

Simple synthesis of polymeric primary aromatic amines

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Summary

A new simple and versatile method of obtaining polymers bearing aromatic primary amino groups was developed. The method consists in the reaction of an alkylating polymer with sodium 4-acetylaminobenzenesulfinate and subsequent deacetylation of the intermediate polymer by acid hydrolysis. Alkylating polymers such as chloromethylated polystyrene resin, tosylated macroporous poly(2-hydroxyethyl methacrylate), macroporous poly(glycidyl methacrylate) and PVC were used in the alkylation performed either in an organic swelling solvent or in an aqueous suspension under phase transfer catalysis conditions. Yields in the alkylation step depend largely on the type of the alkylating group, hydrolysis yields are essentially quantitative.

Introduction

Polymers with reactive electrophilic groups such as alkylating or epoxy polymers are well known and widely used both in science and technology. On the other hand, the assortment of commercially available reactive nucleophilic polymers is still small. The choice is mainly limited to polymers with aliphatic hydroxy or amino groups, and their drawback is a rather narrow range of possible reactions.

In this communication, a simple and versatile synthesis of polymers bearing primary aromatic amino groups based on chemical transformation is described.

Experimental

Materials

1a chloromethylated styrene-divinylbenzene (2 %) copolymer, Cl content 19.82 %; 1b chloromethylated styrene-divinylbenzene (2 %) copolymer, Cl content 23.02 %; 1c chloromethylated macroporous styrene-divinylbenzene copolymer, Cl content 14.62 %; 1d tosylated macroporous 2-hydroxyethyl methacrylate (76 %)-ethylene dimethacrylate (24 %) copolymer prepared by a reaction of the copolymer with an equimolar amount of p-toluenesulfochloride in dry pyridine, S content 4.71 %, N content 0.81%; 1e brominated macroporous 2-hydroxyethyl methacrylate (76)-

ethylene dimethacrylate (24 %) copolymer prepared by a reaction of the copolymer with hydrobromic acid, Br content 25.86 %; 1f macroporous 2,3-epoxypropyl methacrylate (60 %)-ethylene dimethacrylate (40 %) copolymer; 1g poly(vinyl chloride) reprecipitated from THF/methanol.

4-Acetylaminobenzenesulfinic acid was prepared according to the literature (1), its sodium salt according to (2). ¹H-NMR of the Na salt in D₂O: τ 7.85(s) CH₃CO, 2.37(m) arom. H. Dimethyl sulfoxide was dried with molecular sieves, water content 0.26 mg/ml.

Alkylation

(A) A mixture of the alkylating polymer and anhydrous sodium 4-acetylaminobenzenesulfinate (25-50 % excess) was heated in anhydrous dimethyl sulfoxide to 45°C or in anhydrous dimethylformamide to 70°C for 20-25 hours. Afterwards, the product was filtered off and washed with the solvent and water, and dried.

(B) A mixture of the alkylating polymer and sodium 4-acetylaminobenzenesulfinate (50% excess) prepared in situ was heated in water in the presence of tetrabutylammonium bromide or Adogen[®] 464 to 80-100°C for 24 hours. The product was filtered off, washed with water, and dried.

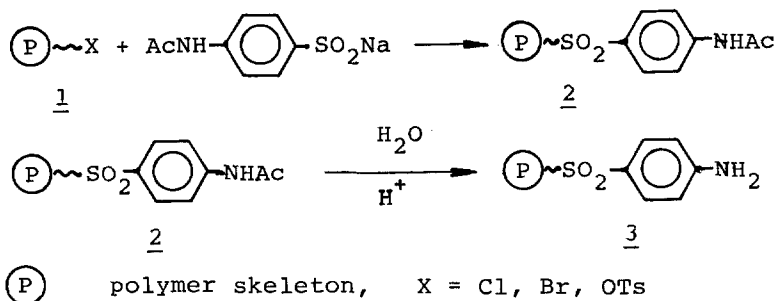
Hydrolysis

Polymeric 4-acetylaminophenyl sulfone was heated in ethanolic HCl (3:1 by vol.) to reflux for 12 hours. The product was filtered off, washed with water, and dried. The properties of the products are given in Table 1.

Results and Discussion

Polymers bearing aromatic primary amino groups are known. Most frequently they are prepared by the nitration of aromatic polymers and subsequent reduction of nitro groups (3). Such procedure however, is not entirely satisfactory: it requires the use of large amount of concentrated acids and reducing agents and, if carried out on a large scale, may even be dangerous. 4-Aminophenylsulfonyl groups can be introduced to hydroxy polymers, such as cellulose (4) or poly(2-hydroxyethyl methacrylate) (5), by a reaction with 2-(4-aminophenylsulfonyl)ethyl sulfate. The synthesis of a polymer with aromatic primary amino groups by a reaction of polyvinylamine with 4-acetylaminobenzenesulfochloride and subsequent hydrolysis has also been mentioned in the literature (6).

In this communication, a simple and versatile two-step synthesis of polymers bearing primary aromatic amino groups is described. In the first step, an alkylating polymer 1 is reacted with the alkali salt of 4-acetylaminobenzenesulfinic acid to give 4-acetylaminophenyl sulfone 2 which is in the second step hydrolyzed to the 4-aminophenylsulfonyl derivative of the starting polymer 3.



Alkylation of sodium 4-acetylaminobenzenesulfinate by polymeric alkylating groups was performed in solvents which swell or dissolve the corresponding polymer, on the one hand, or, in an aqueous medium under phase transfer conditions, on the other hand. As anticipated, the alkylation yields are considerably dependent on the reactivity of the alkylating group and on the reaction medium. Excellent yields of polymeric sulfones comparable with those of low-molecular compounds (7) were obtained using a chloromethylated gel-type polystyrene resin or tosylated macroporous poly(2-hydroxyethyl methacrylate) in the dimethyl sulfoxide medium. Dimethyl sulfoxide seems to be the solvent of choice in nucleophilic reactions of alkylating polymers other than chloromethylated polystyrene (8). Poorer results were obtained in the alkylation of sulfinate with poly(vinyl chloride), the chlorine atoms of which are little reactive. A heterogeneous arrangement in an aqueous suspension under phase transfer catalysis conditions is attractive for its simplicity in spite of only medium or low yields. In all cases the products obtained are sulfones and not sulfonic acid esters, as follows from their stability towards acid hydrolysis (nitrogen contents increase after hydrolysis) and also from their infrared spectra (9).

In the alkylation, corresponding polymeric hydroxy derivatives are obviously always formed due to the hydrolysis of polymer alkylating groups. In the reactions carried out in dimethyl sulfoxide or dimethylformamide, traces of water present in the reaction medium are sufficient to promote the hydrolysis (10). In most cases, however, hydroxy groups in the product do not interfere.

Hydrolysis of acetyl groups in 4-acetylaminophenyl sulfones 2 with ethanolic hydrochloric acid proceeds smoothly and with practically 100% conversions, judging by the absence of the characteristic infrared absorption of acetyl groups.

The synthesis of polymers bearing aromatic primary amino groups described here is simple and versatile. Both starting reaction components, the alkylating polymer and 4-acetylaminobenzenesulfonic acid are easily available. This renders the synthesis a method of choice for the preparation of polymeric primary aromatic amines which can further serve as intermediates for a series of useful polymer products. At the same time, the reaction sequence represents a general method for the transformation of a polymer electrophile to a polymer nucleophile.

Table 1 Polymeric 4-acetylamino-phenyl sulfones 2^a

| Starting polymer | Method | Reaction medium | N % | S % | Conversion % | Note |
|------------------|----------------|-------------------------------|-------------------|------|--------------|------|
| <u>1a</u> | A | DMSO | 3.92 ^b | 9.00 | 92 | c,d |
| <u>1b</u> | B ^e | H ₂ O ^f | 2.58 ^g | 5.24 | 40 | - |
| <u>1c</u> | A | DMSO | 1.33 | 3.09 | 27 | - |
| <u>1d</u> | A | DMSO | 2.12 | - | 100 | h |
| <u>1e</u> | A | DMSO | 1.28 | - | 32 | h |
| <u>1f</u> | B | H ₂ O ^f | 1.14 | 2.19 | 23 | h |
| <u>1g</u> | A | DMF ^k | 1.38 | 3.32 | 8 | i,j |
| <u>1g</u> | B | H ₂ O ^k | 0.18 | - | 0.8 | - |

^aAll the polymers have IR absorption at 1690-1695 cm⁻¹ (CONH) and at 1140 and 1320 cm⁻¹ (SO₂). After hydrolysis the amide absorption entirely disappears. ^bCl content 1.01 %. ^cSwelling ratios in methanol and H₂O are 1.4 and 2.1, resp. After hydrolysis, the ratio of swelling ratios in water and concd. HCl is 3:4. ^dN content after hydrolysis 4.28 %. ^ePotassium 4-acetylaminobenzenesulfinate was used. ^fIn the presence of Bu₄N⁺Br⁻ ^gCl content 6.74 %. ^hThe IR amide absorption overlapped by a massive ester absorption. ⁱ¹H-NMR (deuterated DMSO): τ 7.87(s) CH₃CO, 7.4-7.9(m) CH₂, 5.51(s) CHX, 2.07(d) arom.H. ^jN content after hydrolysis 1.38 %. ^kIn the presence of Adogen[®] 464 (Ashland Chemical Co.).

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