833. *Properties of Ion-exchange Resins in Relation to Their Structure. Part VI.* Anion-exchange Resins derived from Styrene–Divinylbenzene Copolymers.*

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Anion-exchange resins have been prepared from styrene–divinylbenzene copolymers by a route which involves chloromethylation of the copolymer and subsequent treatment with amines. Experiments on the chloromethylation of soluble polystyrene, chloromethyl methyl ether being used with stannic chloride as catalyst, showed that a side-reaction giving insoluble, cross-linked products may occur when monochloromethylation is approached. If styrene–divinylbenzene copolymers are pre-swollen in the ether, the rate of chloromethylation is largely independent of the particle size or the degree of cross-linking of the copolymer (from 2 to 7½% divinylbenzene content).

Trimethylamine reacts with chloromethylated copolymers to give resins containing the strongly basic, quaternary ammonium grouping. With certain copolymers, each chloromethyl group reacts quantitatively with 1 molecule of amine, the products being monofunctional. Dimethylamine behaves similarly, forming monofunctional resins which contain weakly basic, tertiary amine groups. Ethylenediamine and monomethylamine give weakly basic resins of less definite structure. For all these resins, the observed exchange capacities agreed with the values calculated from the nitrogen contents.

The swelling of the chloride form of weakly basic resins is greater than that of the free base; with strongly basic resins, the reverse is true. At fixed cross-linking, the swelling of strongly basic resins (chloride form) increases with increasing exchange capacity; moreover, the proportion of water absorbed increases up to a fractional substitution of about 0·5 quaternary ammonium group per benzene ring.

A CONVENIENT method for the preparation of anion-exchange resins from styrene–divinylbenzene copolymers has been discovered independently by the Rohm and Haas Co. (B.P. 654,706), by the Dow Chemical Co. (B.P. 662,314, 677,350, 679,850—3) and, in these laboratories, by Hawdon, Linstead, and Thomas (B.P. Appln. 7732/50). The method

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involves two steps: (1) Introduction of chloromethyl groups as substituents for aromatic nuclei in the styrene–divinylbenzene copolymer, by treatment of the copolymer with, for example, chloromethyl methyl ether in presence of a Friedel–Crafts catalyst: $RH + CH_2Cl{\cdot}OMe \longrightarrow R{\cdot}CH_2Cl + MeOH$ (R represents the styrene–divinylbenzene residue). (2) Introduction of basic groups into the copolymer by treatment of the chloromethylated intermediate with ammonia or amines. This route has many advantages over earlier methods for the preparation of anion-exchange resins. In particular, the chloromethylated intermediate may be treated with different amines to give a series of resins possessing a common polymeric structure, but different functional groups. Tertiary amines form the strongly basic, quaternary ammonium grouping, *e.g.*, $R{\cdot}CH_2Cl + NMe_3 \longrightarrow R{\cdot}CH_2{\cdot}N^+Me_3\}Cl^-$, whilst ammonia and primary or secondary amines give weakly basic groups, *e.g.*, $R{\cdot}CH_2Cl + NHMe_2 \longrightarrow R{\cdot}CH_2{\cdot}NMe_2 + HCl$. Hence an opportunity is provided for studies of the effect of the nature of the functional group on anion-exchange behaviour. Alternatively, anion-exchange resins possessing different degrees of cross-linking may be prepared by varying the divinylbenzene content of the original styrene–divinylbenzene copolymer and subsequent treatment of the chloromethylated products with the same amine. A series of this type would be of value for comparison with the sulphonated polystyrenes of different degrees of cross-linking previously examined (Part V, *J.*, 1953, 844).

The exchange capacity of the final product is ultimately controlled by the extent of chloromethylation. The chloromethylation reaction is, however, subject to complications which are not encountered, to any extent, in the corresponding sulphonation reaction. In an investigation of the chloromethylation of simple aromatic compounds, Vavon, Bolle, and Calin (*Bull. Soc. chim.*, 1939, **6**, 1025) showed that a *secondary* reaction may take place between a chloromethyl group attached to one benzene ring and another aromatic nucleus, $R{\cdot}CH_2Cl + RH \longrightarrow R{\cdot}CH_2{\cdot}R + HCl$. In polymeric systems, an intermolecular reaction of this type would give rise to cross-linking, which, being difficult to control and to estimate, would be a serious disadvantage. Moreover, in the event of a secondary reaction, the chlorine content of a product is not, by itself, a sufficient criterion of the extent of reaction. Vavon *et al.* also observed that the reaction may proceed beyond monochloromethylation, albeit slowly.

In this work, the chloromethylation of soluble polystyrene was first investigated in an attempt to find conditions under which the secondary reaction—giving insoluble, cross-linked products—might be avoided. The chloromethylation of styrene–divinylbenzene copolymers, of different degrees of cross-linking and of different particle diameters, was then examined. Bead polymers were treated with chloromethyl methyl ether in presence of stannic chloride as catalyst, either under reflux (58°) or at 25°. The preparation of various basic resins from the chloromethylated intermediates and certain of their properties have also been studied.

Chloromethylation

Polystyrene.—When free from cross-linking, polystyrene and its chloromethylated derivative are readily soluble in chloromethyl methyl ether, benzene, and other solvents. Hence in the chloromethylation of polystyrene, the onset of gelling or the formation of an insoluble product indicates cross-linking. Results obtained with 0·12 mole of stannic chloride to 1 mole of polymer are shown in Fig. 1, where the broken line indicates the chlorine content of monochloromethylated polystyrene (23·3%). With the more dilute solutions (16½ moles of ether to 1 mole of polymer), it will be seen that, at 58°, 50°, and 45° (curves 1, 2, and 3), all products containing less than about 22% of chlorine were soluble, the only insoluble product being the last sample of the run at 58° (Cl, 22·8%). Results obtained at 25° with the same molecular proportions were:

Reaction time (days)	1	7	14	21
Cl, %	17·3	20·4	21·9	22·0
Product	Soluble	Soluble	Soluble	Insoluble

The run at 45° (Fig. 1, curve 4), with double the concentration of polymer (8¼ moles of the ether to 1 mole of polymer), closely followed that for the more dilute solution (curve 3) except that, in this case, the last sample was insoluble. This result agrees with Jones's findings (*Ind. Eng. Chem.*, 1952, **44**, 2686), that increased concentration favours the onset of cross-linking.

With the addition of a poor solvent, light petroleum (curve 5), insoluble products were formed at very low chlorine contents.

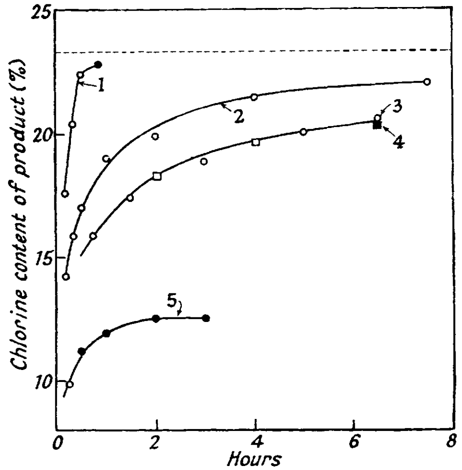
It appears from these results that the secondary cross-linking reaction must be expected when monochloromethylation is closely approached—at least with stannic chloride as catalyst. No advantage can be gained by reducing the reaction temperature to 25°. In absence of poor solvents, the risk of cross-linking may not be great with products containing less than about 20% of Cl, corresponding to a fractional substitution of about 0·8 chloromethyl group per benzene ring.

In applying these conclusions to the chloromethylation of styrene–divinylbenzene copolymers, it must be borne in mind that the *effective* concentration of copolymer in chloromethyl methyl ether will probably be determined by the amount of ether absorbed by the fully swollen copolymer. This would result in high effective concentrations, *e.g.*, a fully swollen 2% divinylbenzene copolymer contains about 2½ moles of ether to 1 mole of copolymer. Secondly, Jones (*loc. cit.*) has shown that the occurrence of cross-linking is favoured by an increase in the molecular weight of the polystyrene. Both of these considerations suggest that the secondary reaction is more likely to occur with cross-linked polymers than with linear polymers.

Styrene–Divinylbenzene Copolymers.—Chloromethylation of cross-linked polystyrene follows a course similar to that of soluble polystyrene; after an initially rapid reaction, curves relating chlorine content and reaction time tend to level off as monochloromethylation is approached. With prolonged reaction, however, chlorine contents greater than that corresponding to monosubstitution are obtained. This fact, together with the risk that prolonged reaction may give rise to additional cross-linking, constitutes a potential difficulty in the use of this route for the preparation of well-defined anion-exchange resins. One of the objectives of this research was to prepare resins of different degrees of cross-linking but possessing the same exchange capacity; it was essential that the capacity should be independent of particle size. With the analogous series of sulphonated cross-linked polystyrenes, these objectives were readily attained, since, with the conditions used, sulphonation proceeds no further than monosubstitution. Hence, whatever the degree of cross-linking (up to 25% of divinylbenzene) or the particle size of a copolymer, it was merely necessary to allow a sufficient reaction period in order to prepare uniform, monosulphonic acids (Pepper, *J. Appl. Chem.*, 1951, 1, 124). For the reasons given above, this simple procedure cannot be adopted with chloromethylation, and hence it became desirable to examine the influence of particle size and degree of cross-linking on the rate of chloromethylation.

FIG. 1. *Chloromethylation of polystyrene.*

			Product soluble	Product insoluble
1.	58°	16½ Moles of chloromethyl methyl ether : 1 mole of polymer	○	●
2.	50°			
3.	45°			
4.	45°	8¼ Moles of chloromethyl methyl ether : 1 mole of polymer	□	■
5.	50°	8¼ Moles of chloromethyl methyl ether : 1 mole of polymer : 4 moles of light petroleum	○	●



Chloromethyl methyl ether is a good swelling agent for styrene–divinylbenzene copolymers, the beads as normally used (dried overnight at 50°) being fully swollen in less than an hour at room temperature or in a few minutes at reflux temperature. Experiments showed that, in absence of catalyst, the ether reacts to a negligible extent with the copolymer. Diffusion of ether, as a rate-controlling process, can thus be avoided by pre-swelling the beads before addition of catalyst. Equal weights of fractions of two sizes (50—100 μ and 150—200 μ) of a 2% divinylbenzene copolymer were mixed and swollen in chloromethyl methyl ether. Stannic chloride, dissolved in the rest of the ether, was then added to give the proportions 1 mole of copolymer : 8·25 moles of ether : 0·12 mole of stannic chloride. Two separate experiments gave the following values for the chlorine content in different sized fractions of the product:

	30 Min. at 25°		1 Hr. at 25°	
Particle diameter (μ)	>150	<150	>150	<150
Cl, %	5·3	5·5	6·2	6·7

In each experiment, the weight-swellings in toluene of the different fractions were the same (1·93 and 1·91 g. of toluene per g. of copolymer after 30 min. and 1 hr. respectively at 25°).

In further experiments with 2% and 7½% divinylbenzene copolymers, where the time required for the beads to become fully swollen was small in comparison with the reaction time, pre-swelling was not used; the full amount of chloromethyl methyl ether together with catalyst was added at once.

2% *D.V.B. copolymer*

	6 Hr. at 25°			
Particle diameter (μ)	230—150	150—125	125—100	100—40
Cl, %	13·9	14·0	14·2	14·2

7½% *D.V.B. copolymer*

	24 Hr. at 25°		30 Min. at reflux temp.		
Particle diameter (μ)	>150	<150	>250	250—125	<125
Cl, %	16·0	15·5	18·1	17·8	18·0
Weight-swelling (g. of toluene per g. of copolymer)	0·45	0·47	0·33	0·35	0·36

The above experiments, taken together, cover the chloromethylation reaction from a fractional substitution of 0·2 to 0·7 chloromethyl group per benzene ring. With an experimental error of ±0·2% of Cl, there is little evidence of an increase in chlorine content with decreasing particle diameter. Moreover, there is no evidence of a decrease in weight-swelling, which might arise from additional cross-linking produced by the secondary reaction. It appears, therefore, that with the above conditions the rate of chloromethylation is controlled by the chemical reaction itself and not by a diffusion process, and hence it becomes possible to chloromethylate uniformly copolymer beads of differing particle diameters. It seems that, whatever the degree of substitution, the chloromethyl groups must be distributed in a more or less random fashion throughout the copolymer beads. Thus by chloromethylating samples of copolymer to different extents, it becomes possible to prepare a series of anion-exchange resins of varying capacity in which the functional groups are distributed randomly.

It may be emphasised that the copolymer beads as used above, *i.e.*, after drying at 50° overnight, contain about 2—4% of monomers which escaped reaction. Diffusion of chloromethyl methyl ether into the beads is apparently facilitated by this small amount of monomer, since, after removal of monomer, by steam-distillation and heating *in vacuo*, the beads are only slowly swollen. If *monomer-free* beads are treated for short periods with chloromethyl methyl ether and catalyst together, the chloromethylation reaction is largely confined to the surface layers.

Chloromethylation of copolymers of different divinylbenzene content (particle diameter, 100—250 μ) was examined at 25° and under reflux, the molecular proportions stated above being used. For the experiments under reflux, the beads were swollen at room temperature in chlorodimethyl ether alone before addition of catalyst; at 25°, no pre-swelling was used. The Tables give the chlorine content in the products.

	Hr. at 25°			
D.V.B., %	5	48	168	336
2	12·0	16·3	18·4	21·3
4½	12·6	16·1	18·0	19·4

	Min. at reflux (58°)		
D.V.B., %	10	60	180
2	15·0	19·5	24·0
4½	13·0	19·5	23·0
7½	12·5	18·5	19·5

The reproducibility of separate experiments at reflux temperatures, under nominally identical conditions, was not good, the variation in chlorine content of the products being about ±1%. The above results are mean values from several experiments. It appears that the divinylbenzene content of the copolymer has little influence on the rate of chloromethylation, although the effective concentration of copolymer in chloromethyl methyl ether must increase with increasing cross-linking. This conclusion is in accord with the observation that the rate of chloromethylation of soluble polystyrene is unaffected by a two-fold increase in polymer concentration (Fig. 1, curves 3 and 4).

The swelling of styrene–divinylbenzene copolymers affords a sensitive measure of the degree of cross-linking, particularly at low divinylbenzene contents (Pepper, *loc. cit.*). Fig. 2, curves 1 and 2, show the weight-swelling (g. of toluene absorbed per g. of copolymer) plotted against fractional substitution (number of chloromethyl groups per benzene ring), for chloromethylated copolymers containing 2% and 4½% of divinylbenzene respectively. Curves 3 and 4 give the molar swellings, *i.e.*, g. of toluene absorbed per mole (corresponding to one benzene ring). Up to a fractional substitution of about 0·75 (Cl $\sim$19%), the molar swellings are almost constant. This suggests that introduction of chloromethyl groups does not affect the amount of toluene absorbed per benzene ring. Presumably, the unsubstituted styrene–divinylbenzene matrix is fully extended when swollen in the good solvent toluene, and there is no change in cross-linking. The marked decrease in molar swelling at higher fractional substitution may be due to additional cross-linking produced during chloromethylation.

Amination of chloromethylated copolymers

Strongly Basic Resins.—Trimethylamine reacts with chloromethylated styrene–divinylbenzene copolymers, giving products which contain quaternary ammonium groups and behave, therefore, as strongly basic anion-exchange resins. The properties of commercial materials of this type have been described by Wheaton and Bauman (*Ind. Eng. Chem.*, 1951, **43**, 1088). The chloromethylated copolymer should be swollen in a suitable solvent, *e.g.*, dioxan, butanone, tetrahydrofuran, or benzene, but, otherwise, conditions for the quaternisation reaction do not appear to be critical. The swollen copolymer may be shaken with an excess of anhydrous amine at 0°, or with an aqueous solution at room temperature.

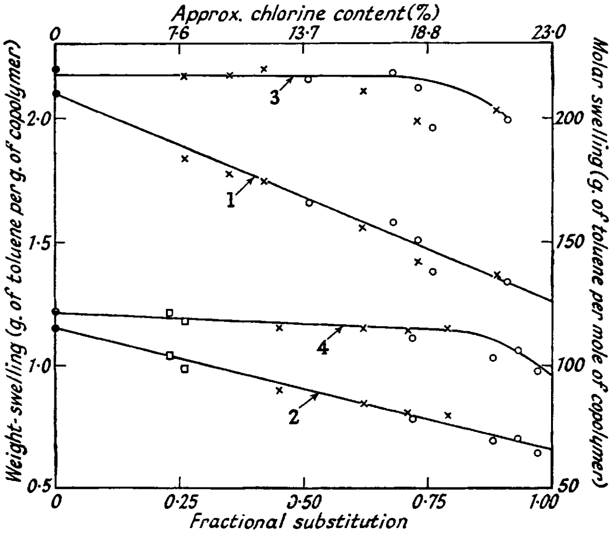


FIG. 2. *Swelling of chloromethylated copolymers.*

Prepared at 0° ☐; at 25° ×; at 58° ○.
1. Weight swelling (g. of toluene per g. of copolymer): 2% divinylbenzene.
2. Weight swelling (g. of toluene per g. of copolymer): 4½% divinylbenzene.
3. Molar swelling (g. of toluene per mole of copolymer): 2% divinylbenzene.
4. Molar swelling (g. of toluene per mole of copolymer): 4½% divinylbenzene.

The Table below gives the nitrogen content and exchange capacities of the dry, *chloride forms* of products obtained by treating a series of chloromethylated copolymers (2% of divinylbenzene) with trimethylamine. The chlorine contents of the intermediates are given in parentheses.

Fractional substitution	N, % (Found)	N, %, ×10/14 (mg.-equiv./g.)	Exchange capacity (mg.-equiv./g.)	
			Calc.	Found
0·26 (8·0%)	2·84	2·02	2·00	2·00
0·35 (10·2%)	3·40	2·43	2·45	2·45
0·42 (12·0%)	3·90	2·78	2·80	2·75
0·62 (16·3%)	5·05	3·60	3·60	3·60
0·73 (18·4%)	5·65	4·03	3·95	4·00

It was shown that the *free-base* forms of the resins contained no chlorine, proving that all chloromethyl groups had reacted. The experimental determination of exchange capacities involved the displacement of chloride ion by nitrate in neutral solution; under these conditions, any weakly basic groups present would exhibit negligible capacity. Values for the exchange capacity in the column headed "Calc." were calculated from the chlorine contents of the corresponding chloromethylated intermediates on the assumption that one molecule of amine reacts with one chloromethyl group. The agreement between these calculated values and the capacities found is well within experimental error (±1%). It will be seen also that the observed capacities agree closely with the values calculated from the nitrogen content (column headed "N, %, ×10/14"). It may be concluded that, with 2% divinylbenzene copolymers of fractional substitution within the range 0·26—0·73, all the chloromethyl groups are quantitatively converted into quaternary ammonium groups, giving monofunctional resins.

This last conclusion cannot, however, be generally applied. With intermediates of higher fractional substitution (0·9 or greater), the observed exchange capacity appears to be some 10% lower than the calculated value.

Weakly Basic Resins.—Anion-exchange resins containing weakly basic groups are obtained by treating chloromethylated copolymers with primary or secondary amines. The next Table gives the nitrogen content and exchange capacities of the dry *free-base* forms of products formed by the reaction of dimethylamine with chloromethylated intermediates of 2, 4½, and 7½% divinylbenzene. Chlorine contents of the intermediates are in parentheses.

	N, % (Found)	N, %, ×10/14 (mg.-equiv./g.)	Total exchange capacity (mg.-equiv./g.) Calc.	Found
2% D.V.B. (19·0%) ...	7·15	5·12	5·10	5·10
4½% D.V.B. (18·2%) ...	6·70	4·80	4·90	4·80
7½% D.V.B. (16·8%) ...	6·30	4·50	4·55	4·45

The free-base forms contained negligible chlorine (2%, nil; 4½%, 0·05%; 7½%, 0·15% Cl), showing that dimethylamine had reacted with virtually all the chloromethyl groups.

The absorption of chloride ion by the free-base forms of the resins was measured from hydrochloric acid solutions of different pH, in presence of potassium chloride. No uptake of chloride ion was observed at pH values greater than 7, proving that the resins contain no strongly basic groups. Below pH 3, a constant value was obtained irrespective of the pH or the concentration of salt. Hence in acidic solutions, as used for the determination of the exchange capacities given in the table above, a well-defined "total" capacity is obtained. These experimental values agree closely with those calculated from the nitrogen content (N, %, ×10/14). Capacities were derived also from the chlorine contents of the intermediates, it being assumed that one molecule of dimethylamine reacts with one chloromethyl group. The agreement is, again, very good, and there can be no doubt that all the chloromethyl groups had reacted quantitatively with dimethylamine, forming tertiary amino-groupings; the latter do not react with other chloromethyl groups to form quaternary ammonium groupings. Quantitative conversion has not been effected, however, when the fractional substitution of the intermediate approaches 1·0.

Whilst dimethylamine gives monofunctional resins, ethylenediamine and monomethylamine yield products possessing a less definite structure. The dry *free-base* forms of the products obtained from intermediates containing 2% of divinylbenzene gave the following results.

			Total exchange capacity (mg.-equiv./g.)		
			Calc.		
	N, % (Found)	N, %, ×10/14 (mg.-equiv./g.)	(*a*)	(*b*)	Found
Ethylenediamine ...	10·4	7·45	9·85	5·80	7·50
Monomethylamine ...	6·0	4·28	6·30	3·50	4·20

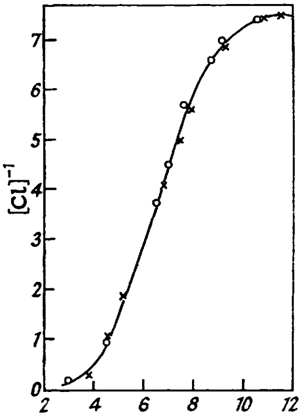
For the ethylenediamine resin, theoretical values of the total exchange capacity were calculated from the chlorine content of the intermediate (19·8%) on the assumption that one molecule of diamine reacts with (*a*) one chloromethyl group to give $R\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\cdot NH_2$ or (*b*) two chloromethyl groups giving either $R\cdot CH_2\cdot NH\cdot CH_2\cdot CH_2\cdot NH\cdot CH_2R$ or $(R\cdot CH_2)_2N\cdot CH_2\cdot CH_2\cdot NH_2$. The observed capacity, which agrees with the value derived from the nitrogen content, is intermediate between the two calculated values. The resin (in the free-base form) contained no chlorine, and therefore the low observed capacity cannot be due to incomplete reaction. It appears that ethylenediamine reacts in part with one chloromethyl group and in part with two or more groups, giving resins which contain primary, secondary, and possibly tertiary amino-groupings. Reaction with chloromethyl groups attached to different polymer chains would give additional cross-linking. The uptake of chloride ion by this resin from solutions of different pH has been determined by Dr. N. E. Topp, using the methods described by Topp and Pepper (*J.*, 1949, 3299). In Fig. 3, [Cl^-], *i.e.*, the number of mg.-

equivs. of chloride taken up per g. of dry resin, is plotted against $\log_{10}$ [Cl]/[OH], *i.e.*, the logarithm of the ratio of the chloride- and hydroxyl-ion concentrations in solution. The results show that the resin contains no quarternary ammonium groups, since such groups would be expected to take up appreciable chloride ion even at values of [Cl]/[OH] as low as unity. The different weakly basic groups known to be present are not revealed separately as inflexions in the curve, and hence, this product behaves as a pseudo-monofunctional resin.

The results obtained by treating a chloromethylated copolymer (Cl, 21·6%) with monomethylamine indicate that this amine reacts, in part, with one chloromethyl group, giving a secondary amino-group, and, in part, with two chloromethyl groups, giving a tertiary amine.

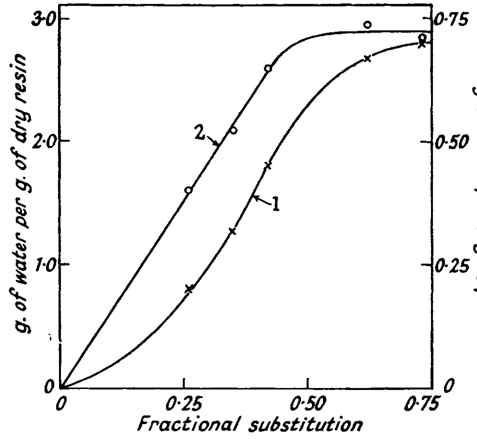
Swelling of Basic Resins.—The weight-swellings of the chloride and free-base forms of anion-exchange resins derived from styrene–divinylbenzene copolymers have been measured by the centrifuge technique (Pepper, Reichenberg, and Hale, *J.*, 1952, 3129). Determinations on the chloride form of the weakly basic resins were made in contact with 0·01N-hydrochloric acid, in order to ensure that the resin remained completely in the chloride form. With water, some conversion into the free-base form might occur. All other measurements were made in contact with water.

FIG. 3. *Uptake of chloride ion by ethylenediamine resin.*



In presence of 0·1M-KCl, ○.
In presence of 1·0M-KCl, ×.

FIG. 4. *Swelling of strongly basic resins.*



1, g. of water per g. of dry resin.
2, g. of water per mg.-equiv.

		Exchange capacity (mg.-equiv./g. of dry resin)		Swelling (g. of H_2O/mg.-equiv.)	
		Chloride	Free base	Chloride	Free base
Weakly basic resins					
2% D.B.V.	DM	4·30	5·10	0·54	0·104
4½% D.V.B.		4·10	4·80	0·23	0·067
7½% D.V.B.		3·85	4·45	0·15	0·055
2% D.V.B.	ED	5·90	7·50	0·21	0·10
2% D.V.B.	MM	3·65	4·20	0·25	0·055
Strongly basic resins					
2% D.V.B.	TM	3·95	4·25	0·70	1·01
7½% D.V.B.		3·50	3·75	0·19	0·32

DM = Dimethylamine; ED = ethylenediamine; MM = monomethylamine; TM = trimethylamine.

With the weakly basic resins, the swelling of the free-base forms is less than that of the chlorides, whilst, with the strongly basic resins, the reverse is true. This difference in behaviour can be related to the different extents of ionisation of the basic groups, the ionised forms being much more hydrated than the non-ionised group. With the weakly basic resins, the chloride form is probably fully ionised but the free base is largely non-ionised and, therefore, possesses low swelling. Both forms of the strong base resins are fully ionised, the higher swelling of the free base being probably due to the higher hydration of the hydroxyl anion. At the same divinylbenzene content, the chloride forms of the dimethylamine and trimethylamine resins possess roughly the same swelling, the values being in reasonable agreement with those for the corresponding sulphonated cross-linked polystyrenes (2% D.V.B., 0·7; 7½% D.V.B., 0·2 g. of water per mg.-equiv.). The swelling of both forms of these resins decreases with increasing cross-linking.

The monomethylamine resin made from a copolymer containing 2% of divinylbenzene possesses lower swelling, in both the chloride and the free-base form, than the dimethylamine resin of the same divinylbenzene content. The values obtained agree fairly closely with those for a dimethylamine resin containing 4½% of divinylbenzene. This reduction in swelling is undoubtedly due to additional cross-linking produced by the reaction of monomethylamine with chloromethyl groups attached to different polymer chains, as described in the previous section. The reduced swelling of the chloride form of the ethylenediamine resin, considered in conjunction with the analytical data, suggests that additional cross-linking was produced during this amination reaction, but if this is true the swelling of the free base form is anomalously high. In practical operations where a weakly basic resin is required, the relatively small difference in swelling between the chloride and the free-base form of the ethylenediamine resin would be an advantage; moreover, this resin has a high exchange-capacity.

Fig. 4 gives the swellings of the chloride forms of a series of strongly basic resins (2% of divinylbenzene) possessing exchange capacities varying from 2·0 to 4·0 mg.-equivs. per g. As expected, the swelling expressed as the number of g. of water per g. of dry resin (curve 1) increases with increasing fractional substitution (or increasing exchange capacity). Rather surprisingly, the amount of water absorbed per mg.-equiv. (curve 2) also increases with increasing fractional substitution up to about 0·5 quaternary ammonium group per benzene ring and then apparently levels off. The behaviour at even higher fractional substitutions would be of considerable interest. The exchange capacity when referred to the apparent volume of swollen resin (as used in a column) decreases from 0·75 to 0·65 mg.-equiv. per ml. of apparent volume, as the fractional substitution increases from 0·26 to 0·73.

EXPERIMENTAL

Suspension Polymerisation of Styrene and Styrene–Divinylbenzene Mixtures.—Redistilled styrene (75 ml.) containing recrystallised benzoyl peroxide (0·75 g.) was added to 400 ml. of an aqueous solution of " Promulsin," a cellulosic derivative manufactured by Watford Chemical Co. (The concentration of " Promulsin " was 3½—4½%, depending on its grade.) The mixture was shaken mechanically for 1 hr. to disperse the monomer, and was then heated at 80° for 18 hr. in a water-thermostat. Hydrolysis of " Promulsin " was effected with 2N-sulphuric acid at 60°, and the resulting polymer beads (50—250 μ particle diameter) were filtered off, washed, and dried at 50° overnight. The number-average molecular weight of the polymer, determined osmometrically in benzene by Mr. R. Townsend (Hookway and Townsend, *J.*, 1952, 3190, 4390), was 24,000.

Divinylbenzene was obtained from the Dow Chemical Co. in the form of a solution containing approx. 50% of divinylbenzenes (mainly *m*-) and 50% of ethylstyrenes. For the copolmer of 2% nominal divinylbenzene content, redistilled divinylbenzene solution (20 ml.) was made up to 500 ml. with redistilled styrene, benzoyl peroxide (5 g.) was added, and the mixture polymerised in 7 batches as above. The weight-swellings of the copolymers were: 2% D.V.B., 2·10; 4½% D.V.B., 1·15; 7½% D.V.B., 0·78 g. of toluene per g. of copolymer (dried at 110° *in vacuo* for 65 hr.).

Chloromethyl Methyl Ether.—Hydrogen chloride was passed through a well-stirred slurry of paraformaldehyde (600 g.) in methanol (500 ml.) at <5°. The system tended to form a gel and, at this stage, vigorous stirring and a rapid flow of hydrogen chloride were essential. The flow of hydrogen chloride was stopped when nearly all the paraformaldehyde had dissolved. The product was purified as described in " Organic Reactions," John Wiley and Sons, Inc., New York, 1942, Vol. I, p. 68. The ether was distilled three times; the fraction collected had b. p. 58—60° (mainly 59—59·5°), d_4^{25} 1·064, n_D^{25} 1·3940. Since chloromethyl methyl ether is toxic (Jones, *loc. cit.*) and hydrolyses in moist air, it was transferred directly, through all-glass apparatus, either to the reaction vessel or to an automatic pipette fitted with a silica gel guard-tube.

Chloromethylation of Polystyrene.—Chloromethyl methyl ether (30 ml., 0·395 mole) was added, with stirring, to polystyrene (5 g., 0·048 mole) in a flask which was immersed in a water-thermostat at the required temperature. The polymer beads dissolved rapidly and then a further 30 ml. of the ether containing 1·52 g. (0·0058 mole) of anhydrous stannic chloride

(B.D.H.) were added. Samples of the reaction mixture were withdrawn and precipitated by pouring into stirred methanol. The product was washed with methanol, dried, and analysed for chlorine.

Chloromethylation of Copolymers.—In a typical experiment under reflux, the ether (200 ml.) was added to copolymer beads (50 g.), which were allowed to swell at room temperature for an hour and then warmed while being stirred. On addition of 100 ml. of the ether containing 15·2 g. of stannic chloride, the mixture boiled, and it was kept at reflux temperature for 1 hr. The product was cooled, filtered off, and washed with aqueous dioxan. In order to remove residual catalyst, the product was transferred to a column and washed slowly with aqueous dioxan containing 10% (v/v) of concentrated hydrochloric acid, and finally with dioxan alone. The experiments at 25° were carried out in sealed tubes which were shaken in an air-thermostat.

Samples of the chloromethylated products required for analysis were washed with dioxan which was progressively diluted with methanol, and finally with methanol alone. They were dried at 90° for 2—3 days under 0·02 mm. with a cold trap at $-78°$ in the vacuum line. Chloromethylated copolymers, if free from stannic chloride, can be heated for several days at 90° without apparent change; above 110°, cross-linking occurs. If the catalyst is not removed, the chloromethylated products darken rapidly on heating. Chlorine was determined gravimetrically, after fusion of the dry copolymer with sodium peroxide in a Parr bomb. Weight-swellings in toluene were measured by a centrifuge technique (Pepper, *loc. cit.*).

Amination of Chloromethylated Copolymers.—Anhydrous trimethylamine (B.D.H.) was used for the preparation of strongly basic resins. 20 G. of chloromethylated copolymer (2% of divinylbenzene) were swollen in dioxan and cooled to 0°. 100 Ml. of the amine at 0° were added and, after slight warming to dissolve the amine, the mixture was kept at 0° for 2 days with intermittent shaking (7½% divinylbenzene copolymers require 7 days at 0°). After filtration, the product was washed in a column with 2N-hydrochloric acid for 2—3 days, and then treated alternately with 0·1N-sodium hydroxide and 2N-hydrochloric acid, three times. The acid and alkali solutions were passed through guard-tubes, containing strongly basic resin in the chloride or the hydroxyl form respectively. Finally, the resin was treated with 2M-sodium chloride solution, and washed with de-ionised water, until the effluent was chloride-free. The de-ionised water was passed through a small mixed bed of strongly acidic and strongly basic resins, immediately above the column. In this way, absorption of carbonate ion by the sample was avoided.

A similar procedure was employed for the preparation of weakly basic resins by use of anhydrous dimethylamine (B.D.H.), the times allowed being: 2% D.V.B., 4 days; 4½% D.V.B., 7 days; and 7½% D.V.B., 10 days at 0°. The products were converted into the free-base form by treatment with 0·1M-sodium hydroxide (passed through a guard-tube) and washed with de-ionised water as above. With these precautions, no carbonate ion was absorbed.

Monomethylamine (B.D.H.), 33% (w/w) in water, and ethylenediamine hydrate (B.D.H.) were shaken with the swollen chloromethylated copolymers for 4 days at room temperature.

Exchange Capacities of Basic Resins.—Strongly basic resins in the chloride form were dried to constant weight in presence of washed and dried sodium hydroxide pellets, and phosphoric oxide. At room temperature with a pressure of 0·02 mm. Hg, 2—3 days were required. About 0·2 g. of the dry resin was shaken overnight with 50 ml. of 5M-sodium nitrate, and the displaced chloride ion was determined gravimetrically. Weakly basic resins were dried in the free-base form; about 0·2 g. of the dry resin was shaken for 3 days with 50 ml. of M-sodium chloride and 50 ml. of 0·05M-hydrochloric acid. Excess of acid in 25-ml. aliquots was titrated with standard alkali. Nitrogen was determined by Kjeldahl's method.

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