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Functional group polysulphones by bromination–metalation

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A variety of functional groups can be substituted on aromatic polysulphones by a process of bromination followed by metalation. Both Udel polysulphone and Radel polyphenylsulphone were brominated at room temperature using bromine without a catalyst. Repeat units containing two bromine atoms at the electrophilic site in the bisphenol portion were obtained when excess reagent was used. These polymers readily undergo metal–halogen exchange with *n*-butyllithium. The resulting polyanionic lithiated polysulphones are reactive to a variety of electrophiles and give polymers containing functional groups such as carboxyl and hydroxyl. These polymers are useful as membrane materials.

(Keywords: aromatic polysulphones; chemical modification; halogenation; bromination; metalation; lithiation)

INTRODUCTION

Applications for new reactive polymers containing functional groups have continued to grow since Merrifield's pioneering work on solid phase synthesis¹. Since then, a substantial proportion of work on reactive polymers has been concerned with a variety of polystyrene derivatives obtained by chemical modification.

Aromatic polysulphones are high performance thermoplastics which are extensively employed as materials for semi-permeable membranes. While these materials have excellent overall properties, their intrinsic hydrophobic nature precludes their use in membrane applications that require hydrophilic character. Significant changes in membrane performance and new applications have been brought about by sulphonation^{2,3} and chloromethylation⁴, resulting in hydrophilic polysulphones of the anionic and cationic varieties as sulphonic acid and quaternary ammonium derivatives. Polymers with other selected functionalities should enable further developments such as enzyme immobilization and better control of the charge on charged membranes.

We are investigating general methods of introducing functional groups into polysulphones by either controlled direct lithiation or by a dual process of bromination/lithiation. Both modification routes make use of ring lithiated polymer intermediates which are reactive to a variety of electrophiles and give their respective products. Surprisingly high degrees of substitution can be achieved compared with similar modification procedures for other polymers. Directed lithiation and bromination/lithiation procedures applied to both polystyrene^{5,6} and poly(2,6-dimethyl-1,4-phenylene ether)^{7,8} give degrees of substitution of about one or less.

In a previous paper we reported that up to two lithium atoms per repeat unit can be substituted *ortho* to

sulphone on polysulphone by directed lithiation⁹. The structural evidence was obtained by ¹H-n.m.r. analysis of simple deuterated and methylated derivatives. Carboxyl¹⁰ and other derivatives¹¹ and their application to semi-permeable membranes have also been reported. In the present study, the site of substitution by a bromination/lithiation approach to modified polysulphones is examined by n.m.r. spectroscopy. Ohmae *et al.*¹² first reported perbrominated polysulphone derivatives using an iron catalyst with bromine. However, these polymers were apparently degraded. Most recently, Daly *et al.*¹³ prepared dibrominated derivatives under more controlled conditions. Our findings on the bromination were arrived at independently¹⁴ and are in close agreement with those of Daly *et al.* We have further modified these brominated polymers by lithiation. A representative variety of functionalized polymers were obtained by reaction of lithiated polymers with different electrophiles.

EXPERIMENTAL

Materials and methods

Udel® 3500 and Radel® were obtained from Union Carbide. Reagent grade bromine and chloroform were used as received for the bromination reactions. For the lithiation reactions, glassware and apparatus were dried in an oven at 120°C overnight prior to use. Reactions were performed under an inert atmosphere of dry argon. The reaction flask was equipped with a gas inlet, bubbler, thermocouple, septum and a magnetic stirrer. Reagent grade tetrahydrofuran (THF) was refluxed over lithium aluminium hydride and under argon, then freshly distilled into a dropping funnel for transfer to each reaction. *n*-Butyllithium as hexane solution was obtained from Aldrich and was used as received. The polymers were dried in a vacuum oven.

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Polymer characterization

^1H -n.m.r. and ^{13}C -n.m.r. spectra were recorded on a Bruker AM-400 spectrometer at room temperature. ^{13}C -n.m.r. spectra were recorded with ^1H noise decoupling. Polymers were dissolved in CDCl_3 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), multiplet (m) and broadened (br). Coupling constants (J) are in Hertz. Infrared measurements were made on a Perkin-Elmer 683 spectrometer. Infrared samples were cast as thin films from polymer solutions in chloroform. Viscosity measurements were made using *N*-methyl-2-pyrrolidinone (NMP) polymer solutions at $25.0 \pm 0.1^\circ\text{C}$ and a Cannon-Ubbelohde dilution viscometer model 75. Thermogravimetric curves were determined using a DuPont 951 Thermogravimetric Module in combination with a DuPont 1090 Thermal Analyzer. Powdered polymer samples were heated at a rate of 10°C per minute under nitrogen.

BROMINATED POLYSULPHONES

Bromination of Udel polysulphone at room temperature

Bromine (11.0 g, 0.0687 mol) was added to a stirred solution of Udel polysulphone 1 (11.05 g, 0.025 mol) in chloroform (60 ml) at room temperature. White clouds of hydrogen bromide soon evolved. The mixture was stirred at room temperature for 24 h and then precipitated into methanol. The recovered dibrominated polymer 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 . 15.00 g (100%) of white dibrominated polymer 2 was recovered; $[\eta] = 0.28$, $[\eta]$ (Udel) = 0.47. Samples for elemental analysis were prepared by reprecipitation of a filtered chloroform solution of polymer.

Elemental analysis: calculated for $\text{C}_{27}\text{H}_{20}\text{SO}_4\text{Br}_2$, Calculated: C = 54.02%, H = 3.36%, Br = 26.62%, Found: C = 53.06%, H = 3.25%, Br = 27.55%, 27.29%.

N.m.r., unmodified Udel polysulphone: $\delta = 7.85$ H-d (4H d), $\delta = 7.24$ H-b (4H d), $\delta = 7.00$ H-c (4H d), $\delta = 6.94$ H-a (4H d), $\delta = 1.69$ CMe_2 (6H s). N.m.r. brominated polysulphone: $\delta = 7.87$ H-d (4H d J 8.8), $\delta = 7.52$ H-e (2H d J 2.0), $\delta = 7.16$ H-b (2H dd J 8.3, J 2.0), $\delta = 6.97$, H-a (d J 8.3), $\delta = 6.96$ H-c (d J 8.8), $\delta = 1.69$ CMe_2 (6H s).

The experiment was scaled-up by starting with 442 g (1 mol) of polymer dissolved in 2.5 l chloroform. Aliquots were taken at the following time intervals and analysed for bromine: 0.5 h, 13.46%; 1 h 13.95%; 1.5 h, 16.95%; 3 h 17.76%; 4.5 h 23.52%; 6 h 26.03%; 24 h 27.10%.

Bromination of Udel polysulphone at elevated temperature

The bromination was repeated following the above procedure but at reflux temperature and using 44.2 g (0.10 mol) of polymer. The yield of dibrominated polymer was 57.2 g (95%); $[\eta] = 0.27$.

Elemental analysis: calculated for $\text{C}_{27}\text{H}_{20}\text{SO}_4\text{Br}_2$, Found: C = 57.58%, H = 4.17%, S = 5.06%, Br = 24.46%.

Bromination of polysulphone with bromine and a catalyst

The procedure of Ohmae *et al.*¹² was modified by adding bromine (7.25 ml, 0.141 mol) to a stirred solution of polysulphone (11.0 g, 0.025 mol) in chloroform (100 ml) containing a suspension of iron filings (20 mg). The mixture was stirred under reflux for a total of 20 h before

the polymer was recovered by precipitation into isopropanol. The product was washed thoroughly with methanol and then purified for elemental analysis as before. The brittle greyish-brown powder was dried at room temperature.

Elemental analysis: C = 45.85%, H = 2.62%, S = 5.61%, Br = 40.52%.

Bromination of Radel polysulphone

Bromine (3.0 ml, 0.058 mol) was added to a solution of Radel polysulphone 6 (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 h at reflux the mixture was cooled and a slurry of polymer solution separated out. The supernatant was discarded and the dibrominated polysulphone was recovered by precipitation into methanol. Excess free bromine was leached out by allowing the polymer to stand in methanol. The dibrominated polymer 7 was purified for elemental analysis as before.

Elemental analysis, calculated for $\text{C}_{24}\text{H}_{14}\text{SO}_4\text{Br}_2$, Calculated: C = 51.63%, H = 2.53%, S = 5.74%, Br = 28.63%. Found: C = 51.37%, H = 2.68%, S = 5.88%, Br = 28.86%.

N.m.r., unmodified Radel polysulphone: $\delta = 7.90$ H-d (4H d), $\delta = 7.58$ H-b (4H d), $\delta = 7.11$ H-a (4H d), $\delta = 7.07$ H-c (4H d). N.m.r., brominated Radel: $\delta = 7.91$ H-d (4H d), $\delta = 7.85$ H-e (2H br s), $\delta = 7.52$ H-b (2H br d), $\delta = 7.14$ H-a (2H d), $\delta = 7.02$ H-c (4H d).

MODIFICATION OF POLYSULPHONES BY BROMINATION/LITHIATION

Lithiation/deuteration of dibrominated Udel polysulphone

n-Butyllithium (0.0105 mol, 10.5 M) was added dropwise to a stirred solution of dibrominated polysulphone 2 (3.00 g, 0.005 mol) in THF (75 ml) at -78°C . A clear red solution formed which was stirred for 30 min before a solution of D_2O in THF was added. The resulting solution was precipitated into methanol, washed and then dried to yield dideuterated polymer 5; $[\eta] = 0.47$.

N.m.r.: $\delta = 7.85$ H-d (4H d), $\delta = 7.24$ H-b and H-e (4H m), $\delta = 7.00$ H-c (4H d), $\delta = 6.94$ H-a (2H d), $\delta = 1.69$ CMe_2 (6H s).

Lithiation/methylation of dibrominated Udel polysulphone

The above procedure was followed, except that excess iodomethane was used in place of D_2O . A dimethylated polymer 4 was obtained.

N.m.r.: $\delta = 7.83$ H-d (d), $\delta = 7.13$ H-e (br s), $\delta = 7.06$ H-b (br d), $\delta = 6.91$ H-c (d), $\delta = 6.84$ H-a (d), $\delta = 2.11$ Me (H-*ortho*-ether s), $\delta = 1.68$ CMe_2 (s). A small percentage of repeat units containing methyl groups *ortho* to the sulphone linkage had minor signals at $\delta = 8.12$ and $\delta = 7.77$ (*ortho*-sulphone), $\delta = 7.25$ (H-b), $\delta = 7.00$ (H-a) and at $\delta = 2.40$ Me (H-*ortho*-sulphone s for monomethyl repeat unit). The degree of substitution (DS) was 1.60 on the bisphenol portion and 0.18 *ortho* to sulphone.

Excess lithiation/methylation of brominated Udel polysulphone

n-Butyllithium (0.022 mol, 10.5 M) was added dropwise to a mechanically stirred solution of dibrominated polysulphone (3.00 g, 0.005 mol) in THF (75 ml) at -78°C . During the addition a clear red gel formed initially,

followed by a purple precipitate. The mixture was stirred for 30 min before excess iodomethane was added. The methylated polymer product was recovered by precipitation of the solution into alcohol.

N.m.r.: δ = 8.09, 7.83 and 7.76 H-*ortho*-sulphone (d's), δ = 7.23 (m), δ = 7.13 (br s), δ = 7.07 (br d), δ = 6.96–6.75 (m), δ = 6.73 (s), δ = 2.39 Me and δ = 2.29 Me (H-*ortho*-sulphone s's, mono- and dimethyl substituted repeat units, respectively), δ = 2.12 Me (H-*ortho*-ether s, dimethyl on bisphenol portion), δ = 1.68 CMe₂ (s). The DS was 2.92 by methyl integration in the n.m.r..

UDEL DERIVATIVES FROM ELECTROPHILES

Carbon dioxide

n-Butyllithium (0.01 mol, 10.0 M) was added dropwise to a stirred solution of dibrominated polysulphone (3.00 g, 0.005 mol) in THF (75 ml) at -78°C . The lithiated polymer solution was stirred for 30 min and then carbon dioxide gas was bubbled into the solution. The polymer was recovered by precipitating the resulting whitish slurry into isopropanol and then washing it with additional alcohol.

Methyl ester: A chloroform soluble methyl ester was prepared for n.m.r. analysis. Excess iodomethane was added to a solution of polymer (0.5 g) in DMSO (5 ml) at 70°C for 5 min. The solution was precipitated into methanol, washed and then dried. The DS was 1.50 by integration.

N.m.r.: δ = 8.06–8.00 (minor m), δ = 7.91–7.84 H-*ortho*-sulphone (m), δ = 7.52 (br s), δ = 7.36 (br d), δ = 7.24 (br d), δ = 7.16 (br d), δ = 7.08–6.94 (m), δ = 3.91–3.85 COOMe-*ortho*-sulphone (COOMe s's), δ = 3.72 and δ = 3.75 COOMe-*ortho*-ether (COOMe s's), δ = 1.77–1.69 CMe₂ (6H, s's).

Dimethyldisulphide

n-Butyllithium (0.01 mol, 2.6 M) was added to dibrominated polysulphone (1.50 g, 0.0025 mol) in THF (50 ml) at -78°C . A reddish precipitate formed, to which dimethyldisulphide was added after 30 min. After 1 h of stirring, the precipitate had redissolved. The solution was precipitated into methanol and the polymer was recovered in the usual manner. The yield of thiomethylated polymer was 1.05 g and the DS was 2.60.

Elemental analysis calculated for C₃₀H₂₈S₄O₄. Calculated: C = 62.04%, H = 4.86%, S = 22.08%; found: C = 62.54%, H = 4.92%, S = 21.79%.

N.m.r. (no TMS added): δ = 8.27 (d), δ = 8.09 (d), δ = 7.91 (d), δ = 7.84 (d), δ = 7.15 H-*ortho*-SMe (s), δ = 7.05 (m), δ = 6.95 (d), δ = 6.94–6.84 (m), δ = 6.60 (d), δ = 2.35–2.30 SMe (s's), δ = 1.72 CMe₂ (s).

Chlorotrimethylsilane

n-Butyllithium (0.006 mol, 10.0 M) was added to dibrominated polysulphone (1.50 g, 0.0025 mol) in THF (50 ml) at -78°C . Chlorotrimethylsilane was added to the resulting gel after 30 min. The mixture was stirred for 30 min at -40°C and the resulting clear liquid was precipitated into isopropanol. The silylated polymer had a DS of 2.36.

N.m.r.: δ = 7.86 (d), δ = 7.74 (m), δ = 7.38 (br s), δ = 7.34 (br s), δ = 7.28–7.19 (m), δ = 6.99 (d), δ = 6.97 (d), δ = 6.91 (m), δ = 6.81–6.77 (m), δ = 1.72 CMe₂ (6H, s), δ = 0.34 SiMe₃ *ortho*-sulphone and δ = 0.18 and 0.16 SiMe₃ *ortho*-ether.

Benzophenone

n-Butyllithium (0.0033 mol, 10.0 M) was added to dibrominated polysulphone (1.50 g, 0.0025 mol) in THF (40 ml) at -78°C . After 30 min, the addition of benzophenone to the red gel caused a pink-red precipitate which was poured into a mixture of isopropanol and water. 1.33 g of hydroxylated polymer was recovered. The DS was 1.30 by n.m.r. integration.

I.r. (film): 3530 cm⁻¹ (OH Stretch). Elemental analysis, found: C = 72.75%, H = 4.59%, Br = 5.26%. N.m.r.: δ = 7.84 (m), δ = 7.64 (d), δ = 7.36 (d), δ = 7.15 benzophenone residue (major m), δ = 7.01 (d), δ = 6.92 (m), δ = 6.70 (m), δ = 6.54 (br s), δ = 4.35 and δ = 4.30 OH (s), δ = 1.69 CMe₂ (minor s) and δ = 1.54 and 1.36 CMe₂ shielded by phenyl substituent (s's).

RESULTS AND DISCUSSION

Bromination of polysulphones

The two step process of bromination/lithiation offers a new modification route to functionalized polysulphones. The reaction scheme is outlined in Figure 1. Unlike polystyrene⁶, bromination of both commercial Udel 1 and Radel 7 polysulphones occurs readily in the presence of elemental bromine without necessity for a catalyst. The reactive substitution position is situated *ortho* to the aryl ether linkage in the bisphenol portion of the repeat units. This is the most favourable site because it is electrophilically activated by the oxygen atom. The *ortho*-ether site in the phenylsulphone portion of the polymer is unreactive to bromination, presumably due to the strong electron withdrawing influence of the sulphone group. Victrex® polyethersulphone, which has all the *ortho*-ether sites in the phenylsulphone portion, did not react with bromine under these conditions.

A chloroform solution of Udel polysulphone, treated with excess bromine at either elevated or room temperature, resulted in a polymer with two bromine atoms per repeat unit. At room temperature, monobromination occurred during the first hour and dibromination after

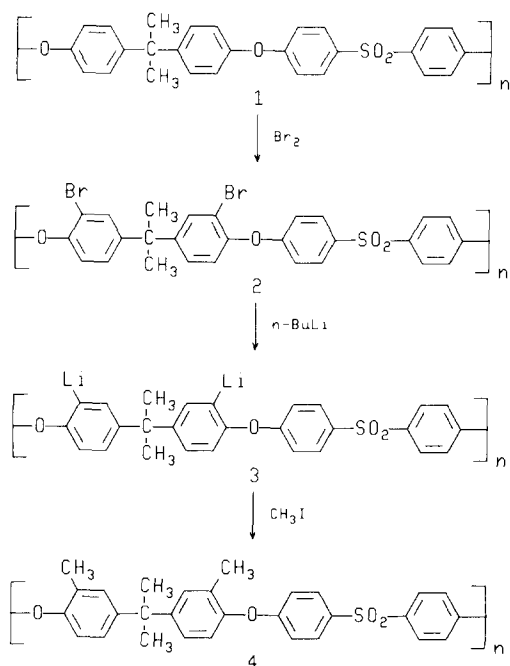


Figure 1 Reaction scheme for polysulphone modification

about six hours. Although the product had a lower viscosity than the starting material, little or no degradation apparently occurred because the subsequently lithiated/deuterated product had a similar viscosity to the original polysulphone. This is in contrast to the perbrominated product obtained using iron catalyst, where degradation is quite evident. Using a similar procedure to Ohmae *et al.*¹², we found this polymer contained four bromine atoms per repeat unit, rather than the six originally reported.

Figure 2 shows the comparative n.m.r. aromatic region spectra of Udel polysulphone and the dibrominated derivative 2. The modification site on the bisphenol portion of the polymer is revealed by a minimal change in phenylsulphone doublets H-c and H-d. Protons H-e

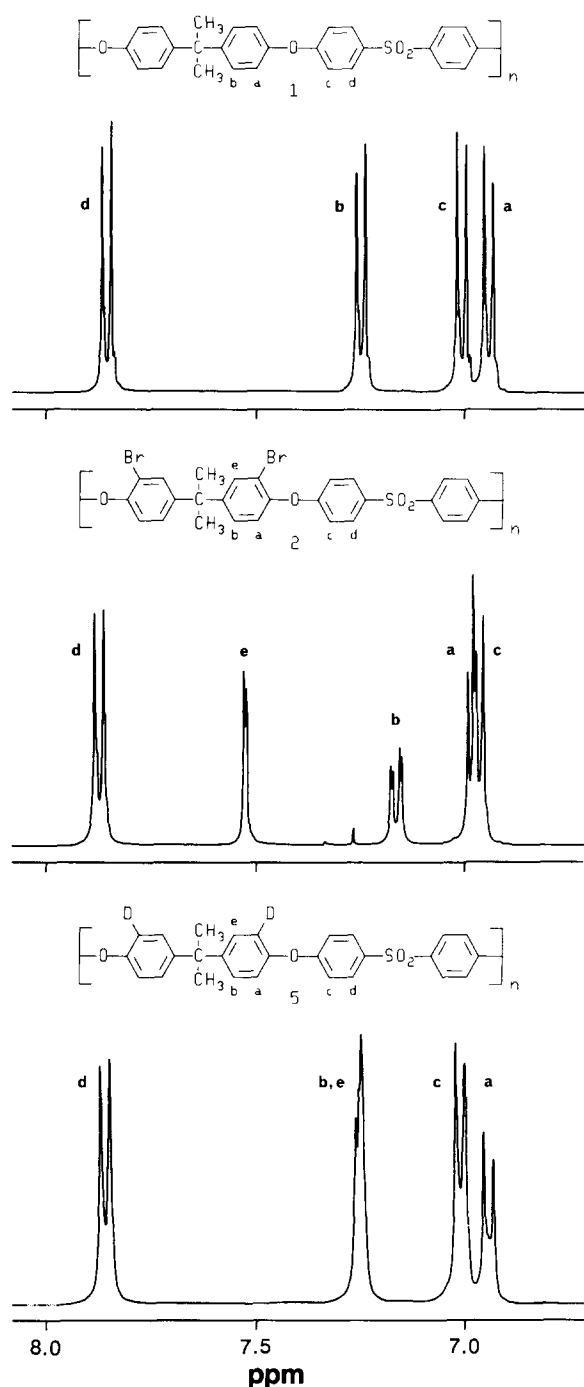


Figure 2 Comparative ^1H -n.m.r. spectra of unsubstituted, dibrominated and dideuterated Udel polysulphone (aromatic region)

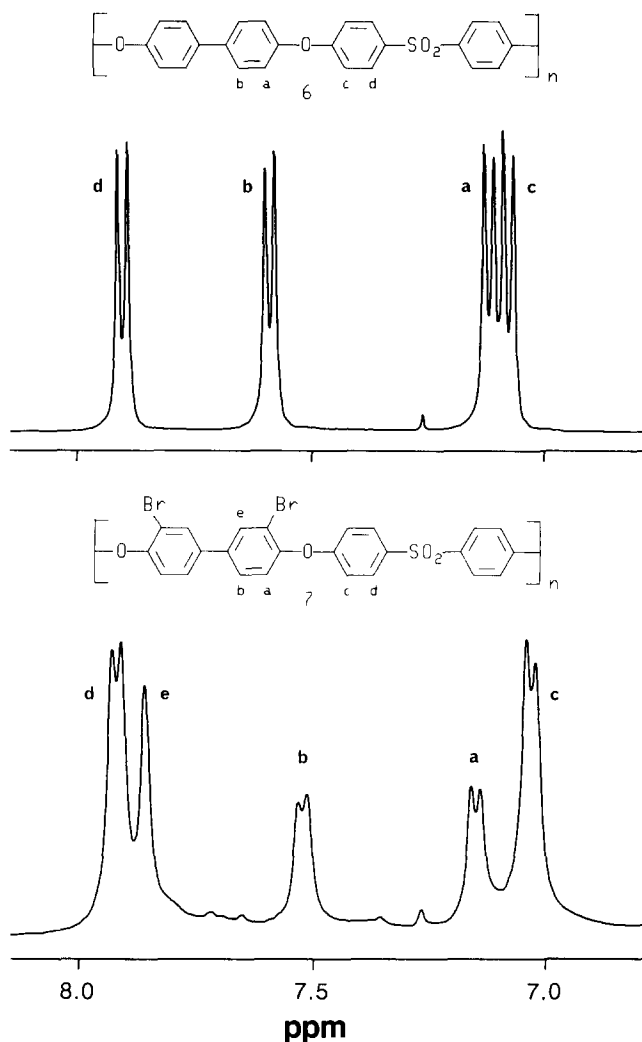


Figure 3 Comparative ^1H -n.m.r. spectra of unsubstituted and dibrominated Radel polysulphone (aromatic region)

ortho to bromine are at $\delta=7.52$ and are *meta*-coupled to H-b. The H-b doublet of doublets at $\delta=7.16$ arises from *ortho* and *meta*-coupling in the dibrominated polymer. The elemental analysis and n.m.r. spectrum are consistent with derivatives having the structure shown. Other isomers are not evident.

Radel polysulphone was also readily dibrominated under the same conditions as Udel. Bromine also substitutes on the bisphenol portion at the electrophilic site *ortho* to the ether linkage. The n.m.r. spectrum in Figure 3 shows unchanged signals from the phenylsulphone portion. The three types of protons in the bromine substituted ring appear as a singlet at $\delta=7.85$ (H-e), a broadened doublet at $\delta=7.52$ (H-b) and a doublet at $\delta=7.14$ (H-a), confirming the site of substitution.

^{13}C -n.m.r. spectra

Both Gagnebien *et al.*¹⁵ and Bulai *et al.*¹⁶ have characterized oligomeric polysulphones and report their ^{13}C -n.m.r. structural assignments. The assignments and the values we obtain for Udel polysulphone are in general agreement with their results. However, it is apparent from changes we observe in the spectra of brominated polysulphone 2 as well as from *ortho*-sulphone substituted derivatives¹⁷ that C-2 and C-8 are misassigned because of their very similar chemical shifts. Because we are able

to substitute groups specifically in either aromatic ring of polysulphone, the signals from the unperturbed ring can be assigned. The ^{13}C -n.m.r. assignments for unmodified and brominated polysulphones are listed in Table 1. The brominated polymers displayed clean unambiguous spectra as shown in Figure 4, confirming the site of substitution in the bisphenol ring. No other type of repeat unit was apparent from either carbon or proton spectra.

Table 1 ^{13}C -n.m.r. chemical shifts of unmodified and brominated polysulphones

Carbon number	Udel ^a	Udel ^b	Dibrominated udel	Radel	Dibrominated radel
1	152.7	152.9	148.7 ^d	154.7	151.6
2	117.5 ^c	119.7	122.0	120.6	122.8
3	128.3	128.4	127.6	128.7	127.7
4	147.1	147.1	149.8 ^d	137.1	137.6
5	128.3	128.4	132.2	128.7	132.6
6	117.5 ^c	119.7	115.8	120.6	116.5
7	161.9	161.9	161.1	161.8	161.0
8	119.6 ^c	117.7	117.1	118.0	117.3
9	129.2	129.6	129.9	129.9	130.0
10	135.0	135.5	135.8	135.9	136.0
C	42.2	42.4	42.6		
Me	30.7	30.9	30.7		

^a Reference 15

^b Authors results

^c Assignment not in agreement with author

^d Assignment uncertain

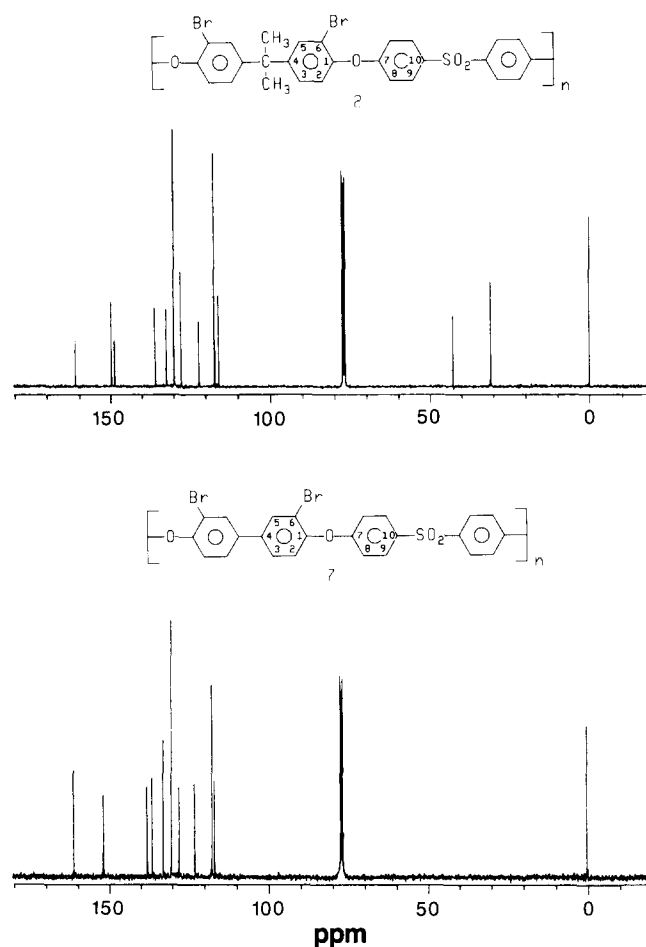


Figure 4 ^{13}C -n.m.r. spectra of brominated polysulphones

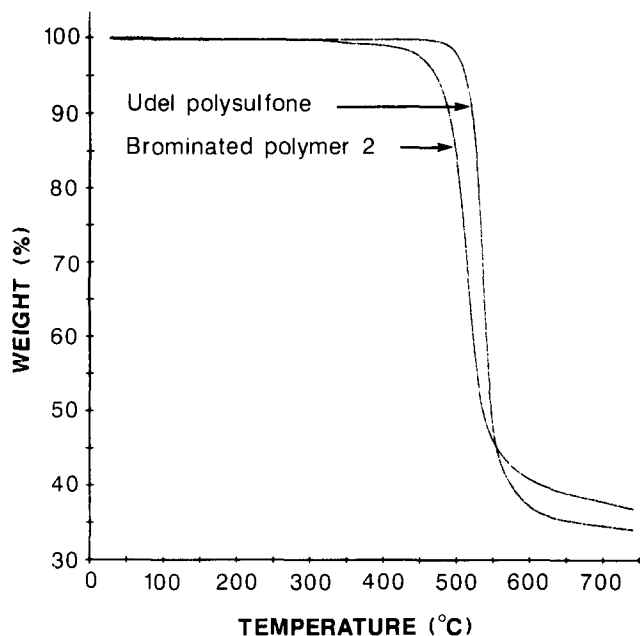


Figure 5 Thermogravimetric curves of Udel and dibrominated polymer

Thermal stability

The thermal stabilities of dibrominated Udel polysulphone and starting polymer were determined by thermogravimetry (t.g.a.). The brominated polymer had an onset of decomposition at approximately 400°C compared with about 470°C for Udel¹⁸. The superimposed t.g.a. curves are shown in Figure 5. Surprisingly, both polymers exhibited similar but offset decomposition t.g.a. curves. No initial loss of bromine was observed.

Lithiation of brominated polymers

Dibrominated polysulphone 2 was metalated with 2.1 mol equivalents of *n*-butyllithium and the lithiated intermediate was quenched with deuterium oxide. Reduced temperature was required to prevent any side reactions. The lithiated intermediate 3 formed as a viscous solution which was easily manageable. Both the bromine and the *ortho*-sulphone position⁹ are potentially reactive metalation sites, the first by simple metal-halogen exchange and the second by heteroatom directed lithiation. A substantial amount of competition between these two sites might be expected. However, the n.m.r. spectrum of the deuterated polysulphone derivative 5 in Figure 2 shows that metal-halogen exchange is the dominant reaction, with a minimal amount of *ortho*-lithiation evident in this derivative. The aryl sulphone doublets remain unaltered while the bisphenol proton signals show dideuteration *ortho* to oxygen by the H-b/H-e multiplet and the diminution of the H-a doublet.

The structure of a methylated derivative 4, obtained by methylation of lithiated intermediate 3, confirmed that metal-halogen exchange occurred preferentially. It also provided evidence for a small degree of competitive *ortho*-lithiation. Relative ratios for these two sites were obtained by n.m.r. integration. The chemical shifts of the methyl singlets at the halogen site and at the *ortho*-sulphone site are well separated, being at $\delta = 2.11$ and $\delta = 2.40$. From this, the DS was 1.60 on the bisphenol portion and 0.18 *ortho* to sulphone. In the aromatic region, two doublets at $\delta = 7.83$ and $\delta = 6.91$ correspond

to the phenylsulphone portion of the polymer. A broadened singlet at $\delta=7.13$ arises from protons *ortho* to the methyl groups and the remaining H-b and H-a protons appear as doublets at $\delta=7.06$ and $\delta=6.84$ respectively.

Higher amounts of substitution could be achieved if brominated polymers were treated with excess metalating agent. Dibrominated polysulphone 2 was metalated with excess n-butyllithium and then methylated. The n.m.r. spectrum of this derivative suggests that three lithium atoms per repeat unit of polymer chain can be substituted. The distribution of methyl groups on the polymer chain could not be accurately established, but the major portion of substitution occurred at the bromine site.

Functional group polymers

Samples of dibrominated Udel polysulphone were

to the ether linkage. The brominated polymers were metalated with n-butyllithium and characterized using deuterated and methylated derivatives. Metal-halogen exchange was the dominant reaction, but in cases where the polymer was lithiated to higher than stoichiometric halogen levels, substantial metalation occurred at the *ortho*-sulphone site also. Almost three groups per repeat unit could be substituted on the polymer chain in this manner. Functional group polymers were prepared by quenching the lithiated intermediates with electrophiles.

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