomogeneous with respect to the segment density distribution. In this cross-linking reaction, dependence between conditions of formation and properties of the corresponding networks exists, e.g. between the degree of swelling and the total polymer concentration at the moment of cross-linking (Ref. 38). Therefore, star-shaped polymers prepared at different concentrations were cross-linked with divinylbenzene.

We tried to prepare ion exchangers from these very inhomogeneous networks. They were shown, however, to be pretty unstable and decomposed during their formation. This statement is in accordance with the supposition that the more regular the matrix, the better properties of the ion exchangers on their basis are to be expected.

Thus, we demonstrated how to prepare inhomogeneous but defined networks; now, the same is to be done also for homogeneous networks.

## ANIONIC STYRENE-DIVINYLBENZENE BLOCK COPOLYMERS

Such a method was developed by Rempp and co-workers from Strasbourg (Ref. 41). It served as a basis for us and consisted in the following items: polystyrene dianions with a definite and chosen molecular weight were prepared and cross-linked with a small amount of divinylbenzene. The whole mixture forms a network consisting of linear polystyrene segments and divinylbenzene knots (Fig. 13).

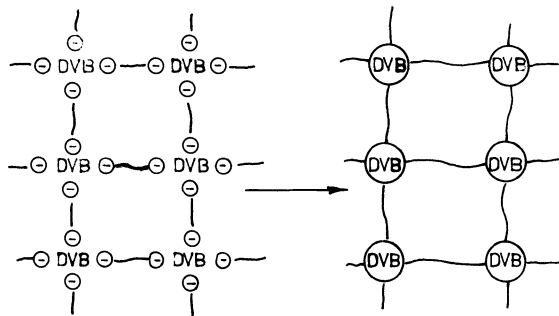


Fig. 13. Synthesis of homogeneous styrene-divinylbenzene copolymers

The principal difficulty in the synthesis consists in a very quick cross-linking in tetrahydrofuran or tetrahydrofuran/benzene mixture so that the divinylbenzene cannot be homogeneously distributed in the reaction mixture before the gelation begins. When a low degree of swelling of the copolymers is wanted, very short polystyrene chains and high polymer concentrations are to be used. Thereby the gel point occurs quickly and there is a natural limit for this method, lying at a degree of swelling of approximately 7 (g toluene/g product). Such degree of swelling is however not suitable for the ion exchanger synthesis. For this reason, a mixture of DVB and diisopropenyl benzene as retarder was used (Ref. 42). Also, this measure led to an insufficient improvement of the swelling behaviour. Thus, we investigated the same synthesis in non-polar hydrocarbons (benzene, toluene). For this purpose a bifunctional anionic initiator soluble in this medium was used. The reaction of *m*-DVB with *sec*-butyllithium in the presence of amines resulted in 1,3-bis-(1-lithio-3-methylpentyl)benzene (Ref. 43). This initiator was tested by us for its initiation capability and functionality (Ref. 44). The polystyrene dianions produced in this way were cross-linked with 3 mol DVB per mol chain end. The synthesis results of some samples are summed up in Table 3 (Ref. 45).

The properties of these cross-linked products were correlated with their structural parameters by us (Ref. 46). The networks obtained were converted into weak basic ion exchangers and tested for their osmotic stability. The same methods, already described above, were applied (Table 4).

It is evident that ion exchangers on the basis of anionic block copolymers styrene-divinylbenzene decompose less at both osmotic loadings, whereas the remaining samples are harder damaged, sometimes six- to eightfold.

We tested these exchangers also on their rate of exchange and opposed them to ion exchangers on the basis of statistic radical and anionic copolymers (Table 5). The half-life period of the load of anionic block copolymers

Table 3. Data on regular networks prepared by anionic block copolymerization of styrene with divinylbenzene (benzene; 25°C; DVB/PS<sup>-</sup> = 3)

| No. | $M_c \times 10^{-3}$ | $v_3^c$ | $G_3$ | $Q_3$ | gel time (s) |
|-----|----------------------|---------|-------|-------|--------------|
| 1   | 10.6                 | 0.105   | 9.15  | 11.0  | 180          |
| 2   | 6.7                  | 0.107   | 6.5   | 7.8   | -            |
| 3   | 5.5                  | 0.105   | 4.85  | 6.2   | 40           |
| 4   | 4.7                  | 0.100   | 4.80  | 6.15  | 35           |
| 5   | 6.8                  | 0.125   | 5.5   | 6.6   | 40           |
| 6   | 4.9                  | 0.125   | 4.0   | 4.7   | 25           |
| 7   | 4.3                  | 0.125   | 3.7   | 4.3   | 18           |
| 8   | 3.6                  | 0.125   | 3.1   | 3.6   | 16           |
| 9   | 2.5                  | 0.125   | 2.8   | 3.2   | 10           |
| 10  | 5.7                  | 0.175   | 3.7   | 4.3   | 12           |
| 11  | 4.6                  | 0.175   | 3.0   | 3.4   | 10           |
| 12  | 16.6                 | 0.260   | 6.4   | 7.6   | 15           |
| 13  | 15.0                 | 0.230   | 4.7   | 5.6   | 12           |
| 14  | 5.7                  | 0.225   | 3.3   | 3.9   | 10           |
| 15  | 4.1                  | 0.260   | 2.4   | 2.7   | 8            |

$M_c$  = distance between the cross-links as molecular weight

$v_3^2$  = volume fraction of polystyrene at the moment of cross-linking

$G_3$  = weight degree of swelling                       $Q_3$  = volume swelling

Table 4. Osmotic test of weak basic ion exchangers (total weight capacity 4.1 mval/g; weight degree of swelling 3.6)

| Production method of the exchanger                  | Decay after 50 OH <sup>-</sup> /Cl <sup>-</sup> exchanging-cycles (%) | Decay after 5 further drying-washing cycles (%) |
|---|---|---|
| Statistic radical copolymers styrene-divinylbenzene | 43  | 30  |
| Statistic anionic copolymers styrene-divinylbenzene | 31  | 10  |
| Anionic block copolymers styrene-divinylbenzene     | 5   | 4   |

Table 5. Exchange kinetic test of weak basic ion exchangers in dependence on the swelling of the matrix  $Q_z$ 

| No. | $Q_z$ | Half-life period of the load, $t_H$ , (min) of the exchange OH <sup>-</sup> /Cl <sup>-</sup> |                              |                          |
|-----|-------|--|------------------------------|--------------------------|
|     |       | statistic radical copolymers   | statistic anionic copolymers | anionic block copolymers |
| 1   | 2.7   | 33.0   | 13                           | 7                        |
| 2   | 3.2   | 21.0   | 9                            | 5                        |
| 3   | 3.6   | 13.5   | 6                            | 6                        |

were found to be the shortest and the radical copolymers exchanged 4 - 5 times more slowly, whereas the statistic anionic copolymers exchanged about 2 - 3 times more slowly.

#### FINAL OBSERVATION

Concerning the questions of synthesis, structure and properties of the cross-linked polymers we proceeded from the postulate that the more regular a network is built up, the better qualitative features the matrix exhibits and this property influences positively the subsequent products.

We provided this proof by synthesizing networks in an unconventional way, converting them into ion exchangers and testing them. In all the investigated cases we found unequivocal connections between the structure of polymers and the properties of ion exchangers derived from them.

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