Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Roos, Frederick H. , Daly, William H. , Aniano-Ilao, Marietta N. and Negulescu, Ioan I.(1996) 'NMR Characterization of Substituted Aromatic Poly (Ether Sulofone)s', Journal of Macromolecular Science, Part A, 33: 3, 275 — 290
To link to this Article: DOI: 10.1080/10601329608014320
URL: http://dx.doi.org/10.1080/10601329608014320

J.M.S.—PURE APPL. CHEM., A33(3), pp. 275–290 (1996)

NMR CHARACTERIZATION OF SUBSTITUTED AROMATIC POLY(ETHER SULFONE)S

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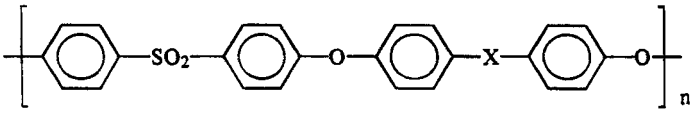
ABSTRACT

The synthesis of a variety of substituted bisphenol A polysulfones, including nitro, amino, aminomethyl, ethyl, and methyl derivatives, is described. Nuclear magnetic resonance (NMR) (both proton and carbon, and several 2-D experiments) data confirm conclusions on the substitution site based on arguments on inductive effects in the phenyl rings. The proton ortho to the oxygen in the bisphenol A (BPA) residue is replaced in electrophilic substitution reactions. The degree of substitution was also calculated from the NMR results. The ethyl and methyl derivatives were expected, from the starting reactants, to each have a BPA ring substituted. The NMR data showed that, on the average, this is true. The nitro derivative also has substitution in every BPA ring, while the amino and aminomethyl derivatives have only intermittent

BPA rings substituted. Measured degrees of substitution (DS) varied from 0.11 to 2.25.

INTRODUCTION

Poly(arylene ether sulfone)s and related structures, such as



(1)

where —X— is, for example, $-C(CH_3)_2-$ (i.e., bisphenol A polysulfone, BPAPSF) are high performance engineering thermoplastics offering an attractive combination of chemical, physical, and mechanical properties. BPAPSF is used in membrane supports for reverse osmosis, ultrafiltration, and gas separation. This amorphous polysulfone has been chosen for membrane applications because of its processability, chemical resistance, toughness, and high T_g, in addition to its gas transport properties [1].

Replacement of phenylene hydrogens of BPAPSF with methyl groups has been shown to have a significant effect on gas transport as well as other properties [2–4]. The nature of these effects was dependent on the placement of the substituents. Symmetric placement resulted in a high degree of chain stiffness, while asymmetric substitution had the opposite effect, yielding a relatively low free-volume structure with moderate chain stiffness. The gas transport properties of substituted BPAPSFs, relative to the parent polymer, do not vary consistently. The usual trade-off between permeability and selectivity may not always be strictly followed: i.e., bulky and immobile substituents may simultaneously increase chain stiffness and decrease packing efficiency and improve separation characteristics [2]. Functional asymmetric phenylene ring substitutions may not impact the chain properties effectively, but their polarity may enhance the membrane selectivity.

This paper deals with a set of polysulfones in which certain phenylene hydrogens are replaced by groups of different polarity and bulkiness. Given the influence of substitution on transport properties, the analysis focuses on modification of the aromatic rings by nitration or phthalimidomethylation of BPAPSF. Amino and methylamino substituents were also afforded by reduction of nitro groups and hydrazinolysis of phthalimidomethylated polymers, respectively. In addition, the symmetric phenylene ring substitution with methyl or ethyl groups was accomplished by reaction of preformed alkyl-substituted BPA with 4,4′-dichlorodiphenyl sulfone (vide infra).

The determination of the degree of substitution (DS) and the site of substitution is important for understanding the physical properties of the products. The application of NMR to these problems is the major subject of this paper. Only substitution in the BPA residue was found in this work. Other researchers have introduced bromine (through direct bromination) [5] and azide (through bromina-

tion followed by lithiation and then reaction with tosyl azide) [6] groups in the BPA residue of BPAPSF. Direct lithiation has been used to introduce azide [6], hydroxyl [7], and carboxyl [8] groups to the sulfone rings of BPAPSF.

EXPERIMENTAL

Materials

Bisphenol A polysulfone (UDEL), purchased commercially, was modified according to procedures described earlier [9–11] as shown in the following.

Nitration of BPAPSF

The method reported by Crivello [12] was utilized for nitration as follows [10, 11]: A solution of 4 g ammonium nitrate in 42 mL trifluoroacetic anhydride was added to 22.1 g BPAPSF dissolved in 200 mL $CHCl_3$. After 24 hours of stirring at room temperature (RT) the volume of the mixture was reduced and the reaction product, labeled as BPAPSF-NO_2, was precipitated in methanol, filtered, and washed sequentially with methanol, aqueous $NaHCO_3$, water, and methanol. Yield: 22.1 g (DF = 0.21, 99.2%). Spectroscopic analysis: FT-IR, 1533 cm^{-1} ($-NO_2$); ^1H NMR ($CDCl_3$), 1.73 ppm (s), 6H, 2-CH_3; 7.01 ppm (d), 7.24 ppm (d), 7.44 ppm (d), and 7.83–7.90 ppm (m), 14H, aromatic protons. ^{13}C NMR ($CDCl_3$): 30.06 ppm ($-CH_3$); 42.6 ppm [$-C(CH_3)_2$]; 119.8, 120.0, 122.8, 129.8, 133.3, 135.5, 141.6, 148.8, 153.3, and 161.8 ppm (aromatic carbons).

Reduction of Nitrated BPAPSF [10]

Aminated polysulfone, BPAPSF-NH_2 (DS = 0.11), was obtained by reacting BPAPSF-NO_2 (3 g) with $SnCl_2$ (5 g)/concentrated HCl (100 mL) in THF (30 mL) at 70°C for 48 hours in the presence of tetrabutylammonium chloride (0.01 g). THF was evaporated, and the residue was neutralized with solid NaOH in an ice bath. The reduced polymer was extracted with $CHCl_3$ and reprecipitated twice from methanol. Yield: 1.2 g (42.6%). Spectroscopic analysis: FT-IR 3475, 3378, 1625 cm^{-1} ($-NH_2$). ^1H NMR ($CDCl_3$): 1.72 ppm (s), 6H, $2CH_3$; 3.67 ppm (broad), 2H, $-NH_2$; 6.58–6.99 (m), 7.24 (d), 7.43 (d), and 7.87 (d) ppm, 14H, aromatic proton. ^{13}C NMR ($CDCl_3$): 30.8 ppm ($-CH_3$); 42.4 ppm ($H_3C-C-CH_3$); 115.6, 116.6, 117.4, 117.7, 119.7, 120.8, 128.4, 129.7, 135.3, 138.3, 139.1, 147.3, 148.6, 152.8, 161.7, and 161.9 ppm, all aromatic carbons.

Phthalimidomethylation of BPAPSF [10, 11]

This modification was achieved by reacting BPAPSF (22.1 g) dissolved in $CHCl_3$ (200 mL) with a solution of *N*-hydroxymethylphthalimide (8.85 g) in a mixture of trifluoromethanesulfonic acid (5 g) and trifluoroacetic acid (200 mL) at RT for 6 hours. The poly(phthalimidomethylarylene ether sulfone), BPAPSF-CH_2-Im, was isolated by precipitation in methanol followed by sequential washing with ammonium hydroxide, water, and methanol. Yield: 25.7 g (DS = 0.64, 99.9%). Spectroscopic analysis: FT-IR, 1773, 1718, 948, 794, and 756 cm^{-1} (absorptions). ^1H NMR ($CDCl_3$): 5.32 ppm (s), $-CH_2-$, phthalimide; 6.92 (d), 7.10 (t), 7.42-7.61

(m), 7.75–7.79 (m), and 7.88–7.92 ppm (m), all aromatic protons. ^{13}C NMR ($CDCl_3$): 66.1 ppm, $-CH_2-$phthalimide; 117.7, 118.0, 120.7, 123.5, 127.6, 127.8, 128.5, 129.9, 131.3, 134.9, 135.1, 135.4, 136.1, 154.1, 157.1, and 161.2 ppm, all aromatic carbons; 167.8 ppm, C=O.

Hydrazinolysis of Phthalimidomethylated BPAPSF [6, 7]

Dried BPAPSF-CH_2-IM polymer 5 g (DS = 0.7–0.8) was dissolved in a mixture of THF (150 mL) and ethanol (150 mL). The reaction was carried out at 70°C for 48 hours using 3.5 mL hydrazine hydrate. The aminomethylated polysulfone, BPAPSF-CH_2NH_2, was precipitated in methanol and washed sequentially with aqueous $NaHCO_3$, water, and methanol. Yield: 12.5 g (95.4%). Spectroscopic analysis: FTIR, 3400 cm^{-1} ($-NH_2$). ^1H NMR ($CDCl_3$): 1.69 ppm (s), 6H, $2CH_3$; 1.92 ppm (broad), 2H, $-NH_2$; 3.73 ppm (s), 2H, $-CH_2NH_2$; 6.78–7.29 (m), and 7.80–7.89 (d), all aromatic protons. ^{13}C NMR ($CDCl_3$): 30.9 ppm, $-CH_3$; 41.8 ppm, $-CH_2NH_2$; 42.5 ppm, $H_3C-C-CH_3$; 115.3, 117.1, 120.0, 125.8, 128.4, 129.7, 135.6, 147.1, 153.0, and 162.0 ppm, all aromatic carbons.

Synthesis of BPAPSF-CH_3 and BPAPSF-CH_2CH_3

High molecular weight alkyl-substituted polysulfones were synthesized from the appropriate bisphenol and a dihalogenated diphenylsulfone according to the procedure described by Johnson and Farnham [13]. For example, 2,2-bis(4-hydroxy-3-methylphenyl)propane was transformed to the corresponding sodium salt by reacting with $NaOH_{(aq)}$ in dimethylsulfoxide (DMSO) at 70°C. The salt was further reacted with 4,4′-dichlorodiphenylsulfone in DMSO at 160°C to yield BPAPSF-CH_3 with DS $\cong$ 2. BPAPSF-CH_2CH_3 with DP $\cong$ 2 was obtained in a similar way. NMR data for the methyl and ethyl derivatives are in the Results and Discussion Section.

Methods

A Perkin-Elmer 1760X FT-IR spectrophotometer was used to record the spectra. Thin films were cast from chloroform.

The NMR data on the polymers were obtained at RT in $CDCl_3$ with TMS as the internal reference. A Bruker 200 MHz spectrometer was used.

For more precise NMR measurements, polymers were dissolved, when possible, in 1,1,2,2-tetrachloroethane-d_2 (TCE) at a concentration of 2 to 5%. Although the amino and aminomethyl derivatives were not very soluble, no other solvent was as good. THF, acetonitrile, and chloroform were not successful at RT. While the TCE can be heated to well over 120°C, this resulted in the formation of the insoluble ammonium chloride derivative. Even at RT this was the outcome with chloroform. Little solvation occurred with dimethylsulfoxide, dimethylformamide, and benzene, even at high temperature. The NMR spectra were then acquired on a Bruker AC-300 spectrometer, the proton frequency being 300 MHz, with a 13C frequency of 75 MHz.

For the proton NMR spectra, the flip angle was 90°. The TCE solvent resonance occurring at 5.97 ppm was used as the spectrum reference. Partly as a result of the spectra being obtained at wide intervals over a period of more than 1 year, the other collection parameters were not identical for all spectra. The delay between

pulses was 7 to 14 seconds; the acquisition time varied between 4 and 9 seconds. No mathematical manipulations were done on the free induction decays to increase either signal-to-noise or resolution. The proton spectrum of the unmodified BPAPSF yielded the expected ratio for the four aromatic proton types and the BPA residue methyl groups of 4:4:4:4:6 with a 7-second delay between pulses. All of the derivative spectra were acquired with longer pulse delays. Comparisons of relative peak areas arising from new proton resonances in the substituted rings indicated that these data were also quantitative. Only in the nitro derivative, where peak overlap prevented this comparison, is the quantification not directly confirmed by relative peak area. It was possible in all of the derivatives to distinguish meta couplings of about 2 Hz.

No attempt was made to obtain quantitative ^{13}C-NMR data, but only to determine peak locations. An inversion-recovery spin-lattice relaxation time experiment on the starting BPAPSF showed T_1 varying between 0.117 and 2.999 seconds. The TCE solvent peak at 75.5 ppm, was used as the spectrum reference in the ^{13}C spectra.

DEPT (distortionless enhancement by polarization transfer) experiments were used to distinguish between protonated and nonprotonated carbons. Several types of 2-D NMR spectra were acquired when such data were expected to aid peak identifications. COSY (homonuclear correlated spectroscopy) spectra were used to identify, through the coupling information, protons arising from substitution that were hidden under other resonances. An F1 spectral width of 1126 Hz and an F2 spectral width of 2252 Hz were used for the data acquisition. The data were digitized to a size of 1 K in the F2 dimension and of 0.5K in the F1 dimension. The number of increments in the F1 direction was 128, with 8 scans being co-added for each.

A 2-D NOESY (nuclear Overhauser enhancement spectroscopy) spectrum was used to make an initial confirmation of assignments for protons in the starting BPAPSF. The spectral widths were 1126 and 2252 Hz for F1 and F2, respectively. Data size was 1024 for F2, with a total of 128 increments (with 8 scans each) being collected.

To determine carbon-proton connectives, both HETCOR (heteronuclear correlation) and COLOC (heteronuclear correlation long range coupling) 2-D experiments were used. The COLOC data permitted the assignment of nonprotonated carbons. Both the HETCOR and COLOC experiments were accomplished using an F1 spectral width of 1351 Hz and an F2 spectral width of 13,157 Hz. Digitization size was 4K in F2 with 128 increments acquired in F1. For the HETCOR experiments, 8 scans were co-added for each increment. For the COLOC studies, 48 scans were collected per increment for the nitro and methyl derivatives, and 128 scans were used per increment for the ethyl derivative. A one-bond C—H coupling of about 150 Hz was assumed for the HETCOR acquisition. Following the example of Guiver and Robertson [6], a coupling of 7.5 Hz was chosen for the COLOC experiment.

RESULTS AND DISCUSSION

The data support the conclusion that substitution occurs only in the enchained rings, which are activated for electrophilic substitution by —OR and —R (isopropylidene) groups. The aromatic sulfonyl protons retain a ratio of 8:6 with the

isopropylidene methyl protons, with the exception of the aminomethyl derivative. Here, the ratio is about 7:6 (probably within experimental error). A similar ratio was obtainable in the highly altered (from that of the starting BPAPSF) spectrum of the nitro derivative if corrections were made for peak overlap.

Two factors suggest that substitution occurs ortho to the oxygen in the BPA residue:

1. The —OR group is more strongly activating than the isopropylidene group.
2. There is likely to be steric hindrance to substitution ortho to the isopropylidene group.

This substitution site has been confirmed through the combination of NMR techniques applied here.

Identification of NMR Peaks

The parent polysulfone and its nitrated, aminated, and aminomethylated derivatives, as well as the alkylated BPAPSFs, were each studied by both ^{13}C-NMR and ^{1}H-NMR spectroscopy. In addition to the one-dimensional spectra, a variety of 2-D spectra were acquired, including COSY (to identify protons on adjacent carbons), NOESY (to detect protons in spatial proximity), and carbon-proton correlation (both HETCOR and COLOC) to identify connectivities between these atoms. The identification of the atoms in the starting BPAPSF polymer and its aminomethylated derivative will be used as an example of the approach used on all the derivatives.

Figure 1 is the NOESY spectrum of the BPAPSF polymer. The off-diagonal peak for the 7.25 ppm proton doublet is also aligned with the methyl group at 1.70 ppm. This demonstrates a spatial proximity of these groups (H_d and the isopropylidene methyl group protons). This information, along with the coupling contents and consideration of the strong electron-withdrawing effect of the sulfone group, particularly at the ortho ring position, allows assignments to be made for all the proton NMR peaks for the starting BPAPSF.

A comparison of the proton 1-D spectra for the starting BPAPSF and the aminomethylated derivative is given in Fig. 2. The BPAPSF spectrum (top) exhibits the predicted four proton types on the aromatic rings. If the area of the methyl peak (not shown) is assigned a value of 6 (for the two methyl groups in the isopropylidene unit), the areas of the aromatic protons should each be about 4. This is indeed the case. The largest deviation from 4.0 is 2.2% relative.

The H_e and H_f peaks in the aminomethylated derivative (Fig. 2, bottom) are readily assigned. The former shows only an ortho coupling, whereas the latter shows both ortho and meta coupling. This leaves the question of the location of the H_g resonance.

The COSY spectrum of this derivative (Fig. 3) shows a coupling (evident through the off-diagonal peaks) of H_f to a peak obscured by H_d. This peak is assigned to H_g. The carbon-proton correlation spectrum (Fig. 4) clearly shows that there are at least two carbon types associated with the area of the H_d doublet. The COSY spectrum, with the NOESY data from Fig. 1, also supports the identifications of H_a through H_d. Also note that the small peaks seen in the aminomethyl derivative in Fig. 2 at about 7.4 to 7.45 ppm are absent in the projections of the

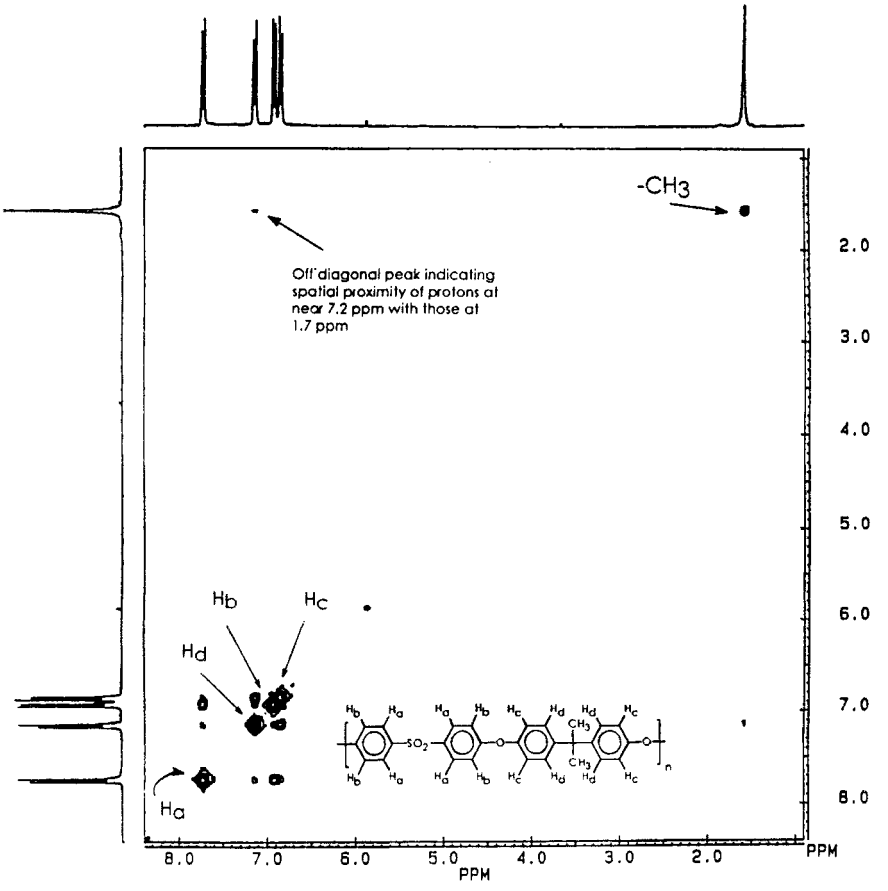


FIG. 1. NOESY spectrum of BPAPSF.

COSY spectrum. These peaks are thought to be impurities; they were not seen in later preparations.

The carbon-proton correlation spectrum in Fig. 4 gives the assignments of protonated aromatic carbons in the polymer. Carbons directly bonded to the protons previously identified are immediately assigned in the figure. In addition, it is possible to separate impurities in the ^{13}C spectrum from the polymer resonances. Unfortunately, this sample was insufficiently soluble to obtain a sufficient signal to permit identification of the nonprotonated carbons in substituted rings through the COLOC experiment.

Tables 1 and 2 give the assignments of the proton and carbon NMR spectra of the starting BPAPSF and the derivatives. In addition, literature data on azide and bromine derivatives (both with DS = 2) are shown for comparison [5, 6].

The degree of substitution (DS) for each polymer type was determined from the proton NMR spectrum. Results are expressed as the percentage of the BPAPSF repeat units that are substituted. Since there are two rings from the BPA residue, there is the possibility that both may be substituted. It is impossible to detect this

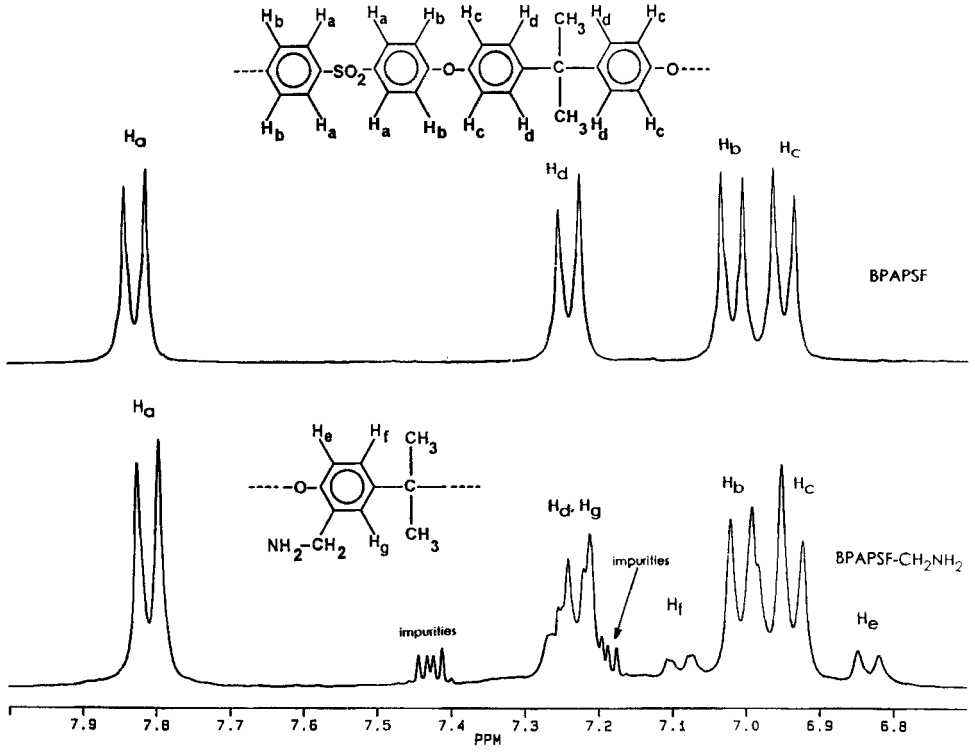
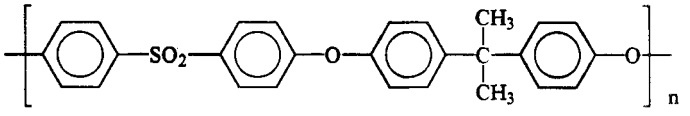


FIG. 2. Proton NMR spectra of the aromatic region of BPAPSF (top) and BPAPSF-CH_2NH_2 (bottom).

situation by NMR spectroscopy. Therefore a DS calculation gives only the average substitution per BPAPSF unit. In all cases the area of the methyl protons in the bisphenol A residue was divided by 6 to give the relative number of BPAPSF repeat units:



(2)

When one of the aromatic ring protons is substituted by another group, the remaining three protons in that ring for the most part no longer occur in the on-substituted ring locations. A ratio of the area from a single one of these, or when possible from the average of two or all three, is obtained. Dividing this area by 1/6 of the isopropylidene methyl area yields the DS.

For the amino and aminomethyl derivatives, the number of substituents was determined directly from the average of these new resonances. As an example, Fig.

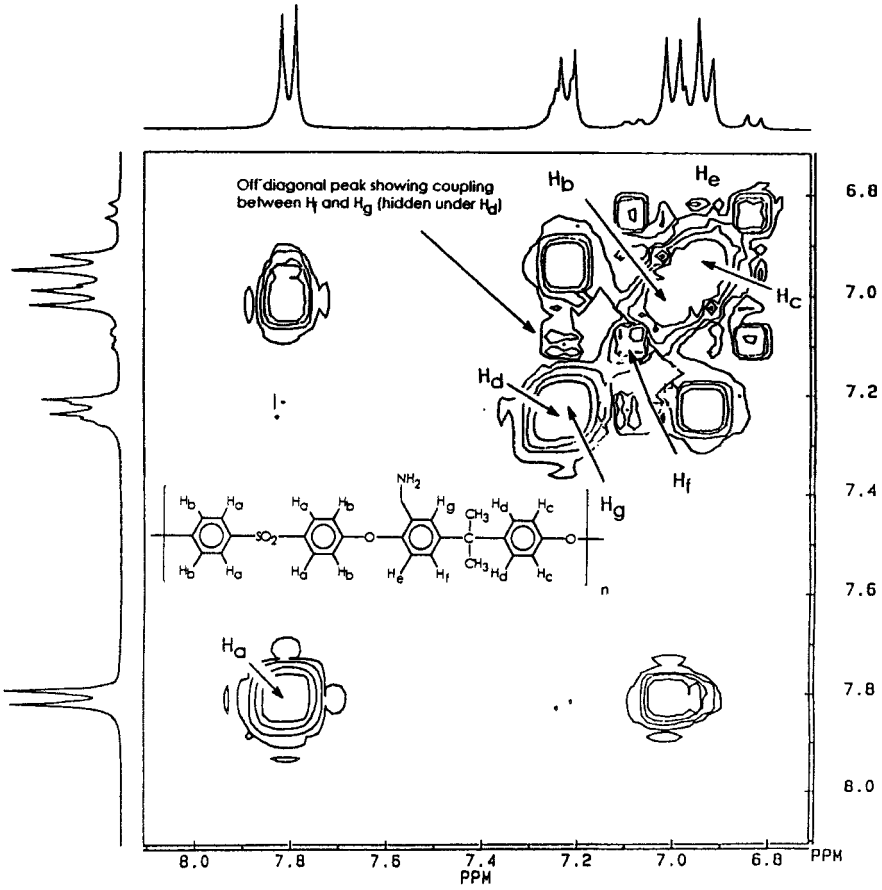


FIG. 3. COSY spectrum of aromatic region of BPAPSF-CH_2NH_2.

5 shows the proton aromatic region of BPAPSF-NH_2. The new proton resonances arising from substitution elsewhere in the ring give an average area of 2.08. No other resonances not present in the starting BPAPSF were seen. The pattern of these peaks (one with ortho coupling, one with meta coupling, and one with both ortho and meta coupling) indicates that when substitution has occurred, there is no more than one substituent per ring. Therefore, the average of the three new peaks directly yields the number of introduced groups. The methyl area is 117.68. Dividing 2.08 by 117.68/6 yields a DS of 0.11.

The same reasoning was applied to the aminomethyl derivative, BPAPSF-CH_2NH_2, synthesized as shown above according to Scheme 1. In this case, however, only two of the three new proton aromatic peaks were resolved. These were averaged for one DS measurement. The amino protons were also utilized for the DS by dividing their area by 2 and obtaining the ratio to one-sixth of the BPA methyl area. It was not possible to make use of the methylene protons in the aromatic side group since it is not a clean resonance.

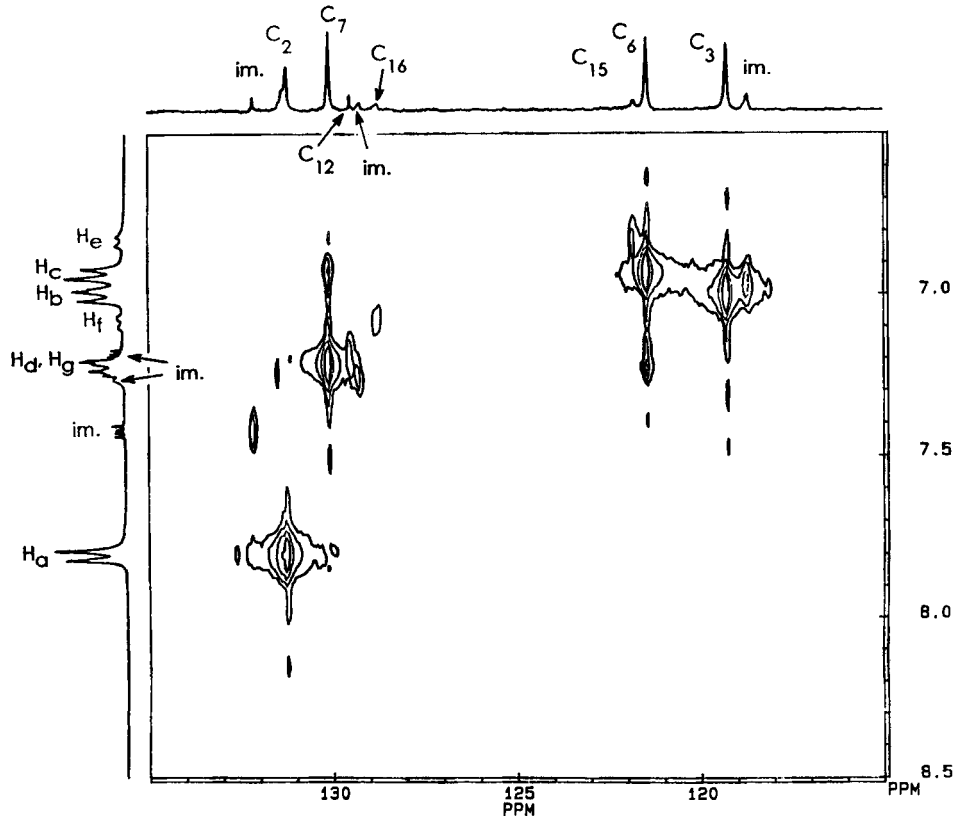
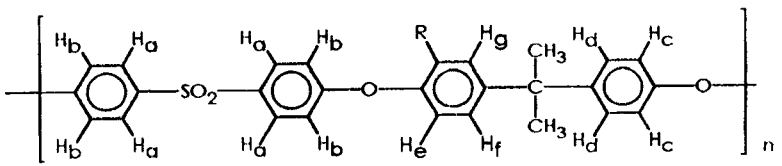


FIG. 4. HETCOR (proton-carbon correlation) experiment for BPAPSF-CH_2NH_2. im. = impurity.

The proton NMR spectrum of the aminomethyl derivative shows no evidence of disubstitution within a single ring. Of course, with an average DS of 0.76, there are many rings that are not substituted at all. The carbon spectrum, however, showed more peaks than can be accounted for with monosubstitution. Nine quaternary aromatic carbon types (and possibly a tenth not well resolved occurring under the 136.55 ppm peak) were detected; only seven would be expected for this derivative if there were no more than one substituent per ring. A total of 10 quaternary aromatic carbons would be predicted for a product with both mono- and disubstitution. This assumes the disubstitution occurred only ortho to the oxygen. The protonated carbon total with the presence of disubstitution ortho to oxygen would be eight. A total of 11 such peaks were found. The origin of the "extra" peaks is not known. They may be impurities. Presumably, peaks in the proton spectrum from distribution within a ring are not resolved and/or are too small to detect. It was concluded that there may be some disubstitution in this product.

For the aminomethyl derivative, the DS was also measured by nitrogen analysis. The determined DS was 0.70, compared to the values of 0.70 and 0.82 by the two proton NMR calculations.

TABLE 1. Proton Spectra Chemical Shifts (in ppm) (J = coupling constant in Hz)



Peak location	H	NO_2	NH_2	CH_2NH_2	CH_3	CH_2CH_3	N=N=N
H_a	7.84 (d) (J ~ 8.8, 4H)	7.88 (d) (J ~ 8.8, 4H)	7.82 (d) (J ~ 8.8, 4H)	7.81 (d) (J ~ 8.7, 4H)	7.81 (d) (J ~ 8.8, 4H)	7.79 (d) (J ~ 8.8, 4H)	7.87 (d) (4H)
H_b	7.03 (d) (J ~ 8.8, 4H)	7.05 (d) (J ~ 8.7, 4H)	7.03 (d) (J ~ 8.8, 4H)	7.01 (d) (J ~ 8.7, 4H)	6.91 (d) (J ~ 8.9, 4H)	6.93 (d) (J ~ 8.9, 4H)	6.95–7.03 (m)
H_c	6.96 (d) (J ~ 8.6, 2H)	–	6.95 (d) (J ~ 8.7)	6.94 (d) (J ~ 8.7)	–	–	6.95–7.03 (m)
H_d	7.25 (d) (J ~ 8.6, 2H)	–	7.25 (d) (J ~ 8.7)	7.23 (d) (J ~ 8.7)	–	–	6.95–7.03 (m)
H_3CCCH_3	1.70 (s)	1.67 (s)	1.70 (s)	1.67 (s)	1.66 (s)	1.68 (s)	1.71 (s)
H_e	–	7.08 (d) (J ~ 8.4, 2H)[f]	6.79 (d) (J ~ 8.4)	6.83 (dd) (J ~ 8.4)	6.83 (d) (J ~ 8.4, 2H)	6.81 (d) (J ~ 8.4, 2H)	6.95–7.03 (m)

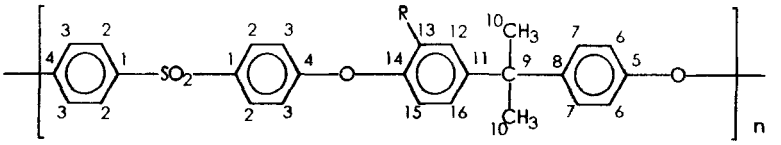
(*continued*)

TABLE 1. Continued

Peak location	H	NO_2	NH_2	CH_2NH_2	CH_3	CH_2CH_3	N=N=N
H_f	–	7.42 (dd) ($J \sim 8.7$; $J \sim 2.3$, 2H)	6.63 (dd) ($J \sim 8.3$)[e]	7.09 (dd) ($J \sim 8.5$; $J \sim 1.8$)	7.03 (dd) (J ~ 8.4; $J \sim 1.8$, 2H)	7.05 (d)[c] ($J \sim 8.5$, 2H)	6.95–7.03 (m)
H_g	–	7.88 (d) ($J \sim 2.5$, 2H)	6.70 (d) ($J \sim 1.2$)	7.23 (d)[b] (2H)	7.11 (d) ($J \sim 1.8$,[a] 2H)	7.13 (s)[d] (2H)	6.95–7.03 (m)
$-NH_2$	–	–	2.82 (s)	–	–	–	–
$-CH_2NH_2$	–	–	–	3.68 (s)	–	–	–
$-CH_2NH_2$	–	–	–	2.41 (s)	–	–	–
$-CH_3$	–	–	–	–	2.08 (s, 3H)	–	–
$-CH_2CH_3$	–	–	–	–	–	2.50 (q) ($J \sim 7.4$, 4H)	–
$-CH_2CH_3$	–	–	–	–	–	1.07 (t) ($J \sim 7.5$, 6H)	–

[a]The meta coupling is visible but not peak-picked by the computer.
[b]This peak is obscured by H_d.
[c]Doublet appears to be broadened by meta coupling but it is not resolved.
[d]Singlet is broadened, apparently from meta coupling.
[e]Meta coupling is visible but not well resolved.
[f]The ortho coupling constant could not be accurately measured because of severe overlap with H_b.

TABLE 2. ^{13}C Spectra Chemical Shifts (in ppm)



Peak location	R							
	H	NO_2	NH_2	CH_2NH_2	CH_3	CH_2CH_3	N=N=N	Br
C_1	136.6	137.9	136.6	136.6	136.0	137.1	135.8	138.8
C_2	131.2	131.6	131.2	131.2	131.2	131.1	129.9	129.9
C_3	119.3	119.7	119.3	119.3	118.2	118.5	117.7	117.1
C_4	163.5	162.0	163.5	163.4	163.7	163.9	161.5	161.1
C_5	154.1	—	154.1	154.1	—	—	—	—
C_6	121.4	—	121.4	121.4	—	—	—	—
C_7	130.1	—	130.1	130.1	—	—	—	—
C_8	148.8	—	148.8	148.8	—	—	—	—
C_9	43.9	44.4	43.9	44.0	43.8	44.1	not assigned	42.6
C_{10}	32.5	32.0	32.5	32.5	32.5	32.4	not assigned	30.7
C_{11}	—	148.4	[a]	149.4	149.2	149.3	148.6	149.8
C_{12}	—	125.4	[a]	129.3	131.6	130.1	119.4	132.2
C_{13}	—	143.0	[a]	131.4	131.1	130.9	131.9	115.8
C_{14}	—	148.0	[a]	151.7	152.5	152.1	143.9	148.7
C_{15}	—	124.6	[a]	121.8	121.6	121.5	122.3	122.0
C_{16}	—	135.1	[a]	128.7	127.3	127.2	124.5	127.6
CH_2NH_2				43.3				
CH_3					17.5			
CH_2CH_3						24.7		
CH_2CH_3						15.6		

[a]The level of substitution was too low to detect these peaks.

The degree of substitution calculation for the nitro derivative was dependent on the single resolved aromatic proton resonance (7.42 ppm) in the substituted rings. This peak shows both ortho and meta couplings, which can only occur if the ring is monosubstituted. Interestingly, this is the only polymer synthesized with unsubstituted BPA that has a DS greater than 1. Indeed, the DS was found to be 2.16, indicating that all the BPA rings in the product are substituted. Five quaternary and five protonated aromatic carbons should be seen for this material. This prediction was confirmed by DEPT experiments.

No degree of substitution calculations were made on the phthalimidomethyl derivative. The spectrum was not clean enough in the alkyl region to measure the side-chain methylene area; the aromatic area was too complex.

The DS for the methyl and ethyl derivatives was expected to be 2.0 since the starting BPA was reported to be substituted once in each of its two rings. For the

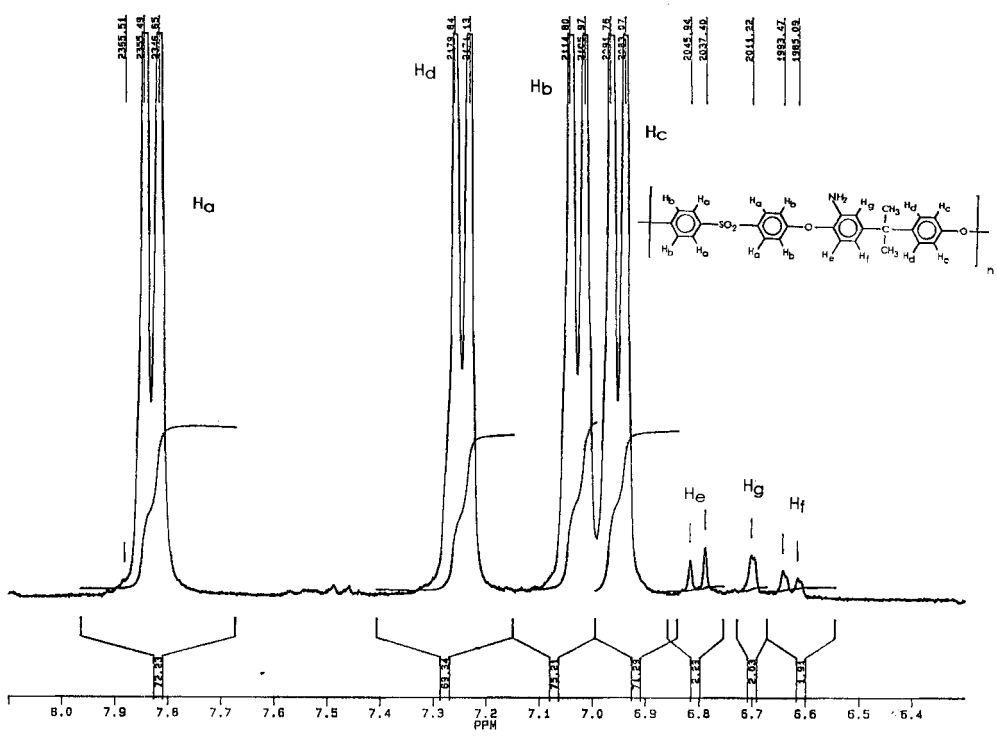
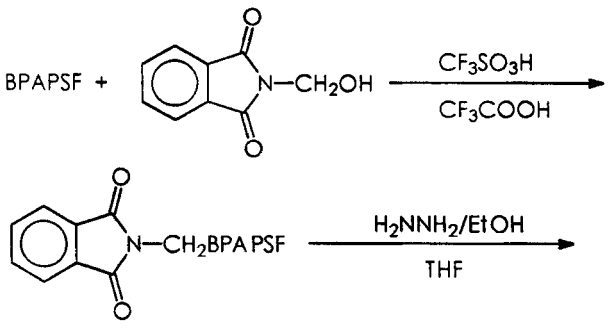


FIG. 5. Proton NMR spectrum of aromatic region of BPAPSF-NH_2.



BPAPSF-CH2NH2

SCHEME 1.

TABLE 3. Estimated Degrees of Substitution for the BPAPSF Derivatives

BPAPSF-R, where R is	Estimated substitution, DS (^{1}H NMR)
$-NO_2$	2.00
$-NH_2$	0.11
$-CH_2NH_2$	0.70[a]; 0.82
$-CH_3$	2.03; 2.20
$-CH_2CH_3$	1.76; 2.25; 2.13

[a]The DS for the aminomethyl derivative was also 0.70 by nitrogen analysis of the phthalimidomethylated precursor.

ethyl derivative, three methods were used to calculate the DS. All relied on the BPA methyl area to supply the relative number of BPAPSF repeating units.

1. Average of the three sets of aromatic proton peaks in the ethyl-substituted rings (at 7.13, 7.04, and 6.81 ppm) over one-sixth the BPA methyl area.
2. One-half the methylene proton area (from the ethyl group) divided by one-sixth the BPA methyl area.
3. One-third the methyl proton area (from the ethyl group), divided by one-sixth the BPA methyl area.

The average of the calculated results (2.05) was close to the expected DS = 2.0 value.

The DS for the methyl substituted UDEL derivative was calculated by two methods.

1. The average of the three new sets of aromatic proton peaks (at 7.11, 7.04, and 6.83 ppm) over one-sixth the BPA methyl area.
2. One-third the methyl substituent area divided by one-sixth the BPA methyl area.

There was no evidence for more than monosubstitution in a ring in the methyl derivative. There are only the predicted five aromatic carbons seen in the carbon-proton correlation experiment. There are, however, only four of the predicted five quaternary carbons. Peak degeneracy may account for this observation.

Table 3 lists the estimated degrees of substitution for the BPAPSF derivatives studied.

CONCLUSIONS

With NMR spectroscopy it was possible to determine the site of electrophilic substitution in BPAPSF. In two of the products, some evidence was found for a small amount of disubstitution within a ring. Three of the polymers had DS values of about 2. The DS for the polymer series ranged from 0.11 to 2.25. In some cases it was possible to use different calculation methods to confirm the DS.

Further NMR work could provide confirmation of the COLOC identifications of quaternary carbons. In high DS products (such as the nitro derivative), it may be possible with NOESY spectrum to determine which of the protons in a substituted ring are in closest proximity to the isopropylidene methyl groups.

In addition, an INADEQUATE (incredible natural abundance double quantum transfer) experiment, which identifies carbon-carbon connectivities, would be useful. To trace out the carbon skeleton involved with substitution, a high DS would be necessary. In addition, the sample must be sufficiently soluble. The starting BPAPSF is soluble in tetrachloroethane, at least up to the 50% level, which is usually mentioned as the minimum concentration for a successful INADEQUATE run.

ACKNOWLEDGMENTS

We wish to thank Dr. P. Neil Nugara of DSM Copolymer for his helpful comments on the NMR work. Thanks are extended to Dr. Cynthia Brinkley and Mr. Danny Purvis of DSM Copolymer for the nitrogen analysis data. Synthesis of alkylated polysulfones by Dr. Soo Lee is also acknowledged. Finally, the access to many hours of NMR instrument time at DSM Copolymer is greatly appreciated.

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Received June 8, 1995