Preparation and Characterization of Brominated Polyethersulfones

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ABSTRACT: A novel derivative of aromatic polyethersulfone (PES) was obtained by bromination. Victrex PES was reacted with bromine under various conditions: in solution, in suspension, and without solvent; with or without catalyst; and at low and elevated temperatures. Practically no bromination occurred in solution; in the other cases, brominated PESs to various extents were obtained. The degree of substitution (DS) varied between 0.3 and 2.3. It was found that no catalyst is required for this reaction; the temperature, the concentrations of bromine and of polymer in the reaction mixture, and the duration of the reaction are the determinant factors of the DS. The modified polymers were characterized by elemental analysis, ¹H-NMR, ¹³C-NMR, and PGC-MS, and their thermal properties were investigated by TGA and DSC methods. Further transformations of brominated PES as well as other new chemical reactions of PES will be the subject of later publications. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1–13, 1999

Key words: aromatic polyethersulfone; bromination; structural characterization; thermal properties

INTRODUCTION

Aromatic polysulfones are a family of high-performance engineering thermoplastics that comprise sulfone groups in the backbone. Since their development in the 1960s, they have been used extensively as membrane materials, mainly in the field of ultrafiltration and reverse osmosis, but other industrial and medical applications are also well known. Three members of this polymer family, shown in Figure 1, are commercially widely distributed. (It should be noted that numerous name variations appear in the literature; the most common trade names are given in parentheses.)

These polymers possess outstanding oxidative, thermal, and hydrolytic stability with excellent strength and flexibility, resistance to extremes of

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pH, and good mechanical and film-forming properties. Despite these benefits, however, they have certain disadvantages. Their rather hydrophobic nature is a considerable limitation in some aqueous membrane applications that demand hydrophilic character. Hydrophilicity enhancement has been achieved by various physical and chemical surface treatment procedures on preformed polysulfone membranes or by doping the casting solution of the membranes with several additives, such as other hydrophilic polymers (PVP). Another different method is the chemical modification (substitution) of either the polysulfones (and making membranes from the modified derivatives) or of the polysulfone membranes (by heterogeneous reactions). The chemical modification also affords the possibility of introducing ion-exchange groups onto the polymer, and certain functionalities can serve as attachment sites for immobilization of enzymes and other bioactive molecules.



polysulfone, PSU (Udel; Amoco Performance Product, Inc.; USA)



polyarylsulfone, PAS (Radel; Amoco Performance Product, Inc.; USA)



polyethersulfone, PES (Victrex; ICI; GB)

Figure 1 Three commercially available types of polysulfones.

For these purposes, a variety of functional groups have been introduced onto polysulfones. Sulfonation procedures¹⁻⁴ have led to hydrophilic and cation exchange membranes. (Further derivatizations of the sulfo group are also possible.) Halomethylation reactions (chloro- and bromomethylation) have resulted in useful intermediates for anion exchange and other specially functionalized polymers.^{4–12} Lithiation is also a versatile polysulfone modification $tool^{4,11,13-17}$ that can be accomplished directly or via bromination and following metal-halogen exchange by n-butyllithium.¹⁵ From the lithiated intermediate, among others, carboxylated polysulfone can be obtained on addition of CO_2 , which is an advantageous membrane material in ultrafiltration¹⁸ and reverse osmosis processes^{19,20} because of its enhanced hydrophilicity. Guiver et al.²¹ and



 $Y = Br, CH_2Hal, NO_2, SO_2OH$

Figure 2 Electrophilic substitutions on Udel polysulfone.

Staude et al.⁴ have reported the heterogeneous lithiation/carboxylation on ready polysulfone membranes. Another route to carboxylated polysulfone is based on acetylation and subsequent transformation of the acetyl group to carboxyl.^{22,23} Polysulfones with N-containing functional groups have also been prepared via lithiation.²⁴⁻²⁷ From among these, the aromatic amino derivative (PSU- NH_2) has the greatest significance, which is available by the nitration/reduction method¹² as well (nitration of PSU is accomplished by NH_4NO_3 + (CF₃CO)₂O). Aminomethylation of PSU has been effected via phthalimidomethylation with N-chloromethylphthalimide and a Lewis acid-type catalyst^{4,11} or with *N*-hydroxymethylphthalimide and CCl₃SO₃H in CF₃COOH¹² followed by hydrazinolysis. Instead of direct phthalimidomethylation, a Gabriel synthesis can also be used, starting from chloromethylated polysulfone.

As this survey shows, the overwhelming majority of chemical modifications cited have been performed on PSU or PAS. The literature is ill provided with publications that deal with the functionalization of polyethersulfone. This is due to the much more inert nature of this polymer compared to the other polysulfones. The strong electron-withdrawing influence of the sulfone group deactivates both aromatic rings of the repeat unit; moreover, polyethersulfone (PES) has less good solvents than PSU or PAS. Attachment points for electrophile reagents are provided by the bisphenol portion in polysulfone and the biphenvl moiety in polyarylsulfone. The ortho ether sites are especially activated by the oxygen atom, so the electrophilic substitutions sulfonation,² halomethylation,⁹ nitration (amination), phthalimidomethylation (aminomethylation),12 and bromination¹⁵ occur in these positions. (In most instances, disubstitution also can occur.) Figure 2 displays these derivatives prepared from Udel PSU.

Lithiation is another case. It is a heteroatomfacilitated process, the sulfone group directs the lithium to the adjacent ortho $position(s)^{14,16}$ as illustrated in Figure 3. This reaction of PSU and PAS can be carried out in tetrahydrofuran (THF), but PES is insoluble in this solvent and in other solvents usually used in lithiations.



Figure 3 Lithiated derivative of Udel polysulfone.

Noshay and Robeson² have reported the sulfonation of PSU (in the range of 0.1-1.0 —SO₃Na groups per repeat unit) by first using a sulfur trioxide–triethyl phosphate complex and then sodium methoxide. Nevertheless, they stated that PES did not undergo sulfonation under the conditions used to sulfonate polysulfone, owing to its deactivated structure. But using more energetic circumstances, CISO₃H as both solvent and reagent and at elevated temperature, Bikson et al.³ prepared sulfonated PES in the form of PES– SO₃H and PES–SO₂Cl in a 1 : 1 ratio and with DS = 2.

Our experiences were negative in relation to the bromomethylation of PES; Warshawsky's bromomethylating agent, bromomethyl octyl ether,^{6,9} failed when applied to this polymer. There was no reaction, even at reflux conditions.

Nitration of a polyetherethersulfone (PEES)– PES copolymer (60% PEES + 40% PES) has occurred on the hydroquinone unit (i.e., on the PEES moiety) exclusively by using the conventional HNO₃ + H₂SO₄ mixture in nitrobenzene without degradation.²⁸ The ensuing reduction by Na₂S₂O₄ has led to the corresponding aminated copolymer. Nitration of PES itself has become possible only under forcible conditions: PES (dissolved in 98% H₂SO₄) + KNO₃/cc. H₂SO₄ or + fuming HNO₃; and PES + NO₂BF₄ (in sulfolane medium), respectively.²⁹ These conditions, however, resulted in substantial chain fission in the polymer; the following reduction step was also problematic.

Bromination of polysulfone was first reported by Ohmae and Takeuchi³⁰; they executed the reaction by using bromine with iron catalyst in alkyl bromides at reflux. The result was an apparently degraded polymer with 6 Br per repeat unit, but it was applicable as a flame-retardant for thermoplastic resins. Daly et al.¹² have effected the bromination under more controlled conditions. They used a CHCl₃ polysulfone solution and a large excess of Br_2 (mixed with $CHCl_3$), at room temperature or below, in the dark and under Ar atmosphere to minimize chain scission. However, no degree of substitution was reported. Reflux conditions or the use of thallium chloride as a catalyst (useful for the bromination of polystyrene) led to substantially degraded products. Most recently, Barbari and Datwani³¹ described the treatment of polysulfone membranes with molecular bromine, which altered the gas separation properties of the membranes. Notwithstanding, the most systematic study about the bromination

of PSU and PAS was published by Guiver et al.¹⁵ They found that in contrast to polystyrene, bromination of both polysulfones occurs easily and does not require the use of any catalysts. Adding a small excess of bromine to the stirred chloroform solution of these polymers at room temperature resulted in monobromination after 1 h and dibromination after about 6 h. At reflux temperature there was no increase in the extent of bromination, but use of an iron catalyst (similar to the method of Ohmae and Takeuchi³⁰) yielded a product with 4 bromine atoms per repeat unit (in contrast with 6 as they had reported previously). This latter polymer was considerably degraded, whereas bromination without catalyst did not cause chain cleavage, neither at elevated temperatures nor at long reaction times. Guiver et al.¹⁵ have verified by NMR spectroscopy that the site of bromination is ortho to the aryl ether linkage in the bisphenol and in the biphenyl portion, respectively, because of the premised activating effect of the oxygen atom. In addition, they have established that the ortho ether position in the phenylsulfone portion of the repeat unit is unreactive to bromination, certainly as a consequence of the powerful electron-withdrawing impact of the sulfone group. This is why Victrex PES, having each ortho ether site in the phenylsulfone portion, did not react with bromine under conditions used for Udel polysulfone and Radel polyarylsulfone. It is fully in keeping with the observation of Esser and Parsons,³² who have described that the bromination of the above-mentioned 40% PES: 60% PEES copolymer occurred solely on the (-OPhO-) subrepeat unit.

We report here a new and efficient method for the bromination of PES^{33-35} without solvent.

EXPERIMENTAL

Materials

Victrex PES (PES 4800) powder was obtained from ICI and was dried at 150°C for 3 h before use. Reagent grade bromine, tetrachloromethane, and methanol were used as received, as well as 1,1,2,2-tetrachloroethane (TCE) and tin(IV) bromide (Aldrich Chemical Co.)

Bromination of PES

Attempted Bromination of PES in Solution

Bromine (4.25 mL, 82.5 mmol) was added dropwise at a rate of 0.5 mL/min to a mechanically

PES (mol)	$\begin{array}{c} \mathrm{Br}_2 \\ \mathrm{(mol)} \end{array}$	$\begin{array}{c} SnBr_4 \\ (mmol) \end{array}$	$\begin{array}{c} \mathrm{CCl}_4 \\ \mathrm{(mL)} \end{array}$	Temp (°C)	Reaction Time (h)	Br Content (%)	$\frac{\text{PES-Br}_x}{(\text{DS})}$
0.500 0.560	$2.00 \\ 2.23$	39 44	$\begin{array}{c} 210\\ 250 \end{array}$	25 50	5 4.5	$\begin{array}{c} 8.93\\ 15.44\end{array}$	$0.28 \\ 0.53$

Table I Bromination of Polyethersulfone in Suspension with Catalyst

stirred solution of PES (4.8 g, 20.7 mmol) in TCE (30 mL) containing SnBr₄ (0.72 g, 1.6 mmol) as catalyst. (It should be noted that of the several chlorinated hydrocarbons examined, only dichloromethane and TCE were found to be good solvents for PES; the latter was preferred because of its higher boiling point.) In this experiment the solution was stirred at room temperature for 5 h and then precipitated dropwise into methanol (150 mL). The polymer was filtered on a glass frit (G2), washed repeatedly with warm methanol until white, and dried in vacuum. The elemental analysis showed 1.71% bromine content only, which corresponds to a DS of 0.05. A similar experiment, but at 55°C, gave a very weak result as well (with a slightly higher Br content of 3.30% and a DS of 0.10.)

Bromination of PES in Suspension I: Adding Bromine to the Stirred Polymer Suspension Containing Catalyst

The reaction was carried out in a half-liter, fournecked, round-bottom flask with ground-glass joints, equipped with a thermometer, condenser, dropping funnel, and stirrer. A special robust, high-torque mechanical stirring apparatus is needed, because the reaction mixture becomes very viscous during the bromination. PES (116.14 g, 0.500 mol) was suspended in CCl₄ (210 mL) containing SnBr₄ (17.10 g, 39 mmol); then Br₂ (103 mL, 2.00 mol) was added dropwise to the stirred suspension in 3 h. During this time, HBr formed and the polymer became swollen, but no heat evolution was observed. The highly viscous reaction mixture was stirred for an additional 2 h. then filtered on a glass frit (G3). The polymer was washed with CCl₄, then with CH₃OH several times until it whitened. (If necessary, it was pounded in a mortar in the presence of methanol to leach out residual free bromine and tin(IV) bromide.) Drying took place in three steps: 1) in air (overnight in a well-ventilating hood), 2) in a vacuum desiccator (in the presence of Nuxit Al III and Klinosorb 4 [Al-silicate molecular sieve] adsorbents for 2 days), and finally 3) in a vacuum oven or in a vacuum-drier of Abderhalden type (60°C for 2–3 days, the same adsorbents) to constant weight. The reaction conditions and the results are recorded in Table I.

Bromination of PES in Suspension II: Adding Bromine to the Stirred Polymer Suspension Without Catalyst

We proceeded according to the foregoing experiment in every respect, except that we did not use catalyst with this series of bromination experiments. The results are shown in Table II.

Solventless Bromination of PES I: Adding Polymer to the Stirred Solution of the Catalyst in Bromine

The same apparatus was used for this reaction as in the previous reaction, with the only difference being that a closable powder-feeding funnel was used instead of the dropping funnel. (It was observed that diffusion of bromine from the flask

Table II Bromination of Polyethersulfone in Suspension Without Catalyst

PES (mol)	$\begin{array}{c} Br_2 \\ (mol) \end{array}$	Temp (°C)	CCl ₄ (mL)	Reaction Time (h)	Br Content (%)	$\frac{\text{PES-Br}_x}{(\text{DS})}$
0.500	1.36	25	210	5	4.34	0.13
0.250	2.00	25	210	8	15.75	0.54
0.250	2.00	25	210	25	27.04	1.07
0.250	2.00	25	210	100	28.03	1.13
0.500	2.00	-20	210	4	2.74	0.08

PES (mol)	$\begin{array}{c} \operatorname{Br}_2 \\ (\operatorname{mol}) \end{array}$	$\frac{\mathrm{SnBr}_4}{(\mathrm{mmol})}$	Temp (°C)	Reaction Time (h)	Br Content (%)	$\frac{\text{PES-Br}_x}{(\text{DS})}$
0.166	0.88	7	0–5	4	19.27	0.69
0.164	0.86	9	15 - 20	4	25.97	1.02
0.165	0.86	3	25 - 30	4	27.58	1.10
0.165	0.88	8	38 - 40	4	31.26	1.31
0.248	1.33	12	50 - 52	4	33.28	1.44
0.246	1.33	12	50 - 52	4	34.81	1.54

Table III Solventless Bromination of Polyethersulfone with Catalyst

was more considerable than in the previous case, because of the absence of solvent for bromine. The use of a gas-tight sealing adapter on the shaft of the stirrer is particularly recommended at higher temperatures.) In these experiments, summarized in Table III, the temperature of the reaction mixture was kept constant (0-5°C in the first two cases, 20-25°C in the others) with an appropriate cooling bath during the polymer feeding (0.5-1.0)h). Heat and HBr evolution indicated the start of the reaction. It should be noted that faster feeding or insufficient stirring led to balling. After the polymer was added, the reaction temperature was raised to the value given in Table III. The reaction time was 4 h. PES and bromine formed a thick, viscous, dough- or pastelike homogeneous material. At least a fourfold excess of bromine was necessary to have a stirrable consistency. At the conclusion of the reaction, the mixture was allowed to cool to room temperature, and then it was poured slowly into a large quantity of methanol (8-10 mol to 1 mol of bromine) during vigorous mixing with a glass rod. Brominated PES

separated out as a yellow precipitate from the bromine solution in methanol. It was filtered (G2) and washed with methanol thoroughly to obtain a white powder, which was dried to constant weight. The washing was performed in a beaker during warming and stirring, the polymer was filtered, and this process was repeated with fresh methanol about 10 times.

Solventless Bromination of PES II: Adding Polymer to the Stirred Bromine Without Catalyst

We proceeded according to the foregoing experiment in every respect except that we did not use catalyst with this series of bromination experiments. The results are shown in Table IV.

Analytical Techniques

Elemental Analysis

Bromine content of the polymer samples was determined by the Schöniger method (burning in O_2 atmosphere and subsequent analysis for Br^-).

 Table IV
 Solventless Bromination of Polyethersulfone Without Catalyst

PES	Br_2	Temp	Reaction Time	Br Content	$PES-Br_x$
(mol)	(mol)	(°C)	(h)	(%)	(DS)
0.336	1.98	-5 - +6	2	13.37	0.45
0.327	1.98	0-10	0.5	13.72	0.46
0.319	1.94	-5-0	5	19.03	0.68
0.341	1.98	-5 - +14	1.5	19.37	0.70
0.339	1.98	-5 - +20	4.5	20.31	0.74
0.335	1.98	-5 - +8	4.5	23.33	0.88
0.197	0.74	50	5	32.19	1.37
0.246	1.33	50 - 52	4	34.33	1.51
0.500	2.50	50 - 52	5	35.31	1.58
0.500	2.82	57 - 59	4.5	40.54	1.96
0.495	2.84	57 - 59	14.5	44.32	2.29
0.501	5.00	49–60	27.5	44.88	2.34

Two parallel measurements were performed; the averages are recorded in the tables.

NMR Spectroscopy

All ¹H and ¹³C spectra were obtained on a Bruker DRX-500 spectrometer. Spectra were acquired at room temperature by using deuterated dimethyl sulfoxide (DMSO- d_6) solvent and referenced to an internal 3-(trimethylsilyl)propionic acid, sodium salt standard. Chemical shifts δ are expressed in parts per million (ppm), and the spectral resonances are designated singlet (s) and doublet (d). Proton-proton coupling constants (J) are in Hertz. Unmodified and monosubstituted rings are denoted by U and M, respectively; P means perturbed unsubstituted rings.

¹H-NMR spectra were recorded at standard parameter conditions; that is, a proton frequency of 500.13 MHz, a 30-degree flip angle, 32 K data points, a spectral width of 10,000 Hz, 16 scans, a 1 s preacquisition delay time, and exponential multiplication with 0.3 Hz line broadening.

¹³C distortionless enhancement by polarization transfer (DEPT) spectra were recorded at a carbon frequency of 125.76 MHz, DEPT-135 pulse sequence, WALTZ16 ¹H decoupling, 4 K data points, spectral width of 4400 Hz, 512 scans, a 1-s preacquisition delay time, and exponential multiplication with 1.0-Hz line broadening. Composite pulse decoupling (CPD) experiments were carried out with similar parameters.

¹³C inverse-gated NMR spectra were recorded at a carbon frequency of 125.76 MHz, inverse-gated pulse sequence with 30 degrees of ¹³C flip angle and WALTZ16 ¹H decoupling, 64 K data points, a spectral width of 22,700 Hz, 51,200 scans, a 5-s preacquisition delay time, and exponential multiplication with 1.0-Hz line broadening.

 1 H/ 13 C proton detected magnetic field gradient heteronuclear multiple quantum coherence experiment (grad-HMQC) was recorded at a proton frequency of 500.13 MHz with an F2 spectral width of 1140 Hz and 2 K data points. A total of 256 increments of 1 scan were acquired in F1 dimension using a carbon frequency of 125.76 MHz and a spectral width of 4400 Hz. A preacquisition delay of 2 s, a GARP composite pulse for 13 C decoupling, and a one-bond coupling of 145 Hz were used for selection of direct C—H correlations.

Pyrolysis–Gas Chromatography–Mass Spectrometry (P–GC–MS)

Pyrolysis was performed in a Chemical Data System Pyroprobe 120 pyrolyzer equipped with a platinum coil and quartz sample tube interfaced to a Hewlett-Packard 5985B GC-MS device. Polymer samples of $350-500 \ \mu g$ were pyrolyzed at 550–650°C for 10 s. A helium carrier gas at a 20 mL/min flow rate purged the pyrolysis chamber into a fused silica capillary gas chromatographic column (25 m \times 0.2 mm) coated with a bonded methyl silicone phase (0.33 μ m). A split ratio of 1 : 20 and a temperature program from 50-300°C at a 10°C/min rate were applied. The mass spectrometer was operated in electron impact (EI) mode at 70 eV, scanning in the mass range from 33 to 360 atomic mass unit (amu). The temperature of the GC–MS interface was held at 300°C.

Thermal Measurements

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were generated by using a Mettler TA-1 instrument. Powdered polymer samples were heated at a rate of 10°C/min in an atmosphere of nitrogen flowing at 50 mL/min. Glass transition temperatures (T_g) were measured by a Netzsch 200 differential scanning calorimeter (DSC). Samples were heated from room temperature to 300°C at 10°C/min in an atmosphere of nitrogen flowing at 50 mL/min and then quenched in liquid nitrogen. For the second run, in which the T_g was determined, the sample was heated to 250°C.

RESULTS AND DISCUSSION

Synthesis

Brominated PES (PES-Br) is a new material whose first production has been achieved by our research group.^{33–35} No or only negligible bromination occurred in solution, as was previously reported by Guiver et al.,¹⁵ but in more forcible circumstances, without polymer solvent, we were able to execute this reaction.

Bromination of PES was carried out in four different ways: in suspension or without solvent, and with or without catalyst. In CCl_4 suspension, only moderate degrees of substitution can be reached. (The designation suspension concerns just the starting point; after adding bromine, a viscous condition sets in.) Tetrachloromethane is



Figure 4 Bromination of Victrex polyethersulfone.

an ideal diluent for bromine in this case, because it does not dissolve the polymer and does not react with bromine. However, for the removal of bromine after reaction, methanol is much better proved than CCl_4 .

When only the polymer and bromine are present in the system, without solvent or suspending agent, brominated PESs of higher DS can be obtained. The extent of bromination is determined principally by the temperature and the duration of the reaction. The higher the temperature and/or longer the reaction time, the higher the DS. Surprisingly, tin(IV) bromide showed no catalytic effect on this reaction; the DS was the same (within experimental error) when $SnBr_4$ was not used, but the reaction conditions were the same in every other respect (1.54 and)1.51, respectively; see Tables III and IV). The most important circumstance is that the polymer is not dissolved. If the polymer is dissolved, the solvent decreases the concentration of the polymer and bromine so much that at such concentration proportions bromine cannot attack the strongly deactivated aromatic rings of polyethersulfone, even in the presence of a Lewis acid catalyst. Naturally, the bromination of PSU and PAS occurs readily in 10% and 5% solution, respectively, due to the nucleophile character of the bisphenol and the biphenyl portions of the repeat units, respectively.¹⁵ Suspension of the polymer in tetrachloromethane leads to the lesser dilution of the reaction mixture. For the attempted solution-phase bromination of PES in TCE, the polymer concentration in the reaction mixture (after

adding bromine) was 7.2% (by weight) compared with 14.7% for the suspension-phase bromination; the bromine concentrations were 19.8% and 40.6%, respectively. If CCl_4 and $SnBr_4$ are omitted, then a two-component system arises in which the polymer and the bromine concentration can be, for example, 21.2% and 78.8%, respectively. The higher the polymer and the bromine concentration, the higher the DS. The maximum observed DS was 2.34, however, brominated polyethersulfones having a DS of more than 2 were apparently degraded. At lower DS only slight degradation occurred as a function of the bromine content as it was studied by matrix-assisted laser desorption ionization with time of flight analyzer (MALDI-TOF) mass spectrometry technique.³⁶ Gel permeation chromatography (GPC) measurements would be of use to compare the molecular weight of brominated products with that of the original polymer; however, the insolubility of PES in THF prevented us from recording GPC profiles. The extent of bromination was determined by elemental analysis, and it was also confirmed by MALDI-TOF. The NMR and PGC-MS spectra showed that the site of bromination was ortho to the ether linkage. (Fig. 4 represents the case when DS = 2.) This orientation, along with being chemically anticipated, was also supported by ab initio calculations.³⁷ According to the charge distribution, the ortho ether carbons have the most negative relative charge from among the carbon atoms of the molecule; thus they are the targets of the electrophilic Br⁺ attack.



Figure 5 ¹H-NMR spectrum of Victrex polyethersulfone.



Figure 6 13 C-NMR spectra of polyethersulfone in DEPT (a) and CPD (b) modes.

Structural Characterization by ¹H- and ¹³C-NMR of PES and PES-Br (DS = 0.70)

In ¹H-NMR, Victrex PES displays an AA'XX'type aromatic spectrum composed of two doublets, as shown in Figure 5. Ortho ether protons $(H_a, \delta 7.28, 4\text{H})$ are coupled to ortho sulfone protons $(H_b, \delta 8.00, 4\text{H})$; the latter are shifted downfield due to the deshielding effect of the sulfone group. However, all of the protons are shifted slightly downfield compared to the analogous protons of Udel and Radel polysulfones on the phenyl sulfone rings.¹⁵

To assign the ¹³C-NMR spectra, substituent constants for the $PhSO_2$ — and PhO— groups

Table VCalculated and Measured ¹³C-NMRChemical Shifts of Victrex PES

Carbon	Calculated	Measured
1	162.8	160.6
2	119.9	121.1
3	128.5	131.3
4	135.5	137.9
5	128.5	131.3
6	119.9	121.1



Figure 7 A typical structural portion and ¹³C-NMR spectra of PES-Br_{0.70} in DEPT mode (a) and with inverse-gated decoupling (b).

were calculated from the literature chemical shifts of diphenyl ether and diphenyl sulfone³⁸ (no NMR data were found for PES):

PhSO₂—: +5.1 (C-1), 0.8 (C-2), -1.4 (C-3), +12.3 (C-4); PhO—: +29.2 (C-1), -9.4 (C-2), +1.4 (C-3), -5.3 (C-4)

With these constants, the shifts for PES were calculated, and the measured peaks were readily assigned (see Fig. 6 and Table V). The deviations

 Table VI
 ¹³C-NMR Chemical Shift Assignments

 of PES-Br_{0.70}
 13

Carbon	δ	Carbon	δ	Carbon	δ
1	160.2	7	156.6	13	160.6
2	120.8	8	119.8	14	116.2
3	131.0	9	131.4	15	133.8
4	137.5	10	136.7	16	139.6
5	131.0	11	131.4	17	130.1
6	120.8	12	119.8	18	122.9

Table VII Calculated ¹³C-NMR Chemical Shifts for the Monosubstituted Repeat Units of 2-Br-PES, 3-Br-PES, and the Corresponding Measured Shifts of PES-Br_{0.70}

Carbon	3-Br-PES	2-Br-PES	Measured ^a
1	162.0	163.6	160.6
2	124.1	115.1	116.2
3	125.3	134.3	133.8
4	140.9	139.3	139.6
5	132.7	129.6	130.1
6	119.4	122.5	122.9

^a These values correspond to the shifts of carbon atoms 13–18 in Figure 7; this table serves only for comparison.

from the shifts of the analogous carbon atoms of Udel and Radel polysulfones reported by Guiver et al.¹⁵ are within 3.5 ppm. From the measured shifts new substituent constants were calculated for the two groups by adding a corrective factor (F) to the old ones. If we apply the approach that this corrective factor is equal for the two substituent constants, the four equations can be solved as follows:

$$160.6 = 128.5 + 29.2 + 5.1 + 2\Delta F1 \quad \text{(C-1)}$$

$$121.1 = 128.5 - 9.4 + 0.8 + 2\Delta F2 \quad (C-2)$$

$$131.3 = 128.5 + 1.4 - 1.4 + 2\Delta F3$$
 (C-3)

$$137.9 = 128.5 - 5.3 + 12.3 + 2\Delta F4 \quad (C-4)$$

The new substituent constants are

 $\begin{array}{l} PhSO_2 &\longrightarrow +4.0 \ (C-1), \ 1.4 \ (C-2), \ 0 \ (C-3), \ +13.5 \ (C-4); \\ PhO &\longrightarrow +28.1 \ (C-1), \ -8.8 \ (C-2), \ +2.8 \ (C-3), \ -4.1 \ (C-4). \end{array}$

The spectrum of PES-Br (DS = 0.70) was recorded with inverse gated decoupling to get true intensity ratios (Fig. 7). DEPT spectrum was also run to remove substituted aromatic carbon signals. We have considered 14 major peaks, listed in Table VI. From these, four belong to unmodified repeat units (δ 160.2, 137.5, 131.0, and 120.8 ppm). A benzene ring can be substituted symmetrically or asymmetrically, in the former case we have four peaks, in the latter six peaks. So the remaining 10 peaks originate from a symmetrically and an asymmetrically substituted ring. To elucidate the position of bromine, a HIPPO–CNMRS 1.2 program³⁹ was used that works with the following



Figure 8 The ortho ether monobrominated polyethersulfone (2-Br-PES).

bromine substituent constants: -6.0 (C-1), +3.0 (C-2), +1.4 (C-3), and -1.7 (C-4). Table VII gives the calculated shifts for the two possible isomeric monosubstituted repeat units and the measured shifts: the ortho ether monobrominated isomer in Figure 8 (2-Br-PES) shows good agreement with the calculated values, whereas the hypothetic meta isomer does not. In addition, this assignment is confirmed by the DEPT spectrum and the peak intensities. However, four peaks remain unassigned: $\delta 156.5$, 136.7, 131.4, and 119.8 ppm. These belong to a symmetrical structure. Efforts to explain them by the appearance of degradation products were un-



Figure 9 $2D \,{}^{1}H/{}^{13}C$ gradient HMQC inverse detected C—H direct correlation experiment on PES-Br_{0.70}.



Figure 10 P-GC-MS total ion chromatogram of PES pyrolysed at 650°C.

successful. They can be assigned only if we suppose that an unsubstituted ring connected with a substituted ring via an ether linkage is perturbed by the bromine (P ring), so it cannot be treated spectroscopically as an isolated unsubstituted (U) ring. The sulfone-coupled unsubstituted ring may be more isolated from this perturbation effect. The shift differences between a U and a P ring can be seen by comparing the first two columns in Table VI.

With the use of the 1D 13 C signal assignation results and the 2D 1 H/ 13 C grad-HMQC inversedetected C—H direct correlation experiment (shown in Fig. 9) we obtained the following correlations for the M ring:

C-15 (δ 133.8), H-15 (δ 8.37, s); C-17 (δ 130.1), H-17 (δ 7.99, d, $J \approx$ 7.5); C-18 (δ 122.9), H-18 (δ 7.35, d).

The ¹³C nuclei of the P ring showed correlation peaks with the directly connected ring protons as well. These correlation peaks were

C-8, C-12 (δ 119.8); H-8, H-12 (δ 7.25, d, $J \approx 7.5$); C-9, C-11 (δ 131.4); H-9, H-11 (δ 8.09, d, $J \approx 7.5$).

Despite the overlapping signals and lower resolution of the 1D ¹H-NMR spectrum, the signal intensities and observable splittings are completely supported with the carbon assignation results explained earlier. However, brominated polyethersulfones of higher DS displayed more complicated spectra as the DS augmented. Theoretically, a DS of 1.96 (close to 2.0) brominated product, as shown in Figure 4, would have mostly one type of



Figure 11 P–GC–MS total ion chromatogram of PES-Br_{0.70} pyrolysed at 550°C.



Figure 12 Mass spectra of peak 5 in the TIC of PES-Br $_{0.70}$ and those of the two bromophenol isomers in question.

repeat unit, and its spectrum would be much simplified. Perhaps degradation may be the reason why the spectrum is complicated.

P-GC-MS

Unmodified PES and PES-Br (DS = 0.70) were subjected to P-GC-MS analysis to ascertain the position of bromine substitution at the aromatic rings in the latter polymer. To obtain comparable pyrolysis chromatograms, the brominated polymer was pyrolyzed at a lower temperature than the original one because bromine substituents enhanced the thermal decomposition of PES. Figures 10 and 11 represent the total ion chromatograms (TIC) obtained. The major thermal degradation products of PES are SO2, phenol, and diphenyl ether, accompanied by a smaller amount of benzene and dibenzofuran. These compounds are also present among the products of PES-Br, together with their bromine-substituted derivatives. Our results conform to the observations of Montaudo et al.⁴⁰ who studied PES by direct pyrolysis-mass spectrometry (DP-MS) and obtained higher molecular mass product as well. However, the isomeric products are not separated in direct MS. In our work GC-MS was applied, so the positional isomers of brominated phenols and diphenyl ethers appear as individual peaks in the chromatogram. The GC peaks were assigned with the help of library spectra. The mass spectra of the peaks corresponding to isomers could not be distinguished in each case, but in the crucial one of bromophenols, 2-bromophenol was unambigously identified. The mass spectrum of the obtained bromophenol (the fifth peak in the TIC of PES-Br in Fig. 11) and that of two bromophenol isomers of the spectrum library are compared in Figure 12. Thus the ortho ether substitution in PES-Br was confirmed again. It was also remarkable to find Cl-containing compounds among the pyrolysis products that can only originate from the polymer end-groups, taking into consideration the synthesis of PES.⁴¹ Elemental analysis and NMR spectroscopy proved to be not sensitive enough to detect such a low degree of chlorine substitution in the investigated polymers.

DSC and TGA Thermal Measurements

The T_g values of brominated polyethersulfones decreased significantly with increasing DS. (DS = 0.00 signifies unmodified PES.) Table VIII and Figure 13 exhibit that the high T_g of Victrex (225.0°C; nearly the same as of Radel, but 37°C higher than that of Udel) lessened 66°C by incorporation of two bromine atoms. The T_g versus DS plot is shown in Figure 14. This considerable decrease might be associated with degradation;

Table VIII	Glass Transition Temperatures of
Brominated	Polyethersulfones

DS	T_g (°C)
0.00	225.0
0.69	195.5
1.31	177.4
1.96	159.2



Figure 13 DSC scans for brominated polyethersulfones of different DS showing $T_{g'}$'s.

however, no comparative DSC data about brominated Udel or Radel are reported in the literature. Guiver et al.¹⁵ studied only the thermal stability of unmodified and dibrominated Udel. In this respect our results are similar to theirs, because the selected brominated polyethersulfones displayed similar but offset decomposition thermogravimetric curves compared to original Victrex, without initial loss of bromine. The superimposed curves and their derivatives are shown in Figure 15. The plots demonstrate the necessity in the P-GC-MS to pyrolyze the unmodified polymer at a 100°C higher temperature than the brominated derivative. The modified polymers had an onset of degradation at about 400°C, whereas Victrex started to decompose at approximately 450°C.



Figure 14 Plot of glass transition temperatures of selected brominated polymers versus degree of substitution.



Figure 15 Thermogravimetric and derivative thermogravimetric curves of selected brominated polymers.

CONCLUSIONS

Bromination of polyethersulfone was investigated under various conditions. In solution, only a very slight degree of bromination occurred. In CCl_4 suspension, the DS was 0.1–1.1, depending on the temperature. By the solventless bromination, where only polymer and bromine are present in the system, a DS of 0.5–2.3 could be obtained. No catalyst is required; the temperature and the duration of the reaction are the determinant factors of the extent of bromination. The novelty and success of our method lies in the fact that no polymer solvent is used, but it must be admitted that under such forcible conditions, the process is accompanied with a little degradation, which becomes noteworthy at high DS (>2). Structural characterization by ¹³C-NMR and P-GC-MS showed that the site of the bromination was ortho to the ether linkage. TGA and DSC measurements indicated good, but reduced thermal properties compared to unmodified polyethersulfone.

Further transformations of brominated polyethersulfone, as well as other new reactions of PES, will be reported in separate publications.

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