Polymer Bulletin 5, 111–116 (1981)

Polymer Bulletin

Chemical Modification of Polystyrene

Introduction of Sulfinate and Sulfone Functionalities

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SUMMARY

Sulfinate functional groups have been introduced on selected positions of the aromatic rings of soluble or crosslinked polystyrene via lithiation reactions followed by quenching with sulfur dioxide. The sulfinate polymers have good stability, can be stored at room temperature, and can be used for ion-exchange or as nucleophiles to produce polymer-bound sulfones. Good functional yields of polystyrene resins with sulfone pendant groups can be obtained by reaction of the polymeric sulfinates with various alkyl halides under phase transfer or classical conditions.

INTRODUCTION

The chemical modification of polystyrene has continued to attract much attention due to the numerous applications of functionalized resins in areas as varied as ion exchange (DORFNER 1972), polymeric protecting groups (FRECHET 1981a), peptide synthesis (MERRIFIELD 1969) and other polymer-supported reactions (HODGE and SHERRINGTON 1980). Chemical modification often affords an easy access route to polymers which are normally difficult to prepare by a direct route (e.g.:polyvinyl alcohol) but it suffers from the fact that it is usually impossible to purify the polymers after modification. Thus, it is important that side-reactions be minimized during chemical modification or that their occurence not affect the final reactivity of the modified polymers (FRECHET 1981b). Numerous functional polymers have been prepared from ring-lithiated (FARRALL and FRECHET 1976, FYLES and LEZNOFF 1976, GRUBBS and SU 1976) or chloromethylated polystyrene (FARRALL and FRECHET 1978, FRECHET and FARRALL 1977, FRECHET et al. 1979a and b, HODGE and SHERRINGTON 1980, RICARD et al. 1981) as both of these intermediates are easily obtained and possess high reactivities.

The present report describes a very efficient method for the formation of a polymeric sulfinate which has ion exchange properties and can be used in nucleophilic substitution reactions to prepare polymers with sulfone pendant groups.

A survey of the literature shows very little previous work in the preparation of polymers containing sulfinate groups. Polymeric sulfinic acids and sulfinates have been prepared by reaction of crosslinked styrene-divinylbenzene resins with gazeous hydrochloric acid and sulfur dioxide in the presence of very large

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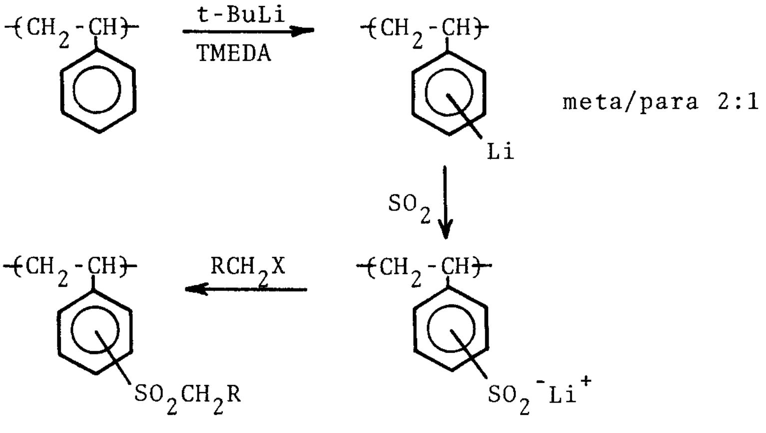
amounts of aluminium chloride. However, the reaction gave low degrees of substitution as evidenced by measurements of the exchange capacities of the modified polymers (AOSHIMA et al. 1974).

REACTIONS WITH SOLUBLE POLYSTYRENE

The reactions were carried out as outlined in scheme I below using a complex of t-butyllithium and tetramethylethylene diamine to generate the lithiated resin. This procedure is known to afford a product in which substitution is in the meta and para positions in 2:1 ratio (EVANS et al. 1974, FARRALL and FRECHET 1979). Treatment of the lithiated polymer with excess sulfur dioxide afforded the polymer-bound lithium sulfinate which could be isolated or used immediately to produce a polymer with pendant methyl sulfone groups by reaction with excess methyl iodide.



SCHEME I.

As expected, the reaction did not result in functionalization of all of the aromatic rings of the starting polymer, and the product had a degree of functionalization of 0.32 as indicated by both NMR and elemental analyses.

The structure of the methyl sulfone polymer was confirmed by its infrared spectrum which included large sulfone bands at 1150 and 1308-1320 cm^{-1}, and by its ^{1}H and ^{13}C NMR spectra which exhibited a prominent methyl resonance and an aromatic carbon pattern which confirmed that substitution had occurred in the meta and para positions in 2:1 ratio (FARRALL and FRECHET 1979).

In contrast to the above reaction for which the alkylation proceeded in close to quantitative yield, the reaction of the sulfinate polymer with 2-chloroethanol was very sluggish with less than 10% of the sulfinate being converted to the corresponding sulfone. Slightly better yields (up to 20%)were obtained using

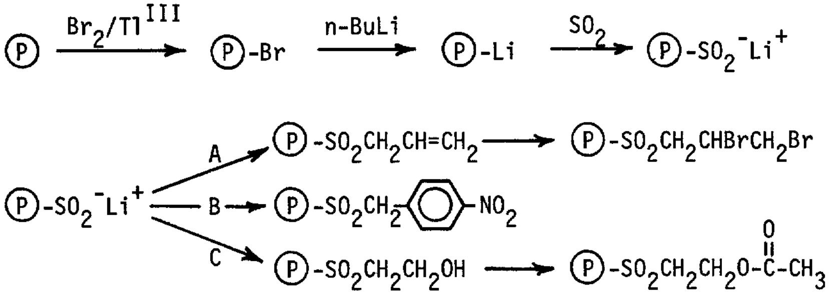
2-iodoethanol.

REACTIONS WITH CROSSLINKED POLYSTYRENE

1% Crosslinked polystyrene was used in a somewhat similar sequence of reactions to test the nucleophilicity of the polymeric sulfinates under phase-transfer conditions as it was expected that the use of such conditions would result in high yields of alkylation. Our earlier work (FRECHET et al. 1979a) on the use of phase transfer catalysis for the chemical modification of crosslinked polymers had shown that although three distinct phases are involved in such reactions, polymers which possess strongly nucleophilic reactive groups (phenolate, thiolate, etc.) react very well with alkyl halides to afford high functional yields of alkylated polymers.

To avoid substitution in the meta positions of the aromatic rings of polystyrene which results from the direct lithiation procedure, our two-step bromination-lithiation reaction sequence (FARRALL and FRECHET 1976) was used to lithiate the resin. The polymeric sulfinate was then obtained by quenching with sulfur dioxide (Scheme II). The functional yield for the transformation of the brominated polymer into the corresponding sulfinate resin could be evaluated from bromine and sulfur analyses and was found to vary between 70 and 80%.

Phase transfer catalyzed reactions involving the polymeric sulfinate and alkyl halides such as allyl bromide, p-nitrobenzyl bromide, or 2-iodoethanol proved that, although sulfinates are not normally considered to be good nucleophiles, very satisfactory results could be obtained. The various reactions involving crosslinked polystyrene are shown in scheme II.



SCHEME II. Ⓟ = 1% crosslinked polystyrene (aromatic subst.)

Some of the changes which are observed in the infrared spectrum of the polymeric sulfinate after reaction with allyl bromide and with p-nitrobenzyl bromide are shown in figure 1. The spectrum of the resin with pendant allyl sulfone groups showed the characteristic sulfone bands at 1143 and 1318 cm^{-1} and a C=C absoption at 1639 cm^{-1}. The IR spectrum of the resin with p-nitrobenzyl sulfone pendant groups also showed large sulfone absorptions at 1145 and 1325 cm^{-1} in addition to very strong bands at 1528 and 1353 cm^{-1} for the nitro group, and a weaker band at 860 cm^{-1} for the C-N absorption.

The weight gains observed in reactions A and B (Scheme II) suggest that these reactions carried out under phase-transfer conditions are quantitative. In contrast, similar reactions carried out with similar amounts of reagents but in the absence of a phase-transfer catalyst were much less successful with only 10-25% of the expected weight increases observed for the reactions shown in Scheme II. These estimates of functional yields were confirmed by the results of nitrogen analyses on the resin with p-nitrobenzyl sulfone pendant groups, and by bromine analyses on the dibromo derivative of the allyl sulfone resin prepared,as shown in reaction A, Scheme II, by reaction of the allyl resin with excess bromine in carbon tetrachloride.

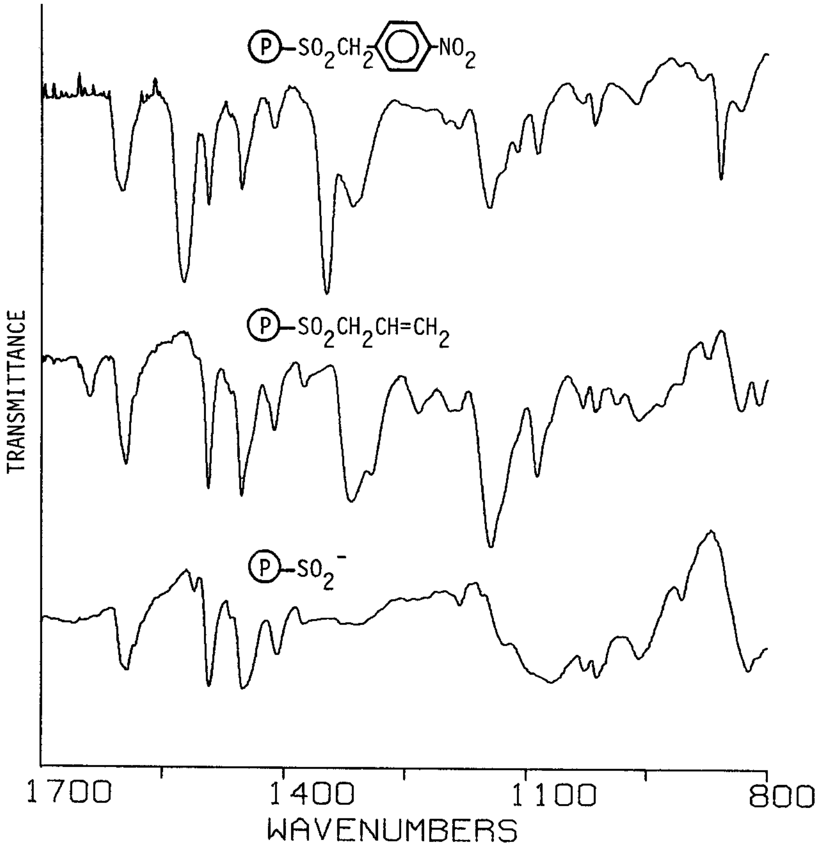


FIGURE 1. Infrared spectra of the resins before and after chemical modification under phase-transfer conditions.

The reaction with 2-iodoethanol (reaction C, Scheme II) was somewhat less successful as indicated by the weight gain of the resin which was only 60-70% of theoretical. The sulfonylethanol resin obtained in this reaction had an infrared spectrum with a large hydroxyl absorption centered at 3400 cm^{-1} and strong sulfone bands at 1143 and 1323 cm^{-1}. After acetylation, a new band at 1738 cm^{-1} was observed.

A final estimation of the activity of the sulfinate resin prepared by the reaction sequence shown in Scheme II was made by measuring its ion exchange capacity. Thus, a sulfinate resin prepared from a crosslinked brominated polystyrene resin containing 3.5 mequiv. of Br/g had an exchange capacity of 2.9 mequiv/g. This value is more than three times higher than that obtained for a sulfinate resin prepared by a different route (AOCHIMA et al. 1974).

CONCLUSION

These reactions show that a useful sulfinate resin can be prepared by sulfur dioxide quenching of metalated polystyrene ; they also confirm that phase-transfer catalysis is an invaluable technique for the chemical modification of polymers. Applications of sulfinate resins as polymeric protecting groups or separation media will be described shortly.

EXPERIMENTAL

Infrared spectra were measured on a Nicolet MX-1 FT-IR spectrometer; NMR spectra were measured on Varian HA-100 or CFT-80 spectrometers. Elemental analyses were performed by MHW Laboratories (Phoenix AZ) or in this laboratory.

Soluble polystyrene (Mn=21,000) was dissolved in cyclohexane and treated with an equivalent amount of t-butyl-lithium/tetramethylethylene diamine complex. After 2 hours of stirring at room temperature, sulfur dioxide was bubbled through the mixture at a rapid rate for a few minutes, then slower for 1 hour. The precipitated polymer was filtered, then treated with a 30% excess of methyl iodide in tetrahydrofuran at 60^{o} overnight. After reaction, the polymer solution was poured into a large amount of water and the precipitate was washed with water. After reprecipitation in methanol, the polymer was dried in vacuo. Similar experiments were carried out only to the sulfinate stage and the polymer was isolated;the polymer could be stored for further reactions.

1% crosslinked polystyrene was brominated and lithiated as previously described (FARRALL and FRECHET 1976). After washing the lithiated resin with dry benzene, it was suspended in dry THF and sulfur dioxide dried over molecular sieves was bubbled through the mixture for 1h at room temperature. Resins containing from 1.5 to 3 mequiv. of functional group per gram could be prepared by this procedure.

A suspension of 1g (ca. 2.1 mmoles) of a polymeric sulfinate in 10 mL dichloromethane containing 2 g of p-nitrobenzyl bromide and 0.1 g Adogen 464 (Aldrich Chem. Co.) was stirred with 3 mL of a 25% solution of NaOH in water. After 4 h of stirring at room temperature, a second portion of p-nitrobenzyl bromide was added and the stirring was continued overnight. After filtration, the polymer was washed extensively, then dried in vacuo at 60° to yield 1.27 g of the p-nitrobenzyl sulfone resin. Similar reaction conditions were used for the reactions with allyl bromide and 2-iodoethanol. Other reactions without phase-transfer catalyst were carried out in DMF or alcohol.

ACKNOWLEDGEMENT. Financial support of this research by the Natural Sciences and Engineering Research Council of Canada, in the form of an operating grant, a postdoctoral fellowship and a summer research assistanship, is gratefully acknowledged.

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Received July 6, 1981