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AROMATIC POLYSULFONES CONTAINING
FUNCTIONAL GROUPS
BY SYNTHESIS AND CHEMICAL MODIFICATION

by

Michael Dominic Guiver, B.Sc., M.Sc.,

A Thesis submitted to
The Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy
Department of Chemistry

Carleton University
Ottawa, Ontario
Canada
June 1987

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ISBN 0-315-46261-2

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ABSTRACT

Aromatic polysulfones containing functional groups were prepared by two synthetic approaches: by copolymerization of a carboxyl containing bisphenol monomer, or by chemical modification of polysulfones. A bisphenol 50 with a pendant fluorene ring was prepared by acid catalyzed phenol condensation of 9-fluorenone-4-carboxylic acid 53. Ionomeric polymers 56 and 57 were obtained by copolymerization of the alkali metal salts of bisphenol 50 and 0-50% of Bisphenol-A with a 4-4'-dihalodiphenylsulfone. The polymers are hydrophilic and have high thermal stabilities and glass transition temperatures. Polymers containing a diversity of functional groups were obtained by direct metalation of Udel 1 or Radel 2 polysulfones. Using organo-lithium metalating agents, the site of lithiation (Figure 6) was exclusively ortho- to the directing sulfone group. A maximum of three lithium atoms per repeat unit could be placed on the polymer chain without degradation. The reaction of electrophiles with the reactive metalated polymer intermediates led to polymers with alkyl, carboxyl, hydroxyl, silyl, halogen and other functional groups. Halogenated polymers 86, 89, and 90 were also prepared by halogenation of polysulfones without a catalyst. The site of halogenation was ortho- to the ether linkages in the bisphenol unit and this underwent metal-halogen exchange preferentially over the site of direct metalation.

ACKNOWLEDGEMENTS

I thank my university supervisor, Prof. John ApSimon for the guidance he has provided. It was a privilege to be allowed to do my research at the National Research Council, Division of Chemistry. I am most grateful to Oleh Kutowy and Edward Capes for their guidance and for arranging generous funding for the project. I also include my thanks to Dave Wiles, the Director and John ApSimon for making this collaboration possible.

Many people at NRC offered their time to help me. Special thanks are due to André Tremblay, Scot Dunlop of the Library, B. McCurdy for some viscometric measurements, D. Cooney for thermal analysis and J. Bornais and S. Brownstein for the large number of NMR measurements. Thanks also to S. Millan, J. Worsfold, P. Black, G. Gardner and to H. Seguin for elemental analysis.

I am especially grateful to my wife, Angela de Wilton, for expertly typing this thesis and offering many helpful suggestions. I appreciate her patience and the endless hours she spent on this. I also thank my parents for the moral support and encouragement they have provided over many years. Since leaving England, I have had too few opportunities to visit them.

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LIST OF SYMBOLS AND ABBREVIATIONS

Ac	acyl
Ar	aromatic
br.	broad
Bu	butyl
d.	doublet
DMA	dimethylacetamide
DMF	dimethylformamide
DMSO	dimethylsulfoxide
D.S.	degree of substitution
DSC	differential scanning calorimetry
Et	ethyl
eq.	equivalent
GPC	gel permeation chromatography
HMPT	hexamethylphosphoric triamide
IR	infrared
J	coupling constant
LDA	lithium diisopropylamide
m.	multiplet
Me	methyl
min.	minutes
M.Pt.	melting point
MS	mass spectroscopy
M.W.	molecular weight
NMP	N-methylpyrrolidinone
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
q.	quartet
s.	singlet
st.	stretch
t.	triplet
T	glass transition temperature
TG	thermogravimetry
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
TMS	tetramethylsilane
t	GPC retention time
$[\eta]$	intrinsic viscosity

to Angela

INTRODUCTION

Aromatic polysulfones are high performance thermoplastics¹ which are suited to applications requiring superior physical and chemical properties. They possess desirable features, such as excellent mechanical strength, thermal stability and chemical resistance, enabling their use in extreme process conditions. Ultrafiltration is one important area in which polysulfones are widely used as membranes or support materials. Although the aromatic polysulfones are considered to be among the best polymers for these purposes, one of the shortcomings has been their relatively hydrophobic nature which has limited their use in some aqueous applications. The hydrophilic/hydrophobic balance is one important polymer characteristic which plays a role in determining membrane separation properties such as flux, adsorption, and selectivity. This balance can be altered by introducing functional groups which increase either the hydrophilicity or the hydrophobicity of the polymer while still maintaining the desirable mechanical and chemical properties of the parent polysulfone. In view of the superior membranes that have resulted from chemical modification, surprisingly few synthetic techniques have been employed. Present modification methods are constrained by less than complete control of the degree of substitution and the limited choice of functional groups

that have been used. The aim of the work described in this thesis is the development of new methods to introduce functional groups on polysulfone with consideration to the control of degree of substitution and variety of functional groups. Two main approaches to the synthesis of functional group modified polysulfones are discussed.

The first approach involves the synthesis of a monomer containing a hydrophilic functional group and subsequent copolymerization leading to a derivatized polymer. The limitation to this approach is that the type of functional group is restricted to the one included in the synthesis of the monomer. The synthesis of the monomer may be time consuming and it may have lower than expected reactivity, revealed only at the polymerization stage. Accordingly, more emphasis was placed on the second more versatile approach.

The second approach is polymer derivatization, which entails the introduction of functional groups by chemical modification of polysulfones. Two methods have been developed. The most significant is the controlled direct metalation of polysulfone leading to a diverse range of products. This technique is the most promising because the degree of substitution and the type of functional group can be controlled. Another merit is the rapidity and simplicity of the procedure and the apparent absence of cross-linking or polymer degradation. The other method is

closely related and consists of a two step process whereby polysulfone is first brominated, providing a site which may then be metalated preferentially over the site of direct metalation. This has similar benefits to the direct metalation with the exception that more steps are required and there is slightly less control over degree of substitution.

The structure and properties of aromatic polysulfones, their synthesis and previous modification procedures will be discussed in the Introduction. Metalation techniques on other polymers are also reviewed.

The Structure and Properties of Polysulfones

Four structural types of polyarylethersulfones are commercially available at present.^{2,3} Udel[®] Polysulfone 1 is more usually known simply as Polysulfone.^{*} Until recently, it was manufactured by Union Carbide but it is now controlled by Amoco. This was the first and most market developed polymer and is available in several grades for different applications.

Amoco also manufactures another less prominent polymer called Radel[®] or polyphenylsulfone 2 which is produced on a small scale for research purposes.

Polyethersulfone 3 is produced by ICI under the trade name Victrex[®] PES. This polymer is the major competitor to

^{*}IUPAC: Poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene]

Udel and has similar market applications.

Another product comprising a copolymer containing repeat units 4 was developed under the name Astrel[®] 360 but is no longer commercially available from this company. ICI also manufactures a copolymer called Victrex 720P containing the same structural repeat units.

The presence of the highly polar sulfone group in aromatic polysulfones is responsible for many of the physical properties of these polymers. With few exceptions, aromatic polysulfones are amorphous, rigid, tough thermoplastics. The reason for the lack of crystallinity is surmised to be due to the difference between the bond angle of the tetrahedral diarylsulfone (105°) and the larger bond angle of the diarylether group which would not readily allow the structure to form a crystal lattice. The polarity and conjugative resonance of the diarylsulfone

group with the aromatic rings impart rigidity, toughness and strength to the polymers and result in high glass transition temperatures (T_g). This chain stiffness would be excessive by itself but it is balanced by the flexibility of the diarylether linkage which imparts tractability. This combination of structural features provides thermoplastics with outstanding performance characteristics to which few other polymers can compare.

The polymers exhibit excellent oxidation resistance and thermal stability. The continuous use temperature is often limited by T_g rather than thermal oxidative degradation. The inherent hydrolytic stability of the bonds in the polymer chain impart chemical resistance to extremes in pH, even at elevated temperatures. However, one disadvantage of these polymers is their poor resistance to many chlorinated and aromatic hydrocarbons, ketones and esters. Polysulfones have been used in areas requiring demanding performance because of their fire, thermal, and hydrolytic resistance, transparency and mechanical and electrical properties. These include materials for appliances, electrical and electronic components, aircraft and automotive parts, medical and surgical components and processing equipment, particularly membranes and membrane supports.

In ultrafiltration applications, polysulfones are important materials which have superior properties over

most other polymer membrane materials. Their high temperature limit allows heat sterilization which is advantageous in biotechnology applications. Polysulfone membranes are stable over the whole pH range (1 to 14) and have a good resistance to chlorine cleaning cycles which are shortcomings of polyamide and cellulosic membranes. Chemical resistance to aliphatic hydrocarbons and other solvents also allows non-aqueous applications such as oil separation. The superior film forming qualities, strength, dimensional stabilities and creep resistance of polysulfones are further desirable qualities which enable their use as both membranes and membrane supports for other polymers.

Synthesis of Polysulfones

Polyarylethersulfones were discovered independently and nearly simultaneously by Union Carbide Corporation,¹⁰ 3M Corporation,¹¹ and ICI.^{11,12} The two principal synthetic routes that have been utilized for these polymers are polysulfonylation (A,B) and aromatic nucleophilic displacement or polyetherification (C,D) which are represented generally by the formulae:

The polysulfonylation reactions A and B are electrophilic aromatic substitutions or Friedel-Crafts acylations. The ether substituents on the aromatic rings activate this type of reaction leading to polyarylether sulfones. The polyetherification reactions C and D are aromatic nucleophilic substitutions whereby an alkali metal phenoxide displaces aromatic halogen activated by the electron withdrawing para-sulfone linkages. ICI examined both processes^{11,12} but eventually adopted the polyetherification method whereas Union Carbide examined only the polyetherification synthesis.¹⁰⁻¹⁶

Synthesis by Polysulfonylation

The polysulfonylation route^{3, 17, 18} to aromatic polyethersulfones was developed independently by both ICI^{11, 13} and 3M.⁹ The general type of reaction involved is an adaptation of the well known Friedel-Crafts¹ condensation of aromatic sulfonyl chlorides with aromatic rings. Although this reaction is similar to a Friedel-Crafts acylation, which normally requires stoichiometric amounts of catalyst, a key difference in this case is the requirement of only small amounts of catalyst. In this respect the reaction more closely resembles a Friedel-Crafts alkylation with the important distinction that polysulfonylation gives predominantly para-substitution because of the electron withdrawing character of the sulfone group rather than branched structures expected in polyalkylations.²⁰

The catalysts that have been found effective in trace amounts are FeCl_3 , InCl_3 , SbCl_5 , MoCl_5 and $\text{CF}_3\text{SO}_3\text{H}$ with anhydrous ferric chloride being the preferred one.²¹ Other typical Friedel-Crafts catalysts such as AlCl_3 , BF_3 or ZnCl_2 are required in stoichiometric quantities and hence are not as favourable because of the inconvenience of eliminating the catalyst from the final product. Two methodologies A and B for polysulfonylation have been used as outlined previously.

One of the earliest reported syntheses of polyether-

sulfone 3 outside the patent literature was by Cudby et al.^{20, 22, 23} The polymer was prepared by ferric chloride catalyzed polysulfonylation of a disulfonyl chloride 5 with a reactive dinuclear aromatic compound 6. The polycondensations were conducted in the melt or more suitably in nitrobenzene. The use of equimolar proportions of AlCl_3 or FeCl_3 catalyst led to low molecular weights, contrary to earlier work by other authors,²⁴ whereas trace amounts of FeCl_3 gave a high molecular weight polymer. The predominant repeating unit of the product was para-substituted polyethersulfone 3 but there was also a significant proportion (c. 20%) of ortho-substituted units 7. The polycondensation was not subject to the classical effects of stoichiometric disturbance and gave high molecular weight material with up to 1.5 mol excess of disulfonyl chloride. Small amounts of branched units were also detected represented by the formula 8.

Polyethersulfones have also been synthesized^{17, 23, 25} by three variants of the polysulfonylation method in the melt and in solution and their structural conformity was compared. The self-condensation of the monosulfonyl chloride 9 led essentially to the all para-substituted polyethersulfone 3.

Similarly, the polysulfonylation of 5 with bis(di-phenylether)sulfone produced the same product 3 with little evidence of ortho-substitution. This exclusive para-formation in these two examples differs from the polysulfonylation of 5 and 6 in the earlier example where approximately 20% ortho-substitution occurs. An explanation suggested²⁰ for these structural differences is that the electronic effects of the sulfone group act via an ether bridge on the orientation of the reactions in

adjacent rings. Other polysulfone structures have been synthesized in the melt^{17,22} and in solution.^{17,21} Two component polysulfonylation in the melt produced predominantly low molecular weight polymers with reduced viscosities in the order of 0.1. Self condensation of various monomers in solution polymerization resulted in generally higher molecular weights.²¹ Astrel 360 4 was prepared by solution condensation of biphenyl with disulfonyl chloride 5. The polymer has an exceptionally high glass transition temperatures of 275°C and is slightly crystalline, unlike most other polyethersulfones.

Polyethersulfones have also been obtained by direct polycondensation of disulfonic acids with aromatic hydrocarbons or by self-condensation of sodium aryl sulfonates using polyphosphoric acid.^{24,26} The molecular weights in these examples were low but a recently reported self-condensation using a sulfonic acid salt 10 with phosphorus pentoxide/methane sulfonic acid led to high molecular weight polyethersulfone 3.²⁷

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Synthesis by Aromatic Nucleophilic Displacement

Johnson et al.¹ first reported in 1967 the synthesis of a series of polysulfones, including Udel, by the aromatic nucleophilic displacement reaction. Almost simultaneously another group² reported the synthesis of polyphenylene sulfide, commercially known as Ryton, by the same type of reaction. Since then a wide variety of high performance engineering thermoplastics such as polyarylethers, polythioethers, polyethersulfones, polyetherketones and polyetherimides have been made by aromatic nucleophilic displacement polymerization.

Although the aromatic nucleophilic displacement reaction, which is a form of the Williamson ether synthesis,³ has been known for a considerable time,⁴ its synthetic importance was not fully recognized until comprehensive reviews appeared much later.⁵⁻⁷ Since then several reviews and key papers relating specifically to polymerization by aromatic nucleophilic displacement have been reported.^{2,4,7,15,16-17} The effectiveness of this reaction to produce high molecular weight polymers depends upon a number of factors, such as reaction conditions and rate, to maximize efficiency. This may be illustrated by the synthesis of Udel polysulfone by polycondensation of the sodium salts of Bisphenol-A 11 with the activated dihalo-aromatic compound dichlorodiphenyl-sulfone 12.¹

In the sulfone monomers, the established order of reactivity of the halogens $F \gg Cl \gg Br \gg I$ is unexpected, implying no bond breaking in the rate determining step^{31, 32} since the C-F bond is the strongest of these. It has been suggested that the high bond polarity and low steric hindrance of the C-F bond contribute to increased electrophilicity of the carbon under attack. Strongly electron withdrawing para-substituents such as sulfone activate the aromatic nucleophilic displacement (S_NAr) by stabilization of the intermediate Meisenheimer complex 13 by accepting negative charge from the bisphenate (resonance structure 14). This further increases the polarity of the carbon-halogen bond.^{22, 39}

The reactivity of various bisphenates is another important consideration which has been studied by several groups.^{4, 33, 41} Electron accepting substituents on bisphenates delocalize the negative charge on oxygen causing the phenolate to become less basic and therefore less reactive. Thus, Bisphenol-A 15 which contains electron donating methyl groups is approximately 800 times more reactive⁴¹ than Bisphenol-S 16 which contains the strongly electron withdrawing sulfone group.

Similarly, polysulfones prepared from bisphenols containing cyclic aromatic residues (referred to as cardic polymers) are obtained as low molecular weight polymers under normal conditions because the electron delocalization of the pendant aromatic substituent increases the acidity of the bisphenol, thus lowering its reactivity. Accordingly, the more reactive 4,4'-difluorodiphenylsulfone 17 must be used with bis(4-hydroxyphenyl)-9-fluorene 18 to obtain high molecular weight polymer 19.

Phenolate reactivity also depends on the counter ion. Potassium phenolates are more reactive than sodium phenolates because of higher charge polarity. However, their

lower solubility may limit their utility. Group I and II metal counter ions other than sodium and potassium are not useful because of insolubility.

A partial summary of polysulfones, prepared by aromatic nucleophilic displacement using different types of bisphenols, is shown in Table I. Glass transition temperatures (T_g) are also shown. Most of the examples shown were prepared by three groups.

Table I

Polysulfones prepared by Nucleophilic Displacement

	T_g ($^{\circ}\text{C}$)	Ref
$\left[\text{O}-\text{C}_6\text{H}_4-\text{X}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_n$ <p style="text-align: center;">20</p>		
X=CMe	195	4
X=nil ²	230, 220	4, 15
X=CH	180	4
X=CF ₃ CCF ₃	205	4
X=O	180	4
X=S	175	4
X=MeCPh	200	4
X=PhCPh	230, 190	4, 41
X=1,1-cyclohexyl	205	4
X=carbonyl	205	4
X=SO ₂	245	4
$\left[\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_n$ <p style="text-align: center;">3</p> <p style="text-align: center;">(Selfcondensation)</p>		
		47
$\left[\text{O}-\text{C}_6\text{H}_4-\text{X}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_n$		
21 X=O		
22 X=S		
X=O ³	210, 207	4, 48
X=S	188	49, 50

Table I (continued)

	T_g ($^{\circ}\text{C}$)	Ref
--	------------------------------	-----

23

X	R ₁	R ₂		
CMe ₂	H	H	184	46
Nil ²	Me	Me	262	46
CMe ₂	Me	H	178	46
CMe ₂	Me	Me	230, 235	46, 4
CMe ₂	CHMe ₂	CHMe ₂	175	46
CMe ₂	Cl	H	205	4

24

Aromatic Residue

Phenolfluorene	270	41
Phenolphthalein	260	41
Phenolphthalein imide	295	41
Phenolanthrone	265	41

25

X=nil

51

X=O

51

Table 1 (continued)

	T_g ($^{\circ}\text{C}$)	Ref
<p>26</p>		
		52, 53
<p>27 $\text{X}=\text{CMe}_2$ 28 $\text{X}=\text{SO}_2$</p>		
$\text{X}=\text{CMe}_2$ $\text{X}=\text{SO}_2$		54, 55 56

The reaction conditions used in these polymer syntheses are generally those developed by Johnson et al. This involves the formation of an alkali metal bisphenate under substantially anhydrous conditions in dimethyl sulfoxide (DMSO) using stoichiometric quantities of sodium or potassium hydroxide. The most useful solvent is DMSO in which the metal counter ion, bisphenate and growing polymer chain are soluble and react with the dihaloarylsulfone at about 160°C. Sulfolane (tetramethylene sulfone) may be used at higher temperatures, but a base consuming side reaction precludes long reaction times. The synthetic conditions of Johnson et al. have some shortcomings because exact quantities of alkali are required. A slight excess of sodium hydroxide causes hydrolysis of dichlorodiphenylsulfone, thus upsetting the stoichiometry. A slight deficiency of sodium hydroxide results in unreacted phenol groups forming hydrogen bonds with phenate, thus reducing nucleophilicity and upsetting stoichiometry.

Recently however, Hendrick et al.,⁵⁸⁻⁶¹ developed a new method using excess potassium carbonate in N-methylpyrrolidinone (NMP). This procedure offers some advantages. Weakly basic potassium carbonate does not hydrolyse dichlorodiphenylsulfone, so excess base may be used. Accordingly, both monomers may be co-reacted simultaneously while the bisphenate is being formed.

Self-condensation by aromatic nucleophilic displace-

ment is an alternative synthetic route to polysulfones. Chlorophenoxide 29, is readily obtained by controlled hydrolysis of dichlorodiphenylsulfone,^{57, 62, 63} and gives polyethersulfone 3 by self-condensation.^{47, 64} This is currently the preferred method of synthesis by over the Friedel-Crafts method^{3, 65, 66} for ICI's polyethersulfone. However, the advantages of a single monomer polymerization are tempered by the lower reactivities of both the halogen and phenoxide by the bridge effect.

Phase transfer catalysis⁶⁷ has also been employed in preparing a fluorinated polysulfone 26 from bisphenol-S 16 and hexafluorobenzene^{52, 53} and also a nitro containing polysulfone 27 using potassium fluoride as the base.⁵⁵ The synthetic advantages of this technique are that the phenolate anion is less solvated in the organic phase and that only the aqueous phase is basic, thus protecting the activated halide from hydrolysis.

Chemical Modification of Polysulfones

The most important chemical modification of polysulfone to date is sulfonation. The sulfonation of Udel polysulfone, first reported by Quentin,⁶ was accomplished by simultaneous addition of polymer solution and a solution of either chlorosulfonic acid, sulfur trioxide or sulfur trioxide/dioxane complex. Later, Noshay and Robeson⁶ reported the sulfonation of Udel utilizing a 2/1 sulfur trioxide/triethyl phosphate complex and obtained compositions varying from 0.1 to 1.0 sulfonate groups per repeat unit of polymer. The use of this complex minimizes crosslinking due to sulfone forming side reactions.⁷ The site of sulfonation occurs at the expected electrophilically activated site as shown in the structure of the polymer repeat unit 30. The sulfur trioxide/triethyl phosphate method is considered superior since chlorosulfonic acid is capable of cleaving polysulfone at the isopropylidene link. The structure and properties of sulfonated polysulfone have been reported elsewhere¹¹⁻¹⁴ as well as in a detailed synthetic account.⁷⁵

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The incorporation of sulfonate ions into polysulfone changes its properties markedly in several ways. The glass transition temperature is elevated from 190°C up to as high as 320°C in examples of higher substitution.¹³ Solvent resistance is enhanced and the material in membrane form displays remarkable selectivity of water versus ion passage. Consequently, these improved materials have found extensive use as ion exchange and hydrophilic membranes for ultrafiltration, electrodialysis and reverse osmosis applications.^{14,15,16} Sulfonated polysulfone membranes that have been produced have excellent salt rejections and water fluxes that are maintained even for high salt concentrations. In addition, their resistance to chlorine containing cleansers is an notable benefit.

Other hydrophilic polysulfones for reverse osmosis membranes have been prepared by sulfonation of a copolymer comprising a mixture of repeat units 3 and 21 with 98% sulfuric acid followed by the conversion of the resulting sodium sulfonate group to sulfonyl chloride using thionyl chloride. The pendant sulfonyl chloride groups were converted to sulfonamide groups from which membranes were made.¹⁷ Similarly, chlorosulfonated Udel was obtained by chlorination of sulfonated polymer with phosphorus pentachloride. Conversion to the sulfonamide with an amine gave a weakly anionic polysulfone sulfonamide.¹⁸

Chloromethylation is another significant modification

procedure for polysulfone but its widespread use depends on the avoidance of the well known carcinogenic reactants chloromethylmethyl ether and bis-chloromethyl ether. Daly et al.¹⁵⁻¹⁷ reported the chloromethylation of Udel polysulfone using chloromethylmethyl ether prepared in situ and stannic chloride catalyst. Chloromethylated polymers 31 were also prepared employing 1,4-bis(chloromethoxy)butane or 1-chloromethoxy-4-chlorobutane with a Lewis acid catalyst. These reagents are as efficacious as chloromethylmethyl ether but their lower vapour pressures minimize personal exposure. Long chain halomethylalkyl ethers with reduced volatility such as bromomethyl octyl ether have also been used effectively in place of more toxic reagents in the bromomethylation of Udel polysulfone.¹⁸ As with sulfonation, chloromethylation or bromomethylation occurs at the electrophilically activated site ortho- to ether on the Bisphenol-A portion of polysulfone as shown by chloromethylated polysulfone 31.

These polymers readily underwent quaternization¹⁵⁻¹⁷ with a variety of amines to give polymers and membranes¹⁸ with

anion exchange capacity. A typical example is the trimethylquaternary ammonium salt derivative 32.

32

A recent Patent Application reports the preparation of chloromethylated polysulfone semipermeable membranes and their subsequent reaction with polyethyleneimine, polyvinylamine or other amines or polyvinylalcohol to give crosslinked products.⁹⁰ Several other post-modification reactions on the chloromethyl group were as follows. Aminomethyl groups were obtained by reaction with potassium phthalimide and then ethanolic hydrazine. Cyanomethylated polymers were obtained by reaction with sodium cyanide. Treatment of chloromethyl groups with sodium acetate followed by sodium hydroxide resulted in hydroxymethylated polymers. A large variety of other derivatives from chloromethylated polysulfone are potentially available by analogy to those prepared from chloromethylated polystyrene via phase transfer catalysis and reviewed by Fréchet.⁹¹

Methyl substituted polysulfone of the formula 23 ($X = \text{CMe}_2$, $R_1 = \text{Me}$, $R_2 = \text{H}$), when treated with *N*-bromosuccinimide (NBS) and benzoylperoxide⁹² or with bromine⁹³ gave a bromo-

methyated product, from which membranes could be cross-linked by treatment with nitrogen compounds. Also briefly mentioned was the preparation of a chlorobutyl polysulfone derivative 33 by lithiation.''

33

Since the work on polysulfone lithiation started for this thesis, another author most recently reported the metalation of Udel polysulfone.''' During re-examination of the lithiation and carboxylation of poly(2,6-dimethylphenylene)oxide 34,''' polysulfone was subjected to the same procedure by treatment of a THF solution of polymer with *n*-butyllithium at room temperature followed by carbon dioxide. Uneven carboxylate substitution resulting from heterogeneous reaction conditions was observed. The structure and degree of substitution of the product were not discussed.

34

Phosphorus containing polysulfones 35a have been synthesized using phosphorus trichloride in the presence of aluminium chloride.¹⁵ Other phosphates were obtained by post-treatment with nitric acid 35b or sodium hydroxide 35c. Similarly, acylated polysulfones 35d for perm-selective membranes were synthesized using acetyl chloride in the presence of aluminium chloride.¹⁶

- 35a R = P(OH)₂
 35b R = PO(OH)₂
 35c R = P(ONa)₂
 35d R = COCH₃

Polyarylethersulfones have been nitrated using the procedure of Crivalo¹⁷ with metal nitrates in trifluoroacetic anhydride^{18,19} thus avoiding degradative nitric/sulfuric acid mixtures. Amine derivatives can be obtained by reduction of nitrated polysulfone with sodium dithionite. Alternatively, direct aminomethylation of polyarylethersulfone can be effected by phthalimidomethylation with N-hydroxymethyl-phthalimide and subsequent hydrazinolysis.^{20,21,22}

Much interest has been shown recently in modifying

thermoplastics, including polysulfone, with pendant or end capped reactive groups for crosslinking.¹⁰¹⁻¹⁰³ The use of these lightweight high strength resin matrices in fibre composites is anticipated in commercial aircraft and other demanding applications where performance under load and exposure to aircraft fluids must be relied upon.¹⁰⁴ Polysulfones or oligomers of polysulfone have been modified by end capping with norbornyl,¹⁰⁵ cyanato,¹⁰⁶ vinylbenzyl¹⁰⁷ and ethynyl groups.¹⁰² These are among the few groups that are able to undergo thermal crosslinking without the release of volatile by-products and result in a resin matrix with improved solvent resistance and other properties. A polysulfone oligomer containing pendant vinyl and ethynyl groups was synthesized in several steps from the parent oligomer.¹⁰⁷ Thus chloromethylated oligomer 36a was transformed to phosphonium salts 36b with $P(Ph)_3$ and then subjected to a phase transfer catalyzed Wittig reaction to give oligomers with pendant vinyl groups 36c. Brominated derivative 36d, obtained by bromination of 36c, was converted to polysulfone oligomer containing pendant ethynyl groups 36e by a base catalyzed dehydrobromination.

- 36a R = CH₂Cl
 36b R = CH₂P(Ph)₂Cl⁻
 36c R = CH=CH
 36d R = CHBr-CH₂Br
 36e R = C≡CH

A different approach was taken by Reinhardt *et al.*¹⁰⁸ in the preparation of a polysulfone containing main chain ethenyl and ethynyl groups derived from an appropriate bisphenol monomer. The relatively mobile linear polymer undergoes an intramolecular cycloaddition reaction upon thermal curing resulting in a rigid polymer backbone containing a cyclic aromatic system.

Numerous block copolymers¹⁰⁹ have been prepared from both hydroxy- and chloro- terminated polysulfone oligomers, but their relevance is outside the scope of this thesis.

Review of Polymer Modification by Lithiation

The major topic of this thesis is concerned with the modification of polysulfone by direct lithiation and, less importantly, by bromination and lithiation. It is therefore appropriate to give a necessarily brief review of other polymer modifications by these methods with special emphasis on direct lithiation.

The greatest activity in functionalized polymers has been with the modification of polystyrene 37 and its divinylbenzene crosslinked counterpart. These functionalized materials have proven useful in applications such as Merrifield's¹¹⁰ polymer supported solid-phase peptide synthesis, as reagents, protecting groups, chromatographic or catalytic supports. These applications of functionalized polymers have been reviewed in several places.¹¹¹⁻¹¹⁶ The advantages associated with polymeric reagents, catalysts or protecting groups are simplification of processing, reduced toxicity over low molecular weight counterparts and a capacity for recycling.

Two reaction routes have been utilized for the lithiation of soluble and crosslinked polystyrene. Both Chalk¹¹⁷ and Yampol'skaya et al.¹¹⁸ independently developed the direct lithiation of soluble polystyrene 37a using excess n-butyllithium/TMEDA^b complex in the non-polar

^bTetramethylethylenediamine

solvent cyclohexane. Later it was shown that the site of lithiation occurred in both the meta- and para- ring positions 37b in the statistical ratio of 2:1, apparently due to the equivalent kinetic acidities of the protons at both sites.¹¹⁹⁻¹²¹

37a	R = H
37b	R = meta:para Li (2:1)
37c	R = COOH
37d	R = OH
37e	R = SH

The nature of the lithiating agent determines the overall degree of substitution. Using excess sec-butyllithium/TMEDA complex, 40% lithiation occurs but where n-butyllithium/TMEDA complex is used only 25% substitution results.¹²²

Similar chemistry has been extended to crosslinked divinylbenzene-polystyrene resins which have greater utility as polymeric supports and catalysts. Fyles et al.¹²³ obtained a carboxylated resin 37c by lithiation of a lightly crosslinked resin with n-butyllithium/TMEDA complex

followed by treatment with carbon dioxide. Analogous mixtures of meta- to para- substitution are found in crosslinked resins as are found in linear polystyrenes.^{122, 124, 125} Lithiation at the ortho-position has not been observed in either linear or crosslinked polystyrene due to the steric effects of the main chain. However, some degree of lithiation at this position was observed in a short chain model compound equivalent to four repeat units of polystyrene.¹²² Up to 23% substitution of carboxyl groups on crosslinked resin has been obtained using *n*-butyllithium/TMEDA with a non-polar solvent such as cyclohexane or heptane.¹²⁶ More polar solvents such as THF or benzene are unsuitable. A detailed account of the lithiation of crosslinked polystyrene and subsequent preparation of some nucleophilic resins containing hydroxyl groups 37d and thiol groups 37e is presented by Frechet et al.^{126, 127}

The second method of preparing lithiated polystyrene is by lithiation of halogenated polystyrene, prepared either by polymerization of halogenated monomer or by polymer halogenation. Polystyrenes have been iodinated with iodine/iodic acid¹²⁸ or brominated using bromine with iron,¹²⁹ bromine with iron (III) salts,^{126, 130} or bromine with stoichiometric¹³¹⁻¹³⁴ or catalytic amounts of thallium (III) salts.¹²⁶

Bromination catalyzed by iron (III) often results in

inhomogeneous substitution and troublesome removal of catalyst. Stoichiometric thallium (III) brominations result in cleaner products but have the obvious disadvantages of cost and toxicity. However, these are somewhat alleviated by using catalytic amounts of thallium (III) salts.¹²⁶ Using these methods, up to 4 meq bromine (approximately 50% ring halogenation) was substituted predominantly in the para-position 38a. Halogenated polystyrene can also be synthesized from appropriately substituted monomers.^{135, 136}

Numerous derivatives have been prepared from reactions of various ~~electrophiles~~ with lithiated p-bromostyrene 38b.^{126, 127, 133, 137-142} A selection of electrophiles and their corresponding derivatives 38 prepared by bromination-lithiation of polystyrene is shown below.

38

Polymer	Substituent	Electrophile
38a	Br	-
38b	Li	-
38c	PhC(OH)Ph	PhCOPh
38d	PhCHOH	PhCHO
38e	PhCO	PhCN
38f	MeCO	MeCN
38g	CHO	CHONMe
38h	COOH	CO ₂
38i	SH	S ₂
38j	SMe	MeSSMe
38k	OH	O
38l	CONHPh	PhNCO
38m	B(OH) ₃	B(OMe) ₃
38n	PPh ₃	PPh ₃ Cl ₂
38o	SiMe ₂ Cl	SiMe ₂ Cl ₂

A further class of functional group polystyrenes is derived from the reactive chain ends of alkylolithium initiated, anionically polymerized styrene.¹⁴³ This type of polymerization usually proceeds without spontaneous termination, resulting in a lithiated carbanionic chain end polystyrene which can be converted to a functional end group by reaction with an appropriate electrophile.¹⁴⁴ For example, polystyrene with a primary amine chain end has been synthesized by terminating anionically polymerized styrene with metalated methoxyamine.¹⁴⁵

Chalk and Hay discovered the direct metalation of poly(2,6-dimethyl-1,4-phenylene ether) 34, a commercial polymer, using a butyllithium/TMEDA complex.¹⁴⁻¹⁶ Both the aromatic ring 39a and the methyl group 39b are lithiated slowly in benzene at 80°C and rapidly in THF at 25°C. There is an apparent kinetic preference for ring lithiation which isomerizes to the thermodynamically favoured benzylic position. Thus, the distribution of lithium on the polymer in benzene is 50% ring substituted and 23% side chain after 21 minutes, with the ratios approximately reversed (46% versus 19% after 19 hours. A similar situation occurs when THF is used. Benzylic substitution products are exclusive when organosodium or potassium metalating agents are employed.

39a

39b

The lithiated polymer 39 reacted smoothly with a variety of electrophiles including carbon dioxide, dimethyl sulfate, several ketones, organophosphoryl and organosilyl chlorides, iodine and diphenyl disulfides. Other electrophiles such as sulfur, carbon disulfide, thionyl chloride

and acid anhydrides or acid chlorides resulted in insoluble gels. A small degree of crosslinking occurred with silylchlorides. Since the initial papers, other authors^{149, 150} have studied the synthesis and properties of the carboxylated derivatives.

Lithiated polymer 39 has also been used as an initiator for the anionic graft polymerization of styrene¹⁵¹ as well as isoprene, methyl methacrylate, hexamethylcyclotrisiloxane and phenyl isocyanate.¹⁵² The styrene graft copolymers contained substantial amounts of styrene homopolymer implying initiation from solvent metalated species. This is consistent with the lack of styrene homopolymer produced in THF where the metalated solvent species, lithium alkoxides, are incapable of initiating styrene polymerization.¹⁵¹ Soluble graft polymers were obtained with the other monomers with the exception of phenyl isocyanate in THF which gave a crosslinked gel.¹⁵²

Structurally similar polymers poly(2-methyl-6-phenyl-1,4-phenylene ether) 40a and poly(2,6-diphenyl-1,4-phenylene ether) 40b have also been metalated.^{147, 153-155} Analogous derivatives and graft copolymers were obtained from the expected main chain and aliphatic side chain reactive lithiated sites on the polymers.

40a R = Me

40b R = Ph

The lithiation of poly(styrenesulfone) 41, a potential resist material in high resolution lithography, has been reported by Fréchet *et al.*^{156, 157} This is an example of a hetero-atom directed lithiation^{158, 159} where the sulfone coordinates the metalating agent, directing lithiation up to a total of three adjacent alpha sites per repeat unit. One (42) or two (43) sites may be lithiated directly and a third (44) by subsequent reaction as shown in Figure 1. The disadvantage of this modification is the substantial loss of molecular weight since the polymer is sensitive to chain scission in the presence of base.

Figure 1

Stepwise Lithiation of Poly(styrenesulfone)

Another interesting hetero-atom directed polymer lithiation is that of poly(vinylthiophene) 45a.¹⁵ Both thiophene and sulfone are efficient directing groups for lithiation¹⁵ which result in high levels of regiospecific substitution in polymers incorporating these functionalities. Thus, the metalation of poly(vinylthiophene) with a stoichiometric quantity of n -butyllithium resulted in one lithium atom per polymer repeat unit exclusively alpha to sulfur 45b.

45

45a R = H
 45b R = Li
 45c R = COOH
 45d R = D
 45e R = CH₃
 45f R = CONHPh

45g R = SMe
 45h R = C(OH)Ph
 45i R = I
 45j R = PPh₂
 45k R = SiMe₃

High degrees of substitution were obtained for 45c-f, derived from electrophiles carbon-dioxide, deuterium oxide, dimethyl sulfate and phenylisocyanate respectively. Other electrophiles less reactive to this system gave intermediate levels of substitutions for derivatives 45g-k.

Other polymers that undergo direct metalation include polyamides,¹⁶¹ poly(vinylfluorene) 46¹⁶²⁻¹⁶⁴ and poly-acenaphthylene 47.¹⁶⁵

46

47

RESULTS AND DISCUSSION

Functional group containing polysulfones were prepared by two distinct synthetic strategies. The general advantages and drawbacks to each approach are outlined here.'''

The first approach entails the synthesis and polymerization of a functional group containing monomer. The synthesis of new functional monomers is frequently tedious or difficult and low yields may be obtained if several synthetic steps are involved. The monomer must be highly purified since condensation reactions require exact stoichiometric ratios of monomers to achieve adequate polymerization and any impurity could interfere with this process. Polymerization of the purified monomer may be slow or incomplete because of several unexpected factors, leading to low molecular weight products. The functional group may have an adverse electronic effect on monomer reactivity or it may interfere sterically. Limited solubility may also prevent homogeneous polymerization. Consequently, this is not the most frequently used method of making functional group polymers. However, one advantage is the well known and defined structure of the functional polymer produced by the condensation polymerization method, providing no unexpected side reaction occurs. Another is the potential for introducing functional groups at different sites, such as, in the main chain, attached to

the main chain (pendant) or as end groups.

A simpler and more usual way to prepare functional group polymers is by starting with a well defined and characterized polymer and then introducing functional groups by chemical modification. The advantages of this approach are that the overall properties and molecular weights of the starting polymer are already established and that usually only one or two steps are required. Frequently, one modification technique can be exploited to produce several different derivatives, a shortcoming of the monomer approach. Several different functionalities may be incorporated on the same polymer to act as solubilizing or compatibilizing agents, anchoring groups or hydrophilic modifiers. Attendant disadvantages are that chain scission or polymer degradation may occur or conversely, cross-linking. Fortunately, aromatic polysulfones are chemically very resistant and chain scission rarely occurs, excepting one sulfonation technique.⁷⁵ The solubility of the modified polymer during synthesis may impede any further derivatization. In cases where reactive groups are replaced by functional groups, complete reaction is desirable to avoid any possible side reactions. In summary, chemical modification is the simplest and most frequently used route to functional group polymers provided that the starting polymer has reactive groups or a structure amenable to derivatization.

Polysulfones are important materials with widespread use in membrane science. Hydrophilic polysulfone, modified by sulfonation, has increased the utility of the material in aqueous and reverse osmosis applications. Despite these achievements, relatively few modification techniques have been developed. For this reason, the work described in this thesis was initiated and addressed the syntheses of novel functional group polysulfones using both the monomer approach and the chemical modification approach.

Synthesis of Bisphenol Monomers

Three carboxyl containing bisphenol monomers 48, 49, 50, were polymerized to synthesize functionalized polysulfones.

48

49

50

The synthesis of these bisphenol monomers, and most other commercially available bisphenols not containing functional groups, is accomplished by the acid-catalyzed phenol condensation reaction (Figure 2). Bisphenols are prepared by condensing a ketone with excess phenol under anhydrous conditions in the presence of acid and usually another catalyst. The mechanism of the reaction proceeds by electrophilic attack of the protonated ketone on the

aromatic ring, followed by acid-catalyzed elimination of water, to give an intermediate cation.^{167, 168, 169} The bisphenol is formed by the reaction of this intermediate with another molecule of phenol.

Figure 2
Mechanism of Bisphenol Formation

Monomer 48 is synthesized by phenol condensation with levulinic acid (4-oxo-pentanoic acid, a hydrolysis product of sucrose) and is available commercially as Diphenolic Acid.^{170, 171} This was purified for polymerization by several crystallizations from a toluene/acetone mixture. Seed crystals were used to initiate the otherwise difficult

γ -hydroxy- γ -(4-hydroxyphenyl)- γ -methyl-benzenebutanoic acid

crystallization. Aromatic hydrocarbons such as benzene or toluene gave crystalline solvates¹⁷⁰ of the formula $C_{11}H_{10}O_4 \cdot 0.5Ar$.

Monomer 49, 2,2-Bis(4-hydroxyphenyl)-propanoic acid,⁴ was synthesized by condensation of pyruvic acid with excess phenol in the presence of glacial acetic acid and hydrogen chloride following the procedure of Parris *et al.*¹⁷² The choice of acid catalyst influences the type of reaction products. Structure 49 was assumed to be the product in a sulfuric acid-catalyzed condensation reported by Böttinger¹⁷³ but was later shown to be a polymeric material 51.¹⁷²

Monomer 49 was purified by several recrystallizations from benzene-ethyl acetate mixtures. The purification was hindered by a tendency for coprecipitation of impurities

⁴4-hydroxy- α -(4-hydroxyphenyl)- α -methyl-benzeneacetic acid

with many solvent systems as well as the susceptibility of the product to aerial oxidation. The structure of the bisphenol was confirmed by mass spectroscopy (MS) and nuclear magnetic resonance (NMR).

9,9-Bis(4-hydroxyphenyl)-fluorene-4-carboxylic acid 50 was prepared by the two step sequence shown in Figure 3.

a: concentrated H₂SO₄
b: phenol, hydrogen chloride, catalyst

Figure 3

Synthesis of 9,9-bis(4-hydroxyphenyl)-fluorene-4-carboxylic acid

Dehydration and intramolecular cyclization of Diphenic acid 52 with concentrated sulfuric acid gave the tricyclic fluorenone-4-carboxylic acid 53 in high yield.^{174, 175} Acid-catalyzed phenol condensation with 53 in the presence of anhydrous hydrogen chloride and a catalytic amount of 3-mercaptopropionic acid led to a 90% yield of crude monomer 50. Evidently, this has not been previously

employed as a bisphenol monomer as there are only early reports of its synthesis as unpurified material using zinc chloride,¹⁷⁶ stannic chloride¹⁷⁷ and sulfuric acid¹⁷⁸ catalysts. The synthesis of 50 has also been reported elsewhere by the author.^{179, 180}

Phenol condensations with ketones containing aromatic or other bulky substituents normally proceed only with difficulty and in low yield because of steric hindrance.¹⁸¹ However, fluorenone and its derivatives are highly reactive ketones in the condensation reactions because of their rigid planar and accessible structure.

Monomer 50 could not be crystallized satisfactorily on a large scale. Toluene/acetone and water/methanol mixtures gave crystals and a water/acetone mixture gave fine needles. The large scale purification was accomplished via aqueous crystallization of the mono-sodium carboxylate salt and subsequent acidification. Structure was confirmed by MS and NMR. Monomer purity is a prime consideration in condensation polymerization for the prevention of side reactions and maintenance of exact stoichiometry.

Synthesis of Carboxyl Substituted Polysulfones

Polymers were prepared by condensation of the trisodium or tripotassium salts of the carboxyl substituted bisphenol monomers with a dihalodiphenylsulfone in DMSO solvent. These are similar conditions to the ones used by Johnson et al. in the preparation of polysulfone, where anhydrous conditions and strict stoichiometry of alkali hydroxide and monomer are observed to avoid hydrolytic side reactions.³⁷ The metal carboxylate salt in the bisphenate monomer did not participate in nucleophilic aromatic substitution but the presence of the carboxyl group is detrimental to polymerization in two ways. First, the trisodium or potassium bisphenate carboxylate is less soluble in DMSO than an unsubstituted monomer and this may lead to low molecular weight polymers due to inhomogeneity or precipitation. Second, the carboxyl group is electron withdrawing and therefore lowers the basicity and reactivity of the bisphenate, especially when the group is situated adjacent to the polymer backbone. During formation of the bisphenates from bisphenols, water was removed azeotropically with a Dean-Stark trap by co-refluxing with either toluene or xylene. Functional monomers were used either alone or mixed with non-functional Bisphenol-A monomer to reduce the concentration of carboxyl groups in the polymer. A high torque motor was used and specialized

stainless steel stirring shaft and blades were made to overcome the very high viscosity in the initial and polymerization stages. After complete removal of water, the azeotrope solvent was distilled off and a solution of the dihalodiphenylsulfone was added. Dichlorodiphenylsulfone 12 is normally used, but with some less reactive carboxyl bisphenates, the more reactive and expensive difluorodiphenylsulfone 17 must be used to achieve higher molecular weights. The polymerizations were conducted at a temperature of about 160°C for a period of up to eight hours.

Chemically and hydrolytically resistant, carboxyl containing aromatic ionomers are being sought to replace other separator membrane materials in electrochemical applications.¹⁸² These applications include membranes for battery separators, electrodialysis of metal wastes and sea water, and as separators in alkali electrolysis. The latter application involves the production of hydrogen by electrolysis of 40% alkali solutions at temperatures of 100°C - 120°C. The asbestos separators currently used degrade under these conditions. Ionomers¹⁸³⁻¹⁸⁵ such as duPont's perfluorosulfonic acid Nafions^{186,187} are thermally and hydrolytically stable, but their high cost precludes their general use. Other interesting carboxyl containing polyarylether ionomers have been developed by Harris et al.^{188,189} The bond forming step during polymer-

ization is a Diels-Alder cyclo-addition between a carboxyl substituted furanone and an ethynyl group. An aromatic ring is formed following extrusion of CO.

Polysulfones prepared from mixtures of Bisphenol-A 15 and Diphenolic acid 48 have been previously synthesized to improve solvent and stress crack resistance^{1,9,10,11} and for attempted compatibilization with styrenic interpolymers^{1,9,12} (eg. α -methyl styrene/methyl methacrylate/acrylonitrile).

Several carboxyl containing polysulfones were synthesized from mixtures of Bisphenol-A and Diphenolic acid, and their structure is represented as 54.

54

54Na	Sodium carboxylate
54K	Potassium carboxylate
54Me	Methyl ester

Polymer 54Na was synthesized from Bisphenol-A, Diphenolic acid and dichlorodiphenylsulfone at 130°C for 24 hours approximately following the procedure of Khattab.^{1,9,10} Some polymer was converted to methyl ester 54Me by heating a solution of the sodium carboxylate ionomer in DMSO and bubbling in chloromethane. It was convenient to use the polymer in the esterified form for some measurements such

as NMR and gel permeation chromatography (GPC) since only polar aprotic solvents like DMSO dissolved the ionic polymer, giving viscous solutions. Esterified polymers readily dissolved in THF for GPC and in CDCl_3 for NMR. In GPC, the methylated polymer 54Me had a molecular weight of 27,600 compared with polystyrene standards. Gel permeation chromatography^{1,2} was used as a comparative rather than an absolute method for molecular weight determination.

Polymerization at a higher temperature (165°C) and for a shorter time (5.5 hours) following the procedure of Olabisi *et al.*^{1,2} also led to ionomer 54Na. The ester 54Me was most similar to the previous polymer and also had identical molecular weight by GPC (M.W. = 27,600).

The bisphenols were rendered more basic by using potassium hydroxide during formation of the bisphenate. These more reactive potassium bisphenates, polymerized with dichlorodiphenylsulfone at 165°C for over 6 hours, led to higher molecular weight polymer 54K. Esterified samples taken during polymerization showed that chain growth was substantial after 3 hours (GPC M.W. = 40,000) and complete by 4 hours (GPC M.W. = 48,000). One hour prior to work-up, chlorophenylphenylsulfone was added to end-cap the reactive phenoxide groups. Chloromethane cannot be used without esterifying the reactive carboxylate groups. The polymer displays NMR signals arising from both types of repeat units containing Diphenolic acid and Bisphenol-A. The most

obvious features of the spectrum of the Diphenolic acid portion are the methyl ester singlet at $\delta=3.64$, two methylene multiplets at $\delta=2.46$ and $\delta=2.14$ and a methyl singlet at $\delta=1.64$. A large singlet at 1.69 corresponds to the methyl groups of Bisphenol-A.

Polymerization of the trisodium salt of Diphenolic acid with dichlorodiphenylsulfone gave a polymer of the structure 55.

55

55Na	Sodium carboxylate
55H	Acid
59Me	Methyl ester

The poor solubility of the growing polymer chain in the reaction solution limited the molecular weight of the product (55Me: GPC M.W. = 30,200). The salt form, 55Na, was water soluble, hence the product was recovered as the acid 55H.

The methylated derivative 55Me was prepared by treatment of the carboxylic acid polymer 55H with methanolic hydrochloric acid. Its NMR spectrum gives the two anticipated AA'XX' patterns arising from the two pairs of

coupled aromatic protons: H-d ($\delta=7.86$) coupled with H-c ($\delta=7.01$) and H-b ($\delta=7.22$) coupled with H-a ($\delta=6.95$). A sharp 3H singlet at $\delta=3.64$ confirms the methyl ester and two 2H triplets at $\delta=2.47$ and $\delta=2.15$ and a 3H singlet at $\delta=1.64$ correspond with the methylene and methyl groups of the Diphenolic acid portion of the polymer repeat units. The carboxylic acid form of the polymer has strong absorption bands at 1715 cm^{-1} (C=O st.) and at $2370\text{--}3600\text{ cm}^{-1}$ (OH st.) and the methyl ester has a band at 1730 cm^{-1} (C=O st.).

Polymers derived from monomer 49 gave universally poor products unsuitable for membranes. The close proximity of the carboxyl group to the polymer chain is the most likely cause of the monomer's low reactivity. The sodium salts of 49, although soluble, produced growing polymer chains that gelled, causing inhomogeneities and preventing further growth (M.W. 16,000). The potassium salts of 49 were simply too insoluble to produce polymers.

Monomer 50 was selected for the following reasons: a) the ease of synthesis because of the planarity of the precursor; b) remoteness of carboxyl group; c) non-conjugation of pendant fluorene with the bisphenol moieties; d) its totally aromatic nature and e) the expected high glass transition temperatures (T_g) of polysulfone derivatives because of rigidity around the spiro centre.

The synthesis of polysulfone ionomers 56 and 57 have

been described by the author elsewhere.^{17,18} The trisodium and tripotassium salts of monomer 50 had adequate solubility in DMSO but they were less reactive than Diphenolic Acid. This is not unexpected since a similar non-carboxylated polysulfone 19 could only be produced in high molecular weight from monomer 18 when the more reactive difluorodiphenylsulfone was used as the co-monomer.¹¹ Equal quantities of the sodium salts of Bisphenol-A 11 and 50 were copolymerized with dichlorodiphenylsulfone at 165°C to give a polymer represented by structure 56Na. The low reactivity of bisphenol carboxyl monomer was manifested by low molecular weight polymer (56Me: GPC M.W. = 18,200). Accordingly, the use of potassium bisphenate salts copolymerized with the more reactive difluorodiphenylsulfone gave a high molecular weight polymer 56K (56Me: GPC M.W. = 125,000) which was polydisperse.

56

56Na
56K
56Me

Sodium carboxylate
Potassium carboxylate
Methyl ester

By analogy, the sodium salts of 50 polymerized with dichlorodiphenylsulfone, led to low molecular weight polymer 57Na(57Bu: GPC M.W. = 18,200) and the potassium salts with difluorodiphenylsulfone gave higher molecular weight polymer 57K (57Bu: GPC M.W. = 27,000).

57

57Na	Sodium carboxylate
57K	Potassium carboxylate
57Me	Methyl ester
57Bu	Butyl ester

The methyl ester was prepared by treatment of the polymer in the ionomer form with iodomethane in DMSO for a short time. The use of chloromethane led to incompletely esterified products. The aromatic region of the NMR spectrum of the methyl ester polymer (Figure 4) displays the expected AA'XX' pattern from the para-substituted benzene rings: protons H-d ($\delta=7.81$) coupled to H-c ($\delta=6.96$) and protons H-b ($\delta=7.18$) coupled to H-a ($\delta=6.86$). The fluorenyl residue displays three 1H doublets, presumably

from singly coupled protons, and a 4H multiplet. The downfield doublet at $\delta=8.31$ corresponds to the shielded proton ortho- to the carboxylic ester. The two other doublets arise from the 1 or 4 positions in the fluorene nucleus. A sharp 3H singlet at $\delta=4.03$ shows the presence of the methyl ester group. This is also confirmed by a strong absorption band at 1725 cm^{-1} (C=O st.) in the IR spectrum.

Figure 4

Aromatic Region of the NMR Spectrum of Polymer 57Me

Selected Properties of Polysulfone Ionomers

Glass Transition Temperatures

The effect of ion incorporation in polymers on the glass transition temperature of ionomers has been studied by several groups.¹⁹⁴⁻¹⁹⁷ A small increase in ion concentration in the polymer results in a significant rise in the glass transition temperature. There is no unanimous agreement on the reason for this but the currently prevailing argument is the presence of ionic crosslinks. Spherical ionic clusters of counterions associated with ordered anionic regions are embedded in an amorphous matrix. Chain stiffening by weak electrostatic ionic interactions results in increased glass transition temperatures.

The effect of ion concentration on T_g has been investigated in sulfonated polysulfones 30.^{69, 73-75} With a degree of substitution of one, sodium sulfonate modified polysulfone has a T_g of 320°C, considerably higher than the value of 190°C for unmodified polysulfone.⁷⁴ Lower values were obtained for correspondingly lower degrees of substitution.

Ionomer 54Na displayed a clear endotherm at 260°C by Differential Scanning Calorimetry (DSC). A large endotherm corresponding to loss of bound water was also evident in samples heated for the initial measurement. The endotherm disappeared on cooling and reheating, however, and its

absence did not affect the T_g endotherm. The important effect of ion concentration on T_g is apparent by the low T_g (154°C) of the methyl ester of the same polymer.^{1,2}

The polysulfone ionomers containing pendant fluorene groups had higher glass transition temperatures than the Diphenolic acid ionomer. Apart from the presence of ions in the polymer, the high T_g values are influenced by the enhanced chain rigidity of the fluorene group. Morgan^{1,3} showed that polyesters with stiff chain segments, containing bisphenols with large planar pendant groups, exhibited marked increases in T_g . Other workers have reported^{1,4} high T_g values for polysulfones containing these types of bisphenols. A polysulfone 19, containing bis(4-hydroxyphenyl)-9-fluorene 18, was amongst the most thermally stable in the series, and had an exceptionally high T_g value of 270°C. DSC measurements on ionomer 56K showed a large water endotherm and a clear endotherm at 330°C, corresponding to the glass transition temperature. Only the single unchanged higher temperature endotherm remained upon reheating the sample to 140°C. However, when the sample was annealed at 330°C for 10 minutes and then re-run, the T_g decreased to 310°C. Lower molecular weight 56Na also had the same lower T_g value, even before drying or annealing. The polymer with the highest ion concentration was 57K, containing only bisphenol 50. Strong water adsorption was evident from a large endotherm. The

glass transition temperature was not clearly defined by the DSC measurement but an endotherm at approximately 380-395°C is believed to represent a glass transition temperature. The small endotherm preceding the glass transition temperature appears to be the onset of the decomposition endotherm. This is further supported by the thermogravimetry curve which indicates that decomposition occurs at or near T_g . The possible reason for the indefinite endotherm is the presence of extraneous ions or solvents retained by the polymer. Johnson *et al.*¹⁴ observed sharp glass transitions in the DSC after careful extraction of impurities from sulfonated polysulfones which previously had ill defined transitions.

Thermal Stability

The thermal stabilities of polymers were measured by thermogravimetry (TG) under a nitrogen atmosphere. Loss of bound water was evident during the initial heating period in the three ionomers under analysis. These polymers had an affinity for water since they re-absorbed water within two hours of being left in the open air.

Ionomer 54Na had an onset of weight loss at 390°C, with rapid loss occurring between 420°C and 500°C. Fluorene containing ionomer 56K had a similar decomposition profile, except that the onset of weight loss occurred at 370°C. The weight loss of the most ionic polymer, 57K, was

more complicated. An initial weight loss at 310°C could be caused by loss of carbon dioxide. The onset of major weight loss occurred at approximately 420°C. Interestingly, the thermal profile of this two stage decomposition resembles that of perfluorinated ionomer Nafion, with similar temperature values for weight loss. One significant difference is that total weight loss occurs at 550°C in Nafion, whereas 50% of the weight loss occurs at approximately 950°C in the polysulfone ionomers. The ionomers are comparatively less thermally stable than Udel Polysulfone which has an onset of weight loss at 475°C. The thermogravimetric curves of Udel and other polysulfones have been reported.^{19, 20}

Water adsorption

The hydrophilicity of the polymers was determined by water adsorption in dried ionomer membranes. Porous membranes approximately 50 μm thick were prepared by casting a 15% N-methylpyrrolidone (NMP) solution onto a glass plate with a doctor blade and then gelling the polymer into water. Dry, weighed films were immersed in 0.1 M aqueous sodium chloride solution for 24 hours at ambient temperature, then blotted dry and reweighed. The polymers with the highest ion concentration adsorbed the most water, as anticipated. The results are listed in Table II.

*kindly measured by H. L. Yeager, University of Calgary.

Table II
Water Adsorption of Polymer Membranes

Polymer	Water Uptake %
Udel	2.6
Radel	2.0
54Na	11.2
56K	15.1
57Na	22.0
57K	21.5

The Chemical Modification of Polysulfones by Directed Metalation'

Directed Lithiation of Aryl Sulfones

The term lithiation denotes the particular case of metalation in which a hydrogen atom is replaced with lithium. The stabilizing influence of a heteroatom or hetero-group in metalation reactions, especially in lithiation, frequently leads to rate enhancement and a high degree of regioselectivity. Several reviews on the synthetic uses of metalation and hetero-atom directed lithiation have been published,^{158, 200-203} notably a comprehensive one by Gschwend and Rodriguez.¹⁵⁹ Hetero-atom directed lithiation is usually divided into two categories: alpha and beta (or ortho) lithiation. Ortho-lithiation is the class of reaction in the metalation of polysulfones where lithium atoms replace hydrogen atoms ortho- to the sulfone containing group. In some ortho-substituted aromatic systems, deprotonation occurs preferentially on this proximal substituent rather than on the sp^2 -carbon atom of the aromatic ring.

The structure of the organolithium metalating agents and the mechanism by which they react are not clearly understood because of their unstable and highly reactive

'Parts' of this work concerning the chemical modifications of polysulfones have already been reported elsewhere (refs. 200-203).

nature. The metalating agents are electron deficient species with a degree of Lewis acid character, capable of coordinating with electron pair containing groups such as ethers. In non-polar hydrocarbon solvents, where *n*-butyllithium exists as a hexameric aggregate, their reactivity or basicity is lower than in less aggregated dimeric states which exist in the presence of strong electron donors such as THF.^{159, 204} Another consideration is the increase in basicity of carbanions which occurs at this site with increased *s* character, whereby alkyl carbanions are more basic than aryl carbanions.²¹⁰ Electron donating alkyl substituents at the carbanionic site have a destabilizing influence causing *sec*-butyllithium to be more basic than the straight chain moiety.²¹⁰ Amine complexed metalating reagents such as *n*-butyllithium/TMEDA complexes have negligible Lewis-acid character compared with uncomplexed organolithium reagents because of the strongly electron donating nature of the amine. Their increased reactivity and rate enhancement in metalation reactions is partly due to their monomeric or dimeric state of aggregation and partly to the greater negative charge at the carbanionic site resulting from the chelation of the cation.

A large number of hetero-atom containing functional groups are able to direct lithiation regiospecifically in substituted benzenes. It might be expected that only electron withdrawing groups such as sulfone, that induct-

ively increase proton acidity, would be capable of this. However, electron donating groups such as ethers readily direct ortho-lithiation. This apparent contradiction arises because, in the coordinated intermediate, the lone pairs of electrons coordinated with lithium are unavailable for interaction with the aromatic π system, making the substituent inductively electron withdrawing.

Once the organolithium is coordinated to the directing group, the nearest carbon is deprotonated, usually the ortho-proton. It has been postulated that there are two limiting mechanisms in ortho-lithiation relating to functional groups: coordination only and acid-base.¹³ Between these lie the majority of cases where both mechanisms contribute simultaneously. Tertiary nitrogen separated by one saturated carbon atom from the aromatic ring is considered a coordination only group whereas halogens, which have little or no coordinating capacity, are effective ortho-directors only because their inductive electron-withdrawing character increases hydrocarbon acidity. Sulfone has an electron withdrawing effect by induction on the ortho-position and also has a moderate capacity for coordination with the lithiating agent. Consequently, the sulfone group is amongst the most effective and powerful directing groups in lithiation reactions.¹³ A simplified mechanism for the lithiation of diphenylsulfone is shown in Figure 5.

Figure 5

Representative Mechanism of Ortho-Lithiation

Arylsulfones are readily mono- or dimetalated using butyllithium at reduced temperatures at or below zero, whereas at higher temperatures, uncharacterized products were originally obtained.²¹¹ Thus, diphenylsulfone 58a is monolithiated 58b or dilithiated 58c exclusively at the ortho-position depending on the quantity of metalating agent used^{212, 213} and these products are converted to their respective carboxylic acids 58d and 58e by treatment with carbon dioxide. Similarly, dibenzothiophene-5,5-dioxide 59a gives metalated 59b and 59c and carboxylated products 59d and 59e exclusively ortho to the sulfone group.²¹³

58

59

a	R ₁ = H	R ₂ = H
b	R ₁ = Li	R ₂ = H
c	R ₁ = Li	R ₂ = Li
d	R ₁ = COOH	R ₂ = H
e	R ₁ = COOH	R ₂ = COOH

The directing influence of selected substituents is evident in the metalation of some monosubstituted diphenylsulfones. The 4-methyl group has a slight deactivating effect, with ortho-lithiation occurring to slight excess in the unsubstituted ring.²¹¹ The ortho-, meta- and para-bromo group has an activating influence such that ortho-lithiation occurs only in the substituent ring.²¹² This extremely unusual example of the meta-substituted product is remarkable because there is neither metal-halogen exchange nor even benzyne formation commonly observed in ortho-situated metal-halogen systems. The inductive effect of the bromine atom reinforces that of the sulfone group at the position ortho- to both groups.²¹² In the case of the para-bromo isomer, predominantly ortho-metalation with only 2% metal-halogen exchange is observed. Metal-halogen exchange is not observed in the dilithiation of para-disubstituted fluoro isomers,²¹⁵ nor in meta-substituted

chloro-derivatives.²¹⁶ The superior directing influence of arylsulfone over arylother and arylthioether groups is exemplified by the mono- and dilithiation of phenoxathiin-10,10-dioxide 60a and thianthrene-5,5-dioxide 61a. Products 60b and 60c^{217,218} and 61b and 61c²¹⁹ demonstrate that lithiation occurs ortho- to the sulfone in preference to the other directing groups.

60

61

a	R ₁ = H
b	R ₁ = Li
c	R ₁ = COOH

Dilithiation of Udel Polysulfone with n-Butyllithium

Polysulfone 1 was rapidly dilithiated by the addition of 2.1 mol equivalents of n-butyllithium (n-BuLi) to a cooled solution of the polymer in THF.^{200,201} It was necessary to exclude moisture from all equipment and reagents and to provide an inert atmosphere of argon or nitrogen. The reaction was suitably performed throughout a temperature range of about -10°C to -78°C. The addition of n-BuLi to a solution of polymer resulted in the formation

of the ortho-sulfone carbanion, which was readily observed initially by a green-brown and later by a red-brown colouration. The dilithiated polysulfone 62 remained dissolved as a coloured clear viscous solution or gel. After an appropriate time, the addition of an electrophile converted the reactive metalated intermediate to a functional group containing polysulfone. The site and degree of lithiation were determined by NMR analysis of dimethylated and dideuterated polymers since these are the most simple derivatives and both electrophiles, iodomethane and deuterium oxide, often react quantitatively with aryllithiums.

Thus, 2 mol eq. *n*-BuLi was added dropwise to polysulfone solution at -78°C over a short period. Samples of solution were withdrawn and immediately methylated with iodomethane at several time intervals. The degree of lithiation/methylation was determined by comparison of the methyl signal integration in the NMR spectrum with that of the Bisphenol-A portion of the polymer. A high degree of substitution was obtained immediately after addition and no further reaction occurred after 15 minutes. The degree of substitution was 1.82 by high field NMR. The reaction scheme is illustrated in Figure 6.

Figure 6

Dilithiation/Methylation of Polysulfone_s

Dimethylated 63 and, dideuterated 64 polysulfone were examined by 400 MHz NMR. Figure 7 shows a 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." In the arylsulfone portion, the most downfield protons H-d at $\delta=7.85$, deshielded by the adjacent sulfone group, are coupled with ortho-ether protons H-c at $\delta=7.00$. Shielded ortho-ether protons H-a at $\delta=6.94$ in the Bisphenol-A portion are coupled with protons H-b at $\delta=7.24$. The spectra of both derivatives show that the bisphenol-A portion remains unchanged and that substitution occurs in the arylsulfone portion.

In the deuterated derivative 64, the chemical shifts remain essentially unchanged, as expected. A significant feature of 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 between the downfield doublet H-d is thought to be caused by this ABX system rather than a small degree of substitution at H-e for which there is no evidence in the methylated derivative. Hence dideuteration/dilithiation occurs primarily at the ortho-sulfone site.

Figure 7

Comparative NMR Spectra of Unsubstituted, Dideuterated and Dimethylated Udel Polysulfone (Aromatic Region)

In the spectrum of the dimethylated polymer 63, the virtual disappearance of the doublet at $\delta=7.85$ and the appearance further downfield, at $\delta=8.12$, of a new 2H doublet H-d 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 2H doublet of doublets at $\delta=6.88$ (H-c ortho and meta coupling) and a 2H doublet at $\delta=6.80$ (H-e meta coupling) corresponding to ortho-ether protons.

In lower degrees of methyl substitution, the spectrum is complicated by all three types of repeat unit simultaneously present: unsubstituted, mono- and dimethyl substituted. A series of lithiation/methylation reactions, with increasing amounts of derivatization, clarified the spectral assignments from which was determined the distribution of mono- and disubstituted repeat units. Monomethyl repeat units ($\delta=2.40$) increase to a maximum at a degree of substitution of 1.0 and thereafter decrease, while dimethyl repeat units ($\delta=2.30$) increase. The results are summarized in Table III.

Table IIIDistribution and Degree of Substitution
in Methylated Polysulfones

<u>n</u> -BuLi mol eq	Total Methyl substitution ^a	%Monomethyl Repeat units ^b	%Dimethyl Repeat units ^c	%Other ^d
0.25	0.27	23.0	2.3	74.7
0.50	0.55	42.5	6.4	51.1
0.75	0.82	57.1	12.5	30.4
1.00	1.01	68.7	16.0	15.3
1.25	1.35	52.1	41.7	6.2
1.50	1.52	36.5	57.7	5.8
1.75	1.70	11.4	79.0	(9.6)
2.00	1.82	6.1	87.7	6.2

^a Total methyl substitution per repeat unit, ratio mono- and dimethyl to 0.5 x Bisphenol-A methyl

^b Ratio monomethyl to 0.5 x Bisphenol-A methyl

^c Ratio dimethyl to Bisphenol-A

^d Remaining percentage of unsubstituted or other repeat units

Directed dilithiation of aromatic rings occurs with only a few other hetero-atom containing molecules such as aromatic thioethers,²²⁰ ethers²²¹ and amides.²²²

The spectrum of the monomethylated (D.S.=1.01) polysulfone (Figure 8) shows three types of deshielded ortho-sulfone protons. The doublet at $\delta=7.85$ corresponds to four protons of an unsubstituted repeat unit. Exclusive to monomethyl repeat units 65 are the two protons H-d' which have similar chemical shifts at $\delta=7.78$. The 2:3

ratio of $\delta=7.78:\delta=2.40$ for all derivatives confirms this assignment. Both the single proton H-d in monosubstituted, and two protons H-d in disubstituted repeat units, are shifted substantially downfield to $\delta=8.12$. The ratio of this signal to the total methyl substitution is 1:3. The disturbance of the bisphenol-A doublets probably results from non-equivalent environments next to methyl- and unsubstituted rings.

Figure 8 .

NMR Spectrum of Monomethylated Udel Polysulfone
(Aromatic Region)

Trilithiation of Udel Polysulfone with n-Butyllithium

The dilithiation of polysulfone occurs rapidly and in high yield (D.S.=1.82) in the temperature range of 0°C to -78°C.²⁰⁰ When an excess of n-butyllithium was added to the polymer solution at -30°C, a slower trilithiation reaction occurred. As the reaction progressed from the dilithiated to the trilithiated species, the polymer solution became very viscous and eventually precipitated as a gum.

The position and degree of substitution were determined as before, by NMR analysis of the deuterated and methylated derivatives. The aromatic regions of the NMR spectrum of the trideuterated 66, trimethylated 67 and unmodified polysulfone are compared in Figure 9.

The ortho-sulfone position of lithiation/deuteration in derivative 66 is confirmed by the diminution of the deshielded ortho-sulfone protons H-d from 4H to 1H. Also, the accompanying partial collapse of the doublet from adjacent proton H-c signifies a loss of ortho coupling at H-e. Proton doublets H-a and H-b on the Bisphenol-A portion remain unchanged. This spectrum has comparable features to the dideuterated derivative 64, but the effect here is greater.

Figure 9

Comparative NMR Spectra of Unsubstituted, Trideuterated and Trimethylated Udel Polysulfone (Aromatic Region)

Two types of methyl groups are present in the trimethylated polymer 67: two situated ortho-sulfone on the same ring and one situated on the second ring. The former appears as a 6H singlet at $\delta=2.48$ and the latter as a 3H singlet at $\delta=2.27$. The deshielded single proton H-d occurs slightly upfield from the dimethylated derivative, at $\delta=7.96$. This is coupled to the broadened doublet H-c at $\delta=6.84$ (ortho- and meta- coupling). Small amounts of mono- and disubstituted polymer are also apparent in the deshielded region. Protons adjacent to methyl occur upfield as a 1H broadened singlet (H-e) and a 2H singlet (H-f). The disturbance of the Bisphenol-A protons H-a probably results from the inequivalent environments next to mono- and disubstituted rings.

A series of methylated polymers were prepared to determine the optimum conditions for trilithiation. At -50°C , the reaction was very slow, and only a small degree of trilithiation was observed. Substantial degrees of trilithiation occurred at -30°C when excess metalating agent was used or at 0°C using a slight excess. The degree of substitution was determined by measuring the ratio of the singlet heights $\delta=2.48:\delta=2.27$ and then matching this ratio with a theoretical ratio plotted on a graph. The results summarized in Table IV were measured from low field NMR spectra and serve only as an approximate comparison. The highest degree of substitution (D.S. = 2.79 per repeat

unit) was achieved using 4.0 mol equiv. *n*-BuLi at -30°C.

Table IV
Optimization of Reaction Conditions
for Trilithiated Polysulfone

BuLi mol eq	Temp (°C)	Time (min)	Ratio Methyl ^a δ2.48:δ2.27	Degree Me Substitution
3.0	-30	90	1.08	2.70
3.0	-50	120	0.41	2.34
3.3	-30	120	1.24	2.77
3.3	-30	150	1.27	2.78
3.3	-30	180	1.26	2.78
3.3	-30	240	1.27	2.78
3.3	0	60	1.72	2.93
3.3	0	120	1.79	2.94
4.0	-70	120	0.09	2.09
4.0	-30	30	0.82	2.58
4.0	-30	90	1.75	2.93
4.0	-30	100	1.81	2.95
4.0	-30	240	1.86 ^b	2.96 ^c

^a Based on methyl signal heights in 60 MHz spectrum.

^b 2.03 in 400 MHz, D.S. = 3.00 by signal height

^c 2.79 in 400 MHz, by integration

This high degree of substitution obtainable by lithiation is exceptional in both polymers and aromatic molecules. Only in a few cases can a single hetero-atom direct trilithiation. For example, the product 1,1,1-trilithiomethyphenylsulfone is a case of aliphatic alpha lithiation.²²³ In ortho-metalation, it is unusual for dilithiation to occur on a single aromatic ring. The

metalation of *t*-butylphenylsulfone^{224, 225} results in a dilithiated aromatic ring, which at higher temperatures forms a benzyne intermediate by loss of lithium *t*-butylphenylsulfone. Also, trisilylated derivatives have been synthesized from ortho-metalated 4,4'-difluorodiphenylsulfone.²²⁶

It is difficult to draw conclusions concerning the conformation of the substituted diphenylsulfone unit from the NMR data. In the solid state, the Ph-S-Ph angle of diphenylsulfone is 102°. The planes of the benzene rings are arranged to allow conjugation across the sulfone by interaction between the π electrons of the benzene rings and the unoccupied 3d orbitals of the sulfur atom.^{228, 229} In this situation, the dihedral angle between the planes of the benzene rings is about 0°.

The crystal structure of tetra-ortho-methyl substituted diaryl sulfone gives an insight into how the large steric strain about the sulfone group is relieved.²³⁰ The Ar-S-Ar bond angle is increased to 104.5° and the O-S-O bond angle is decreased from 130° to 117°. Methyl groups are forced away from the sulfone and each other by an increase in the Ar-CH₃ angle to 125°, a lengthening of the Ar-S-Ar bond, and a change in the dihedral angle of the aromatic rings to 77°. In other more sterically hindered tetra-ortho substituted arylsulfones, the dihedral angle is increased to 87° and the Ar-S-Ar bond angle is greatly

increased to 117.9 τ .^{231, 232}

The solution conformation of mono-, di- and trimethyl ortho-substituted diphenyl sulfones have been studied by Montando *et al.*²³³ using NMR. The angular geometry and close proximity of the aromatic rings in diarylsulfones enable the ortho-sulfone protons to be within the shielding region of the opposite ring in certain conformation as shown in Figure 10.

The ortho-sulfone aromatic proton and methyl chemical shifts of mono-, di- and trimethyl substituted polysulfones are in close agreement with the model compounds. However, no conclusion regarding conformational preferences could be drawn because of the absence of any marked shielding effect.

Figure 10
Conformationally Dependant Shielding in Diphenylsulfone

Dilithiation of Radel Polysulfone With n-Butyllithium

The lithiation of Radel Polysulfone 2 gave similar results to Udel 1, but slightly lower degrees of substitution were observed at both the temperatures used, -40°C and -78°C . The comparative NMR spectra of unmodified and dimethylated Radel (Figure 11) also have very similar characteristics to the Udel spectra. However, the absence of the Bisphenol-A methyl groups prevents the determination of the degree of substitution in the usual way. The unsubstituted Radel spectrum is characterized by deshielded ortho-sulfone H-d protons ($\delta=7.90$) coupled to the most upfield H-c protons ($\delta=7.07$). The other ortho-ether H-a protons ($\delta=7.11$) have a very similar upfield chemical shift and these are coupled to H-b at $\delta=7.58$. The dimethylated Radel 68 spectrum shows a downfield shift for the ortho-sulfone protons (H-d, $\delta=8.16$). Small amounts of unsubstituted ($\delta=7.90$) and monomethyl substituted ($\delta=7.83$) repeat units are also apparent. The 4H doublet at $\delta=7.07$ is replaced by a broadened 2H doublet H-c ($\delta=6.96$) and a broadened 2H singlet H-e ($\delta=6.85$, meta coupling). No changes in the biphenyl portion are evident. The degree of lithiation/methylation was 1.72. This was calculated by comparison of the dimethyl singlet at $\delta=2.34$ and the small monomethyl singlet at $\delta=2.44$ with unchanged H-b.

Figure 11

Comparative NMR Spectra of Unsubstituted and Dimethylated Radel Polysulfone (Aromatic Region)

Lithiation of Polysulfones with other metalating agents

Metalating agents other than *n*-BuLi were not as efficacious in the lithiation of Udel polysulfone. The methyl derivatives were analyzed by NMR as before.

Both methyllithium and phenyllithium were reasonably good metalating agents and gave clean products. Lithium bis(trimethylsilyl) amide was unreactive. Lithium diisopropylamide (LDA) alone or in conjunction with hexamethylphosphoric triamide (HMPT) was a surprisingly poor metalating agents. LDA gave apparently inhomogeneous products and uniformly low degrees of substitution and crosslinked. The results of the various metalating agents are presented in Table V.

Table V
Effect of Metalating Agents on Udel Polysulfone

Metalating agent 2 mol eq	Temp (°C)	Time (min)	D.S. (methyl)
MeLi	-70	60	1.1
"	-70	300	1.49
PhLi	-70	250	1.58
"	-30	175	1.73
(TMS) ₂ NLi	-30	60	0
"	0	120	0
"	+25	16hr.	0
LDA	-70	90	0.28*
"	-40	120	0.35*
"	-10	60	0.21*
LDA/HMPT	-70	60	0.34*

* Some degree of crosslinking evident

Lithium 2,2,6,6-tetramethylpiperidide (LiTMP) has been effectively used to dimetalate diphenylsulfone while in the presence of an electrophile, resulting in cyclic thiasilin-5,5-dioxide derivatives.²³⁴ This metalating agent was not used for polysulfone.

Lithiation of Polysulfone at Elevated Temperatures

An insoluble polymer was formed if the solution temperature of dilithiated polysulfone 62 was allowed to rise slowly above 0°C. Precipitation began at about +10°C and the product coalesced into a single mass at +15°C. At a temperature of +40°C over a period of several hours, the polymer darkened and became insoluble in every solvent tested.

Analogous reactions on diphenylsulfone derivatives provide some insight into the possible products. Brinon *et al.*^{226, 235, 236} observed the formation of a substituted benzothiophene-10,10-dioxide at +10°C by the loss of LiH and ring closure in ortho-dilithiated 4,4-difluorodiphenylsulfone. At +45°C, a dibenzothiophene derivative was formed, presumably by the action of released LiH. Under the same conditions, dibenzothiophene 59a was the exclusive product from 2,2'-dilithio-diphenylsulfone 58c. This same reductive ring closure has also been accomplished using cupric chloride.²³⁷

Elemental analysis of the product of polymer lithi-

2

Micro-D

ation at +40°C revealed no increase in the percentage of carbon which would be expected for a polysulfone containing dibenzothiophene repeat units. It is therefore reasonable to assume that some of the polymer repeat units are of the structure 69.

69

The insolubility of the product synthesized at +40°C made NMR analysis impractical. The soluble portion of the product lithiated at +15°C revealed only unchanged starting material in the NMR. Accordingly, IR was used as a probe to determine whether the O=S=O stretching bands were diminished or absent. Johnson *et al.*⁷⁵ have assigned the IR bands of polysulfone. Asymmetric O=S=O stretching occurs at 1325 cm⁻¹ and at 1298 cm⁻¹ and symmetric stretching occurs at 1152 cm⁻¹. The spectrum of the insoluble polymer was the same as unmodified polymer in most respects, but with a broadening of some bands. However, the bands at 1325 cm⁻¹ and 1152 cm⁻¹ were slightly diminished. No conclusions could be drawn from these results.

Another type of reaction can also occur in arylsulfone metalation at room temperature. *t*-Butyl-1-naphthylsulfone

undergoes conjugate addition with *n*-butyllithium giving dihydronaphthalene products or 2-*n*-butyl naphthoic acid and *t*-butylsulfinate elimination when trapped with carbon dioxide.²³⁸

Lithiation of Dimethylated Udel Polysulfone

Dimethylated polysulfone 63 was metalated by 2 mol eq. of *n*-BuLi at -78°C, immediately forming a deep blood-red lithiated species. This was shown by derivatization to be predominantly 70.

This is an example of hetero-atom directed metalation that is neither alpha- nor ortho- (beta-), but which may be classed as gamma-lithiation. This type of metalation has also been observed in a variety of ortho-substituted diarylsulfones which, under appropriate conditions, rearrange to give ortho-benzylphenylsulfonates.²³⁹⁻²⁴⁴ The general Smiles rearrangement also occurs with many other substrates by nucleophilic attack at the aromatic carbon adjacent to a leaving group. However, ortho-lithiomethyl-

diarylsulfones are among the best substrates that readily undergo the specific Truce-Smiles rearrangement without additional activating groups because of the presence of both a strong nucleophile (ArCH_2^-) and a good electron withdrawing leaving group (ArSO_2). Accordingly, the polymer metalation was performed at -78°C to avoid these sulfinic acid containing rearrangement products.

Metalated dibenzyl polymer 70 was trapped with either iodomethane or dimethyl disulfide and the products were examined by NMR spectroscopy. The formation of 70 as the predominant product is clearly illustrated by the resulting diethyl polymer derivative 71. This transformation is apparent by the virtual disappearance of the two methyl groups (singlet at $\delta=2.30$) and the replacement by two ethyl groups, shown by a 6H triplet at $\delta=0.93$ coupled with a quartet at $\delta=2.75$. In the polymer chain, the degree of substitution was 1.60 for ethyl, 0.15 for unreacted units and 0.25 for other ring methylated species ($\delta=2.44$ and $\delta=2.50$). The downfield spectrum reveals similar features and chemical shifts to the starting dimethylated polymer 63, with the exception of a downfield shift of the ortho-methyl proton signal from $\delta=6.80$ to $\delta=6.92$. Ortho-methyl proton singlets originating from minor amounts of other repeat units are present at $\delta=6.81$, 6.69 and 6.66.

71

The aromatic protons in the thiomethylated derivative 72, with the exception of ortho-sulfone ($\delta=8.11$, d.), are masked under the Bisphenol-A AA'XX' spectrum. The pertinent new proton singlets are thiomethylene ($\delta=3.83$) and thiomethyl ($\delta=1.84$) which also appear with several other minor singlets arising from a variety of unreacted, partly reacted and ring thiomethylated repeat units.

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Polysulfones with Functional Groups derived from Lithiated Intermediates and Electrophiles

Udel polysulfones containing functional groups were obtained by the reaction of a variety of electrophiles with the lithiated intermediates. Derivatives originating from the following electrophilic reagents were characterized.

Carbon Dioxide

Carboxylated polysulfone derivatives were prepared by the addition of excess carbon dioxide to lithiated polysulfone. Carbon dioxide gas was used for small samples whereas powdered dry ice was required for rapid quenching of larger quantities. A large excess is required to prevent possible crosslinking reactions from the addition of aryllithium to carboxylate sites:"

Carboxylated derivatives 58d and 58e have previously been synthesized from lithiated diphenylsulfone 58b and 58c^{212, 213, 245} and other aromatic sulfones.^{215, 217-219} Diortho-substituted carboxylic acids form thioxanthone-10,10-dioxide derivatives by acid-catalyzed dehydration and ring closure.^{216, 246}

Highly substituted polysulfone carboxylates were soluble in water and insoluble in many organic solvents. Organic soluble methyl ester derivatives were used for NMR

measurements. The comparative downfield NMR spectra of unmodified and dicarboxymethylated polysulfone 73 are shown in Figure 12. The ortho-sulfone substitution is evident by the absence of the H-d doublet of the unmodified polymer and the presence of a 2H ortho-sulfone doublet at $\delta=8.02$. Other pertinent features are the disappearance of the H-c doublet at $\delta=7.00$ and the appearance of two ortho-ether signals: a doublet of doublets H-c ($\delta=7.08$, ortho and meta coupling) and a doublet H-e ($\delta=7.13$, meta coupling). No substitution is apparent in the Bisphenol-A portion as indicated by the unchanged AA'XX' spectrum. The degree of carboxylation, determined by comparison of the ester methyl singlet at $\delta=3.87$ with the Bisphenol-A methyl, was 1.81.

The NMR spectrum (Figure 12) of a polymer 74 containing a lower degree of carboxylation (0.5) was complicated by three structures being present simultaneously: unsubstituted, mono- and dicarboxylated repeat units. In monosubstituted repeat units, an additional doublet at $\delta=7.90$ corresponding to two ortho-sulfone protons in the unsubstituted aromatic ring and a monomethyl ester singlet at $\delta=3.91$ were present.

A film of the polymer in the lithium carboxylate form had an IR absorption at 1687 cm^{-1} (COO^-) and in the methyl ester form, one at 1735 cm^{-1} (C=O).

Solubility data for carboxylated polysulfone are summarized in Table VI.

Figure 12

Comparative NMR Spectra of Unsubstituted and Carboxymethylated Udel Polysulfones (Aromatic Region)

Table VISolubility of Carboxylated Polysulfone (D.S.=0.5)

Solvent	COOLi form	COOH form
NMP	partly soluble-swells	readily soluble
DMA	soluble/hazy-swells	readily soluble
DMF	swells	soluble-hazy
DMSO	soluble	partly soluble/hazy-swells
BLO	swells	partly soluble
CHCl ₃	swells	swells
THF	swells	partly soluble/hazy-swells
Water	insoluble	insoluble

Dimethyl Disulfide

Thiomethylated polysulfone 75 was obtained by reaction of dilithiated polymer with dimethyl disulfide. This electrophile has the same high reactivity as iodomethane and gave a D.S. of 1.82 by comparison of the thiomethyl singlet ($\delta=2.29$) with Bisphenol-A. Figure 13 shows the uncomplicated aromatic NMR. Deshielded H-d protons ($\delta=8.29$) are coupled with the most upfield doublet of doublets, protons H-c ($\delta=6.75$). H-e protons ortho- to the thiomethyl group occur at $\delta=6.82$ and show meta-coupling. The AA'XX' spectrum of the Bisphenol-A portion remains unchanged.

Figure 13

NMR Spectrum of Dithiomethylated Polysulfone
(Aromatic Region)

Sulfur Dioxide

Sulfur dioxide combined with monolithiated polysulfone to give a lithium sulfinate derivative which, when acidified, was isolated as the sulfinic acid polymer 76.

Elemental analysis indicated a degree of substitution of approximately 1.0, suggesting that sulfur dioxide is a good electrophile for metalated polymer. The material was only sparingly soluble in THF or chloroform. Thin polymer films cast from these solutions had a broad IR absorption band at $3660\text{--}2400\text{ cm}^{-1}$ confirming the presence of $\text{-SO}_2\text{H}$. Interestingly, when these films were heated overnight at 125°C , crosslinking occurred. Another unusual feature of the sulfinic acid derivative is its apparent photosensitivity. Natural light darkened the polymer over a period of several weeks. Sulfinic acids have limited stability and readily undergo disproportionation or decomposition. The thermal crosslinking can be rationalized by the disproportionation of sulfinic acids which readily occurs below 100°C and gives thiolsulfonates and sulfonic acids:²⁴

The chemistry of sulfinates or sulfinic acids can be elaborated to provide other derivatives. Sulfinic acids are more acidic than aliphatic carboxylic acids (PhSO_2H , $\text{pK}_a=1.29$). They are readily oxidized to sulfonic acids, they add to the carbonyl group of aldehydes, and also give thioisulfonates from disulfides. Both sulfinic acids and sulfinates are nucleophilic and combine with alkyl or benzyl halides to afford sulfones, or give Michael-type addition reactions with the suitable olefin substrates.

Chlorotrimethylsilane

The reactions of mono- and dilithiated polysulfones with chlorotrimethylsilane at -20°C led to polysulfones containing predominantly monosilylated 77 and disilylated 78 repeat units respectively.

Apart from the unchanged Bisphenol-A portion, the NMR aromatic spectrum of disilylated polymer 78 was considerably different from that of the starting material or dimethylated polymer 63 (Figure 14). The substituent effect of the trimethylsilyl group on protons H-e occurs with an expected downfield chemical shift to $\delta=7.37$ (doublet, meta coupling). H-c ($\delta=6.84$, dd.) protons are coupled to ortho-sulfone protons H-d at $\delta=7.41$. This considerable upfield shift of 0.43 for H-d gives an indication about the conformational preference of the severely hindered diaryl-sulfone unit.

Figure 14

Comparative NMR Spectra of Unsubstituted, Mono- and Disilylated Udel Polysulfones (Aromatic Region)

Molecular models show that free rotation about the sulfone group is limited by H-d/silyl, and prevented by silyl/silyl interactions. A conformation where the ortho-sulfone proton is within the shielding region of the opposite aromatic ring enables these interactions to be relieved (see Figure 10).

Mono-silylated repeat units 77 have a lesser degree of restricted rotation and their spectral signals do not coincide with those of the fully substituted units. The ortho-sulfone protons (H-d, $\delta=7.71$; H-d', $\delta=7.75$) are less shielded indicating a conformation less within the aromatic shielding region. Protons H-e ($\delta=7.31$, d.) and H-c ($\delta=6.92$, dd.) also have different chemical shifts.

Shielded trimethylsilyl protons occur as a sharp singlet at $\delta=0.34$ in the disubstituted product (D.S.=1.83) and as two singlets at $\delta=0.38$ and $\delta=0.34$ (D.S.=1.13) at lower substitution levels where both mono- and disilylated repeat units occur. Minor singlets at $\delta=0.11$ and $\delta=0.49$ may account for small amounts of lithiation at other sites or different conformers.

It is anticipated that silyl modified polysulfones will be useful membrane materials in gas separation processes, particularly for oxygen enrichment. Membranes from silyl and siloxane modified poly(2,6-dimethyl-1,4-phenylene oxide) 34, prepared via metalation, showed enhanced oxygen permeability compared to unmodified

polymer.²⁴⁸ Polystyrenes containing silicon are of current interest for oxygen permeable membranes²⁴⁹ and as cross-linking groups.²⁵⁰ Other silicon and tin polymers have usefulness as resist materials.^{251, 252}

Cyclic thiasilin-5,5-dioxide derivatives 79^{234, 253, 254} have been generated from 2,2'-dilithiodiphenylsulfone 58c quenched with dichlorodimethylsilane or dichlorodiphenylsilane.

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This approach could provide an interesting polymer and an unusual instance of the introduction of a functional group into the main chain by chemical modification.

Chlorotrimethylstannane

A polymer containing trimethyl tin groups (D.S.=1.60) was synthesized by reaction of dilithiated polysulfone 62 with chlorotrimethylstannane. Incomplete substitution could be due to the steric bulk of the trimethyltin group hindering the accessibility of the metalated polymer chain. In the NMR spectrum, one major upfield signal at $\delta=0.32$ and

three minor signals at $\delta = -0.13$, 0.03 and 0.77 are in accordance with the highly shielded environment of the methyltin protons. The synthesis and applications of tin-containing polymers has been reviewed by Kowalski *et al.*²⁵⁵

Benzaldehyde

Polymers with 1,1-hydroxyphenylmethane substituents 80 were obtained by reaction of dimetalated polysulfone with benzaldehyde. The presence of the hydroxyl group is confirmed by an IR absorption at 3520 cm^{-1} and by two D₂O exchangeable broadened singlets at $\delta = 3.43$ and $\delta = 3.05$ in the NMR. Two new doublets in the ortho-sulfone deshielded region ($\delta = 8.00$ and $\delta = 7.90$) and the absence of this proton in an unsubstituted repeat unit implies a degree of substitution higher than one. The spectrum is complicated by the phenyl substituent overlying Bisphenol-A protons ($\delta = 7.24-7.12$). Two shielded singlets at $\delta = 6.53$ and $\delta = 6.43$, each 1H, could be assigned to shielded protons ortho- to the substituent and/or -CHOH. The presence of other signals at $\delta = 7.03$ and $\delta = 6.94$ is not clear but these could reflect rotationally restricted conformations. Indeed, a sample methylated with sodium hydroxide/iodomethane displayed seven major singlets between $\delta = 3.40$ and $\delta = 2.79$. The degree of substitution was 1.60 by comparison of these singlets with Bisphenol-A, although the conversion

was incomplete as hydroxyl protons were still evident. The degree of substitution by total integration of the aromatic region versus methyl was 2.0 and by hydroxyl versus methyl was 1.90.

Acetone

Acetone reacted incompletely with dilithiated polysulfone. Presumably, unfavourable keto-enol tautomerism and the greater steric hindrance of ketones compared with aldehydes are a factor. The presence of the hydroxyl group is confirmed by an absorption at 3470 cm^{-1} in the IR and two D_2O exchangeable singlets at $\delta=5.13$ and $\delta=4.70$ in the NMR, possibly arising from restricted rotations.

It has been shown by X-ray and NMR data that some ortho-substituted diaryl sulfone iso-propanol derivatives have a distorted tetrahedral geometry about sulfur and restricted rotation.^{231, 232} The dihedral angle between the planes of the phenyl rings was 87.1° and the Ar-S-Ar angle opened from 104.5° to 117.9° in one derivative. In addition, two signals were observed for diastereotopic

geminal methyl groups in the room temperature NMR.

In the NMR spectrum of the iso-propanol substituted polysulfone 81, these methyl groups have a similar chemical shift to the Bisphenol-A methyl groups. The degree of substitution was estimated to be 0.52 based on the peak heights at $\delta=1.71$, $\delta=1.69$ and $\delta=1.64$. The Bisphenol-A methyl groups in substituted and unsubstituted repeat units probably correspond to the former two signals while the methyl substituents give only one upfield singlet at $\delta=1.64$. Ortho-sulfone protons (doublets: $\delta=8.09$, 7.85 (unsubstituted repeat units), $\delta=7.76$ and $\delta=7.74$) are coupled with ortho-ether protons (broadened doublets: $\delta=6.81$ and $\delta=6.73$). Protons ortho- to the substituent appear as broadened singlets at $\delta=7.13$ and $\delta=7.10$. Other aromatic protons lie within multiplets resulting from the slightly different environments of each repeat unit.

Benzophenone

A tertiary alcohol containing polymer predominantly of the structure 82 was obtained by reaction of mono- or dilithiated polysulfone with a solution of benzophenone in THF. Polymers with a degree of substitution greater than one could not be synthesized regardless of the degree of metalation. This is not unexpected in view of the large steric effect that the triphenylcarbinol group would have on the polymer chain and the incoming second group. The polymer is readily soluble in chloroform, unlike the derivative from benzaldehyde which gives hazy solutions. This enhanced solubility could be ascribed to the greater hydrocarbon residue, lower hydroxyl content and altered chain conformations.

The structure determination is confirmed by two carbinol carbons in the ^{13}C -NMR at $\delta=81.5$ and $\delta=81.8$. The presence of hydroxyl group is confirmed by two sharp NMR singlets, exchangeable by D_2O , at $\delta=5.70$ and $\delta=6.91$ and an IR absorption band at 3400 cm^{-1} . Much of the aromatic proton spectrum (Figure 15) is masked under the phenyl residue. Signals outlying this region include the ortho-sulfone doublets at $\delta=8.15$, $\delta=7.76$ and $\delta=7.84$ (unsubstituted repeat units). The presence of a 3-4H doublet at $\delta=6.80$ is puzzling. Conceivably, H-a could be shifted upfield by a through space shielding interaction with the phenyl substituents. Therefore, the doublet at $\delta=6.94$

could be assigned to H-c' rather than H-a. Protons H-e, ortho- to the substituent appear as a shielded upfield signal at $\delta = 6.39$. Interestingly, the Bisphenol-A methyl protons display five major signals ranging from $\delta=1.72$ to $\delta=1.64$. The maximum degree of substitution obtained from dilithiated polysulfone was 1.0 based on total aromatic versus aliphatic integration. Diphenylsulfone bearing this diphenylcarbinol substituent has been synthesized by Köbrich using the metalation procedure.²⁴⁵

Figure 15

NMR Spectrum of Diphenylcarbinol Substituted Polysulfone
(Aromatic Region)

Iodine

Iodine substituted polymers were readily obtained by the reaction of iodine solution in THF with metalated polysulfone. The efficiency of the reaction is evident from the high degrees of substitution obtained: 1.0 and 1.78 from mono- and dilithiated polysulfone respectively, determined by iodine analysis. The NMR spectrum shows

several deshielded doublets due to the different environments of ortho-sulfone protons in the mono- and disubstituted repeat units. Broad singlets at $\delta=7.58$ and $\delta=7.56$ correspond to protons ortho- to iodine in mono- and disubstituted repeat units respectively. The iodinated polymers are readily soluble in THF and chloroform and contain repeat units 83a and 83b.

83a R=H
83b R=I

Iodinated polymers, particularly polystyrene derivatives, are currently of interest as negative electron beam resists.^{256, 257} The aryl iodine group is also useful for the elaboration of further chemistry. For example, processable poly(aryl esters) containing pendant phenyl acetylenyl groups have been synthesized by reaction of cuprous phenylacetylide with an iodinated polyester.²⁵⁸ Intramolecular cyclization, accomplished by curing at 270°C, gave an insoluble aromatic polyester. This reaction could be applied to iodinated polysulfone to attain a thermally curable polymer with phenyl acetylenyl groups.

Benzonitrile

The addition of benzonitrile to monolithiated polysulfone resulted in the formation of a lithium imide derivative which precipitated out of solution as a red gum. Upon work up, the polymer was recovered in the imide form and did not undergo the expected hydrolysis to a ketone. The bright yellow polymer is soluble in NMP, DMSO, DMA, DMF and partly soluble in THF and chloroform. Repeat units of the imide substituted polymer are of the structure 84.

Elemental analysis for carbon, hydrogen and nitrogen are consistent with the above structure. New absorptions in the IR spectrum include a major band at 1688 cm^{-1} and a minor band at 3260 cm^{-1} (N-H stretch). The range for C=N stretch is $1690\text{--}1580\text{ cm}^{-1}$, with conjugated imines typically occurring at about 1625 cm^{-1} . The polymer has a complicated NMR spectrum which includes a downfield D_2O exchangeable signal at $\delta=9.62$ corresponding to N-H proton. The degree of substitution was 0.87 by NMR integration.

Phenylisocyanate

A yellow polymer was obtained from the reaction of phenylisocyanate with monolithiated polysulfone. During synthesis, a thick red gel formed, presumably the lithium amide intermediate. The polymer is only partly soluble in THF and chloroform, and some has repeat units of the structure 85.

The polymer had a lower than expected nitrogen analysis suggesting a degree of substitution of only 0.43. The carbon analysis was also slightly higher than expected. Three new absorption bands in the infrared spectrum were observed at 1540 cm^{-1} , 1675 cm^{-1} and a broad band centred at 3300 cm^{-1} . The latter is consistent with N-H stretching vibration in solid samples. The strong absorption at 1675 cm^{-1} corresponds to the Amide I band for C=O stretch and has a typical value for anilide structures, where there is competition between phenyl and carbonyl for the nitrogen lone electron pair. A medium intensity Amide II band at 1540 cm^{-1} corresponds to N-H bending vibrations. The N-H group is evident in the NMR spectrum by a broad downfield

signal at $\delta=8.32$, exchangeable by D_2O . The remainder of the spectrum is ill defined and characterized by a series of broad downfield signals. The poor resolution is probably partly caused by the inhomogeneity of the sample in the chosen solvent.

Other Electrophiles

Preliminary experiments with other electrophiles gave derivatives which have not been fully elucidated by structural analysis. These electrophiles were: ethylene oxide, allyl bromide, propargyl bromide, acetyl chloride, dimethylformamide and bromobutane.

The Modification of Polysulfones by Bromination and Metalation

The two step process of bromination/metalation offers an alternative synthetic route to modified polysulfones. This synthetic strategy has already been used successfully in other polymeric systems to produce derivatized polystyrenes^{1,2} and poly(2,6-dimethyl-1,4-phenylene oxide).^{3,4} Apart from the utility of introducing further functional groups, brominated polymers are of interest because of their enhanced properties as fire retardants. Typically, brominated polymers or oligomers are synthesized from brominated monomers such as tetrabromo-Bisphenol-A. However, there are only a few reports of direct bromination of polysulfones. A method of treating polysulfone surfaces with bromine has been reported to enhance metal plating.⁵ Fire retardant polymer has been synthesized by bromination of Udel polysulfone with bromine and an iron catalyst.⁶ The polymer contained six bromine atoms per repeat unit.

Halogenation of Udel and Radel polysulfone occurs readily by electrophilic substitution. The reactive substitution position is situated ortho- to the aryl ether linkage in the Bisphenol-A portion of the repeat units. This is the most favourable site because of the greater electron density supplied by the lone electron pair on the oxygen atom. Dihalogenated polysulfones were obtained by

reaction of the polymer with an excess of elemental halogen in the absence of catalyst.

Thus, a solution of Udel polysulfone in chloroform, treated with excess bromine at room temperature, gave dibrominated polysulfone 86 in high yield.

The degree of substitution after 18-24 hours was typically 1.80 to 2.05 by bromine analysis. Lower degrees of substitution were obtained with shorter reaction times as shown in Table VII.

Table VII
Progressive Bromine Uptake of Udel Polysulfone

Time/hr.	%Br
1	13.25
2	16.07
3	17.18
4	19.53
5	19.38
24	23.46
$C_{27}H_{20}SO_4Br_2$	26.62

When an iron powder catalyst was used in conjunction

with excess bromine, following a similar procedure to Ohmae *et al.*,²⁴ a brittle greyish-brown polymer with a halogen content of 40.5% was obtained. The apparently low molecular weight polymer contained slightly less than four bromine atoms per repeat unit, as opposed to six reported by Ohmae *et al.*

Figure 16 shows the NMR spectrum of dibrominated Udel polysulfone compared with the unmodified polymer. The modification site in the Bisphenol-A portion of the polymer is reflected by the largely unchanged aryl-sulfone doublets. Protons ortho- to bromine appear as a meta-coupled doublet at $\delta=7.52$. The in unmodified polymer H-b doublet is replaced by a doublet of doublets at $\delta=7.16$ arising from ortho- and meta-coupling in the dibrominated polymer. Although the product had a low viscosity, little or no degradation occurred since the subsequently metalated/deuterated product had a similar viscosity to polysulfone.

Dibrominated polysulfone 86 was metalated with *n*-butyllithium and the lithiated intermediate was trapped with deuterium oxide. Both the bromine and the ortho-sulfone position are potentially reactive metalation sites; the first by simple metal-halogen exchange and the second by hetero-atom directed lithiation. A substantial amount of competition between these two reactions might be expected. However, the NMR spectrum of the dideuterated polysulfone derivative 87 in Figure 16 shows that metal-

halogen exchange is the dominant reaction, with a minimal amount of ortho-lithiation evident in this derivative. The aryl sulfone doublets remain unaltered while the Bisphenol-A proton signals show dideuteration ortho- to oxygen by the H-b/H-e multiplet and the diminution of the doublet H-a.

Figure 16

Comparative NMR Spectra of Unsubstituted, Dibrominated and Dideuterated Udel Polysulfone (Aromatic Region)

The structure of dimethylated polysulfone 88, obtained by dilithiation and subsequent methylation with iodomethane, also confirms that metal-halogen exchange occurs preferentially. However, the NMR spectrum of this derivative, shown in Figure 17, provides evidence for a small degree of competitive ortho-lithiation. The two major doublets at $\delta=7.83$ and $\delta=6.91$ correspond to the aryl-sulfone portion of the polymer. A broadened singlet at $\delta=7.13$ arises from protons ortho- to the methyl groups. The remaining H-b and H-a protons appear as a broadened doublet at $\delta=7.06$ and a doublet at $\delta=6.84$ respectively. A small percentage of repeat units containing methyl groups ortho- to the sulfone linkage have obvious signals at $\delta=8.12$ & $\delta=7.77$ (ortho-sulfone), $\delta=7.25$ (H-b) and at $\delta=7.00$ (H-a).

Figure 17

NMR Spectrum of Dimethylated Udel Polysulfone
Derived from Dibrominated Polymer (Aromatic Region)

The degree of metalation at the bromine atom was 1.60, and at the ortho-sulfone site was 0.18. This was measured by integration of the singlets at $\delta=2.11$ and $\delta=2.40$ respectively.

Udel polysulfone was also reactive to chlorination with elemental chlorine. A dichlorinated polysulfone of the structure 89 was obtained, as confirmed by elemental analysis. The 60 MHz NMR spectrum, recorded shortly after

the derivative was synthesized, was very similar to the dibrominated derivative. However, the high field NMR, recorded over a year later, showed degradation and some loss of chlorine.

Radel polysulfone was also readily brominated by excess elemental bromine in the absence of catalyst. The degree of substitution was two bromine atoms per repeat unit as shown by bromine analysis. The position of bromination also occurs at the electrophilic site ortho- to the ether linkage and the polymer consists of repeat units of the formula 90. The NMR spectrum (Figure 18) shows unchanged signals from the aryl-sulfone portion. The three types of protons in the substituted ring appear as a singlet at $\delta=7.85$ (H-e), a broadened doublet at 7.52 (H-b) and a doublet at $\delta=7.14$ (H-a), confirming the site of substitution in the biphenyl ring. Victrex polysulfone was not amenable to bromination under the same conditions and resulted only in unchanged starting material.

The bromination/lithiation method of polysulfone modification, by analogy to the direct metalation, allows

the same number and diversity of functional group derivatives to be synthesized. While only deuterated and methylated derivatives have been prepared, many other substituents are accessible by the appropriate choice of electrophile. Just as substituents on the ortho-sulfone site may affect the conformation of the relatively rigid aryl-sulfone linkage, so the rotational freedom of the ether linkage may be affected by bulky substituents. This may increase the rigidity in the polymer chains. This phenomenon has been observed in tetramethyl Bisphenol-A polysulfones 23 where methyl substitution hinders chain rotation resulting in an increase of 40°C in the glass transition temperature.^{6,60} However, chain stiffening does not occur in the dimethyl derivatives.

Figure 18

Comparative NMR Spectra of Unsubstituted and Dibrominated
Radcl Polysulfone (Aromatic Region)

Selected Properties of Modified Polysulfones

Glass Transition Temperatures

The glass transition temperatures of modified polysulfones were determined by differential scanning calorimetry. The substitution of functional groups on the polymer chain reduced the T_g in all but one of the derivatives. The T_g of polymer 88, where the methyl groups are ortho- to the ether linkage, was slightly higher than polymers 63 or 67, where the methyl groups are ortho- to the sulfone group. This lower value in the latter two polymers could be due to a decrease in rigidity about the sulfone linkage. The T_g was also reduced by the introduction of thiomethyl groups in polymer 75, and reduced substantially in both mono- and disilylated derivative 77 and 78. The bulky silyl group apparently does not further hinder the chain rotation in the already stiff sulfone linkage. The expected effect of side-chain mobility is well illustrated by the low T_g of dibutylated Udel polysulfone. However, the inflexible diphenylcarbinol derivative 87 had a slightly higher T_g value than the unmodified polymer. Carboxylic ester derivatives 73 and 74 had lower T_g values with increasing substitution. For these polymers in the ionomeric form, endotherms were observed for loss of bound water, but no glass transition endotherms could be determined. In conclusion, functional groups situated ortho- to the

resonant and relatively inflexible sulfone group do not generally increase chain rigidity and usually result in a drop of 10-20°C in the glass transition temperature. However, tetramethyl substitution ortho- to the flexible ether linkage has been shown to increase the chain rigidity and the T_g value by 40°C. The DSC results are summarized in Table VIII.

Table VIII
Glass Transition Temperatures of Modified Polysulfones.

Polysulfone Derivative	T_g , °C
Udel	189
Radel	212
Dimethyl 63	171
Dimethyl 68	202
Dimethyl 88	179
Trimethyl 67	168
Thiomethyl 75	181
Hydroxyl 82	192
Trimethylsilyl 77	168
Trimethylsilyl 78	168
Carboxylic ester 74	182
Dicarboxylic ester 73	155
Dibutylated Udel	113

Thermal Stability

The thermal stabilities of several modified polysulfones were determined by thermogravimetry. The hydroxyl containing polymer, 82, had a low onset of decomposition at 235°C. A rapid weight loss of 25% corresponded to the loss

of the bulky diphenylcarbinol group. The TG curve displayed a plateau between 350°C and 455°C, followed by a rapid weight loss. A similar plateau was observed in the TG curve of polymer 74 (lithium carboxylate form). The loss of the functional group occurred at 315°C and the major onset of decomposition occurred at 415°C. The TG curve of thiomethylated polymer 75 exhibited a single onset of decomposition at 380°C. These three modified polysulfones were less thermally stable than unmodified polysulfone which has an onset of weight loss at 475°C.

CONCLUSIONS

Polysulfones containing functional groups were prepared by three synthetic routes.

A technique of purifying monomer 50 was developed, from which ionomeric polymers with pendant fluorene rings, 56 and 57, were synthesized. The presence of ions in these polymers, and the rigidity and aromatic content of the bisphenol portion resulted in exceptionally high glass transition temperatures. An increase in hydrophilicity was evident from the water adsorption of these polymers which was an order of magnitude more than for polysulfone. Polymer 57 had a thermal stability comparable with Nafion.[®]

The chemical modification of polysulfones by direct metalation provides a versatile synthetic pathway to a diverse range of functional group containing polymers. The metalation technique is both simple and rapid and results in products with a high degree of substitution. Up to two lithium atoms per repeat unit were substituted rapidly on the polymer chain ortho- to the sulfone linkage. The degree of substitution was well controlled and required little or no excess of metalating agent. Longer reaction times and an excess of metalating agent resulted in the substitution of three lithium atoms. The most effective metalating agent was *n*-butyllithium, but methyllithium and phenyllithium were also effective. However, LDA was not

effective and led to polymer gelation. The lithiated polymer intermediate, by its inherent nature, was reactive to a variety of electrophiles. Carbon dioxide, sulfur dioxide, dimethyldisulfide, iodine, chlorotrimethylsilane and benzonitrile reacted efficiently with the reactive intermediate, providing the corresponding functional group derivatives. Some ketones and phenylisocyanate resulted in lesser amounts of substitution. In most cases the addition of a functional group only moderately reduced the glass transition temperature compared to the parent polymer.

Polysulfones were also brominated or chlorinated with elemental halogen in the absence of a catalyst. Two halogen atoms per recurring unit were substituted at the site ortho- to the ether linkage on the Bisphenol-A rings. When these products were metalated, lithium-halogen exchange occurred preferentially to direct ortho- sulfone lithiation. Hence, a functional group may be placed at either site depending on the synthetic route employed.

Metalation provides a facile route to a new series of materials which have hitherto been inaccessible. Preliminary experiments with carboxylate polymer 74 showed that materials were considerably more hydrophilic than polysulfone. It is anticipated that these polymers will be useful in aqueous ultrafiltration and reverse osmosis applications, particularly in view of the control of

derivatization. Hydroxyl polymers also appear to be promising materials for hydrophilic membranes. Conversely, silyl polymers are more hydrophobic and may have utility in oil or gas separations. The development of these new polymer materials should make a significant contribution to membrane materials.

A number of opportunities exist for further development. There are several possible routes to ethynyl substituted polysulfones. These polymers are expected to be thermally cross-linkable and have improved solvent resistance. Aromatic bromo or iodo groups can be displaced in high yield with trimethylsilylacetylene using a $(PPh_3)_2PdOAc$ catalyst. Aromatic iodo groups can also be displaced with cuprous phenylacetylide. Alternatively, lithiated polymers may react directly with propargyl bromide. Similarly, cross-linkable allyl substituted polymers may be obtained from allyl bromide. In addition lithiated polysulfones could provide a convenient route to a variety of graft polymers.

EXPERIMENTAL

Polymer characterization

^1H -NMR spectra were recorded on a Varian EM-360 60MHz spectrometer and a Bruker AM-400 400MHz spectrometer at room temperature. ^{13}C -NMR spectra were recorded on the latter machine. Samples were dissolved in CDCl_3 or $\text{DMSO}-d_6$ with an internal tetramethylsilane (TMS) standard. Chemical shifts δ are expressed in parts per million (ppm) and the spectral resonances are designated: singlet (s.), doublet (d.), triplet (t.), quartet (q.), multiplet (m.) and broadened (br.). Coupling constants (J) are in Hertz. Unsubstituted, monosubstituted, disubstituted and trisubstituted repeat units are designated U, M, D and T respectively.

Infrared measurements were made on a Perkin-Elmer 683 spectrometer. Samples were cast as thin films from polymer solutions in THF or chloroform.

Melting points were determined on a Büchi SMP-20 melting point apparatus and are uncorrected.

Gel permeation chromatography measurements were made on a Waters GPC 301 using a range of μ -styragel columns, from 10^7 - 10^2 Å. The eluent was THF at 1 mL min^{-1} at ambient temperature. The elution time (t_r) was compared with polystyrene standards. All polymers except 56K.

examined by GPC gave a chromatogram showing a symmetrical peak.

Viscosity measurements were made on a Cannon-Ubbelohde dilution viscometer model 75 following ASTM D 2857-70. The constant temperature bath was controlled to 25.0°C using a Lauda Brinkmann Instruments thermoregulator. Polymer solutions were normally filtered through 0.5 μ m teflon Millipore filters or occasionally through coarser filters. Intrinsic viscosity $[\eta]$ was measured at 25.0°C in NMP and was determined by the Huggins equation.²⁶²

Glass transition temperatures were determined using a duPont 910 Differential Scanning Calorimetry (DSC) module in combination with a duPont 1090 Thermal Analyzer. Samples were heated under nitrogen at a rate of 10°C or 20°C per minute.

The thermogravimetric curves were determined using a duPont 951 Thermogravimetric Module in combination with a duPont 1090 Thermal Analyzer. Samples were heated at a rate of 10°C per minute under nitrogen.

Synthesis of Carboxyl Substituted Polymers

General experimental details

The carboxyl substituted bisphenol monomers were synthesized and purified as described. Diphenolic acid was obtained from Raylo Chemicals. Bisphenol-A (Pfaltz and Bauer Inc.) was supplied pure (M.Pt. = 158.5-159.5°C) and was used as received. Dichlorodiphenylsulfone (Pfaltz and Bauer Inc.) and difluorodiphenylsulfone (Aldrich Chemical Co.) were purified by recrystallization from ethanol. Chlorophenylphenylsulfone (Aldrich Chemical Co.) was recrystallized from iso-propanol. Toluene, xylene and DMSO were distilled prior to use.

The reaction vessel consisted of a resin kettle equipped with a gas inlet, Dean-Stark trap with condenser, thermocouple and mechanical stirrer. A high torque motor drove a specially made heavy duty stainless steel stirrer. All reactions were performed under an inert atmosphere of dry nitrogen or argon. Polymer solutions were precipitated into a non-solvent in a large stainless steel Waring Blender.

4-Hydroxy- γ -(4-hydroxyphenyl)- γ -methyl-benzenebutanoic acid (Diphenolic acid 48)

Approximately 500 g of Diphenolic acid was dissolved in ethyl acetate and stirred with decolourizing charcoal at

room temperature for 10 minutes. After filtering off the charcoal, the solvent was evaporated down to a viscous oil which started to crystallize after a short time. The oil was dissolved in 1700 mL of toluene and stirred vigorously until a white mass of Diphenolic acid precipitated. The mixture was heated to 80°C-90°C while stirring and acetone added in small amounts until the solids dissolved and the solution cleared. In some cases, a small quantity of brown oil remained which was discarded by decanting the crystallization liquor. The solution was allowed to cool to 30°C and then seeded with crystals from a previous recrystallization. Following crystallization, the process was repeated and then the product was dried in a vacuum oven for 4 days at 100°C. M.Pt. = 175.5-176°C (Lit.¹⁷⁰ M.Pt. = 171-172°C).

Mass spectrum: m/e (relative intensity), M 286(12), M-CH₃ 271(3), 214(20), M-CH₂CH₂COOH 213(100), 197(6), 119(24), C₆H₅ 91(18), 69(32).

4-Hydroxy- α -(4-hydroxyphenyl)- α -methyl-benzeneacetic acid

49

Following a similar procedure to Parris et al.,¹⁷² phenol (1410 g, 15.0 mol) was dissolved in glacial acetic acid (1500 mL) in a 5 L four neck round bottomed flask equipped with a mechanical stirrer, nitrogen inlet, condenser, and thermometer. After twenty minutes all the phenol had dissolved to give a clear colourless solution at a temperature of -1°C. Freshly distilled pyruvic acid (264

g, 3.0 mol) was added and hydrogen chloride was bubbled in. No reaction occurred until the solution had warmed up to room temperature at which point it turned to an orange colour and the temperature rose spontaneously to 56°C. Treatment with hydrogen chloride was continued for a total of four hours and the solution was left to stand at room temperature for 24 hours after which time the mixture was again saturated with hydrogen chloride for an additional 4 hours. After 5 days the mixture was poured over crushed ice and the oil was extracted with ethyl acetate in a 6 L separating funnel. The organic phase was washed with saturated sodium chloride (15x) until the washings were neutral and then the product was extracted with saturated NaHCO₃ solution and the organic layer discarded. The product in the aqueous phase was acidified by pouring it into excess dilute hydrochloric acid and the resulting light yellow oil was extracted with ethyl acetate and washed with saturated sodium chloride solution (10x) until the washings were neutral. The organic phase was dried over MgSO₄, concentrated to an oil and then crystallized from an ethyl acetate/benzene mixture. The product was recrystallized to give 251 g (32%) of pure monomer 49. M.Pt. = 182-183.5°C (Lit.¹⁷ M.Pt. = 177.5-179°C.

Mass spectrum: m/e(relative intensity), M 258(15), 214(13), M-COOH 213(100), 197(5), 119(20), C₆H₅ 91(10).

9,9-Bis(4-hydroxyphenyl)-fluorene-4-carboxylic acid 50

Diphenic acid 52 (500 g, 2.06 mol) was reacted with concentrated sulfuric acid (1250 mL, S.G. 1.84) at 140°C for 35 minutes following the procedure of Huntress *et al.*

¹⁷⁵ The red solution was cooled and precipitated by pouring the mixture into 15 L of distilled water. The yellow precipitate was boiled with 10 L of water, filtered and boiled again with 10 L of water. The dried yellow product 9-fluorenone-4-carboxylic acid 53 (Yield 463 g, 81%) was used in the next step without further purification.

In a 5 L three neck round bottom flask equipped with a gas inlet bubbler, mechanical stirrer and condenser, was placed 538 g (2.4 mol) of finely ground crude 9-fluorenone-4-carboxylic acid 7, 1130 g (12.0 mol) of molten phenol and 12 mL of 3-mercaptopropionic acid. The mixture was stirred at 50°C while bubbling in anhydrous hydrogen chloride gas. After an initial period, an exothermic reaction began, and heating was stopped. After two to three hours the yellow colour was replaced by a brown colour. Stirring and treatment with hydrogen chloride was continued for a total of six hours and then the mixture was allowed to stand overnight under an inert atmosphere. Phenol was removed from the reaction products by steam distillation and the remaining hot slurry was poured into a 20 L beaker and boiled with 10 L of water. The mixture was

allowed to cool for half an hour and then the supernatant was decanted off from the settled solids and discarded. The product was washed again in the same way and then filtered to give 875 g (92%) of crude 9,9-bis(4-hydroxyphenyl)-fluorene-4-carboxylic acid 50 which was shown to be the major product by thin layer chromatography.

The product was not readily purified on a large scale by direct crystallization. However, the monosodium carboxylate salt was amenable to crystallization in aqueous medium providing that excess sodium bicarbonate was used. A 1:1 weight ratio of monomer 50 to sodium bicarbonate led to efficient crystallization and gave a product that was filtered more easily. Thus 400 g of crude product was placed in a 20 L beaker with 8 L of water and heated to approximately 60°C. 400 g of NaHCO₃ was added in portions and then the total volume was made up to 14 L with water and heated to boiling. The sodium salt product was filtered on a Buchner funnel after overnight crystallization. The crystals were redissolved in 14 L of hot water and decolourizing charcoal was added. The solution was stirred at 70°C-85°C for one hour and then filtered hot on a cellulose fiber bed. The clarified solution was neutralized by adding concentrated hydrochloric acid with stirring and then the suspension was heated to boiling to coagulate the precipitate. After filtering, washing and drying, the product weighed 259 g (65% of crude).

This material was further purified by suspending the product in 6 L of water and adding 280 g NaHCO_3 . Following the same purification technique, 242 g of pure monomer 50 was recovered. The structure was confirmed by elemental analysis, MS and NMR. M.Pt. $296-297^\circ\text{C}$ (Lit.¹⁷ M.Pt. = $276-279^\circ\text{C}$).

Elemental analysis: calculated for $\text{C}_{12}\text{H}_{10}\text{O}_4$
 Calc. C:79.17%, H:4.60%
 Found C:79.36%, H:4.78%

Mass spectrum: m/e(relative intensity), M+1 395(25), M 394(93), 350(35), $\text{M}-\text{COOH}$ 349(97), 348(19), 302(14), 301(60), 255(30), 227(20), 226(50), 188(26), 150(16), 97(16), 83(18), 73(33), 71(28), 69(33), 60(26), 57(56), 55(75), 44(100), 43(96), 41(58).

NMR 400 MHz ($\text{DMSO}-d_6$): $\delta=8.36$ H-ortho-COOH (1H d. $J\approx 7.7$), $\delta=7.74$ (1H d. $J\approx 7.6$), $\delta=7.60$ (1H d. $J\approx 7.6$), $\delta=7.45$ (1H d. $J\approx 7.3$), $\delta=7.39-7.30$ (3H m.), $\delta=7.01$ H-meta-OH (4H d. $J\approx 8.7$), $\delta=6.73$ H-ortho-OH (4H d. $J\approx 8.7$).

Copolymer 54Na from Diphenolic acid 48, Bisphenol A 15 and dichlorophenylsulfone

Method 1

The polymer was prepared following a procedure similar to the one of Khattab.¹⁹ In the 500 mL resin kettle was placed Bisphenol-A (21.1124 g, 0.0925 mol) and Diphenolic acid (30.7864 g, 0.1075 mol) with toluene (120 mL) and DMSO (125 mL). Sodium hydroxide (20.502 g, 0.5125 mol) was added as a 50% aqueous solution and the mixture was stirred under reflux at 120°C for six hours after which time no more water collected in the Dean-Stark trap. Toluene was distilled off from the viscous mixture until the reaction

temperature reached 142°C and then the mixture was allowed to cool for a short time. Dichlorodiphenylsulfone (57.4332 g, 0.2000 mol) and DMSO (120 mL) were added and then heating was resumed at a reaction temperature of 130°C for 24 hours. The viscous solution was allowed to cool to room temperature and then precipitated into methanol in a Waring blender. After washing and drying, the yield of polymer 54Na was 84.0 g (86%).

Methylation. 20 g of polymer was dissolved in DMSO (75 mL) at a temperature of 130°C. The solution was treated with chloromethane gas for two hours and then chlorobenzene (75 mL) was added to precipitate out the salt. After filtering the solution, it was precipitated into methanol and dried to give methylated polymer 54Me. M.W. (GPC) = 27,600; t_v = 33.8 minutes.

Method 2

The polymer was prepared following a similar procedure to the one of Olabisi and Farnham.^{1,2} Diphenolic acid (76.9660 g, 0.2688 mol), Bisphenol-A (52.7812 g, 0.2312 mol), DMSO (250 mL) and toluene (450 mL) were placed in a one litre resin kettle equipped in the usual manner. Sodium hydroxide (99%, 51.256 g, 1.281 mol) was added as a 50% aqueous solution. The mixture was stirred vigorously under reflux for 6 hours and under nitrogen until no more water collected in the trap. Toluene was distilled off until a reaction temperature of 130°C was reached and then

dichlorodiphenylsulfone (143.5832 g, 0.5000 mol) dissolved in hot toluene (250 mL) was added carefully to the viscous mixture. An additional 50 mL of DMSO was added and then the toluene was distilled off until the temperature reached 165°C. The mixture was stirred and maintained at this temperature during which time the viscosity increased considerably. The polymer was recovered by precipitation into methanol, washed with several portions of hot water and dried in a vacuum oven at 85°C for 3 days. Yield 234.88 g (97%), M.W.(GPC) 54Me = 27,600, t_v = 33.8 minutes.

Copolymer 54K from Diphenolic acid 48, Bisphenol-A 15 and dichlorodiphenylsulfone

The polymer was prepared following a similar procedure to the one of Olabisi and Farnham.¹⁹² Diphenolic acid (71.5826 g, 0.2500 mol) and Bisphenol-A (57.0734 g, 0.2500 mol) were dissolved in DMSO (250 mL) at 100°C in a one litre resin kettle equipped in the usual manner. Potassium hydroxide (86.6%, 81.40 g = 1.256 mol) solution (50% aqueous) followed by xylene (250 mL) were added and the mixture was stirred at reflux temperature (143°C) in an argon atmosphere for 5 hours until no more water collected in the trap. Dichlorodiphenylsulfone (143.5832 g, 0.500 mol) dissolved in hot xylene was added cautiously to the stirred heated slurry. Xylene was distilled off until the temperature reached 165°C and stirring was continued at this

temperature. Samples of the viscous mixture were withdrawn after 2 and 4 hours and methylated for GPC analysis. After 5.5 hours, the reactive phenoxide chain ends of the polymer were end-capped by the addition of chlorophenylphenylsulfone (4.5 g). After half an hour, the polymer 54K was recovered by precipitation into water and then left to stand in several changes of fresh water. Yield 247 g (100%).

M.W. (GPC) 54Me 2hrs: 40,000, t_r = 33.0 minutes
 4hrs: 48,000, t_r = 32.7 minutes
 6hrs: 48,000, t_r = 32.7 minutes

NMR 400 MHz (CDCl₃) methylated polymer 54Me: δ =7.85 H-ortho-sulfone (8H br.d.), δ =7.32-7.20 H-ortho-alkyl (8H m.), δ =7.00 H-meta-sulfone (8H d.), δ =6.94 H-meta-alkyl (8H br.d.), δ =3.64 COOMe (s. incomplete methylation), δ =2.48-2.44 CH₂ (2H m.), δ =2.16-2.12 CH₂ (2H m.), δ =1.69 CMe₂ (6H s.), δ =1.64 CMe (3H s.).

Copolymer 55Na from Diphenolic acid 48 and dichlorodiphenylsulfone

Diphenolic acid (28.633 g, 0.100 mol), DMSO (200 mL), toluene (350 mL) and sodium hydroxide (12.00 g, 0.30 mol) as a 50% aqueous solution, were placed in a 500 mL resin kettle equipped in the usual way. The mixture was stirred at reflux until no more water collected in the Dean-Stark trap and then toluene was distilled off until the reaction temperature reached 125°C. Dichlorodiphenylsulfone (28.717 g, 0.100 mol) was added to the mixture as a slurry in DMSO (100 mL). Heating was resumed at a reflux temperature of 130°C and maintained over the next 40 hours at 130°C-135°C.

Toluene was then distilled off until the reaction temperature was 160°C and then the mixture was maintained at this temperature for 3 hours. The resulting polymer 55Na was difficult to recover in the ionomeric form, being soluble in water and methanol. Hence, the mixture was precipitated into ethanol and then acidified with hydrochloric acid. The polymer 55H was washed with water and then dried in a vacuum oven. Yield = 44.77 g (89%).

Methylation. Polymer 55Me was prepared by treatment of a solution of the acid polymer 55H (1 g) in THF (150 mL) and methanol (30 mL) with hydrogen chloride for two hours. The solvent was evaporated off and water was added to precipitate the methylated polymer. The product was washed several times with water, then redissolved in THF and precipitated into methanol and dried. M.W.(GPC) 55Me = 30,200, t_r = 33.5 minutes.

IR (film) 55H : 2370-3600 cm^{-1} (br. OH st.),
1715 cm^{-1} (C=O st.)

IR (film) 55Me: 1730 cm^{-1} (C=O st.)

NMR 400 MHz (CDCl_3) methylated polymer 55Me: δ =7.86 H-d (4H d. $J \approx 8.8$), δ =7.22 H-b (4H d. $J \approx 8.7$), δ =7.04 H-c (4H d. $J \approx 8.8$), δ =6.95 H-a (4H d. $J \approx 8.7$), δ =3.64 COOMe (3H s.), δ =2.47 CH_2 (2H t.) δ =2.15 CH_2 (2H t.), δ =2.15 CH_2 (2H t.), δ =1.64 CH_3 (3H s.).

Copolymer derived from bisphenol 49, Bisphenol-A 15 and dichlorodiphenylsulfone

Bisphenol-A (10.960 g, 0.048 mol), Bisphenol 49 (13.427 g, 0.052 mol) and a 50% aqueous solution of sodium hydroxide (10.08 g, 0.25 mol) were mixed with DMSO (60 mL),

toluene (100 mL) and chlorobenzene (75 mL) in a 500 mL resin kettle equipped in the usual way. After stirring at reflux for 220 minutes, no more water was collected, and the cosolvents were distilled off until the reaction mixture reached 160°C. The reaction was cooled to approximately 100°C and dichlorodiphenylsulfone (28.716 g, 0.100 mol) was added as a toluene slurry. Stirring was continued at 160°C-165°C for 3.5 hours and then the polymer solution was precipitated into methanol, washed with water and methanol and dried under vacuum at 80°C. A sample of polymer was methylated for GPC analysis by treatment of a solution of ionomer in DMSO with iodomethane. M.W.(GPC) = 16,000, $t_v = 34.8$ minutes.

Copolymer 56Na from bisphenol 50, Bisphenol-A 15 and dichlorodiphenylsulfone

Bisphenol-A (11.4157 g, 0.0500 mol), Bisphenol 50 (19.7215 g, 0.0500 mol) and a 50% aqueous solution of sodium hydroxide (10.00 g, 0.25 mol) were mixed with DMSO (50 mL) and toluene (150 mL) in a 500 mL resin kettle equipped in the usual way. The mixture was stirred at reflux for 4 hours until no more water was removed and then the reaction temperature was increased to 150°C by distilling off toluene. Dichlorodiphenylsulfone (28.7166 g, 0.100 mol) was added as a slurry in toluene, and the remained was washed in with DMSO (50 mL). Toluene was

distilled off and the reaction was stirred at 165-170°C for 5.5 hours. The polymer was precipitated into ethanol, then dried under vacuum for 24 hours at 90°C. The yield of polymer was 51.8 g (99%). The polymer is soluble in aprotic solvents such as NMP, DMA, DMSO and DMF.

Methylation. The ionomer was incompletely esterified where chloromethane was employed. Instead, 5 g of the ionomer was dissolved in 20 mL DMSO at 60°C and iodomethane added. After a few minutes the solution became less viscous and the esterified polymer derivative was precipitated into alcohol, washed with water and dried. M.W.(GPC) 56Me = 18,200, t_r = 34.5 minutes, $[\eta]$ 56Me = 0.23.

Copolymer 56K from bisphenol 50, Bisphenol-A 15 and difluorodiphenylsulfone

Bisphenol-A (11.4147 g, 0.0500 mol), bisphenol 50 (19.7215 g, 0.0500 mol) and a 50% aqueous solution of potassium hydroxide (86.6%, 16.36 g = 0.252 mol) were mixed with DMSO (150 mL) and xylene (200 mL) in a 500 mL resin kettle which was equipped in the usual way. The mixture was stirred at reflux for 5 hours until no more water was removed and then the reaction temperature was increased to 150°C by distilling off xylene. Difluorodiphenylsulfone (25.4258 g, 0.1000 mol) dissolved in hot xylene (60 mL) was added to the reactor slowly with continuous stirring. Xylene was distilled off until the temperature reached

165°C and a further 50 mL of DMSO was added. The mixture was stirred vigorously at 165°C for 8 hours by which time it had become very viscous. The polymer was precipitated into iso-propanol in a Waring blender, washed with iso-propanol and then left to stand overnight in the same solvent. Polymer 56K was boiled with 3x3 L of water, once with alcohol and then dried in a vacuum oven at 70-90°C for 3 days. The polymer is soluble in aprotic solvents such as NMP, DMA, DMSO, and DMF.

Methylation 8 grams of the ionomer were dissolved in 30 mL of DMSO and chloromethane was bubbled into the solution. After 20 minutes the solution had turned a lighter colour and had become less viscous. The polymer solution was precipitated into iso-propanol, washed several times with water and alcohol and then dried. The product was later shown to be incompletely esterified. The molecular weight samples could not be filtered through a 0.5 μ m filter. M.W. (GPC) 56Me = 125,000, t_v = 30.9 minutes, $[\eta]$ 56Me = 1.30.

NMR 400 MHz (CDCl₃) 56Me: δ =8.31 (d.), δ =7.86-7.80 (m.), δ =7.52 (d.), δ =7.39-7.29 (m.), δ =7.23 (d.), δ =7.18 (d.), δ =7.01-6.85 (m.), δ =4.03 COOMe (s.), δ =2.85 and 2.63 impurities, δ =1.68 CMe₂ (s.).

Polymer 57Na from bisphenol 50 and dichlorodiphenylsulfone

Bisphenol 50 (39.4431 g, 0.1000 mol) and a 50% aqueous solution of sodium hydroxide (12.03 g, 0.30 mol) were mixed with DMSO (100 mL) and toluene (150 mL) in a 500 mL resin

kettle equipped in the usual manner. The mixture was stirred at reflux temperature for 4 hours until no more water collected in the Dean-Stark trap and then the temperature was increased to 150°C by distilling off the toluene. Dichlorodiphenylsulfone (28.7166 g, 0.1000 mol) was added slowly as a slurry in toluene and then the temperature was increased to 160-165°C. Stirring was continued for 6 hours at this temperature and then the mixture was precipitated into iso-propanol, washed several times with alcohol and water and then dried in a vacuum oven to give 59.5 g (94%) of ionomer 57Na. If an ethanol or water suspension of this polymer was heated when residual DMSO was present, the polymer would dissolve.

Esterification. Initial attempts to methylate the polymer with chloromethane resulted in partly esterified product which was not soluble in THF or chloroform. A butylated derivative 57Bu was prepared by dissolving 4 g of ionomer in 20 mL of DMSO and adding 10 mL 1-bromobutane. The mixture was refluxed in an inert atmosphere of nitrogen for 30 minutes and then precipitated into iso-propanol, washed and dried. This derivative was soluble in THF and chloroform. A fully methylated derivative was also prepared using iodomethane. $M.W.(GPC)$ 57Bu = 18,200, t_r = 34.5 minutes. $[\eta]$ 57Bu = 0.22, $[\eta]$ 57Me = 0.18.

Polymer 57K from bisphenol 50 and dichlorodiphenylsulfone

Potassium hydroxide (86.6%, 40.82 g $\pm$ 0.63 mol) and xylene (190 mL) were added to a solution of bisphenol 50 (78.8862 g, 0.2000 mol) dissolved in DMSO (200 mL). The mixture was stirred at reflux in a 1 litre resin kettle equipped in the usual way. After 5 hours, no more water was collected in the Dean-Stark trap and a solution of difluorodiphenylsulfone (50.8514 g, 0.2000 mol) in hot xylene (60 mL) was added cautiously to the viscous solution. An additional 170 mL of DMSO was added. Xylene was distilled off until the temperature reached 165°C and then stirring was continued for 1.5 hours when a further 100 mL DMSO was added to the now more viscous solution. Stirring was continued for a total of 7 hours and then the polymer was precipitated into iso-propanol and then left to stand overnight in alcohol. The following day the polymer was treated with hot water (3 x 3 L) and alcohol and then dried in a vacuum oven at 30-90°C for 2 days. The polymer is soluble in aprotic solvents such as DMA, NMP and DMSO and made very viscous solutions.

Esterification. Samples were methylated and butylated as described previously. M.W.(GPC) 57Bu = 27,000, t_r = 33.7 minutes, $[\eta]$ 57Bu = 0.33, $[\eta]$ 57Me = 0.27.

IR (film) 57Me: 1725 cm^{-1} (C=O st.)

IR (film) 57Bu: 1718 cm^{-1} (C=O st.)

NMR 400 MHz (CDCl₃) 57Me: δ =8.31 H-ortho-COOMe (1H d. J ≈7.5), δ =7.81 H-d (4H d. J ≈8.8); δ =7.77 (1H d. J ≈7.3), δ =7.52 (1H d. J ≈7.3), δ =7.39-7.28 (4H m.), δ =7.18 H-b (4H

d. $J \approx 8.5$), $\delta = 6.96$ H-c (4H d. $J \approx 8.8$), $\delta = 6.86$ H-a (4H d. $J \approx 8.8$), $\delta = 4.03$ COOMe (3H s.).

Synthesis and Structural Characterization of Deuterated and Methylated Derivatives of Polysulfones Modified by Metal-ation

Experimental Conditions for Lithiations

Udel 3500 Polysulfone was converted to fibrous form from commercial pellets by dissolving the polymer as an 18% solution in CH_2Cl_2 , and precipitating it into iso-propanol in a Waring blender. The precipitated polymer was dried in a vacuum oven for 24 hours at 100°C and then 24 hours at 120°C .

All glassware and apparatus were dried in an oven at 120°C overnight prior to use. Reactions were performed under an inert atmosphere of high purity research grade argon which has been passed through a silica gel tower. The reaction flask was equipped with a gas inlet, bubbler, thermocouple, septum and a magnetic stirrer unless otherwise specified.

Tetrahydrofuran (THF) was refluxed over lithium aluminium hydride (LAH) and under argon for at least 1 hour and then freshly distilled into a dropping funnel for each reaction.

n-Butyllithium, methyllithium and phenyllithium were purchased from the Aldrich Chemical Company as solutions of known concentration. The solutions were used as received.

The polymer derivatives were precipitated into iso-

propanol, ethanol or methanol, filtered and then treated with fresh alcohol and water. The polymers were dried either in a vacuum oven at between room temperature and 100°C depending on the expected stability, or in a convection oven at 120°C.

Mono- and Dilithiation of Udel 3500 Polysulfone with n-Butyllithium

Monolithiation and Deuteration at -78°C

n-Butyllithium (0.005 mol, 10.2 M) was added to a solution of Udel Polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -78°C. A solution of D₂O (0.2 mL) in THF (5 mL) was added after 20 minutes of stirring. The resulting polymer had an average of one deuterium atom per repeat unit.

NMR 400 MHz (CDCl₃): δ =7.85 H-d (3H d.), δ =7.24 H-b (4H d.), δ =7.00 H-c & H-e (4H m.), δ =6.94 H-a (4H d.), δ =1.69 CMe₂ (6H s.)

Dilithiation and Deuteration at -78°C

n-Butyllithium (2.1 mol eq., 0.0105 mol, 10.5M) was added dropwise to a stirred solution of polysulfone (2.21g, 0.005 mol) in THF (75 mL) at -78°C, during which time a red-brown viscous solution developed indicative of lithiated polymer. After 30 minutes a solution of D₂O (0.4mL) in THF (5mL) was added dropwise to the reaction. The resulting dideuterated polymer 64 was precipitated into iso-propanol and then dried in vacuo.

NMR 400 MHz (CDCl₃) Unmodified Polysulfone:
 δ =7.85 H-d (4H d. J $\approx$ 8.8), δ =7.24 H-b (4H d. J $\approx$ 8.6),

$\delta=7.00$ H-c (4H d. $J\approx 8.8$), $\delta=6.94$ H-a (4H d. $J\approx 8.8$),
 $\delta=1.69$ CMe₂ (6H s.)

NMR 400 MHz (CDCl₃) 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.),
 $\delta=1.69$ CMe₂ (6H s.)

Dilithiation and Deuteration at 0°C

To a stirred solution of Polysulfone (2.20g; 0.005 mol) in THF (75 mL) at 0°C was added *n*-butyllithium (2 mol eq, 0.010 mol, 10.2 M) over a period of 5 minutes. During this time the temperature in the reaction flask increased to 6°C. The clear red solution was stirred for an additional 5 minutes before the addition of D₂O. Dideuteration occurred ortho- to the sulfone linkage as shown by a decrease in the integration of signal area H-d in the 60MHz NMR spectrum.

Dilithiation and Methylation at 0°C

Iodomethane was added to a sample of the dilithiated polymer solution above. The degree of methyl substitution after 5 minutes was 1.77 by 60 MHz NMR.

Dilithiation and Methylation at -30°C

Polysulfone (2.00 g, 0.0045 mol) was dissolved in THF (75 mL) and the temperature of the solution was reduced to -30°C. *n*-Butyllithium (2 mol eq., 0.009 mol, 2.6M) was added dropwise over 12 minutes, during which time the mixture turned to a red brown colour. Iodomethane was added after two hours. The degree of methyl substitution was 1.70 by 60 MHz NMR.

Dilithiation and Methylation at -50°C

Polysulfone (2.20 g, 0.005 mol) was dissolved in THF (75 mL) and the temperature of the solution was reduced to -50°C. *n*-Butyllithium (0.01 mol, 2.6M) was added dropwise over 12 minutes. Samples were withdrawn and methylated at -50°C at the following time intervals: 30, 60, 90, 120 and 180 minutes. No increase in the degree of methylation (D.S. = 1.82 by 60 MHz NMR) occurred after 30 minutes.

Dilithiation and Methylation at -78°C

Polysulfone (4.42 g, 0.01 mol) was dissolved in THF (150 mL) and the solution was cooled to -78°C. *n*-Butyllithium (0.02 mol, 10.2M) was added over a period of three minutes. A clear red solution was formed. Iodomethane was added to samples withdrawn at 0, 5 and 15 minutes. The degrees of methylation were 1.81, 1.86 and 1.92 respectively by 60 MHz NMR. The values are useful for comparative purposes but were higher than actual values shown by 400 MHz spectra. No increase in the degree of substitution was observed between 15 and 90 minutes.

Series of Methylated Polysulfones

A series of polymers with various amounts of methylation were prepared to determine the degree of substitution and, to aid in NMR assignments. The polysulfones were lithiated at -78°C for one hour and then methylated by the addition of excess iodomethane. The results obtained from 400 MHz NMR spectra are recorded in Table III.

Monolithiation and Methylation at -78°C

Monomethylated polysulfone 65 was prepared by using the above procedure. The degree of substitution was 1.01.

NMR 400 MHz (CDCl₃): δ =8.12 H-d (M,D) (d.), δ =7.85 H-d (U) (d.), δ =7.78 H-d' (M) (d.), δ =7.24-7.26 H-b (U,M,D) (d.), δ =7.00 H-c (U) & H-c' (M) (d.), δ =6.94-6.96 H-a (U,M,D) (d.), δ =6.88 H-c (M,D) (dd.), δ =6.80 H-e (M,D) (br. s.), δ =2.40 ArMe (M) (s.), δ =2.30 ArMe (D) (s.), δ =1.70 CMe₂ (6H s.)

Dilithiation and Methylation at -78°C

n-Butyllithium (0.105 mol, 10.5M) was added dropwise to a mechanically stirred solution of polysulfone (22.0g, 0.05 mol) in THF (400 mL) at -78°C. The red-brown viscous solution was stirred for 30 minutes and then excess iodomethane was added. After recovery, the dried polymer weighed 22.55g (96% yield) and the degree of substitution was 1.82. The dimethylated polymer 63 has the following spectrum.

NMR 400 MHz (CDCl₃): δ =8.12 H-d (2H d. $J \approx 8.8$), δ =7.26 H-b (4H d. $J \approx 8.6$), δ =6.96 H-a (4H d. $J \approx 8.8$), δ =6.88 H-c (2H dd. $J \approx 8.8$ $J \approx 2.4$), δ =6.80 H-e (2H d. $J \approx 2.4$), δ =2.30 ArMe (6H s.), δ =1.71 CMe₂ (6H s.).

$[\eta] = 0.54$ (Two samples of Udel 3500 had $[\eta] = 0.47$ and $[\eta] = 0.51$). (Lit. $M_v \approx 50,000$.)

Lithiation of Polysulfone at +15°C

Dilithiated polysulfone was allowed to warm up to +15°C from -30°C. Precipitation began at about +10°C and the product coalesced into a single mass at +15°C. After stirring for 2 hours, the product was precipitated into methanol and recovered in the usual manner. The product was partly soluble in chloroform and THF. An NMR spectrum

(CDCl₃) showed unchanged starting material.

Lithiation of Polysulfone at +40°C

Dilithiated polysulfone at -30°C was heated and maintained at +40°C for 3 hours. During this time, a dark coloured rubbery mass precipitated out. Following recovery by precipitation into methanol, the material was insoluble or only swelled slightly in all solvents tested, hot or cold. These solvents were: NMP, DMSO, DMA, DMF, THF, chloroform, thiophene, pyridine, diphenylsulfide and carbon disulfide. The structure of the polymer is uncertain, but it probably contains repeat units 69. Elemental analysis of the product revealed no increase in the percentage of carbon, which would be expected for a polysulfone containing dibenzothiophene repeat units. The elemental percentages were similar to Udel.

Elemental analysis: calculated for Udel (C₂₂H₂₂SO₂)

	Calculated	Found
C	73.28%	72.32%
H	5.01%	4.87%
S	7.24%	7.21%

Trilithiation of Udel Polysulfone with n-Butyllithium

The following examples illustrate the trimetalation of Polysulfone with various amounts of n-butyllithium and at different temperatures. The degrees of substitution of the methylated derivatives were determined solely by signal height ratios in the 60 MHz NMR spectra and are summarized in Table IV.

3 mol eq. at -30°C

To a solution of Polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -30°C, stirred using a magnetic bar, was added *n*-butyllithium (0.015 mol, 10.2M). After 1 hour the mixture had precipitated and stirring was no longer possible. After 90 minutes a sample was quenched with iodomethane and recovered in the usual manner. D.S. = 2.70.

3 mol eq. at -50°C

Polysulfone (2.20 g, 0.005 mol) was dissolved in THF (75 mL) and cooled to -50°C. *n*-Butyllithium (0.015 mol, 10.2M) was added dropwise via syringe to the mechanically stirred solution over a period of three minutes. After 2 hours, the red solution was quenched with iodomethane. D.S. = 2.34.

3.3 mol eq. at -30°C

n-Butyllithium (0.0165 mol, 10.5 M) was added to a mechanically stirred solution of Polysulfone (2.20 g, 0.005 mol) in THF (75 mL). After 1 hour the polymer solution began to precipitate. Samples were withdrawn and quenched with iodomethane at 2, 2.5, 3 and 4 hour periods. D.S. = 2.77, 2.78, 2.78 and 2.78 respectively.

3.3 mol eq. at 0°C

n-Butyllithium (0.0165 mol, 10.5 M) was added dropwise to a mechanically stirred solution of Polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at 0°C over a period of 7 minutes. The solution precipitated soon after the addition

and samples were withdrawn at 1 and 2 hours and quenched with iodomethane. D.S. = 2.93 and 2.94 respectively.

4 mol eq. at -70°C and -30°C

n-Butyllithium (0.02 mol, 10.2 M) was added dropwise to a mechanically stirred solution of polysulfone (2.20 g, 0.005 mol) in THF (100 mL) at -70°C, during which time the reaction mixture turned green. A sample was methylated with iodomethane after two hours and then the mixture was warmed to -30°C. Further samples were methylated after 30 and 90 minutes at this temperature. D.S. = 2.09, 2.58 and 2.93 respectively.

4 mol eq. at -30°C

Polysulfone (4.42 g, 0.01 mol) was dissolved in THF (150 mL) and cooled to -70°C. *n*-Butyllithium (0.04 mol, 10.2 M) was added dropwise via syringe to the mechanically stirred solution over a period of 10 minutes and the solution was allowed to warm up to -30°C. After 30 minutes at this temperature the red solution became more viscous and effective stirring was more difficult. A sample of polymer gel was removed after 100 minutes and quenched with iodomethane. The polymer solution progressively became less soluble and eventually precipitated as one mass when a small sample was methylated with iodomethane after 4 hours. D.S. = 2.95, 2.96 respectively. The trimethylated polymer 67 has the following spectrum.

NMR 400 MHz (CDCl₃): δ = 7.96 H-d (1H d. $J \approx 8.8$), δ = 7.25 H-b (4H d. $J \approx 8.3$), δ = 6.95-6.94 H-a (4H d. $J \approx 8.8$), δ = 6.84 H-

c (1H br.d. $J \approx 8.8$), $\delta = 6.81$ H-e (1H br.s.), $\delta = 6.67$ H-f (2H s.), $\delta = 2.48$ ArMe (6H s.), $\delta = 2.27$ ArMe (3H s.), $\delta = 1.71$ CMe₂ (6H s.).

A trideuterated Polysulfone 66 prepared using deuterium oxide had the following spectrum.

NMR 400 MHz (CDCl₃): $\delta = 7.84$ H-d (1H d.), $\delta = 7.24$ H-b (4H d.), $\delta = 7.00$ H-c, H-e (4H m.), $\delta = 6.94$ H-a (4H d.), $\delta = 1.69$ CMe₂ (6H s.).

Dilithiation of Radel Polysulfone with n-Butyllithium

Radel Polysulfone 2 (2.00 g, 0.005 mol) was dissolved in THF (75 mL) and cooled to -78°C . n-Butyllithium (0.0105 mol, 10.5 M) was added dropwise to the mechanically stirred solution during which time a light orange-brown colour developed. Samples were withdrawn and quenched with iodomethane after 20, 30, and 60 minutes. NMR analysis of the product indicated that the dimethylation of Radel Polysulfone was essentially complete after 20 minutes. Another experiment at -40°C produced the same results. Dimethylated Radel 68 was sparingly soluble in chloroform, and gave a hazy solution.

NMR 400 MHz (CDCl₃) Unmodified Radel Polysulfone:
 $\delta = 7.90$ H-d (4H d. $J \approx 8.5$), $\delta = 7.58$ H-b (4H d. $J \approx 8.3$), $\delta = 7.11$ H-a (4H d. $J \approx 8.5$), $\delta = 7.07$ H-c (4H d. $J \approx 8.5$).

NMR 400 MHz (CDCl₃) Dimethylated Radel Polysulfone:
 $\delta = 8.16$ H-d, (2H $J \approx 8.8$), $\delta = 7.60$ H-b (4H d. $J \approx 8.0$), $\delta = 7.13$ H-a (4H d. $J \approx 8.0$), $\delta = 6.96$ H-c (2H br.d.), $\delta = 6.85$ H-e (2H br.s.), $\delta = 2.34$ ArMe (6H s.).

Lithiation of Udel Polysulfone with other Metalating agents
Methylolithium at -70°C

Methylolithium (0.01 mol, 1.4 M in ether) was added dropwise to a solution of Polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -70°C over a period of 10 minutes. Samples of the lime green polymer solution were quenched with iodomethane after 60 and 300 minutes and recovered by precipitation from methanol. The 60 MHz NMR spectra showed that the degrees of methylation were 1.10 and 1.49 respectively.

Phenylolithium at -70°C

Phenylolithium (0.01 mol, 1.8 M in cyclohexane/diethyl ether) was added dropwise to a solution of Polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -70°C over a period of 20 minutes. The mixture was stirred for 250 minutes before it was quenched with iodomethane. The degree of methylation was 1.58 by 60 MHz NMR.

Phenylolithium at -30°C

Phenylolithium (0.01 mol, 1.8M in cyclohexane/diethyl ether) was added dropwise to a solution of Polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -30°C. After 175 minutes, iodomethane was added to the mixture and the polymer was recovered by precipitation from methanol. The degree of methylation was 1.73 by 60 MHz NMR.

Lithium bis(trimethylsilyl)amide

Lithium bis(trimethylsilyl) amide (0.01 mol, 1M in

THF) was added to a solution of Polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -70°C . Three samples were withdrawn and quenched with iodomethane after one hour at -30°C , two hours at 0°C and overnight at room temperature. The samples were recovered by precipitation from methanol. The NMR spectra of the three products showed unchanged starting material.

Lithium diisopropylamide at -70°C

Lithium diisopropylamide (LDA) (1.07 g, 0.01 mol) solid was weighed out in a glove box and transferred to a solution of Polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -70°C . Iodomethane was added to the viscous red brown mixture after 90 minutes and the product was recovered. $[\eta] = 0.45$. D.S. = 0.28.

Lithium diisopropylamide at -40°C

LDA (1.07 g, 0.01 mol) was added to a solution of Polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -40°C . Iodomethane was added after 2 hours and the polymer recovered by precipitation into methanol. The NMR spectra showed a D.S. of 0.35.

Lithium diisopropylamide at -10°C

LDA (1.07 g, 0.01 mol) was added to a solution of Polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -10°C . Iodomethane was added to the resulting thick reddish gel after one hour and the mixture stirred until it turned a pale yellow. The polymer was recovered by precipitation

into methanol. D.S. = 0.21.

Lithium diisopropylamide/hexamethylphosphoric triamide

Hexamethylphosphoric triamide (HMPT, $[\text{Me}_2\text{N}]_3\text{PO}$) (1.8 g, 0.01 mol) was added to Polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -70°C . LDA (1.07 g, 0.01 mol) was added to the mixture which formed a thick red gel immediately upon addition. Iodomethane was added after one hour and the mixture was precipitated into methanol. A chloroform solution of the polymer was more viscous than in the previous example and the higher viscosity indicated crosslinking had occurred. The viscometric sample could not be filtered through a $0.5\mu\text{m}$ filter. $[\eta] = 0.78$. D.S. = 0.34.

Lithiation of Dimethylated Polysulfone with n-Butyllithium
Dilithiation and methylation at -78°C

To a mechanically stirred solution of dimethylated Udel Polysulfone 63 (2.35 g, 0.005 mol) in THF (75 mL) at -78°C was added dropwise n-butyllithium (0.0105 mol, 10.5 M). Upon addition the solution immediately developed a clear deep blood red colour. After a total of 5 minutes, a precipitate had formed, a sample of which was methylated. Stirring was continued for 30 minutes after which time an insoluble mass had formed at the bottom of the reaction flask. Samples of the precipitate were methylated by treatment with iodomethane. After 5 minutes, the degree of

substitution was approximately 1.50 by 60 MHz NMR. At 30 minutes, the reaction was virtually complete and at 60 minutes the degree of substitution was 1.60 by 400 MHz NMR. The polymer had predominantly repeat units of the structure 71.

NMR 400 MHz (CDCl₃): δ =8.12 H-d (2H d.), δ =7.27 H-b (4H d.), δ =6.97 H-a (4H d.), δ =6.92 H-e (2H br.s), δ =6.87 H-c (2H br.d.), δ =2.75 CH₂ (4H q.), δ =1.72 CMe₂ (6H s.), δ =0.93 CH₃ (6H t.), minor singlets at δ =6.81, 6.69, 6.66 and at δ =2.50, 2.44, 2.30.

Dilithiation and Thiomethylation at -78°C

To a mechanically stirred solution of dimethylated Udel Polysulfone 63 (2.35 g, 0.005 mol) in THF (50 mL) at -78°C was added *n*-butyllithium (0.0105 mol, 10.5M) dropwise. The deep-red mixture was stirred vigorously for 60 minutes after which time a dark rubbery paste had formed. The lithiated polymer 70 was thiomethylated with dimethyl-disulfide to give a polymer of structure 72.

NMR 400 MHz (CDCl₃): δ =8.11 H-d (2H d.), δ =7.27 H-b and others (d. and m.), δ =6.97 H-a and others (d. and m.), δ =3.83 CH₂ (4H s.), δ =1.84 SCH₃ (6H s.), δ =1.72 CMe₂ (6H s.) and minor signals at δ =2.51, 2.29, 2.25 and 1.95.

Functional Group Containing Polymers Derived from the
Reaction of Various Electrophiles with Lithiated Udel
Polysulfones

Functional group containing Udel polysulfones were obtained by addition of various electrophiles to mono- and dilithiated polysulfones which were prepared with 1.05 mol eq. and 2.1 mol eq. of *n*-butyllithium respectively at reduced temperature. In a few cases, polysulfones with other degrees of metalation were used.

Carboxylated polymer 74 from carbon dioxide

n-Butyllithium (0.025 mol, 10.5 M) was added dropwise to a mechanically stirred solution of polysulfone (22.1 g, 0.05 mol) in THF (500 mL) at -70°C. After 30 minutes, anhydrous carbon dioxide gas was bubbled through the mixture which precipitated as a thick white gel. After a further 30 minutes the gel was precipitated into *iso*-propanol, washed in hot water and finally washed with methanol before drying in a vacuum oven. Yield 19.55 g (84%).

Samples of polymer were converted to the carboxylic acid form by boiling with dilute hydrochloric acid. Samples of methyl ester derivative 74 were prepared by addition of iodomethane to a gently heated solution of polymer carboxylate salt in DMSO. $[\eta]$ Methyl ester = 0.56

NMR 400 MHz (CDCl₃) Methyl ester: δ =8.02 H-d (d.), δ =7.90 H-d' (d.), δ =7.85 H-d (U) (d.), δ =7.24 H-b (br.d.), δ =7.08-6.93 (m.), δ =3.91 Me (M) (s.), δ =3.87 Me (D) (minor s.), δ =1.69 CMe₂ (6H s.).

The degree of carboxylation was 0.54 by comparison of the methyl ester signals with the Bisphenol-A methyl groups. The solubility of the polymers are listed in a Table VI.

Carboxylated polymer 73 from carbon dioxide

n-Butyllithium (0.21 mol, 10.5 M) was added dropwise to a mechanically stirred solution of polysulfone (44.2 g, 0.10 mol) in THF (750 mL) at -70°C. After one hour, the solution was treated with carbon dioxide gas and powdered dry ice for a total of three hours. The intractable precipitate was mixed by hand several times and then precipitated into *iso*-propanol. This water soluble polymer was washed with alcohol several times before drying in a vacuum oven at 40°C. Yield 54.0 g (99%).

Methyl ester: Dilithium carboxylate polymer (41.5 g) was dissolved in DMSO (500 mL) and heated with iodomethane at 40°C for two hours. The solution became less viscous and was precipitated into *iso*-propanol. The dicarboxylic ester polymer 73 was treated with hot water, washed with methanol and dried in a vacuum oven at 70°C. Yield 37.0 g (87%). $[\eta]$ = 0.54 (slight amount of gelation). D.S. = 1.81.

NMR 400 MHz (CDCl₃) Methyl ester: δ =8.02 H-d (2H d. $J \approx 8.8$), δ =7.27 H-b (4H d. $J \approx 8.5$), δ =7.13 H-e (2H d. $J \approx 2.4$),

$\delta=7.08$ H-c (2H dd. $J\approx 8.8$, $J\approx 2.4$), $\delta=6.97$ H-a (4H d. $J\approx 8.5$), $\delta=3.87$ Me (6H s.), $\delta=1.71$ CMe₂ (6H s.).

Thiomethylated Polymer 75 from Dimethyldisulfide

Excess dimethyldisulfide was added to a solution of dilithiated polysulfone (0.005 mol) in THF (75 mL) at -78°C . After 30 minutes, the dithiomethylated polymer 75 was recovered by precipitation into iso-propanol.

$[\eta] = 0.44$

NMR 400 MHz (CDCl₃): $\delta=8.2$ H-d (2H. d.), $\delta=7.26$ H-b (4H d.), $\delta=6.97$ H-a (4H d.), $\delta=6.82$ H-e (2H d. J), $\delta=6.75$ H-c dd.), $\delta=2.29$ SMe (6H s.), $\delta=1.71$ CMe₂ (6H s.).

Sulfinic Acid Polymer 76 from Sulfur Dioxide

Sulfur dioxide gas was bubbled into a solution of monolithiated polysulfone (0.005 mol) in THF (75 mL) at -30°C . An off-white precipitate formed which was poured into methanol in a blender. The precipitate was transferred to a beaker and acidified with dilute hydrochloric acid since it was not possible to filter the polymer in the $-\text{SO}_2\text{Li}^+$ form. The precipitate was filtered and washed with distilled water and dried in a vacuum oven at room temperature. The sulfinic acid polymer appeared to undergo crosslinking when dried at 125°C . Oven dried samples were insoluble in THF and showed some discoloration. Exposure to light over a period of weeks darkened a sample of the room temperature dried polymer. An analytical sample was prepared by reprecipitating a filtered THF solution of

polymer, followed by room temperature drying in a vacuum.

$[\eta] = 0.58$. D.S. ≈ 1.0

Elemental analysis: calculated for $C_{12}H_{22}O_6S_2$

	Calculated	Found
C	64.01	63.51
H	4.38	4.18
S	12.66	12.20

IR(film from THF): $3660-2400\text{ cm}^{-1}$ (SO_2H).

Silylated Polymer 77 from Chlorotrimethylsilane

Chlorotrimethylsilane was added dropwise to a solution of monolithiated polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -20°C . At lower temperatures, the silyl chloride was unreactive. The resulting colourless solution was stirred for 30 minutes, precipitated in ethanol, washed with water and dried. The silylated polymer 77 was readily soluble in chloroform and THF. Yield 2.57 g (98%). $[\eta] = 0.42$

NMR 400MHz^a (CDCl_3 , no TMS): $\delta=7.85$ H-d (U) (d.), $\delta=7.75$ H-d' (M) (d.), $\delta=7.71$ H-d (M) (d.), $\delta=7.41$ H-d (D) (d.), $\delta=7.37$ H-e (D) (d.), $\delta=7.31$ H-e (M) (d.), $\delta=7.27-7.23$ H-b (m.), $\delta=7.00$ H-c (U,M) (d.), $\delta=6.97-6.94$ H-a and others (d. and m.), $\delta=6.92$ H-c (M) (dd.), $\delta=6.84$ H-c (D) (dd.), $\delta=1.70$ CMe₃ (6H s.), $\delta=0.38$ SiMe₃ (M) and $\delta=0.34$ SiMe₃ (D) (9H s.s.). D.S. = 1.13.

Silylated Polymer 78 from Chlorotrimethylsilane

n-Butyllithium (1.00 mol, 10.0M) was added slowly to a mechanically stirred solution of polysulfone (210.5 g, 0.475 mol) in THF (2L) at -50°C . The dark red solution was

warmed to -20°C while stirring over one hour. Chlorotrimethylsilane (190 mL) was added dropwise and the mixture was stirred for 2 hours at -20°C to -10°C . The silylated polymer 78 was recovered by precipitation into ethanol, then treated with aqueous ethanol followed by methanol. The silylated polymer 78 was air dried for 3 days and then dried in a vacuum oven. Yield 273 g (98%). $[\eta] = 0.36$.

Elemental analysis: Calculated for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{SSi}$,

	Calculated	Found
C	67.53	67.82
H	6.53	6.47
S	5.46	5.64

NMR 400 MHz (CDCl_3 , no TMS): $\delta=7.41$ H-d (2H d. $J\approx 8.8$), $\delta=7.37$ H-e (2H d. $J\approx 2.4$), $\delta=7.25$ H-b (4H d. $J\approx 8.3$), $\delta=6.96$ H-a (4H d. $J\approx 8.3$), $\delta=6.84$ H-c (2H dd. $J\approx 8.8$, $J\approx 2.4$), $\delta=1.70$ CMe (6H s.), $\delta=0.34$ SiMe (18H s.) and minor singlets at $\delta=0.11$ and $\delta=0.34$.

Tin Containing Polymer from Chlorotrimethylstannane

A solution of chlorotrimethylstannane in THF was added dropwise to dilithiated polysulfone (2.20 g, 0.005 mol) in THF (75 mL) at -30°C . The solution was stirred for three hours at -30°C and then the polymer was recovered by precipitation into methanol. Yield 3.10 g. The trimethylstannyl substituted polymer had the following NMR.

NMR 60 MHz (CDCl_3): $\delta=7.70-7.46$ (m.), $\delta=7.46-6.70$ (m.), $\delta=1.70$ CMe (6H s.), $\delta=0.32$ SnMe (s.), minor singlets at $\delta=0.77$, 0.03 and -0.13 . D.S. = 1.60.

Hydroxylated Polymer 80 from Benzaldehyde

Benzaldehyde (4 mL in 8 mL of THF) was added dropwise to a stirred solution of dilithiated polysulfone (0.005 mol) in THF (75 mL) at -78°C . A clear red gel formed which turned white upon standing. The gel was kept at 0°C for 60 minutes and then precipitated into iso-propanol, washed several times and dried to give polymer 80. $[\eta] = 0.41$.

The solubility characteristics are listed below.

NMP and DMSO	readily soluble
DMA and DMF	soluble/slightly hazy
THF and Chloroform	sparingly soluble/hazy

IR (film from chloroform): 3520 cm^{-1} (OH st.)

NMR 400 MHz (CDCl_3): $\delta=8.00$, 7.90 H-ortho-sulfone (d.'s), $\delta=7.24-7.12$ H-a and Ph (m.), $\delta=7.03$ (br.s.), $\delta=6.94$ (br.s.), $\delta=6.89-6.77$ (m.), $\delta=6.53$, 6.43 CH (br.s.'s), $\delta=3.43$, 3.05 OH (br. s.'s, D_2O exchangeable), $\delta=1.64$ CMe₂ (6H s.).

D.S. (aromatic versus aliphatic integration) = 2.0

D.S. (hydroxyl versus aliphatic integration) = 1.9

Methylation: A sample of hydroxylated polymer was dissolved in DMSO containing powdered sodium hydroxide. The mixture was heated to 100°C for one hour and then iodomethane was added. The conversion to methoxyl was incomplete as a small hydroxyl signal was evident in the NMR. However, seven singlets at $\delta=3.40$, 3.14 , 3.11 , 3.07 , 3.07 , 3.00 and 2.79 corresponding to rotationally restricted methoxyl were present.

Polymer 81 from Acetone

Anhydrous acetone was added to dilithiated polysulfone (0.005 mol) in THF (75 mL) at -78°C . A gel formed which turned white after 15 minutes. The mixture was allowed to warm to 0°C while stirring, and then precipitated into methanol, washed several times and finally dried to give polymer 81.

IR (film from chloroform): 3470 cm^{-1} (OH st.).

NMR 400 MHz (CDCl_3): $\delta=8.09$, 7.85 , 7.76 , 7.74 H-ortho-sulfone (d.'s), $\delta=7.25$ H-b (br.d.), $\delta=7.13$, 7.10 H-e (br. s.'s), $\delta=7.00$ H-c (U) (d.), $\delta=6.99-6.96$ (m.), 6.94 H-a (U) (d.), $\delta=6.81$, 6.73 H-c (br.d.'s), $\delta=5.13$ and 4.70 OH (s.'s D_2O exchangeable), $\delta=1.71$, 1.69 CMe_2 (s.'s), $\delta=1.64$ Me (s.).

Hydroxylated Polymer 82 from Benzophenone

A solution of benzophenone in THF was added slowly to a mechanically stirred solution of monolithiated polysulfone (0.05 mol) in THF (750 mL) at -30°C . After 5 minutes a thick translucent gel formed which was stirred for 2 hours at -30°C and then precipitated into methanol, washed with dilute hydrochloric acid followed by water and finally methanol. (Yield 28.47 g, 91%). The degree of substitution was 0.95 based on total aromatic versus aliphatic integration in the 60 MHz NMR.

The solubility characteristics are as follows:

NMP, DMA and chloroform	soluble
THF	soluble/hazy
DMSO	swells

Elemental analysis: calculated for $C_{10}H_8O_2S$

	Calculated	Found
C	76.90%	77.00%
H	5.16%	5.06%
S	5.13%	5.14%

IR (film from chloroform): 3400 cm^{-1} (OH st.)

Hydroxylated Polymer 82 from Benzophenone

Benzophenone (3.5 g in THF) was added to a stirred solution of dilithiated polysulfone (0.005 mol) in THF (75 mL) at -30°C . A thick red gel resulted which was stirred at -20°C to -10°C for three hours. The hydroxyl containing polymer 82 was recovered by precipitation into methanol and washed first with dilute HCl and then water, followed by alcohol. Yield 3.06 g. $[\eta] = 0.43$

IR (film from chloroform): 3400 cm^{-1} (OH st.)

NMR 400 MHz (CDCl_3): $\delta=8.15, 7.84, 7.76$ H-ortho-sulfone (d.'s), $\delta=7.28-7.05$ H-b and Ph (m.), $\delta=7.00$ H-c (U) (d.), $\delta=6.94$ H-a (U) (d.), $\delta=6.91$ OH (s., D₂O exchangeable), $\delta=6.80$ (d.), $\delta=6.39$ H-e (br. s.), $\delta=5.70$ OH (s., D₂O exchangeable), $\delta=1.72, 1.70, 1.68, 1.67, 1.64$ CMe₂ (s.'s).

D.S. (aromatic versus aliphatic integration) = 1.0.

Iodinated Polymer 83a from Iodine

A solution of iodine in THF was added dropwise to a stirred solution of monolithiated polysulfone (0.005 mol) in THF (75 mL) at -30°C . A brownish gel formed which was stirred for one hour and then the polymer was recovered by precipitation into methanol. The white iodinated polymer

83a was dried at room temperature in a vacuum oven. Yield 2.65 g (93%). D.S. $\approx$ 1.0 by elemental analysis.

Analytical samples were prepared by reprecipitating a filtered THF solution of the polymer.

Elemental analysis: Calculated for $C_{27}H_{21}O_4I_1S$

	Calculated	Found	Found	Found
C	57.05%	60.42%	58.18%	-
H	3.72%	3.88%	3.79%	-
I	22.32%	19.04%	22.10%	21.93%
S	5.64%	6.81%	-	-

NMR 400 MHz ($CDCl_3$): δ =8.52, 8.30, 7.88, 7.85 H-ortho-sulfone (d.'s), δ =7.58, 7.56 H-ortho-iodine (br.s.'s), δ =7.28-7.24 H-a (m.), δ =7.07-6.92 (m.), δ =1.70 CH_3 (6H s.).

Iodinated Polymer 83b from Iodine

A solution of iodine in THF was added dropwise to a stirred solution of dilithiated polysulfone (0.005 mol) in THF (75 mL) at $-30^\circ C$. A brownish gel formed which was stirred for 2 hours at $-30^\circ C$ and then the polymer was recovered by precipitation into methanol. The iodinated polymer 83b was dried in a vacuum oven at $50^\circ C$. Yield 2.50 g. The degree of substitution was 1.78 based on the results for iodine analysis.

Elemental analysis: calculated for $C_{27}H_{20}O_4I_2S$

	Calculated	Found	Found
I	36.55%	32.48%	32.51%

NMR 400 MHz ($CDCl_3$): δ =8.52, 8.30, 7.88 and 7.85 H-ortho-sulfone (d.'s), δ =7.58, 7.56 H-ortho-iodine (br.s.'s), δ =7.28-7.24 H-a (m.), δ =7.07-6.92 (m.), δ =1.71 CH_3 (6H s.).

Polymer 84 from Benzonitrile

Excess benzonitrile was added dropwise to a solution of monolithiated polysulfone (0.005 mol) in THF (75 mL) at -30°C. The resulting red gummy product was stirred for one hour at this temperature and precipitated into ethanol, washed and dried to give a yellow imine containing polymer 84. Yield 2.55 g, (94%). The polymer was soluble in NMP, DMSO, DMA and DMF and somewhat soluble in chloroform and THF. Samples for elemental analysis were prepared by reprecipitating a filtered THF solution of polymer.

IR (film from NMP) 1688 cm^{-1} (C=N st.)
3260 cm^{-1} (N-H st.)

Elemental analysis: calculated for $\text{C}_{11}\text{H}_7\text{O}_2\text{NS}$

	Calculated	Found	Found
C	74.84%	74.45%	75.09%
H	4.99%	4.92%	5.03%
N	2.57%	2.35%	2.69%
S	5.88%	6.10%	(10.46%)

The NMR spectrum is complicated in the aromatic region. The integration of the aromatic region versus the aliphatic region shows a degree of substitution of 0.87.

NMR 400 MHz (CDCl_3): δ =9.62 NH (br.s. D₂O exchangeable), δ =8.22 (br.s.), δ =7.90 H-ortho-sulfone (d.), δ =7.85 H-ortho-sulfone (d.), δ =7.60 (d.), δ =7.51 (br.s.), δ =7.44 (d.), δ =7.39 (br.s.), δ =7.29 (d.), δ =7.23 Ph (br.s.), δ =7.09-7.05 (m.), δ =7.02-6.91 (m.), δ =6.86 (br.s.), δ =6.80 (br.s.), δ =6.70 (br.s.).

Polymer 85 Phenylisocyanate

Phenylisocyanate (1 mL) was added dropwise to a solution of monolithiated polysulfone (0.005 mol) in THF (75 mL) at -40°C. A thick red gel resulted which could not

be stirred. The gel was maintained at a temperature of -40°C for 2 hours and then the polymer was precipitated into methanol. The yellow amide substituted polymer 85 was washed with methanol and then dried. Yield 2.50 g. The polymer was partly soluble in chloroform and THF. An analytical sample was prepared by reprecipitating a filtered THF solution of the polymer.

IR (film) 1540 cm^{-1} (N-H def. Amide II band)
 1675 cm^{-1} (C=O st. Amide I band)
 3300 cm^{-1} (N-H st.)

Elemental analysis: calculated for $\text{C}_{11}\text{H}_{12}\text{O}_2\text{NS}$

	Calculated	Found	Found
C	72.71%	73.87%	74.29%
H	4.85%	4.91%	5.10%
N	2.49%	1.02%	1.08%
S	5.71%	6.88%	(9.96%)

NMR 400 MHz (CDCl_3): $\delta=8.32$ NH (br. D₂O exchangeable), $\delta\approx 8.00$ (br.), $\delta=7.84$ H-ortho-sulfone (br. d.), $\delta\approx 7.78$ (br.), $\delta=7.52$ (br.), $\delta=7.24$ H-b (d.), $\delta=7.00$ H-c (br.d.), $\delta=6.94$ H-a (br.d.).

The degree of substitution was 0.46 by NMR integration and 0.43 by nitrogen analysis.

Chemical Modification of Polysulfones by Halogenation and Lithiation

Bromination of Udel Polysulfone at room temperature

Bromine (11.0 g, 0.0687 mol) was added to a stirred solution of polysulfone (11.05 g, 0.025 mol) in chloroform (60 mL) at room temperature. The three necked flask was equipped with a magnetic stirrer, condenser and argon gas inlet. White clouds of hydrogen bromide soon evolved. The mixture was stirred at room temperature for 24 hours and then precipitated into methanol. The recovered dibrominated polymer 86 was left standing in fresh methanol to leach out residual free bromine, then filtered and dried in a vacuum oven for two days at 40°C. Yield = 15.00 g (100%). $[\eta] = 0.28$. Samples for elemental analysis were prepared by precipitation of a filtered chloroform solution of polymer.

Elemental analysis: calculated for $C_2H_2SO_2Br$:

	Calculated	Found	Found
C	54.02%	53.06%	-
H	3.36%	3.25%	-
Br	26.62%	27.55%	27.29%

NMR 400 MHz ($CDCl_3$): $\delta=7.87$ H-d (4H d. $J \approx 8.8$), $\delta=7.52$ H-e (2H d. $J \approx 2.0$), $\delta=7.16$ H-b (2H dd. $J \approx 8.3$, $J \approx 2.0$), $\delta=6.97$ H-a (d. $J \approx 8.3$), $\delta=6.96$ H-c (d. $J \approx 8.8$), $\delta=1.69$ CMe₂ (6H s.).

Bromination rate of Udel Polysulfone

Bromine (11.0 g, 0.0687 mol) was added to a stirred solution of polysulfone (11.05 g, 0.025 mol) in chloroform (100 mL). Samples of reaction mixture were withdrawn at 1,

2, 3, 4, 5 and 24 hour intervals and the polymer was recovered and analyzed for bromine.

Elemental analysis:

Sample/time(hr.)	%C	%H	%Br
1	62.07	4.10	13.25
2	60.25	3.92	16.07
3	60.30	3.93	17.18
4	57.40	3.69	19.53
5	57.74	3.71	19.38
24	54.93	3.45	23.46
$C_{2.7}H_{2.0}SO_4Br_2$	54.02	3.36	26.62

Bromination of Udel Polysulfone at elevated temperature

Udel Polysulfone (44.2 g, 0.1mol) was dissolved in chloroform (250 mL) in a 3 necked, 500 mL flask equipped with magnetic stirrer, condenser and argon gas inlet. Bromine (44.0 g, 0.275 mol) was added and the reddish mixture was stirred at reflux temperature. Five minutes following the addition, dense white clouds of hydrogen bromide were evolved which continued at a lesser rate for several hours. The mixture was refluxed for 24 hours and then precipitated into methanol, filtered and left to stand in fresh methanol. The analytical sample of the dibrominated polysulfone 86 was prepared by reprecipitation of a filtered polymer solution. Yield = 57.2 g (95%).

$[\eta] = 0.27$.

Elemental analysis: calculated for $C_{2.7}H_{2.0}SO_4Br_2$

	Calculated	Found
C	54.02%	57.58%
H	3.36%	4.17%
S	5.34%	5.06%
Br	26.62%	24.46%

Bromination of Udel Polysulfone with Bromine and an Iron Catalyst

Modifying the procedure of Ohmae *et al.*,²⁶ bromine (7.25 mL, 0.141 mol) was added to a stirred solution of polysulfone (11.0 g, 0.025 mol) in chloroform (100 mL) containing a suspension of iron filings (20 mg). The mixture was stirred for 1 hour at room temperature and then two hours under reflux. A small sample was extracted and purified for elemental analysis. Stirring under reflux was continued for a total of 20 hours before the polymer was recovered by precipitation into *iso*-propanol. The product was washed thoroughly with methanol four times and then purified for elemental analysis by reprecipitation of a filtered chloroform solution of the polymer. The brittle greyish-brown polymer was dried in a vacuum oven for two days at room temperature.

Elemental analysis:

	2 hours	20 hours
C	49.88%	45.85%
H	3.03%	2.62%
S	6.39%	5.61%
Br	31.70%	40.52%

Chlorination of Udel Polysulfone

Chlorine gas was bubbled into a solution of polysulfone (44.2 g, 0.10 mol) in chloroform (250 mL) at 40°C for 150 minutes. During this time, the evolution of acidic hydrogen chloride gas was shown by moist indicator paper. The dichlorinated polymer 89 was recovered by precipitation

into methanol, washed and dried at room temperature in a vacuum. A sample for elemental analysis was prepared by reprecipitation of a filtered THF solution of polymer. The dichlorinated polymer was brittle and had a low intrinsic viscosity. $[\eta] = 0.13$.

Elemental analysis: calculated for $C_{22}H_{20}SO_4Cl_2$

	Calculated	Found
C	63.41%	63.57%
H	3.94%	4.02%
S	6.27%	6.19%
Cl	13.86%	14.04%

NMR 400 MHz ($CDCl_3$): $\delta=7.87$ H-d (4H d.), $\delta=7.36$ H-e (br.s.), $\delta=7.25$ (d.), $\delta=7.13$ H-b (br.d.), $\delta=7.01$ H-a (br.d.), $\delta=6.96$ H-c (d.), $\delta=1.70$ CMe_2 (6H s.).

Bromination of Radel Polysulfone

Bromine (3.0 mL, 0.058 mol) was added to a solution of Radel polysulfone 2 (4.00 g, 0.01 mol) in chloroform (50 mL). Hydrogen bromide gas evolution began soon after the mixture was brought to reflux temperature. After stirring for 18 hours at reflux the mixture was cooled and a slurry of polymer solution separated out. The supernatant was discarded and the dibrominated polysulfone was recovered by precipitation into methanol. Excess free bromine was leached out by allowing the polymer to stand in methanol. The dibrominated polymer 90 was purified by two reprecipitations of chloroform solutions into methanol and then dried under vacuum.

Elemental analysis: calculated for $C_{12}H_{10}SO_2Br_2$

	Calculated	Found
C	51.63%	51.37%
H	2.53%	2.68%
S	5.74%	5.88%
Br	28.63%	28.86%

NMR 400 MHz ($CDCl_3$): δ =7.91 H-d (4H d.), δ =7.85 H-e (2H br.s.), δ =7.52 H-b (2H br.d.), δ =7.14 H-a (2H d.), δ =7.02 H-c (4H d.).

Attempted Bromination of Victrex Polysulfone

Bromine (3.0 mL, 0.058 mol) was added to Victrex polysulfone (2.32 g, 0.01 mol) gelled with chloroform (50 mL). The mixture was refluxed for 20 hours and then precipitated into methanol, washed and dried. An NMR (CH_2Cl_2) of the aromatic region revealed unchanged starting material.

Lithiation/Deuteration of Dibrominated Udel Polysulfone 86

n-Butyllithium (0.0105 mol, 10.5 M) was added dropwise to a stirred solution of dibrominated polysulfone 86 (3.00 g, 0.005 mol) in THF (75 mL) at $-78^\circ C$. The clear red solution was stirred for 30 minutes before a solution of D_2O in THF was added. The resulting dideuterated polymer 87 solution was precipitated into methanol, washed in methanol and dried under vacuum. $[\eta] = 0.47$.

NMR 400 MHz ($CDCl_3$): δ =7.85 H-d (4H d.), δ =7.24 H-b and H-e (4H m.), δ =7.00 H-c (4H d.), δ =6.94 H-a (2H d.), δ =1.69 CMe_2 (6H s.).

Lithiation/Methylation of Dibrominated Udel Polysulfone 86

n-Butyllithium (0.0105 mol, 10.5 M) was added dropwise to a stirred solution of dibrominated polysulfone 86 (3.00 g, 0.005 mol) in THF (75 mL) at -78°C. The clear red solution was stirred for 30 minutes before excess iodomethane was added. The dimethylated polymer 88 was recovered by precipitation of the solution into methanol. The product was washed into methanol and then dried under vacuum.

NMR 400 MHz (CDCl₃): δ =8.12 and 7.77 H-ortho-sulfone (minor d.'s), δ =7.83 H-d (d.), δ =7.25 (minor d.), δ =7.13 H-e (br.s.), δ =7.06 H-b (br.d.), δ =7.01 (minor d.), δ =6.91 H-c (d.), δ =6.84 H-a (d.), δ =2.40 Me (minor s.), δ =2.11 Me (s.), δ =1.68 CMe₂ (s.).

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APPENDIX ASelected ^1H -NMR Spectra

54 Me

55Me

56 Me

71

73

83b

APPENDIX BSelected ^{13}C -NMR Spectra

C	Ref	Ref	Udel
1	153.5	152.7	152.9
2	118.6*	117.5*	119.7
3	129.1	128.3	128.4
4	147.9	147.1	147.1
7	162.7	161.9	161.9
8	170.5*	119.6*	117.7
9	130.3	129.2	129.6
10	136.1	135.0	135.5
C	43.0	42.2	42.4
Me	31.5	30.7	30.9

*values disagree with the author

C	Ref. 1
1	154.7
2	120.6
3	128.7
4	137.1
7	161.8
8	118.0
9	129.9
10	135.9

C	63
1	153.0
2	119.7
3	128.4
4	147.0
7	161.8
8	114.3
9	132.1
10	132.9
11	140.3
12	121.1
C	42.4
Me	30.9
Me	20.2

C	68
1	154.8
2	120.6
3	128.6
4	137.0
7	161.7
8	114.6
9	132.3
10	133.3
11	140.5
12	121.2
Me	20.3

C	75
1	153.0
2	119.8
3	128.4
4	147.2
7	162.1
8	112.0
9	134.8
10	130.4
11	142.0
12	115.2
C	42.5
Me	31.0
Me	16.1

C	7b
1	153.1
2	119.8
3	128.4
4	147.1
7	160.5
8	116.5
9	131.5
10	140.7
11	143.1
12	125.7
C	42.5
Me	31.0
TMS	1.1

C	86
1	(148.7)
2	122.0
3	127.6
4	(149.8)
5	132.2
6	115.8
7	161.1
8	117.1
9	129.9
10	135.8

C	90
1	151.6
2	122.8
3	127.7
4	137.6
5	132.6
6	116.5
7	161.0
8	117.3
9	130.0
10	136.0

APPENDIX CThermal Analysis Data

DSC

DSC

DSC

TG

TG

TG

TG

TG

END

07|07| 89|

FIN