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A novel way to prepare anion exchangers based on crosslinked polystyrene

Xu Hui, Hu Xizhang*

Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, P. R. China

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Summary

A novel method for preparing anion exchangers based on crosslinked polystyrene is proposed which comprises first acetylation of crosslinked polystyrene by Friedel-Crafts reaction, then reductive amination of acetylated products by Leuckart reaction. Aminated products, if desired, are readily converted to corresponding tertiary amino anion exchangers or optionally quaternized to form corresponding strong base, quternary ammonium anion exchangers. The new method, overcome the toxic problem of classic chloromethylation process, is safe, economical and convenient.

Introduction

The classic process for preparing anion exchangers based on crosslinked polystyrene involves chloromethylation which introduce the chloromethyl functional groups to the crosslinked polystyrene usually using chloromethyl methyl ether (CME) in the presence of catalysts such as aluminum or zinc chloride(1). Unfortunately, CME has been proved to be linked to respiratory cancer, which puts serious restriction on its use(2). In addition, the chloromethylation involves the secondary crosslinking which is harmful to the resins(3).

In view of the stated deficiencies of the prior art method, it remains highly desirable to effectively prepare anion exchangers by a method which does not involve the use of CME. Many researchers have worked hard on it and a variety of alternative routes(4-7) have been proposed. However, these methods are not entirely satisfactory since they can not wholly meet the needs of safe, economical and effectiveness. Here, we wish to report to have now found another new method which comprises first acetylation of crosslinked polystyrene by Friedel-Crafts reaction, then by Leuckart reaction converting acetylated polymers to weak base anion exchangers bearing primary amino groups. Aminated resins, if desired, are readily converted to corresponding tertiary amino anion exchangers by alkylation and then optionally quaternized to form corresponding strong base, quternary ammonium anion exchangers. Alternatively, the strong base anion exchangers can be prepared directly from the primary amino resins by employing methyl iodide and alkali in excess molar amounts. The whole process is shown in scheme 1.

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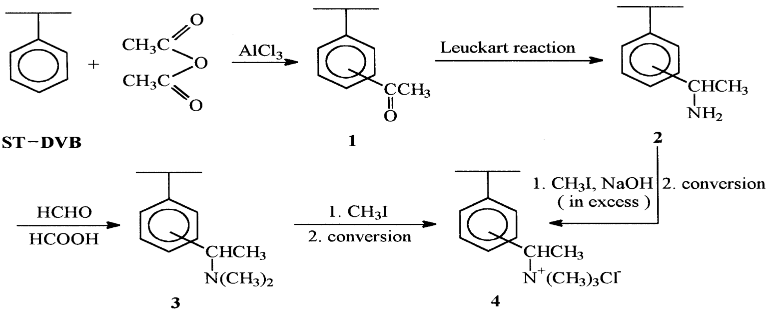
* Corresponding author



Scheme 1

Experimental

Materials and analysis methods

Styrene-Divinylbenzene copolymers (8% DVB) of macroporous types, with beads of a diameter of 0.3~1.0 mm, are obtained by radical suspension copolymerization of comonomers in presence of heptane as a porogenic agent. All the other reagents and solvents are commercially available and of analytical grade.

FT-IR spectra is recorded on Perkin-Elmer 2000 system FT-IR spectrometer. Nitrogen and oxygen contents are determined by element analysis. Exchange capacity is measured by titration(8).

Synthesis

1) Preparation of acetylated crosslinked polystyrene **1** by Friedel-Crafts reaction.

52 g of crosslinked polystyrene is swollen in 400 ml of carbon disulfide for 2 hours. To this solution is added 140 g of powered anhydrous aluminum chloride and then, with rapid stirring, 50 g of acetic anhydride is slowly added through the dropping funnel. After all the acetic anhydride has been added, the reaction mixture is stirred at 50°C for 4 hours. The resin is filtered and thoroughly washed with 10% HCl, 10% NaOH, water, ethanol and methanol. The resin is dried overnight under vacuum.

2) preparation of primary amino weak base anion exchangers **2** by Leuckart reaction.

To a three-necked flask is added 1.2 g of acetylated copolymers, 10 ml of 99.5% formamide and 10 ml of 88% formic acid. The temperature of the solution is raised to 160°C, and then maintained for 10 hours. The resulting formyl derivative is hydrolyzed by refluxing 20 hours with 20 ml of concentrated hydrochloric acid. The beads are washed with water, 10% NaOH, and water until neutral. Upon drying the dried beads are found to have a dry weight capacity of 3.75 meq./g. and contain 5.54% nitrogen.

3) preparation of tertiary amino weak base anion exchangers **3** by alkylation.

To 1.0 g of resulting beads above is added 4 ml of 88% formic acid while the flask is maintained at 50°C. Following said addition, 6 ml of formaldehyde and 10 ml of water to make a stirrable slurry are added. The resulting mixture is heated to 50°C for 1 hour, then heated to 75°C for 1.5 hours, followed by heating 4 hours at 90°C. The mixture is then cooled, filtered, and washed with water, 10% NaOH and water. The beads are vacuum dried, found to have a dry weight capacity of 3.64 meq./g.

4) preparation of strong base anion exchangers **4** by quaternization.

In a suitable size three-necked flask, 1.0 g of tertiary amino resins is swollen in 20 ml of ethanol for 1 hour. To this solution is added 1.0 g of K_2CO_3 (in 10 ml of water), and then 2.0 g of methyl iodide through dropping funnel. The mixture is stirred at 42~44°C for 12 hours, cooled naturally, filtered and washed. The resin has a strong base anion exchange capacity of 2.76 meq./g.

Results and Discussion

Acetylation of crosslinked polystyrene by Friedel-Crafts reaction.

The procedure for acetylation is as follows: styrene-divinylbenzene copolymers, swollen in suitable solvent, reacts with acetic anhydride or acetyl chloride in presence of anhydrous aluminum or zinc or stannic chloride as catalyst.

As acetylation agent, acetic anhydride and acetyl chloride are both effective. However, the handling of acetyl chloride is disagreeable, and the grade of acetyl chloride purchased commercially is generally variable in purity while acetic anhydride is much more stable that make it easy to be handled, and the grade of acetic anhydride is standard and may be used directly in the synthesis. The shortcoming of utilizing acetic anhydride as acetylation agent is that there requires more catalysts.

Catalysts employed here could be anhydrous aluminum chloride, anhydrous zinc chloride and anhydrous stannic chloride etc.. Preferred of the catalysts is anhydrous aluminum chloride. The amounts of catalyst employed in reaction affects the yields greatly and is variable with different acetylation agent used (Table 1).

Table 1 Effects of amount of anhydrous $AlCl_3$ on acetylation

Run	Ratio of $AlCl_3$/Aromatic nucleis	Oxygen content (%)	
		Acetyl chloride as acetylation agent	Acetic anhydride as acetylation agent
1	0.4	5.00	4.05
2	0.6	5.92	4.85
3	0.8	7.32	5.66
4	1.0	8.60	6.47
5	1.5	8.72	7.68
6	2.0	8.64	8.90
7	2.5	8.62	8.95

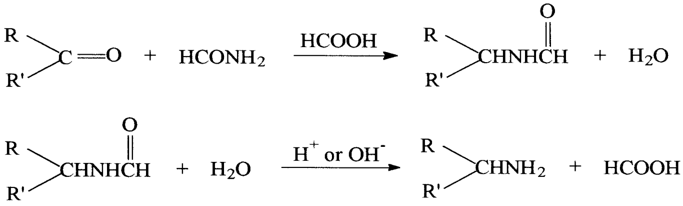
It is observed that, in order to achieve excellent yields, no less than one equivalent of anhydrous aluminum chloride as to acetylation agent is needed when acetyl chloride is used as acetylation agent while no less than two equivalents of anhydrous aluminum chloride as to acetylation agent is needed when acetic anhydride is used as acetylation agent.

Solvents such as carbon disulfide, nitrobenzene, dichloromethane and dichloroethane etc., can be used for swelling the copolymers. Preferred of the solvent is carbon disulfide for it is not only a good swelling agent for copolymer particles, but also a good carrier of anhydrous aluminum chloride.

Dry environment is important for Friedel-Crafts reaction to achieve high yields, so all the reagent must be dried prior to use, especially for anhydrous aluminum chloride which should be treated by sublimation.

Reductive amination of acetylated products by Leuckart reaction.

The Leuckart reaction is well known(9-13) as a process for the reductive amination of aldehydes and ketones. The reaction is carried out by heating a mixture of the carbonyl compound and formic acid salt or formyl derivative of ammonia or the amine. Primary and secondary amines produced in the reaction often are obtained as the formyl derivatives and must be recovered by hydrolysis. The reaction may be illustrated by the following equations.



Scheme 2

In this paper we extended the Leuckart reaction to acetylated crosslinked polystyrene to prepare anion exchangers. A number of reagents such as ammonium formate, ammonium formate-formic acid, formamide-formic acid, or formamide-ammonium formate are often used in this reaction(10). The mixture of formamide-formic acid is preferably used because it could produce satisfactory results. The carbonyl groups and formamide are usually employed in a molecular ratio of above 1:5. The excess of formamide tends to diminish the side-reaction of formation of secondary of tertiary amines. Formic acid is to maintain a slightly acidic medium and serves as a active reducing agent(11). One to three equivalents of formic acid as to formamide is generally required (Table 2). Formamide, meanwhile, served as swelling agent for resins in reaction and no other solvents are needed.

Table 2 Effects of variation in amounts of formamide and formic acid on yields of formyl derivatives

Run No.	Formamide (ml)	+	Formic acid (ml)	Temperature (°C)	Nitrogen content (%)
1	20	+	0	170~180	1.18
2	15	+	5	170~180	4.12
3	10	+	10	160~170	4.73
4	5	+	15	150~160	3.19
5	10	+	20	155~165	4.79
6	10	+	30	150~160	4.82

The optinum reaction temperature for this reaction is 160~175°C (Fig. 1); whenever it falls below about 160°C, accumulated water is allowed to distil until the temperature rises again. When refluxing occurs, a deposit of ammonium carbonate is soon found to appear in the condenser. The reaction is considered complete when ammonium carbonate is deposited only very slowly in the condenser.

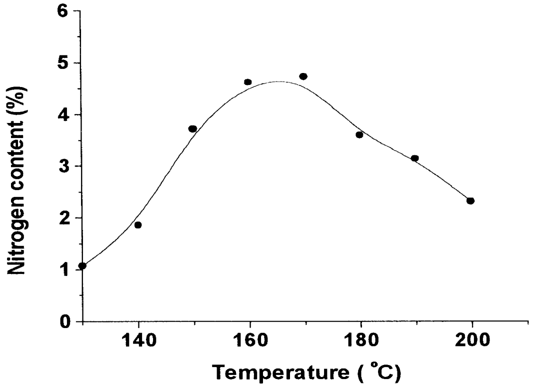


Fig. 1 Effect of temperature on the Leuckart reaction

In the process of hydrolysis, the best yield was obtained by hydrolyzing the formyl derivative directly in the reaction mixture with concentrated hydrochloric acid. Hydrolysis with aqueous sodium hydroxide usually requires a long time of refluxing, and the yield of amine is not as good (Table 3).

Table 3 Effect of reagents on the hydrolysis of formyl derivatives

Run No.	Hydrolytic reagent	Time of hydrolysis (hrs)	Nitrogen content (%) Before hydrolysis	Nitrogen content (%) After hydrolysis	Yield of hydrolysis (%)
1	Concd. HCl	20	4.73	5.54	90
2	10% HCl	22	4.73	5.47	82
3	30% NaOH	37	4.73	4.87	16
4	10% NaOH	40	4.73	5.13	44

After the Leuckart reaction is obtained a weak base anion exchangers bearing primary amino groups.

Characterization of resins.

FT-IR spectra of resins is shown in Fig. 1.

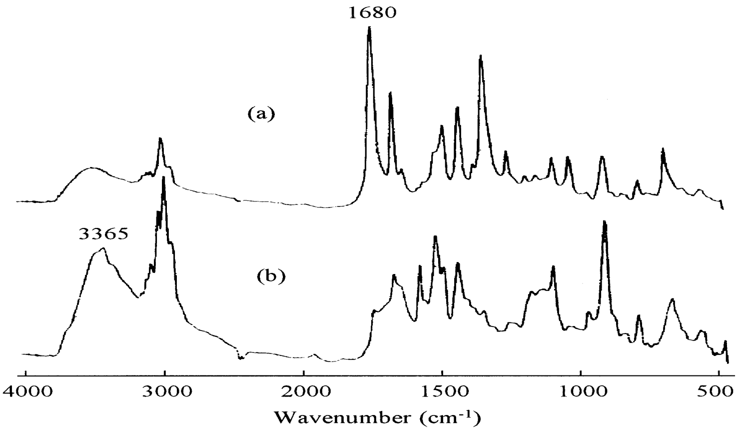


Fig. 2 FT-IR spectra of acetylated crosslinked polystyrene (a) and aminated product (b) resulted from Leuckart reaction

Acetylated resins showed strong IR band at 1680cm^{-1} which is assigned to carbonyl groups, indicating the pesence of carbonyl groups(14). The peak of carbonyl groups decreases sharply after Leuckart reaction, meanwhile, there appears a new peak at 3365 cm^{-1} which is characteristic of amino groups, indicating carbonyl groups have been converted to amino groups. The residue peak of carbonyl groups might result from incomplete reaction or incomplete hydrolysis of formyl derivatives during the second step of Leuckart reaction or both.

Aminated resins, if desired, are readily converted to corresponding tertiary amino, weak base anion exchangers by alkylation according to G. R. Buske(15), or are optionally quaternized to form corresponding strong base, quternary ammonium anion exchangers. The nitrogen content, exchange capacity and water content of obtained resins are listed in Table 4.

Table 4 The nitrogen content and exchange capacity of anion exchangers

Type of anion exchangers	Form	Nitrogen content (%)	Exchange capacity (meq./g.) Calc.	Exchange capacity (meq./g.) Found	Water content (%)
Weak base (primary amine)	Free base	5.54	3.96	3.75	57.5
Weak base (tertiary amine)	Free base	5.35	3.82	3.64	53.2
Strong base (quternary ammonium)	Chloride	4.16	2.97	2.76	62.4

The observed exchange capacities appear to be a little lower than the theoritical values calculated from the nitrogen contents, which is supposed to the incomplete hydrolysis of formyl derivatives during the second step of Leuckart reaction. The exchange capacities is also found to be slightly lower than that of same type of resins prepared by chloromethylation method, but they are enough for practical use.

The water contents are a little higher than those of commercial resins prepared by conventional method, according to the contrast with products of Shanghai resin factory, Shanghai, China. It is probably resulted from the relatively high reaction temperature (~160 °C) associated with Leuckart reaction since the high temperature is usually favourable for the resins to swell more sufficiently, that enable the resins to hold more of water and therefore, to have a relatively high water content.

Apparently, the chemical structure of the obtained anion exchangers is a little different from that of conventional resins, that is, there exists an additional side-methyl on the obtained structure of $-CH(CH_3)N<$ in comparison with $-CH_2N<$ which is the typical structure of conventional resins. However, the side-methyl seems to have little negative effect on the stability of the obtained resins because there is hardly any sign of decrease of exchange capacity after the resins are subjected to the repeatedly treatment with alkali solution.

Conclusions

The outstanding virtue of this new method for preparing anion exchangers based on crosslinked polystyrene is that it avoids the use of carcinogenic chloromethyl methyl ether which is broadly used in classic chloromethylation process, and eliminate secondary crosslinking due to the absence of methylene bridging, which improve performance of resins. In addition, all the reagents used in reaction are nontoxic, simple and commercially available, and some of them such as solvents and catalysts may be recycled. All of these show that the new method is safe, economical and effective hence it predicts a great prospects in the future and might replace classic chloromethylation process.

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