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The Modification of Polysulfone by Metalation

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INTRODUCTION

Chemical modification of aromatic polysulfones by sulfonation^{1,2} and chloromethylation³ provides polymers with functional groups which make them more versatile as membrane materials. Lithiation has been employed in the modification of polystyrene,^{4,5} poly(2,6-dimethyl-1,4-phenylene)ether,⁶ polyvinylthiophene,⁷ and styrene-sulfur dioxide copolymers,⁸ but has not been investigated as a method of modification of polysulfone. Polysulfone possesses aryl sulfone groups in the structure which strongly activate towards ortho-lithiation⁹ as previous studies on simple diphenyl-sulfones have shown,^{10,11} making this polymer a particularly suitable substrate. A recent paper concerning the preparation of carboxyl containing polysulfone by room temperature lithiation¹² prompts us to disclose our own related work¹³ on the subject.

Our studies of changes in membrane characteristics brought about by various types of functional groups led to the development of this versatile modification approach in which a diverse range of substituted polymers are attainable. In this letter, the position and degree of lithiation was examined by ¹H-NMR spectral analysis of two simple derivatives.

EXPERIMENTAL

Materials

All glassware and Udel® P-3500 polysulfone were dried overnight at 120°C. Tetrahydrofuran (THF) was freshly distilled from Lithium Aluminum Hydride. *n*-Butyllithium was obtained commercially as a 10.5 M solution in hexane. Reactions were performed under a dry argon atmosphere.

Analysis

¹H-NMR spectra were recorded on a Bruker AM 400, 400 MHz spectrometer. Samples were dissolved in CDCl₃ with an internal TMS standard. Chemical shifts δ are expressed in parts per million and are described as singlet (s), doublet (d), or multiplet (m).

Lithiation and Deuteration of Polysulfone

n-Butyllithium (2.1 eq., 0.0105 mol) was added dropwise to a stirred solution of polysulfone (2.21 g, 0.005 mol) in THF (75 mL) at -78°C, during which time a red-brown viscous solution developed indicative of lithiated polymer 2. After 30 min, a solution of D₂O (0.2 mL) in THF (5 mL) was added dropwise to the reaction. The resulting deuterated polymer was precipitated into isopropanol and then dried in

vacuo.

NMR (Unmodified Polysulfone): $\delta = 7.85$, H-d(4H, d); $\delta = 7.24$, H-b(4H, d); $\delta = 7.00$, H-c(4H, d); $\delta = 6.94$, H-a(4H, d); $\delta = 1.69$, CCH₃(6H, s).

NMR (Dideuterated Polysulfone): $\delta = 7.85$, H-d'(2H, d); $\delta = 7.24$, H-b'(4H, d); $\delta = 7.00$, H-c' and H-e'(4H, m); $\delta = 6.94$, H-a'(4H, d); $\delta = 1.69$, CCH₃(6H, s).

Lithiation and Methylation of Polysulfone

Excess iodomethane was added dropwise to a solution of lithiated polysulfone (2.21 g, 0.005 mol) prepared in an identical manner to the previous example. The resulting methylated polymer was recovered as before. Yield = 2.20 g (94%); Degree of substitution ≈ 1.84 NMR: $\delta = 8.12$, H-d''(2H, d); $\delta = 7.26$, H-b''(4H, d); $\delta = 6.96$, H-a''(4H, d); $\delta = 6.88$, H-c''(2H, dd); $\delta = 6.80$, H-e''(2H, d); $\delta = 2.30$, ArCH₃(6H, s); $\delta = 1.71$, CCH₃ (6H, s).

RESULTS AND DISCUSSION

The lithiation of polysulfone (1) was satisfactorily conducted in THF solution with *n*-butyllithium throughout a temperature range of -10°C to -78°C (Figure 1). Temperatures of about 5°C and above resulted in precipitation of the lithiated polymer possibly caused by an intramolecular rearrangement.¹⁴ The presence of the lithiated polysulfone carbanions 2 was manifested by the formation initially of a green-brown and later a red-brown homogenous gel or viscous solution. Upon addition of the electrophile iodomethane or deuterium oxide, the color was immediately discharged. The progress, extent, and position of lithiation was conveniently monitored by high field ^1H -NMR of the methylated and deuterated derivatives.

^1H -NMR Analysis

Figure 2 shows the comparison of the aromatic region of the spectrum of the dideuterated and dimethylated derivative with that of unmodified polysulfone. The unmodified polymer displays two AA'XX' systems arising from each of the pairs of coupled protons on the bisphenol-A portion and the arylsulfone portion.¹ The spectra

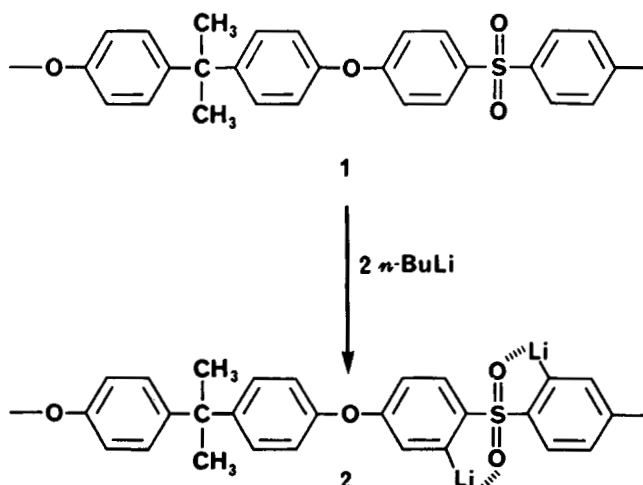


Fig. 1. Metalation of polysulfone with *n*-butyllithium.

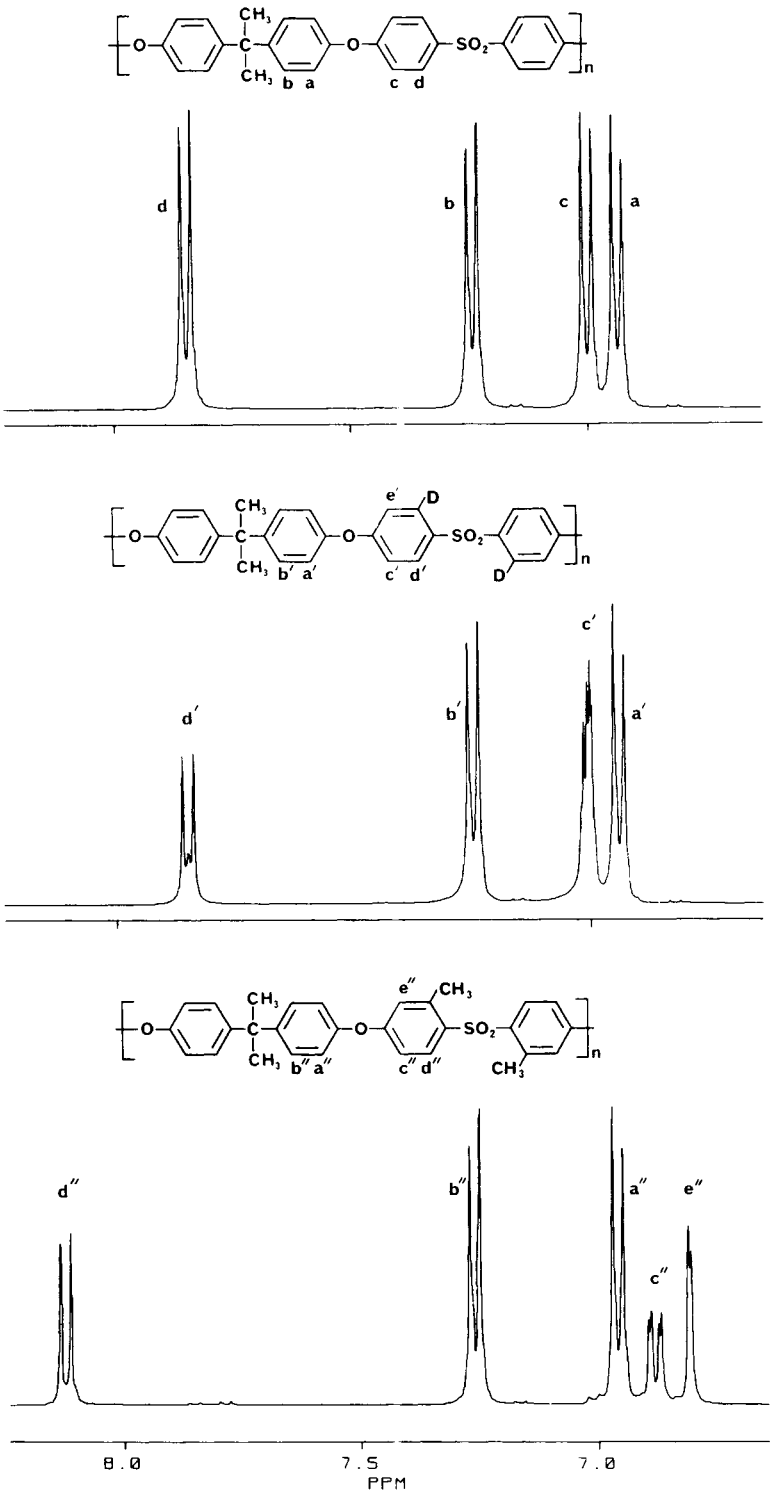


Fig. 2. Partial ^1H -NMR spectra of polysulfone and disubstituted derivatives.

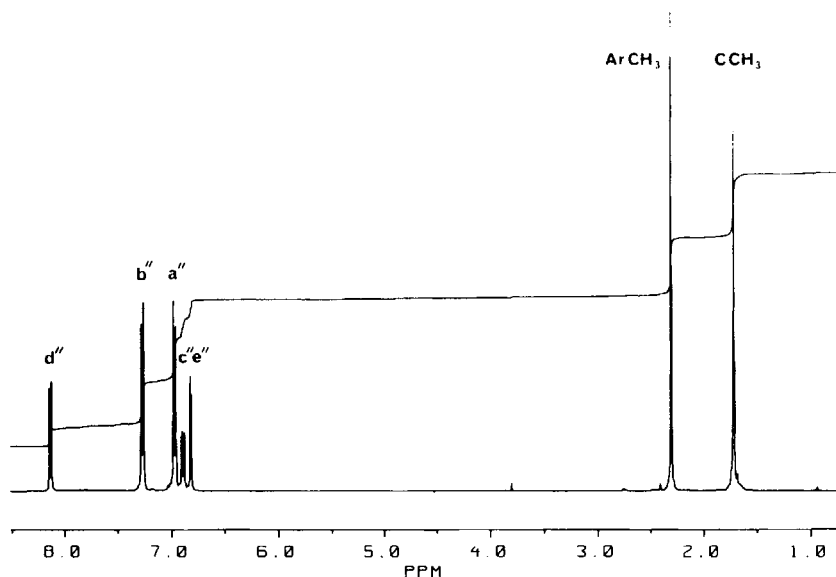


Fig. 3. Complete ^1H -NMR spectrum of dimethyl polysulfone derivative.

of both derivatives show that the bisphenol-A portion remains unchanged and that substitution occurs in the arylsulfone portion.

In the dideuterated derivative, the chemical shifts remain essentially unchanged as expected. A significant feature in the spectrum is the diminution of the downfield ortho-sulfone H-d' from 4H to 2H and the partial collapse of the doublet of the adjacent proton H-c' signifying loss of ortho coupling at H-e' . This multiplet is the result of a complex ABX system where H-c' and H-e' have very similar chemical shifts. The minor signal in the downfield doublet H-d' is thought to be caused by this ABX system rather than a small degree of substitution at H-c' for which there is no evidence in the methylated derivative. Hence, dideuteration/dilithiation occurs primarily at the ortho-sulfone site.

In the spectrum of the dimethylated polymer, the virtual disappearance of the doublet at $\delta = 7.85$ and the appearance further downfield of a new doublet H-d'' of 2H suggests the lithiation/methylation occurs exclusively on separate aromatic rings rather than dilithiation in one ring. Other changes in the aromatic region are the disappearance of the H-c doublet, which is marked by the appearance further upfield of a doublet of doublets (H-c'' ortho and meta coupling) of 2H and a doublet (H-e'' meta coupling) of 2H corresponding to ortho-ether protons. Figure 3 shows the complete spectrum of the dimethyl derivative. The degree of methylation was readily observable by comparison of the dimethyl singlet at $\delta = 2.30$ with that of the bisphenol-A dimethyl. Typically, the degree of dimethylation was over 90%. The chemical shifts of the methyl group ($\delta = 2.30$) and the ortho-sulfone proton ($\delta = 8.12$) are in close agreement with those reported by Montaudo et al. for 2,2'-dimethyldiphenylsulfone.¹⁵

CONCLUSIONS

Polysulfone was controllably lithiated by *n*-butyllithium in THF at temperatures of 0°C and below. The reaction proceeded rapidly and homogeneously in high yield and required little or no excess of reagent and no catalyst. ^1H -NMR analysis of the methyl

and deuterio derivatives indicated that the site of lithiation was at the ortho-sulfone position. Up to two lithium atoms per repeat unit were readily substituted, although lower degrees of substitution were obviously equally readily attainable. The high degree of substitution possible by direct metalation is somewhat unusual in low molecular weight systems and exceptional in polymeric systems where lower degrees of substitution and poor regiospecificity and control are typical.

Lithiation is a versatile method of polysulfone modification because of the known reactivity of lithium aryls with numerous electrophiles.⁹ A more detailed description of the direct metalation of polysulfone and its reactions with other electrophiles will be the subject of further publications.

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