Anion Exchange Resins Prepared from Polystyrene Crosslinked Via a Friedel–Crafts Reaction

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Synopsis

The preparation of anion exchange resins from polystyrene crosslinked via a Friedel–Crafts reaction is investigated. Chloromethylation of a highly swollen styrene–hexahydrotriacrylolyl-*s*-triazine copolymer with a mixture of chlorosulfonic acid and methylal is accompanied by the crosslinking of the initially flexible copolymer. The crosslinking efficiency is dependent on the conditions (temperature, nature of solvent) of chloromethylation and can be explained by cationic postpolymerization of polystyrene or poly(benzylchloride), which takes place concurrently with the chloromethylation.

INTRODUCTION

The production of insoluble crosslinked polystyrene from the linear polymer by Friedel–Crafts reactions was described as early as 1948.[1] Solutions of polystyrene in ethylene dichloride or nitrobenzene formed a crosslinked product in the presence of stannic chloride or other Friedel–Crafts catalysts, presumably in a reaction involving the solvent.

Recently, it has been reported that a number of crosslinked copolymers can be prepared by the condensation of 1,4-bis(chloromethyl)benzene with aromatic compounds containing carboxylic or heterocyclic groups, in the presence of Friedel–Crafts catalysts.[2] In particular, a crosslinked polystyrene can be produced from benzene and 1,4-bis(chloromethyl)benzene allowed to react in 1,2-dichloroethane, with SnCl$_4$ as a catalyst.

It has been also shown that insoluble crosslinked polystyrene used for ion exchange resins can be prepared by treating polystyrene or a styrene–divinylbenzene (DVB) copolymer containing less than 1 mole-% DVB with 1,4-bis-(chloromethyl)benzene or 4,4'-bis(chloromethyl)biphenyl in the presence of a Friedel–Crafts catalyst.[3]

Conventional anion exchange resins derived from crosslinked styrene–DVB copolymers are usually prepared via a chloromethylated polystyrene intermediate. The intermediate is obtained by treating copolymer with chloromethyl methyl ether in the presence of a Friedel–Crafts catalyst.[4-6] It is well known that during this process the side reactions, which take place simultaneously with the principal reaction,[6] result in the formation of new intermolecular bonds between the polymer chains. In this manner the extent of crosslinking in the three-dimensional matrix of the resin is increased. The side reactions are often defined as additional or postpolymerization crosslinking.

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The chloromethylation of styrene–DVB beads in conditions either promoting or excluding additional crosslinking have been described in detail in many publications. A number of authors[7,8] have noted that the type of catalyst determines the extent of crosslinking. Most researchers have concluded that catalysts such as $ZnCl_2$ and $SnCl_4$ promote crosslinking to a smaller degree than do $AlCl_3$ and $FeCl_3$.

There is a small body of information in the literature[9,10] as to how this additional crosslinking can be controlled and on its influence on the properties of anion exchange resins. Our aim was to make several different anion exchangers by aminating a crosslinked chloromethylated copolymer, which we prepared by chloromethylation of a slightly crosslinked polystyrene matrix. Styrene-1–hexahydrotriacryloyl-s-triazine (TAT) copolymer was synthesized as the starting matrix, and a mixture of chlorosulfonic acid and methylal was used as the chloromethylating agent. (Some groups of researchers have successfully used this reaction mixture or a mixture of methylal and sulfuryl chloride for the chloromethylation of styrene–DVB copolymers.[11–16])

Our work can be divided into three main sections: (1) the selection of the optimal conditions for the production of chloromethylated intermediates of high chlorine content for subsequent transformation into anion exchangers; (2) the determination of the effects of temperature and solvent on crosslinking efficiency and crosslinking rate in the chloromethylation; and (3) the investigation of the amination conditions required for the production of the anion exchange resins.

RESULTS AND DISCUSSION

Chloromethylation of Styrene–TAT Copolymer under Various Conditions

Our first set of experiments was aimed at producing chloromethylated styrene–TAT copolymers with a high chlorine content. In addition to the conventional chloromethylation procedures, we investigated the chlorine content obtained by using different ratios of our chloromethylating agent (methylal/chlorosulfonic acid) to copolymer at different temperatures (Table I).

The data in Table I clearly demonstrate that the styrene–TAT matrix is accessible to electrophilic substitution of one of the hydrogen atoms in the styrene ring by a chloromethyl group. The high degree of introduction of chloromethyl groups into styrene units, which was achieved by conventional methods with chloromethyl methyl ether and a Friedel–Crafts catalyst, confirms this conclusion (samples 1–3, Table I). It can also be seen from the table that our chloromethylating agent gives a chloromethylated copolymer with a high chlorine content. As was the case for the conventional method of chloromethylation, raising the temperature and increasing the amount of our chloromethylating agent resulted in a higher chlorine content in the final product.

The results of sulfur analysis show that the introduction of SO_2Cl groups (which may take place during the reaction) has no practical effect.

TABLE I
Chloromethylation of Styrene–TAT Copolymer Under Different Conditions[a]

Sample no.	Chloromethylating agent	Copolymer: chloromethylating agent ratio	Temp., °C	Cl, %	S, %
1	Chloromethyl methyl ether + ZnCl$_2$	1:8	50	20.6	—
2	Chloromethyl methyl ether + AlCl$_3$	1:8	50	20.8	—
3	Chloromethyl methyl ether + FeCl$_3$	1:8	50	23.4	—
4	Chlorosulfonic acid + methylal	1:1	40	4.1	0.1
5		1:3	40	16.4	0.1
6		1:4	40	19.6	0.2
7		1:6	40	22.8	0.5
8		1:4	20	9.5	0.1
9		1:4	30	13.2	0.1
		1:4	50	23.1	0.2

[a] All reactions were allowed to proceed for 6 hr.

Postpolymerization Crosslinking

The aim of the next part of our experiments was to examine the effects of temperature and solvent on the postpolymerization crosslinking which takes place during the chloromethylation process.

Nature of the Solvent

To eliminate as far as possible the occurrence of substitution and to direct the interaction in such a way that crosslinking occurs as the main reaction, the reaction between the styrene–TAT copolymer and the chloromethylating agent was carried out at a low temperature (in an ice bath). The copolymer was allowed to swell in a solvent before the chloromethylating agent was added. Four solvents with different dielectric constants were investigated. The results are plotted in Figures 1 and 2 as swelling value in toluene* versus time of reaction.

We can see from Figure 1 that the swelling decreases very sharply during the first 30 min of the reaction between styrene–TAT and methylal/chlorosulfonic acid, i.e., at the beginning of the reaction the crosslinking proceeds rapidly. A significantly higher degree of crosslinking was achieved in dichloroethane or nitrobenzene than in methylal or cyclohexane (Figs. 1 and 2 and Table II). In the latter two solvents the swelling decreased twofold with respect to that of the initial product; and, as we can see from Figure 2(b) and Table II, there was no introduction of CH$_2$Cl. In dichloroethane and nitrobenzene, both crosslinking

* We determined the swelling in toluene of a series of reaction products which were isolated at different times during the reaction. The swelling of styrene copolymers affords a sensitive measure of the degree of crosslinking, particularly when the starting copolymer is only slightly crosslinked.[5] The introduction of chloromethyl groups does not affect the amount of toluene absorbed by the benzene ring: the marked decrease in swelling is a result of additional crosslinking produced during chloromethylation.
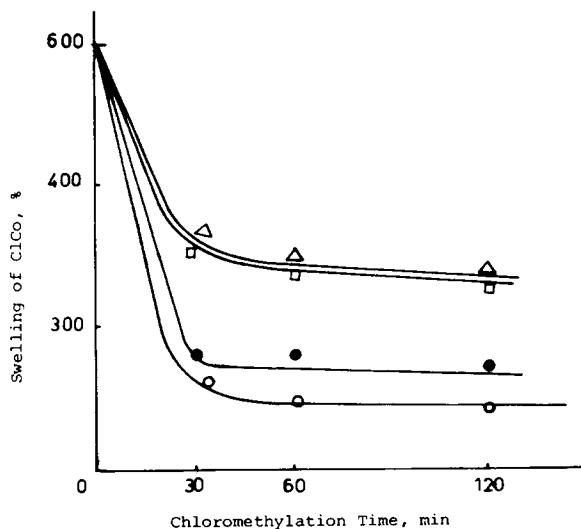
Fig. 1. Swelling vs. time of reaction at 0°C in different solvents: (△) methylal; (□) cyclohexane; (●) nitrobenzene; (○) dichloroethane.

TABLE II
Swelling and Chlorine Introduction during Chloromethylation in Various Solvents at 0°C[a]

Solvent	ϵ	30 min[b]		60 min		120 min	
		Swelling, %	Cl, %	Swelling, %	Cl, %	Swelling, %	Cl, %
Methylal	—	300	<0.4	270	<0.5	270	<0.5
Cyclohexane	2.02	310	0.2	300	—	300	0.2
Dichloroethane	9.2	100	8.65	90	10.5	90	—
Nitrobenzene	34	130	5.7	130	7.2	110	8.7

[a] The initial swelling of styrene-TAT copolymer in toluene was 580%.
[b] Reaction time.

and substitution took place, but the former proceeded more rapidly than the latter, Figure 2(a).

Effect of Temperature

It was also of interest to establish the effect of the temperature during the first stages of the chloromethylation reaction. The results of these experiments, which were conducted in methylal as the solvent, are given in Figure 3. Surprisingly, there was only a slight difference between the swelling of the products obtained at 40°C and the swelling of those formed at 0°C during the first 5 to 10 min of the reaction. The difference increased as the reaction proceeded, and after 30 min the swelling of the chloromethylated copolymer obtained at 40°C was threefold smaller than that produced at 0°C.

The relationship between the degree of conversion to the chloromethylated product and the degree of crosslinking is presented in Figure 4. Crosslinking efficiency increased to a maximum when about 25% to 40% conversion to the chloromethylated product had taken place and remained approximately constant
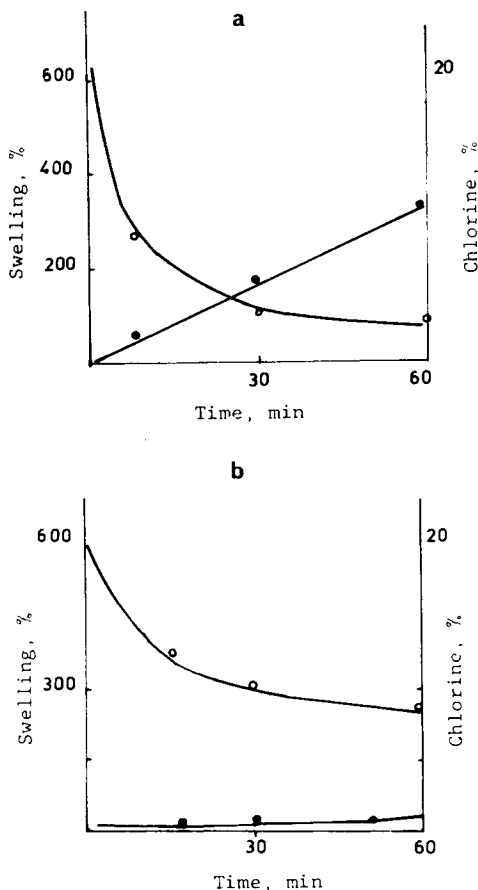
Fig. 2. Effect of solvent on the degree of swelling and introduction of chloromethyl groups in di-
chloroethane (a) and methylal (b): (O) decrease of swelling; (●) increase of chlorine content.

at that level up to 80% to 90% conversion. The dependence of the swelling of
the final chloromethylated product (80% to 90% conversion) on temperature is
given in Figure 5. As can be expected, the higher the temperature, the lower the
value of the swelling of the chloromethylated product and consequently the
higher the degree of crosslinking.

Proposed Reaction Mechanism

The exact nature of the reactive chloromethylating species in electrophilic
aromatic chloromethylation has not yet been established. $\overset{+}{C}H_2OH$ and $\overset{+}{C}H_2Cl$
are frequently suggested as the active species.[17] It has recently been demon-
strated that chloromethyl alcohol can exist in acid media in a relatively stable
protonated form.[18] It can therefore be proposed that a chloromethyloxonium
ion is the reactive intermediate in chloromethylation with methylal–chlorosul-
fonic acid. Accordingly, for chloromethylation with methylal and chlorosulfonic

Fig. 3. Swelling vs. time of reaction at different temperatures: (O) 40°C; (△) 20°C; (□) 0°C.

acid, the following reaction pathway may be suggested:

The formation of the alkoxymethyl intermediate can be expected as a result of the attack of the protonated oxonium ion on the aromatic substrate.[19] The reaction can, in principle, then proceed via two simultaneous pathways: (1) cleavage of the alkoxymethyl derivative and substitution of the hydroxy group by chlorine, or (2) interaction with a second aromatic substrate to form crosslinks. Either one of the pathways may predominate, depending on the reaction conditions.

Thus, in both methods of chloromethylation (with methylal + chlorosulfonic acid or with monochloromethyl methyl ether), the same reactive chloromethylating agent evidently attacks the aromatic nucleus in an electrophilic substitution reaction.   In accordance with this suggestion, the results of Table I show
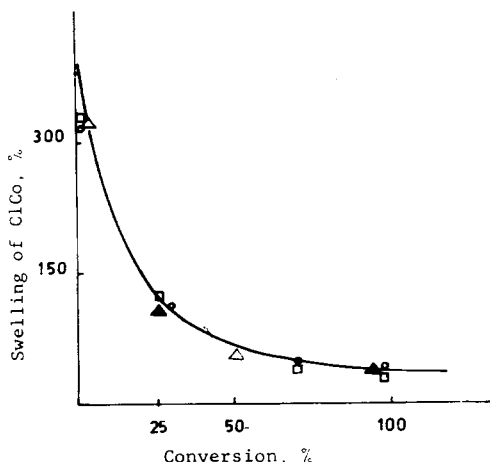
Fig. 4. Effect of conversion to chloromethylated copolymer on crosslinking efficiency in different solvents. Solvents are the same as those in Fig. 1.

that both an excess of our chloromethylating agent (methylal + chlorosulfonic acid) and a relatively high temperature are necessary for the introduction of a high number of chloromethyl groups into the polymer matrix.[20]   (It is well known that the conventional method of chloromethylation requires a considerable excess of chloromethyl methyl ether and is conducted at 55–58°C.)[4-6,19]

In a number of publications which have appeared on crosslinking occurring during the chloromethylation of linear polystyrene or polystyrene–DVB copolymers, the crosslinking has been described as a side reaction.[6]   In view of the results presented here, it seems likely that the crosslinking plays a dominant role, particularly during the primary steps of the reaction, and may take place before the substitution reaction occurs.   From Figures 1 and 2 it seems that the crosslinking begins as soon as the swollen polymer has made contact with the reaction mixture and proceeds more rapidly than the introduction of the chloromethyl groups.
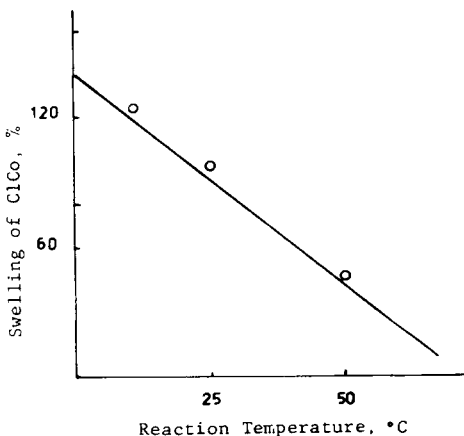

Fig. 5. Effect of reaction temperature on the swelling of chloromethylated copolymer (80–90% conversion).

Our observations together with the mechanism of chloromethylation with chlorosulfonic acid and methylal described above may explain the crosslinking process in terms of cationic polymerization. According to this theory, the initial step in cationic polymerization is the formation of carbonium ions, without which polymerization cannot take place. In our case, the formation of a polymeric carbonium ion is evidently due to the attack of protonated chloromethyl ether on the styrene unit of the polymer backbone. As a result of the polymeric nature of this carrier and the relative proximity of the polymer chains, the generation of active centers and the subsequent formation of crosslinks are readily facilitated.

Influence of the Nature of the Solvent and of Temperature on Crosslinking Efficiency

The nature of the solvent determines the crosslinking efficiency. It is well known that the solvent plays an important role in cationic polymerization; its mode of action is based on its polarity and its basicity.[21] The dependence of the rate of crosslinking on the dielectric constant of the solvent is attributed to the dependence of the formation of the positive ion on the dielectric constant; this process is favored in media with a high dielectric constant in which the electrostatic attraction between charged bodies is small. Therefore, crosslinking efficiency in nitrobenzene, which is an extremely polar solvent ($\epsilon = 34$), is higher than that in apolar solvents, such as cyclohexane.

The main factor influencing the initial reaction is the course of cationic polymerization is the basicity of the solvent. In our case, methylal, which possesses strong electron-donating characteristics, can solvate the primary complex and thus retard the initiation of crosslinking. Therefore, the degree of crosslinking of the chloromethylated copolymer obtained in methylal is more than threefold smaller than that in dichloroethane (Fig. 1). Moreover, in the presence of methylal the degree of crosslinking at the beginning of the reaction at 40°C is lower than that at 0°C (Fig. 3). This indication of a negative temperature effect is further evidence that a cationic mechanism is involved in the formation of crosslinking, at least in the initial stage of reaction.

At higher temperatures the copolymer undergoes chloromethylation more rapidly. Since at high temperatures the interaction between polystyrene and chloromethylating agent is complicated by a number of parallel or competing reactions, an explanation of the mechanism is more difficult.

The following trends were observed in our experiments the results of which are given in Figures 3–5. The crosslinking efficiency increases with the number of chloromethyl groups introduced to the polymer matrix, irrespective of the nature of the solvent; it is however influenced by temperature. Examination of the swelling of chloromethylated copolymers containing 17–20% chlorine, produced at different temperatures between 25° and 50°C, leads us to conclude that crosslinking efficiency of a chloromethylated copolymer synthesized at 50°C is higher than that of a copolymer synthesized at room temperature. It is likely that p-chloromethylstyrene, formed as a result of the introduction of a CH_2Cl group, can itself initiate the crosslinking reaction. There is some evidence in the literature[22] that polymeric benzyl chloride can be used to initiate the polymerization of styrene by a carbocationic technique. Thus, during the whole

process of chloromethylation the crosslinking reaction, which occurs either as the primary reaction or parallel to the substitution reaction, causes significant changes in the structure of the polymer backbone from which ion exchange resins are produced.

Amination

A series of experiments was conducted on the production of aminated chloromethylated styrene–TAT copolymers. Attempts were made to ascertain the relationship between the chlorine content, the percent swelling of the chloromethylated copolymer, and the amination conditions on the one hand and the physical properties of the anion exchange resin on the other hand. The results of the reactions of three types of chloromethylated copolymer with a number of amines are shown in Table III.

We should remember that the various chloromethylated copolymers were synthesized under different conditions and do not swell to the same degree. The changes in the extent of swelling, attributed to the crosslinking efficiency, explain the difference in accessibility of these polymer matrices to the introduction of the amines. As can be seen from Table III, samples 1 through 6 are open to a high degree of substitution with a large number of different amines. The high value of the total exchange capacity attained with amines such as pyridine and trimethylamine confirms this conclusion.

A relatively high extent of substitution was achieved with ethylenediamine for all the chloromethylated copolymers tested, irrespective of the crosslinking efficiency and the swelling capacity of the matrix. We observed only a small reduction in the degree of introduction of the amine (as reflected in decreased total exchange capacity) into chloromethylated products with low degrees of swelling.

The introduction of the bulky trimethylamine molecule into the resin is obstructed by steric hindrance. Contrary to the results obtained for ethylenediamine, it was found that the introduction of trimethylamine became much less successful as the percent swelling of the chloromethylate copolymer decreased.

TABLE III
Amination of Chloromethylated Styrene–TAT Copolymer with Various Amines

Sample no.	Chloromethylated copolymer		Amination conditions		Anion exchange resin	
	Swelling, %	Cl, %	Amine, excess in dioxane	Temp., °C	Total exchange capacity, meq/g	Moisture, %
1	120	22.3	ethylenediamine	70	6.50	55.3
2	120	22.3	dimethylamine[a]	40	4.96	56.4
3	120	22.3	diethylamine	40	4.88	47.5
4	120	22.3	diethanolamine	70	4.14	47.1
5	120	22.3	pyridine	70	3.50	44.6
6	120	22.3	trimethylamine[a]	40	3.90	60.2
7	100	18–20	ethylenediamine	75	5.42	52.4
8	100	18–20	trimethylamine[a]	40	2.9	59.5
9	50	23	ethylenediamine	75	5.28	49.6
10	50	23	trimethylamine[a]	40	1.37	46.7

[a] 30% solution in water.

The impossibility of achieving complete amination of the highly crosslinked rigid copolymer matrix with trimethylamine may also be due to electrostatic repulsion. In the reaction between trimethylamine and the chloromethylated copolymer, charged quaternary ammonium groups are formed on the polymer. When a number of chloromethylated groups have been aminated, the charge on these groups may repel an incoming unreacted group.

CONCLUSIONS

The investigations directed toward the elucidation of the role of the different variables in the synthesis of chloromethylated styrene–TAT copolymers lead us to conclude that the properties of postpolymerization crosslinkage can be successfully utilized to select chloromethylation conditions for the synthesis of a wide range of anion exchange resins.

APPENDIX: EXPERIMENTAL

Copolymerization

A solution of TAT and styrene was prepared by vigorous stirring at 60°C. Benzoyl peroxide was then added all at once to the styrene–TAT solution. The resulting mixture was poured into a reactor containing starch solution in 20% sodium chloride brine, which was kept at 60°C and stirred constantly during the addition. The suspension in the reactor was maintained at 80–85°C for 4 hr and then at 90°C for a further 4 hr. The polystyrene–TAT bead polymer thus obtained was filtered off, washed, and dried. The yield was 90–95%, based on styrene.

Chloromethylation

Polystyrene–TAT beads were allowed to swell in an organic solvent (Table II). A mixture of chlorosulfonic acid and methylal was added dropwise to the swollen beads, and the resulting mixture was stirred for a fixed time at a particular temperature. After the reaction was stopped, the polymer was isolated by filtration and poured into a large quantity of methanol. The polymer was then extracted with methanol in a Soxhlet apparatus and dried in vacuo. The Cl and S contents were analyzed. The chloromethylation procedure was carried out at different temperatures (Table I).

Amination

The chloromethylated copolymer was allowed to swell in a mixture of dioxane and an amine (Table III) for 3 hr, after which time a further quantity of the same amine was added. The reaction was allowed to proceed for 10 hr at a temperature which depended on the nature of the amine. The resin was obtained by filtration and then washed to neutrality and stored.

Total Exchange Capacity

The total exchange capacity (in meq/g dry resin) of the anion exchange resin was obtained by means of a batch method.   The weakly basic anion exchanger was equilibrated with an excess of 0.1N HCl, and the unreacted acid was then back-titrated with an alkali.

Swelling of Copolymers and Resins

Percent swelling was determined by placing the air-dried copolymer or resin in a graduated cylinder and reading the volume measurement.   An excess of solvent was added, and the volume was read again after the resin had ceased to swell.   Percent swelling (k) was calculated as

$$k = \frac{\text{final volume} - \text{initial volume}}{\text{initial volume}} \times 100\%$$

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