Restricted Chain Rotation in Polymers Containing Pendant Groups: Structural Characterization of Hydroxyl-Functionalized Polysulfones[†]

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ABSTRACT: Proton and carbon resonance spectra have been obtained for 9- and 9,9′-substituted polysulfones with progressively bulkier substituents. The degree of substitution and the changes in stereochemistry caused by the substituents have been determined by analysis of the spectra.

Introduction

Aromatic polysulfones are high-performance thermoplastics which are extensively employed as materials for semipermeable membranes. Significant changes in membrane performance and new applications have been brought about by introducing chemical functionality into the polymer. Principal examples of modification chemistry for aromatic polysulfones are sulfonation,[1,2] halomethylation,[3-5] lithiation,[6,7] bromination,[8,9] and aminomethylation.[9,10] Proton and occasionally carbon-13 resonance spectroscopies have been used to determine the location and degree of substitution (DS) on the aromatic rings of the polysulfone.[8,11-13] It has been shown that nonpolymer aromatic sulfones with bulky substituents ortho to sulfone exhibit restricted rotation about the sulfur-aryl bonds with free energies of activation of about 22 kcal mol^{-1}.[14] In this paper we examine the ^{1}H and ^{13}C resonance spectra of a series of partially *o*-sulfone-substituted derivatives of UDEL polysulfone in which the steric bulk of the substituents is systematically increased. The effects upon the spectra by inherently chiral centers in the substituents, and by chiral centers created by hindered rotation, will be presented and interpreted.

Experimental Section

Magnetic Resonance. All spectra were obtained with a Bruker AM 400 spectrometer operating at a proton frequency of 400.13 MHz. Spectra were normally obtained at room temperature in either deuteriochloroform or deuterated dimethyl sulfoxide as solvent according to the solubility of the particular polymer. Proton spectra were collected with a spectral width of 4000 Hz and a 16K data table. All results are reported for Fourier transformation of the free induction decay without apodization. In some cases, to aid spectral interpretation, the free induction decay was apodized to narrow the spectral peaks. In these cases the data table was increased to 32K. A pulse width of 1.0 μs (7.2°) and a delay of 0.5 s between pulses were employed to insure that there was no saturation. Carbon-13 spectra were collected with a spectral width of 20 000 Hz and a 16K data table. Apodization corresponding to a line broadening of 1.0 Hz was employed. Two-power-level proton decoupling was employed to minimize dielectric heating of the sample. A pulse width of 5.0 μs (72°) and a delay of 5.0 s between pulses were used to avoid saturation. Proton-carbon one-bond connectivities were obtained from two-dimensional spectra using a modified HETCOR sequence[15] with a final data table of 4K points in the carbon frequency domain of 5500 Hz and 512 points in the proton domain of 250 Hz. Longer range proton-carbon connectivities were determined using the COLOC sequence[16] with 4K data points in the carbon frequency domain of 5500 Hz and 256 data points in the proton domain of 1000 Hz. The appropriate delays for these two-dimensional experiments were calculated from the proton-carbon coupling constants measured on a proton-coupled carbon-13 spectrum. All chemical shifts are referred to internal tetramethylsilane as reference.

Polymer Synthesis. Functionalized polysulfones containing pendant carbinol groups, substituted by combinations of hydrogen, methyl, and phenyl groups, were prepared via the direct lithiation route.[7,17] To synthesize each type of hydroxyl derivative, three lithiated intermediates were prepared from polysulfone: approximately 0.5, 1.0, and 2.0 lithium atoms per repeat unit. The degree of substitution (DS) of the lithiated intermediate was controlled by the addition of 0.5-, 1.0-, and 2.0-mol quantities of *n*-butyllithium to a tetrahydrofuran (THF) solution of polysulfone. The reaction selectively lithiates each aromatic ring of polysulfone ortho to the sulfone linkage up to a total of two per sulfone group.[6] Carbinol derivatives of various DS were produced by reaction of carbonyl electrophiles with the lithiated intermediates. The least hindered substituent, a primary alcohol, was obtained from formaldehyde. Methyl- and phenyl-substituted secondary alcohols were obtained from acetaldehyde and benzaldehyde, respectively. Tertiary alcohols were derived from acetone, acetophenone, and benzophenone. A lower than expected DS of carbinol groups resulted from the reactions of acetaldehyde, acetone, and acetophenone, presumably due to competitive keto-enol tautomerism side reactions from protons α to the carbonyl. Full experimental details for the preparation of hydroxylated polysulfones will be reported elsewhere.[18] The polysulfone derivatives synthesized and their actual DS's are summarized in Table I.

Results and Discussion

The numbering system shown in Chart I will be used throughout the discussion. The primed numbers are only significant for the monosubstituted derivatives. Proton and carbon chemical shifts and proton-carbon coupling constants for the unsubstituted polysulfone are listed in Table II. There has been a controversy concerning the assignment of chemical shifts to the carbon atoms 2 or 6 versus 8 or 12.[8,12] The one-bond connectivity data clearly show that the proton at 6.94 is bonded to the carbon atom at 119.8 and that at 7.00 to 117.6, confirming the assignment of ref 8. The three-bond couplings C_1–H_3, C_4–H_2, C_7–H_9, and C_{10}–H_8 found in the COLOC experiment confirm the assignments of the carbon atoms not directly bonded to hydrogen.

The synthesis of a polymer in which only one of the hydrogens 9 or 11 is replaced by a substituent is not possible by this lithiation modification. Depending on the total degree of substitution, there will be a distribution of unsubstituted, monosubstituted, and disubstituted species as previously described.[13] In order to assign chemical shifts to the monosubstituted derivatives, polymers were syn-

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Table I
Actual Degree of Substitution Obtained for Various Functionalized Polysulfones

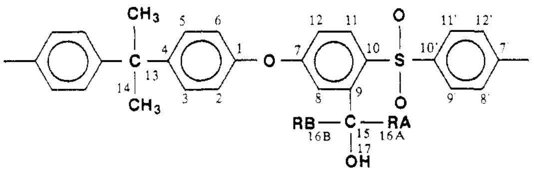
electrophile	substituent	low DS	mid DS	high DS
formaldehyde	$-CH_2OH$	0.31	0.84	1.85
acetaldehyde	$-C(OH)HCH_3$	0.35	0.73	1.60
benzaldehyde	$-C(OH)HC_6H_5$	0.48	1.00	2.00
acetone	$-C(OH)(CH_3)_2$	0.34	0.71	1.40
acetophenone	$-C(OH)(CH_3)C_6H_5$	0.50		1.47
benzophenone	$-C(OH)(C_6H_5)_2$	0.46	0.97	2.00

Table II
Chemical Shifts for Unsubstituted and CH_2OH-Substituted Polysulfone Polymers

				RA = RB = H			
	DS[a] = 0.0			DS[a] = 1.0		DS[a] = 2.0	
atom	δ(H)[b]	δ(C)[b]	J_{C-H}[c]	δ(H)	δ(C)	δ(H)	δ(C)
1		152.8	9.8 (1,2) 3.7 (1,3)		152.2		152.3
2	6.94	119.8	161.1 (2,2) 5.8 (2,3)	7.07	119.8	7.09	119.8
3	7.24	128.2	121.5 (3,3) 5.8 (3,2)	7.31	128.3	7.33	128.3
4		147.1	3.7 (4,5)		146.7		146.7
5	7.24	128.2	121.5 (5,5) 5.8 (5,6)	7.31	128.3	7.33	128.3
6	6.94	119.8	161.1 (6,6) 5.8 (6,5)	7.07	119.8	7.09	119.8
7		161.9	9.8 (7,8) 3.1 (7,9)		161.3		161.8
7′					161.3		
8	7.00	117.6	164.8 (8,8) 6.4 (9,8)	7.12	117.6	7.34	115.3
8′				7.00	117.7		
9	7.85	129.8	128.8 (9,9) 6.4 (8,9)		129.7		129.7
9′				7.87	129.7		
10		135.3	8.5 (10,9)		144.9		144.8
10′					134.5		
11	7.85	129.8	128.8 (11,11) 6.4 (11,12)	8.05	130.3	8.03	131.6
11′				7.87	129.7		
12	7.00	117.6	164.8 (12,12) 4.9 (12,11)	7.00	115.1	7.06	114.8
12′				7.00	115.1		
13		42.4			41.8		41.9
14	1.69	30.9	128.2 (14,14)	1.66	30.4	1.69	30.4
15					58.8		58.4
16				4.66		4.53	
17				5.47		5.49	

[a] The degree of substitution at carbon atom 9 (maximum 2.0). [b] In parts per million from tetramethylsilane. [c] In hertz.

Chart I



thesized with a total degree of substitution of about 0.5. Under these circumstances, there is a negligible concentration of the disubstituted species and the signals of the monosubstituted species can be distinguished from those established for UDEL itself. A confirmation of these assignments was made with polymers which were synthesized with a total DS in the range of 1.4–2.0. For these polymers one sees primarily signals from the disubstituted and monosubstituted species.

Proton and carbon chemical shifts for polysulfones with a CH_2OH substituent in the 9 position are listed in Table II. There is no evidence for hindered rotation in these polymers since only single, sharp signals are observed for the substituent. The most significant changes in chemical shift with substitution are observed for H_{11} and C_{10} which move to lower field. These are consistent with observations with monomeric diaryl sulfones which have been attributed to the magnetic anisotropy of the phenyl rings perpendicular to each other.[19]

Table III
Chemical Shifts for $C(CH_3)HOH$-Substituted Polysulfones ($RA = CH_3$, RB = H)

	DS[a] = 1.0		DS[a] = 2.0[c]			
atom	δ(H)[b]	δ(C)[b]	$\delta(H_{meso})$	$\delta(C_{meso})$	$\delta(H_{SS,RR})$	$\delta(C_{SS,RR})$
1		152.7		152.4		149.9, 150.0
2	6.88	116.5	7.02	118.6	7.02	118.6
3	7.25	128.4	7.32	127.7	7.32	127.7
4		148.0		146.0		146.0
5	7.25	128.4	7.32	127.7	7.32	127.7
6	6.88	116.5	7.02	118.6	7.02	118.6
7		162.7		160.9		160.7, 161.1
7′		162.1				
8	7.34	115.7	7.31	115.4	7.31	115.3
8′	7.00	115.7				
9		129.5		128.9		129.1
9′	7.78	129.5				
10		135.4		131.4		131.3
10′		135.4				
11	8.02	131.7	7.89	130.1	7.89	130.0
11′	7.78	129.5				
12	7.00	115.7	7.00	116.1	7.00	116.2
12′	7.00	115.7				
13		42.4		41.5		41.5
14	1.69	30.9	1.70	30.0	1.70	30.0
15		64.9		63.0		62.9
16A	1.29	23.6	1.06	25.1	1.13	24.8
16B	2.73				3.50	
17	5.47		5.35		5.35	

[a] The degree of substitution at carbon atom 9 (maximum 2.0). [b] In parts per million from tetramethylsilane. [c] Dissolved in dimethyl sulfoxide–d_6 at 100 °C.

Proton and carbon chemical shifts for polysulfones with a $C(CH_3)HOH$ substituent in the 9 position are listed in Table III. This substituent has a chiral center at C_{15}. Therefore, barring long-range effects along the polymer chain, two stereoisomers (*SS,RR* and meso species) are expected for a disubstituted segment. These have been observed via some of the carbon and proton signals, as detailed in Table III. It has been shown that magnetic nonequivalence may be observed for geminal dimethyl groups of a substituent in tetra-ortho-substituted diphenyl sulfides and sulfones which are unsymmetrically substituted in each phenyl ring.[14] We propose that the inherent asymmetry in the diphenyl sulfone grouping produces magnetic nonequivalence in the *SS* and *RR* disubstituted isomers, regardless of hindrance to rotation, in a manner analogous to that of methylene protons adjacent to a chiral center.[20] This has been observed for signals arising from some of the nuclei and is included in Table III. The changes in the proton and carbon resonance spectra with temperature arise from changes in chemical shift and in the rate of overall polymer motion rather than from restricted rotation about a particular bond. This is illustrated for the proton spectrum in Figure 1 where the chemical shift of the OH group in one isomer and one set of CH_3 signals from the *SS* or *RR* isomers change with temperature. In Figure 2 for the same polymer the effect of temperature is shown for the chemical shifts of carbons 3, 5, 9, 10, and 11.

Proton and carbon chemical shifts for polysulfones with a $C(CH_3)_2OH$ substituent in the 9 position are listed in Table IV. The spectra may be interpreted and assigned in the same fashion as those with CH_2OH substituents.

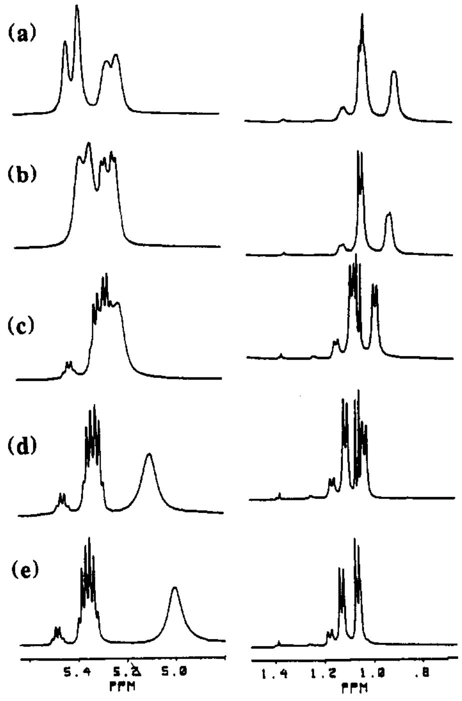


Figure 1. Portions of the proton spectrum of UDEL partially substituted with the $C(CH_3)HOH$ group as a function of temperature: (a) 28 °C, (b) 40 °C, (c) 60 °C, (d) 80 °C, (e) 100 °C.

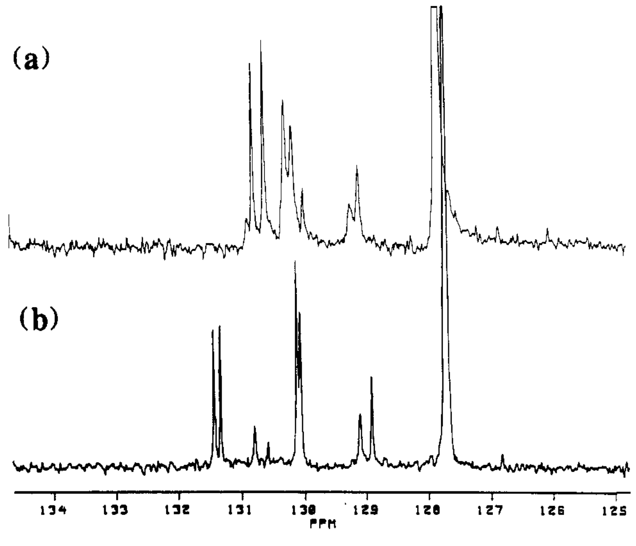


Figure 2. A region of the carbon resonance spectrum of UDEL disubstituted with the $(CH_3)HOH$ group: (a) 28 °C, (b) 100 °C.

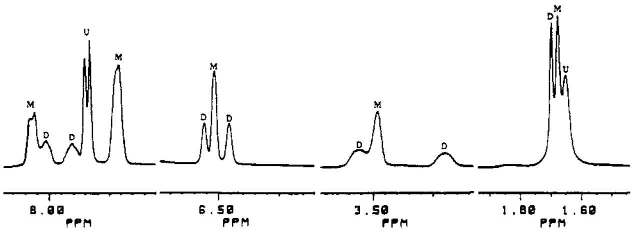


Figure 3. Portions of the proton spectrum of UDEL partially substituted with the $C(C_6H_5)HOH$ group. Peaks labeled U, M, and D are assigned to protons in unsubstituted, monosubstituted, and disubstituted regions of the polymer, respectively.

Table IV
Chemical Shifts for $C(CH_3)_2OH$-Substituted Polysulfones ($RA = RB = CH_3$)

	DS[a] = 1.0		DS[a] = 2.0	
atom	δ(H)[b]	δ(C)[b]	δ(H)	δ(C)
1		152.7		153.2
2	6.81	119.8	6.73	119.8
3	7.25	128.4	7.27	128.5
4		147.2		147.2
5	7.25	128.4	7.27	128.5
6	6.81	119.8	6.73	119.8
7		161.0		161.6
7′		161.5		
8	7.14	117.6	7.13	117.6
8′	6.97	119.8		
9		128.8		128.5
9′	7.76	133.1		
10		136.8		134.4
10′		135.1		
11	8.09	128.8	7.73	131.7
11′	7.76	133.1		
12	7.12	114.0	6.72	114.3
12′	6.97	119.8		
13		42.4		42.4
14	1.69	30.9	1.69	30.9
15		73.5		73.5
16	1.64	32.2	1.69	32.3
17	5.13		4.73	

[a] The degree of substitution at carbon atom 9 (maximum 2.0). [b] In parts per million.

Table V
Chemical Shifts for $C(C_6H_5)HOH$-Substituted Polysulfones (RA = Phenyl, RB = H)

	DS[a] = 1.0		DS[a] = 2.0	
atom	δ(H)[b]	δ(C)[b]	δ(H)	$\delta(C_{meso})$ and $\delta(C_{SS,RR})$
1		152.3		152.3, 152.4
2	6.86	119.3	6.82	119.8
3	7.15	127.4	7.15	128.3
4		146.1		146.1, 147.2
5	7.15	127.4	7.15	128.3
6	6.86	119.3	6.82	119.8
7		162.5		162.5, 162.6
8	6.89	115.7	6.89, 6.95	115.7, 115.8
8′	6.86	115.7		
9		132.1		132.4, 132.5
9′	7.74	129.4		
10		141.1		140.9, 141.3
11	8.08	131.9	7.89, 7.99	131.0, 131.1
11′	7.74	129.4		
12	6.86	115.7	6.82	119.5, 119.6
13		42.4		42.3
14	1.68	30.9	1.64	30.9
15		70.1		69.5, 69.6
16	6.53		6.43, 6.53	
17	3.44		3.17, 3.55	

[a] The degree of substitution at carbon atom 9 (maximum 2.0). [b] In parts per million from tetramethylsilane.

The spectral assignments with a chiral $C(C_6H_5)HOH$ substituent in the 9 position are listed in Table V. For this set of polymer derivatives we also observe diastereoisomerism of meso and *SS,RR* units, as described when RA is methyl. There is no evidence for hindered rotation since only single, sharp signals of the appropriate multiplicity are observed for the substituents.

Proton and carbon chemical shifts for polysulfones with a chiral $C(C_6H_5)(CH_3)OH$ substituent in the 9 position are listed in Table VI. Both in $CDCl_3$ solution at room temperature and in $(CD_3)_2SO$ at 100 °C, there is evidence for hindered rotation in the monosubstituted species since two signals of unequal intensity are observed for some of the carbon species. Two equal signals are observed for some of the proton and carbon species for the disubstituted regions of the polymer in the same manner as with the polymers containing $-C(CH_3)HOH$ substituents. Because of severe overlap of the backbone aromatic proton and carbon signals with those of the substituents, it was

Table VI
Chemical Shifts for $C(C_6H_5)(CH_3)OH$-Substituted Polysulfones (RA = C_6H_5, RB = CH_3)

	DS = 1.0				DS = 2.0			
atom	$\delta(H_{CDCl_3})$[a]	$\delta(H_{(CD_3)_2SO})$[b]	$\delta(C_{CDCl_3})$	$\delta(C_{(CD_3)_2SO})$	$\delta(H_{CDCl_3})$	$\delta(H_{(CD_3)_2SO})$	$\delta(C_{CDCl_3})$	$\delta(C_{(CD_3)_2SO})$
1			153.0, 153.1	151.2, 152.9			152.6, 153.0	152.5, 153.1
2	6.91		119.6, 119.9	119.3, 119.5	6.91		119.0, 119.1	119.0, 119.1
3	7.25		128.0, 128.8	127.5, 127.6	7.25		128.0, 128.4	128.1, 128.3
4			147.1, 147.6	146.9, 148.3			147.1, 147.9	146.5, 147.9
5	7.25		128.0, 128.8	127.5, 127.6	7.25		128.0, 128.4	128.1, 128.3
6	6.91		119.6, 119.9	119.3, 119.5	6.91		119.0, 119.1	119.0, 119.1
7			161.1, 161.6	159.4, 160.7			160.6, 161.6	158.5, 160.4
8	6.94		115.0	115.0	6.75		114.4, 114.6	115.0, 115.3
8′	6.73		117.3, 117.7	117.5				
9			129.7	129.7			129.7	128.9, 129.7
9′	7.85	7.93	129.7	128.9				
10			135.5, 136.0	134.8			134.5	134.8, 135.7
11	8.15	8.17	135.5	136.3, 136.4	7.85	7.75 → 7.87		129.7, 128.9, 129.7
11′	7.85	7.93	129.7	128.9				
12	6.73		117.3, 117.7	118.0	6.73		119.0	
13			42.4	42.0			42.4	42.0
14	1.70	1.65	30.9	30.6	1.69	1.65	30.9	30.6
15			76.7	76.4			76.7	76.6, 76.8
16	1.79	1.82	33.8	31.6	1.84, 1.87	1.80, 1.85	32.3, 33.8	31.1, 31.9
17	5.07	5.61			5.23	5.37		

[a] In parts per million from tetramethylsilane at 25 °C. [b] In parts per million from tetramethylsilane at 100 °C.

Table VII
Chemical Shifts for $C(C_6H_5)_2OH$-Substituted Polysulfones (RA = RB = C_6H_5)

	DS[a] = 1.0		DS[a] = 2.0		
atom	δ(H)[b]	δ(C)[b]	δ(H)[b]	δ(C)[b]	δ(C)[c]
1		151.9, 152.2 152.87, 152.94		149.3, 150.8	152.3
2	6.8, 6.9	119.7, 119.8	6.80	117.4, 117.7	
3					
4		146.0, 146.7		147.0, 147.1	148.3
5					
6	6.8, 6.9	119.7, 119.8	6.80	117.4, 117.7	
7		160.0, 162.0		160.8	159.0
8	6.39	121.2	6.39	121.3, 129.7	
9		129.0		129.7	
10					
11	8.15	135.1, 135.4 135.8, 136.0	7.76	133.1, 133.9	
12			6.85		
13		42.32		42.42	42.0
14	1.67, 1.69 1.70, 1.72	31.0	1.64	31.0	30.6
15		82.5		82.8	82.5
16					
17	5.70, 6.91		5.70		

[a] The degree of substitution at carbon atom 9 (maximum 2.0). [b] In parts per million from tetramethylsilane for a $CDCl_3$ solution at 25 °C. [c] In parts per million from tetramethylsilane for a dimethyl sulfoxide-d_6 solution at 100 °C.

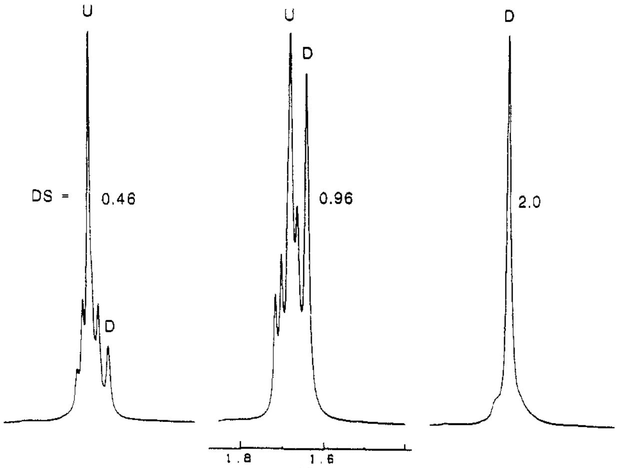


Figure 4. Proton resonance spectra of the *gem*-dimethyl region of $C(C_6H_5)_2OH$-substituted UDEL as a function of the degree of substitution.

necessary to make some of the assignments with the aid of two-dimensional proton–carbon correlation spectra.

The assignment of some signals to particular proton and carbon atoms of polysulfones with a $C(C_6H_5)_2OH$ substituent in the 9 position are listed in Table VII. Severe overlap of the signals from the aromatic ring protons and carbons makes a complete assignment impossible at this time. An explanation of the assignments can best be made with the aid of Figure 4 which shows the proton resonance spectra of the *gem*-dimethyl group 14, as a function of the degree of substitution. The polymer in which all of the 9 positions of the repeating unit are substituted has only one signal, as does the polymer in which the 9 positions of the repeating unit are unsubstituted. For the polymer in which one of the 9 positions per repeat unit is substituted with a $C(C_6H_5)_2OH$ moiety, four signals are found. These results may be explained by invoking hindered rotation about the sulfur–carbon 10 and carbon 9–carbon 15 bonds which effectively produces chiral-like centers at sulfur and carbon 9. The configuration of the disubstituted species is analogous to that of a meso isomer so only a single signal is observed. The 14-*gem*-dimethyl group is approximately equidistant from the sulfone groups of two adjacent repeating units. Therefore, although in isolation *SS* and *SR* are not distinguishable by NMR from *RR* and *RS*, in this polymer they should be distinguishable in principle because of the effect of the adjacent repeat unit. In fact this is observed for the protons in the 14 position and the carbons in the 1 and 11 positions. In some other positions two signals are observed for the monosubstituted unit. It is not necessary that there be stereochemical equivalence for all positions in the disubstituted repeat unit, although it is observed for the 14 position. In fact two signals are observed for several of the carbon resonances of the disubstituted species in deuteriochloroform solution. Although these becomes single lines in dimethyl sulfoxide-d_6 at 100 °C, they do not split at room temperature, but some are broadened.

Since we invoke hindered rotation to explain some of the observed spectral features, it is necessary to get some independent evidence for it. It has not been possible to

Table VIII
Enthalpy Barriers to Rotation Calculated for Some Substituted 9,9′-Bis(hydroxymethyl)diphenyl Sulfones

substituent		sulfone rotation barrier, kcal/mol	substituent rotation barrier, kcal/mol
9	9′		
H	H	2.0	
CH_2OH	H	6.5	5.3
CH_2OH	CH_2OH	7.7	3.8
$C(CH_3)HOH$	H	12.2	10.9
$C(CH_3)HOH$ (*S*)	$C(CH_3)HOH$ (*S*)	9.0	11.8
$C(CH_3)HOH$ (*S*)	$C(CH_3)HOH$ (*R*)	11.2	13.2
$C(CH_3)_2OH$	H	11.2	10.0
$C(CH_3)_2OH$	$C(CH_3)_2OH$	20.8	8.8
$C(C_6H_5)HOH$	H	9.0	7.7
$C(C_6H_5)HOH$ (*S*)	$C(C_6H_5)HOH$ (*S*)	21.8	12.4
$C(C_6H_5)HOH$ (*S*)	$C(C_6H_5)HOH$ (*R*)	10.8	9.5
$C(C_6H_5)CH_3OH$	H	13.2	7.4
$C(C_6H_5)CH_3OH$ (*S*)	$C(C_6H_5)CH_3OH$ (*S*)	19.5	13.6
$C(C_6H_5)CH_3OH$ (*S*)	$C(C_6H_5)CH_3OH$ (*R*)	21.3	7.0
$C(C_6H_5)_2OH$	H	7.5	18.3
$C(C_6H_5)_2OH$	$C(C_6H_5)_2OH$	64	81

clearly overcome the rotation barrier by increasing the sample temperature. Visual examination of molecular models clearly shows strongly preferred conformations. In order to quantify this, theoretical mechanical modeling was done via the molecular mechanics program Sybyl of Tripos Associates. The overall enthalpy of the various structures was minimized for given torsional angles about the aryl–sulfone and aryl–substituent bonds. The difference between the maximum and minimum calculated values for 360° of the torsional angle was taken to be the enthalpy barrier to rotation about that bond. These values are listed in Table VIII. The program uses a commonly accepted force field and standard molecular mechanics calculations.[21] Energies for substituted 9,9′-bis(hydroxymethyl)diphenyl sulfones were initially calculated at 20° intervals and then at 4° intervals for the angular regions about the maximum and minimum energy values. A few different starting coordinates were used for each minimization routine in order to lessen the chances of reaching a local minimum rather than a global minimum. This danger was greatest for the more bulky substituents. As a result of these procedures, one can state that the barriers to rotation listed in Table VIII could be somewhat greater but are unlikely to be smaller. Free energy barriers to rotation will be larger than the enthalpy barriers because of the significant degree of ordering required for the molecule at the maximum of the enthalpy barrier.

From the calculated values of Table VIII we may conclude that separate NMR signals due to hindered rotation should be observable in principle for the disubstituted sulfone polymers where the substituents are $(CH_3)_2OH$, $(C_6H_5)HOH$, $(C_6H_5)CH_3OH$, and $(C_6H_5)_2OH$ and the monosubstituted polymer with the $(C_6H_5)_2OH$ substituent. These calculations therefore confirm the assignments of some spectral features as arising from hindered rotation. Small chemical shift differences may be invoked to explain the absence of separate lines for the different stereoisomers in all of the proton and carbon signals.

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