^{13}C NMR Studies on Some Poly(alkene sulfone)s

A. H. Fawcett,[1a] F. Heatley,[1b] K. J. Ivin,*[1a] C. D. Stewart,[1a] and P. Watt[1a]

Departments of Chemistry, The Queen's University of Belfast, BT9 5AG, U.K., and The University of Manchester, M13 9PL, U.K. *Received January 31, 1977*

ABSTRACT: ^{13}C NMR spectra are reported for 15 poly(alkene sulfone)s; spin–lattice relaxation times T_1 were determined for seven of these. In the alk-1-ene series well-resolved tacticity effects were generally observed in DMSO as solvent but not in $CDCl_3$. Main-chain CH_2 and side-chain α-C carbons showed dyad sensitivity; for the propene polymer an assignment was made to m and r dyads and used to derive information concerning the conformation about the main-chain bonds. The 2-methylpent-1-ene polymer in $CDCl_3$ gave two peaks for both the side-chain α-CH_2 and the quaternary C. For the but-2-ene polymer evidence is presented that the hydrocarbon units are present almost entirely as r_c structures, unless the polymer is made from *trans*-but-2-ene at −78 °C, when m_c units may also be present. The fine structure is markedly sensitive to solvent (DMSO and $CDCl_3$) and is interpreted in terms of m_s and r_s $-CH(CH_3)SO_2CH(CH_3)-$ units in the ratio 35:65; a complete assignment of four CH peaks is given in terms of the r_c-centered "tetrads" $r_sr_cr_s$, $m_sr_cr_s$, $m_sr_cm_s$. The cyclopentene polymer in DMSO shows a similar kind of fine structure for both CH and α-CH_2. The cyclohexene polymer in $CDCl_3$ gives two CH peaks of equal intensity, indicating an atactic structure. T_1 values of 75 ± 10 ms and 43 ± 8 ms were observed for backbone CH and CH_2 respectively in the polysulfones of propene, but-1-ene, hex-1-ene, 2-methylpent-1-ene, cyclopentene, and cyclohexene. This independence of structure indicates that the dominant magnetic relaxation process of backbone nuclei does not involve rotation about the main-chain C–C bond. T_1 was independent of molecular weight in the three cases tested, in marked contrast to the dielectric relaxation behavior of the hex-1-ene and 2-methylpent-1-ene polymers.

Those poly(alkene sulfone)s which are soluble in organic solvents[2a] have either one or two chiral centers in each repeat unit and so exhibit tacticity effects which can be studied by NMR spectroscopy. Hitherto it was necessary to work with selectively deuterated polymers in order to simplify the interpretation of the ^{1}H NMR spectra.[2b,3] The advent of routine ^{13}C NMR spectroscopy removes the need for deuteration and provides an opportunity for a much closer look at tacticity effects in these polymers. In addition, the pulse-Fourier transform technique allows measurements of spin–lattice relaxation times T_1 from which information about the mobility of the chains can be derived. This is of special interest in view of the unexpectedly high barriers to rotation about certain of the main-chain bonds revealed by dielectric measurements.[4] This aspect is reported in more detail by Stockmayer[5] and by Bovey[6] in the accompanying papers.

A preliminary account of the poly(but-2-ene sulfone) spectrum has been given[7] but a study of model sulfones[8] now allows a more reliable and complete analysis of the spectrum. The main results from the study of 27 monosulfones and 13 disulfones may be expressed, for the purposes of this paper, as three rules, and will be referred to as such.

(1) A carbon atom situated α to a sulfone group experiences the following shifts as a result of methyl substitution at positions α, β, γ_c, δ_c, γ_s, δ_s with respect to the carbon atom: 5.5 ± 0.1, 6.3 ± 0.2, −0.6 ± 0.4, 0.2 ± 0.5, −2.7 ± 0.1, 1.0 ± 0.2 ppm, provided *tert*-butyl compounds are omitted from consideration. The subscripts c and s denote that the effect occurs through a chain containing C atoms only or one S atom, respectively.

(2) A carbon atom situated β to a sulfone group experiences the following shifts as a result of methyl substitution at positions α, β, γ_c, δ_c, δ_s with respect to the carbon atom: 8.3 ± 0.2, 8.7 ± 0.2, −3.4 ± 0.4, 1.8 ± 0.6, 0.1 ± 0.2 ppm.

(3) Carbon atoms situated β to a sulfone group experience a marked upfield effect compared with the same carbon in the hydrocarbon formed by replacement of the SO_2 group with a CH_2 group. This effect is sensitive to the conformation about the C–S bond: β carbons in the trans position (gauche to both oxygens) are shifted upfield by 9.4 ± 1.6 ppm compared with those in the gauche position (gauche with respect to one oxygen, trans with respect to the other). The conformationally sensitive effect is not directly expressed by the parameter set of rule (2), being lost in the averaging process.

Experimental Section

All the polymers used here had been prepared by radical copolymerization of mixtures of alkene and sulfur dioxide and most were available from previous work.[9] Molecular weights were in the range 10^4–10^7.

The NMR spectra were obtained for 5–15% solutions using a Bruker WH90 (22.63 MHz) spectrometer, with decoupling of protons by broad band irradiation (24 μs pulse ≡ 90° angle). Off resonance experiments were performed where necessary to confirm the assignments.

^{13}C spin–lattice relaxation times were measured on a Varian Associates XL-100 spectrometer at 25.14 MHz using the standard inversion recovery (π–τ–$\pi/2$) pulse sequence. Overhauser enhancement measurements were obtained from the ratios of integral intensities of spectra recorded first with the protons noise-decoupled and then with the decoupler offset by 30 KHz in the single-frequency mode.

Results

The chemical shift data are presented in Table I for 15 polymers. The T_1 data are given in Table II for 7 polymers.

Poly(propene sulfone) (1). The spectrum of this polymer (Figure 1) shows two peaks for each of the methyl and methylene carbons but only one for the methine carbon. The assignment of the fine structure to m and r dyads was made by examining the spectrum of a polymer rich in isotactic (m) dyads prepared by oxidation of an isotactic-rich sample of poly(propene sulfide).[10]

Poly(but-1-ene sulfone) (2). The spectrum is shown in Figure 2 for DMSO-d_6 as solvent. The side chain α-CH_2 is clearly resolved into two peaks of equal area, while both main chain CH_2 and CH show partially resolved triad structure; the CH_3 carbon gives a single sharp peak. The line order for the two α-CH_2 peaks is likely to be the same as for CH_3 in **1**, although the splitting is smaller. In chloroform as solvent none of the carbon atoms showed fine structure. Instead there was a steady broadening of the peaks in the order a, b, d, c.

The positions of the peaks are in general accord with those expected from rules (1) and (2), thus (expected differences shown in brackets): 1(a) → 2(b), α = 7.8 (8.3); 1(c) → 2(d), β = 4.9 (6.3); 1(b) → 2(c), $\gamma_c + \delta_s = -0.1$ (+0.4) ppm.

Poly(pent-1-ene sulfone) (3). The spectrum of **3** has many features in common with that of **2**. The α-CH_2 again gives two peaks separated by 0.4 ppm when the solvent is DMSO and both the main chain carbons give broad peaks with incipient splitting. In $CDCl_3$ there is no splitting and the lines broaden progressively through the series a, b, c, e, d. The positions of

Table I
^{13}C Shifts in Poly(alkene sulfone)s

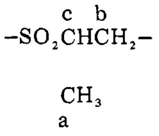
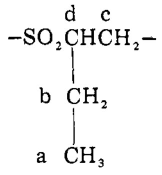
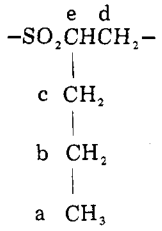
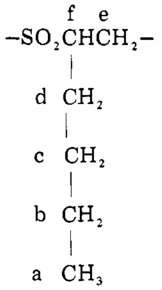
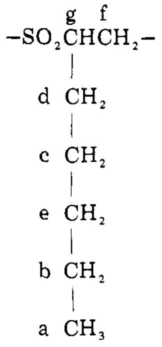
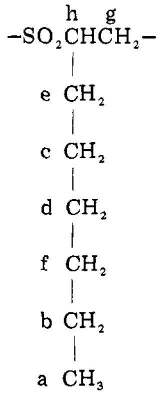
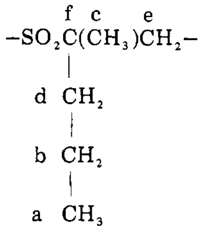
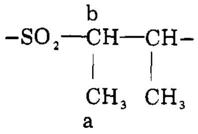
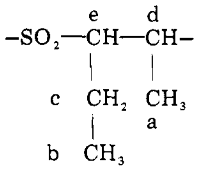
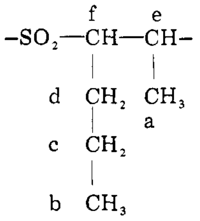
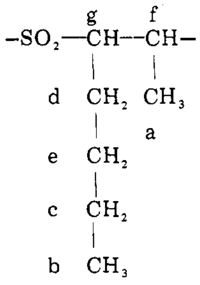
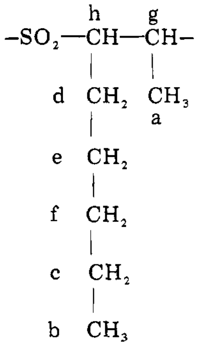
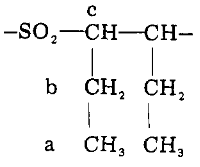
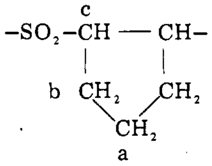
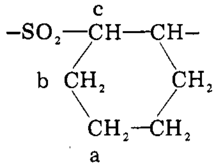
Compd No.	Repeat unit	Carbon	δ, ppm, in solvent indicated[a]	
			DMSO[b]	$CDCl_3$
1	 $-SO_2CH(CH_3)CH_2-$	a	13.02 r 14.00 m	
		b	47.86 r 48.51 m	
		c	52.80	
2	 $-SO_2CH(CH_2CH_3)CH_2-$	a	10.07	10.5
		b	20.92 21.41	22.25[d]
		c	47.73 48.05 48.22	49.4[d]
		d	57.28 57.71 58.28	58.7[d]
3	 $-SO_2CH(CH_2CH_2CH_3)CH_2-$	a	13.51	13.8
		b	18.67	19.65
		c	29.81 30.22	31.0[d]
		d	48.2[e] 48.6	50.5[d]
		e	56.4[e] 56.65[d]	57.75[d]
4	 $-SO_2CH(CH_2CH_2CH_2CH_3)CH_2-$	a		13.6
		b		22.45
		c		28.15
		d		28.15
		e		50.3
		f		57.75
5	 $-SO_2CH(CH_2CH_2CH_2CH_2CH_3)CH_2-$	a		13.85
		b		22.3
		c		25.8
		d		29.0[d]
		e		31.5[d]
		f		50.4[d]
		g		57.8[d]
6	 $-SO_2CH(CH_2CH_2CH_2CH_2CH_2CH_3)CH_2-$	a		14.0
		b		22.6
		c		26.2[d]
		d		29.2[d]
		e		29.2[d]
		f		31.5
		g		50.6[d]
		h		57.7[d]
7[i]	 $-SO_2C(CH_3)(CH_2CH_2CH_3)CH_2-$	a		14.36
		b		17.74
		c		19.95
		d		36.33 36.65
		e		48.87
		f		67.78 67.91
8[i]	 $-SO_2-CH(CH_3)-CH(CH_3)-$	a	8.65[h] 9.73[g] 12.74[h]	9.55 10.20[g]
		b	51.15 52.12[g] 53.37 53.69 56.5 58.3 } [h]	50.79 51.11 51.50[g] 51.93 52.28 53.39
9	 $-SO_2-CH(CH_2CH_3)-CH(CH_3)-$	a		10.79[d]
		b		12.84
		c		17.80 18.99
		d		54[d]
		e		59[d]
10[c]	 $-SO_2-CH(CH_2CH_2CH_3)-CH(CH_3)-$	a		10.36[d]
		b		13.70
		c		21.15[d]
		d		27.19[d]
		e f		51–59[d]
11	 $-SO_2-CH(CH_2CH_2CH_2CH_3)-CH(CH_3)-$	a		10.84[d]
		b		13.60
		c		22.61
		d		24.28[d] 25.30[d]
		e		30.10[d]
		f g		49–58[d]
12	 $-SO_2-CH(CH_2CH_2CH_2CH_2CH_3)-CH(CH_3)-$	a		10.73[d]
		b		13.97
		c		22.34 22.60
		d		26.27 27.78[d]
		e		29.13
		f		31.51 31.78
		g h		49–58[d]
13[f]	 $-SO_2-CH(CH_2CH_3)-CH(CH_2CH_3)-$	a		12.80[d] 13.13[d]
		b		19.5[d]
		c		59–63[d]

Table I (*Continued*)

			δ, ppm, in solvent indicated^a					δ, ppm, in solvent indicated^a	
Compd No.	Repeat unit	Carbon	DMSO^b	$CDCl_3$	Compd No.	Repeat unit	Carbon	DMSO^b	$CDCl_3$
14		a	25.31	26.16	15		a		19.96
		b	27.26	27.49			b		22.66^d
			27.84	28.24			c		52.76^d
			28.75^g	29.08					53.95^d
			29.14	29.67					
		c	59.17						
			59.72	59.90					
			60.14	61.12					
			60.63^g						

[a] At 60 °C except where stated; relative to TMS. Precision ±0.04 ppm or better. [b] In dimethyl-d_6 sulfoxide the center peak was used as a secondary standard, 39.67 ppm. [c] Solvent CCl_4 with 10% C_6D_6 to provide the lock signal. [d] Broadened peak (unresolved fine structure). [e] Shoulder. [f] Spectrum in $CDCl_3$ at 30 °C. [g] Main peak. [h] Only observed in polymer made from *trans*-but-2-ene at −78 °C or lower. 8.65 ppm peak usually observed as shoulder of 9.73 ppm peak. [i] Spectrum in $CDCl_3$ at 40 °C.

Table II
^{13}C Spin–Lattice Relaxation Times (T_1) and Nuclear Overhauser Enhancement Factors (η) for Poly(alkene sulfone)s^a

Polymer^b	Solvent	Nucleus^b	T_1 ms^c	η^c
1	DMSO-d_6	a	260	
		b	45	1.0
		c	76	1.2
2	DMSO-d_6 ($CDCl_3$)	a	470 (460)	
		b	75 (65)	1.2 (0.8)
		c	51 (50)	1.0 (0.5)
		d	92 (78)	0.8 (0.5)
4	80/20 PhMe/ C_6D_6	c, d	65, 73^d	1.0
		e	35, 38^d	1.0
		f	74, 69^d	1.1
4	$CDCl_3$	c, d	80, 85^d	
		e	41, 40^d	
		f	66, 74^d	
7	$CDCl_3$	a	400	
		b	68	
		c	133	
		d	51	
		e	45	
8	$CDCl_3$	a	260	1.4
		b	91, 113^e	0.9
14^f (mol wt 5×10^6)	$CDCl_3$	a	138 (151)	
		b	75 (80)	
		c	78 (85)	0.8 (0.8)
14^f (mol wt 2×10^5)	$CDCl_3$	a	132 (127)	
		b	67 (58)	
		c	80 (62)	1.0 (1.0)
15 (mol wt 2.4×10^5)	$CDCl_3$	a	43	
		b	43	
		c	67	1.1
15 (mol wt 4.5×10^4)	$CDCl_3$	a	42	
		b	43	
		c	68	1.2

[a] Polymer weight fraction = 0.08 ± 0.01 except where noted. Solvent as indicated. Temperature 30 °C. [b] Labeling scheme as in Table I. [c] Experimental error ±12%. [d] Pairs of values are for two samples prepared in such a way as to have widely different molecular weights. [e] The times refer to the peaks at 51.50 and 53.39 ppm, respectively. [f] Data in parentheses are for solutions of polymer weight fraction 0.045.

the peaks are as expected from the substitution rules: **2**(a) → **3**(b), α = 8.6; **2**(b) → **3**(c), β = 8.7 (8.7); **2**(d) → **3**(e), $\gamma_c = -1.2$ (−0.6); **2**(c) → **3**(d), $\delta_c = 0.3$ (0.2) ppm.

Poly(hex-1-ene sulfone) (4). This polymer is insoluble in DMSO. Its spectrum in $CDCl_3$ is as expected from that of **2** and **3**. Peaks a and b (Table I) are very sharp, c and d are coincident and somewhat broader, while e and f are broader still. The positions of the peaks are as expected from the substitution rules: **3**(a) → **4**(b), α = 8.65; **3**(b) → **4**(c), β = 8.5; **3**(c) → **4**(d), $\gamma_c = -2.85$ (−3.4); **3**(e) → **4**(f), $\delta_c = 0.0$ (0.2) ppm. All comparisons were made using $CDCl_3$ as solvent.

Poly(hept-1-ene sulfone) (5). In $CDCl_3$ the breadth of the peaks again increases progressively along the side chain, in the order a, b, e, c, d, and the main-chain peaks are broader still (about 1.5 ppm at half-height). The substitution shifts are: **4**(a) → **5**(b), α = 8.7; **4**(b) → **5**(e), β = 9.05; **4**(c) → **5**(c), $\gamma_c = -2.35$; **4**(d) → **5**(d), $\delta_c = 0.85$ (1.8) ppm.

Poly(oct-1-ene sulfone) (6). In $CDCl_3$ peaks a, b, and f are all sharp, d and e coincide and are somewhat broader, as also is c; h and g are much broader still. The resonance lines all occur at the expected frequencies.

Poly(2-methylpent-1-ene sulfone) (7). This polymer is insoluble in DMSO; its spectrum in $CDCl_3$ is shown in Figure 3. It is remarkable that the main-chain quaternary carbon f gives two very sharp peaks of separation 0.13 ppm, just as sharp as for the terminal methyl carbon a. The other main-chain carbon e and the α-methyl carbon c give single, broader peaks. The side chain α-CH_2 is split into two peaks of separation 0.33 ppm.

Poly(but-2-ene sulfone) (8). The spectrum of this polymer is at its simplest when the polymer is made from either *cis*- or *trans*-but-2-ene at temperatures of −60 °C or higher and the spectrum taken in DMSO-d_6. An example is shown in Figure 4b: CH_3 gives a single line but CH gives four peaks of unequal intensity. There were only minor variations of this intensity pattern with polymer preparation temperature (down to −60 °C). Somewhat different behavior is observed in $CDCl_3$; see Figure 4a. The CH_3 signal is split into two peaks of unequal intensity and at least six peaks are resolved in the CH region. The chiral shift reagent, Eu(TFC)$_3$, did not have any effect on the resolution of the spectrum in $CDCl_3$.

When the polymer was made from *cis*-but-2-ene at −78 °C the spectra were similar to those in Figures 4a or 4b, but when made from *trans*-but-2-ene the spectrum shown in Figure 4c was obtained in DMSO. The CH_3 resonance has an upfield shoulder (which in one spectrum appeared as a separate peak at 8.65 ppm) while another CH_3 peak appears downfield at 12.74 ppm. In addition a new set of CH peaks appears downfield from, but less well resolved than, the first set. In contrast

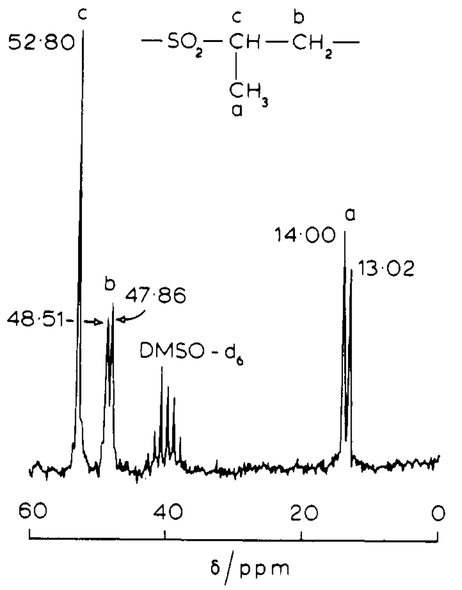


Figure 1. ^{13}C-$\{^1H\}$ NMR spectrum of poly(propene sulfone) prepared by radical copolymerization of propene and sulfur dioxide. Solvent DMSO-d_6/60 °C, 2048 pulses, 11 μs width, repetition time 0.7 s, spectral window 6024 Hz. For assignments see Table I.

the spectrum in chloroform did not show any additional peaks. In dioxane the spectrum was similar to that in $CDCl_3$, and in mixtures of DMSO and $CDCl_3$ the spectrum was intermediate between that in the pure solvents although in a 1:1 mixture the spectrum was essentially the same as in DMSO. No significant difference could be seen in the appearance of the CH_3 peaks in DMSO when the temperature for the NMR spectrum was raised from 30 to 85 °C.

An attempt was made to study the *trans*-but-2-ene system as a function of preparation temperature but the spectrum of the product was found to be very sensitive to small changes of preparation temperature around −78 °C and the temperature control was such that the results were not very reproducible. In one preparation we succeeded in obtaining a spectrum in which the new peaks were actually more intense than those corresponding to the positions of the peaks in Figure 4b.

Other Poly(alk-2-ene sulfone)s (9–12). Distinct but broad resonances are observed for the main-chain carbons in **9** but as the side chain is lengthened these signals merge into a single broad resonance. The α-CH_3 signal is broad but shows a shoulder or incipient splitting. The α-CH_2 signal d generally shows fine structure, being quite marked in the case of **12** where splitting was also observed rather surprisingly for c and f but not for e.

Poly(hex-3-ene sulfone) (13). The methyl resonance was a clear doublet with two outer shoulders. The α-CH_2 signal likewise appeared to have at least four components. The main-chain carbon gave a broad peak with some sign of fine structure.

Poly(cyclopentene sulfone) (14) and Poly(cyclohexene sulfone) (15). The spectra of these two polymers in $CDCl_3$ are shown in Figure 5. The spectrum of **14** in DMSO is also shown (**15** is insoluble in DMSO). The α-CH_2 (b) carbons in **14** give an unsymmetrical pattern of four lines in both solvents, the most intense peak being one of the downfield pair. The CH carbons in **14** also give an unsymmetrical pattern of four lines when the solvent is DMSO and two lines of unequal intensity in $CDCl_3$; in each case the greater weight is in the downfield part of the signal. In **15**, only the CH carbons show tacticity effects and here there are essentially two lines of equal intensity.

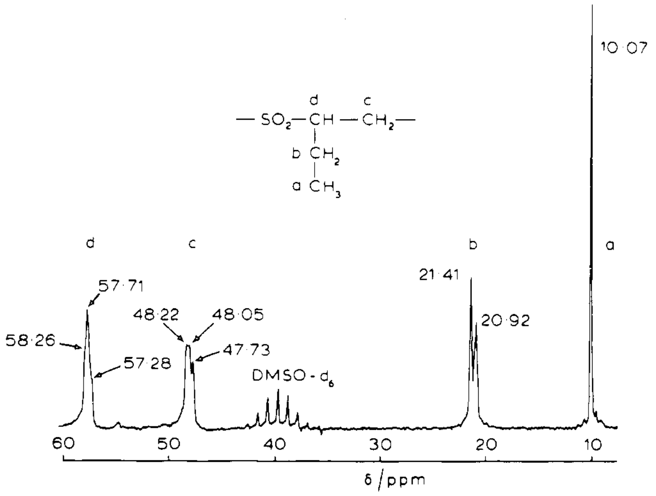


Figure 2. ^{13}C-$\{^1H\}$ NMR spectrum of poly(but-1-ene sulfone). Solvent DMSO-d_6/60 °C, 43600 pulses, 24 μs width, repetition time 1.5 s, spectral window 3012 Hz.

Relaxation Times. ^{13}C spin–lattice relaxation times (T_1) and nuclear Overhauser enhancement factors[11] (η) are collected in Table II. The relaxation of selected polymers was studied as a function of solvent (**3** and **4**), molecular weight (**4**, **14**, and **15**), and concentration (**14**), as indicated in Table II.

Discussion

We shall discuss in turn the chemical shift data for polymers **1**, **7**, **8**, **14**, and **15** and conclude with a discussion of the relaxation data.

Poly(propene sulfone). In the spectrum shown in Figure 1 the heights of the two peaks for each of the methyl and methylene signals are about the same indicating that the radical copolymerization of propene and sulfur dioxide produces essentially atactic polymer, confirming the conclusion previously drawn from ^1H NMR spectra.[2b]

Next we may note some striking contrasts with the spectrum of poly(propene sulfide).[10] Compared with the polysulfide the methyl resonance is upfield by about 7 ppm while the methylene and methine resonances are downfield by about 10 ppm. The upfield shift for CH_3 is presumably a consequence of the major influence of the β-sulfone group (rule (3)), whereas the downfield shifts for CH_2 and CH indicate that the inductive effect of the α-sulfone group outstrips the effect of the β-sulfone group.

The second point of difference from poly(propene sulfide) is the complete inversion of the tacticity effect. In the polysulfide only the methine resonance is split (by 0.2 ppm) whereas in the polysulfone only the methine resonance is not split. Furthermore the line order is reversed (m upfield from r for CH in the polysulfide). Compared with the polysulfide the splittings are also a good deal larger: 0.65 and 1.0 ppm for CH_2 and CH_3, respectively.

Before attempting to interpret the line order we may make a comparison with chemical shifts predicted from those of the model compound[8] $CH_3CH_2CH_2SO_2CH(CH_3)CH_2SO_2CH_2CH_2CH_3$ by application of rules (1) and (2), substituting methyl groups at the appropriate points on the terminal propyl groups. For CH the predicted shift is 51.2 + 1.0 + 0.1 = 52.3 ± 0.3 (obsd 52.8); for CH_2, 50.6 − 2.7 = 47.9 ± 0.1 (obsd 47.9, 48.5); for CH_3, 13.54 (obsd 13.0, 14.0) ppm. This agreement suggests that the conformational populations about the two internal C–S bonds are similar for the model compound and **1**, otherwise substantial differences would be expected because of rule (3). The evidence from the model compound[8]

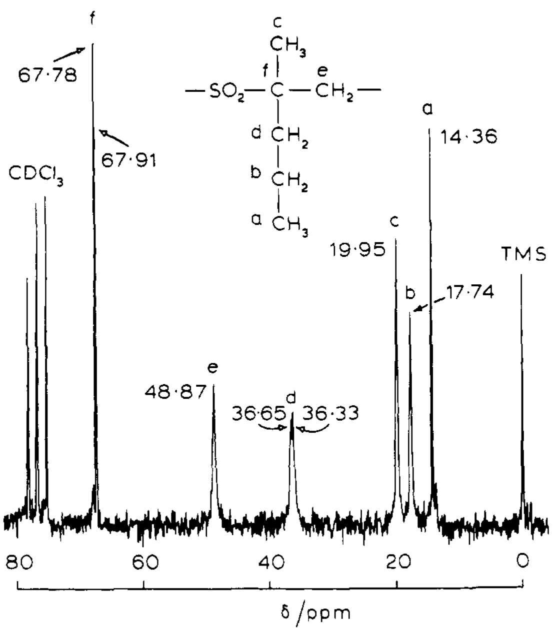


Figure 3. ^{13}C-{^{1}H} NMR spectrum of poly(2-methylpent-1-ene sulfone). Solvent CDCl$_3$/40 °C, 860 pulses, 24 μs width, repetition time 8 s, spectral window 6024 Hz.

suggests that trans CH$_2$–SO$_2$ has a weight of less than 0.5, and that the CH(CH$_3$)–SO$_2$ trans weight is about 0.5.

Two factors will determine the line orders: first, the relative weights of the various possible conformational sequences within each repeat unit, and second, the difference in the interactions, in particular the gauche interactions, for m and r dyad structures. Detailed consideration shows that the nature of these interactions is determined solely by the conformational states of the two main-chain bonds adjacent to the chiral center and that these are likely to be restricted to five possibilities,[12] namely for -CH$_2$–CH(CH$_3$)–SO$_2$–, g^-g^+, g^+g^-, tt, tg^-, tg^+. In all cases there is no difference in the type of gauche interactions experienced by *C*H in m and r dyads. This does not necessarily account for its insensitivity to dyad structure, since the conformational populations may depend on the dyad structure. For *C*H$_2$ the difference in the gauche interactions for m and r dyads is determined by the conformation about the -CH(CH$_3$)–SO$_2$– bond and may result in zero effect (for t), r upfield from m (for g^+), or m upfield from r (for g^-). For *C*H$_3$ the gauche interactions with sulfur are not likely to be significant since the sulfur atoms are attached to two oxygen and two carbon atoms but there will be gauche interactions with carbon and oxygen and there are three possible end results for the five sequences listed, rising to five if the interaction with sulfur is also significant. However, it would be unrealistic to suppose that the conformational properties were independent of dyad structure and it seems preferable to make deductions from the observed line order on the assumption that it is primarily determined by rule (3). The insensitivity of the *C*H shift to dyad structure then implies that the -CH$_2$–SO$_2$– bond conformational populations are independent of dyad structure. On the other hand the upfield line position of r-*C*H$_2$ relative to m-*C*H$_2$, and of r-*C*H$_3$ relative to m-*C*H$_3$ implies that for the -SO$_2$–CH(CH$_3$)CH$_2$– bond there is 5–10% more chance of *C*H$_3$ or *C*H$_2$ being found in the trans position with respect to the sulfone group (zero dihedral angle to the $O\hat{S}O$ bisector) in the r dyad than in the m dyad. One should add that as far as the methyl carbon is concerned it is not possible to say, a priori, which of the two next nearest chiral centers determines its chemical shift. A similar problem is encountered and has been solved for *C*H in poly(propene sulfide).[13]

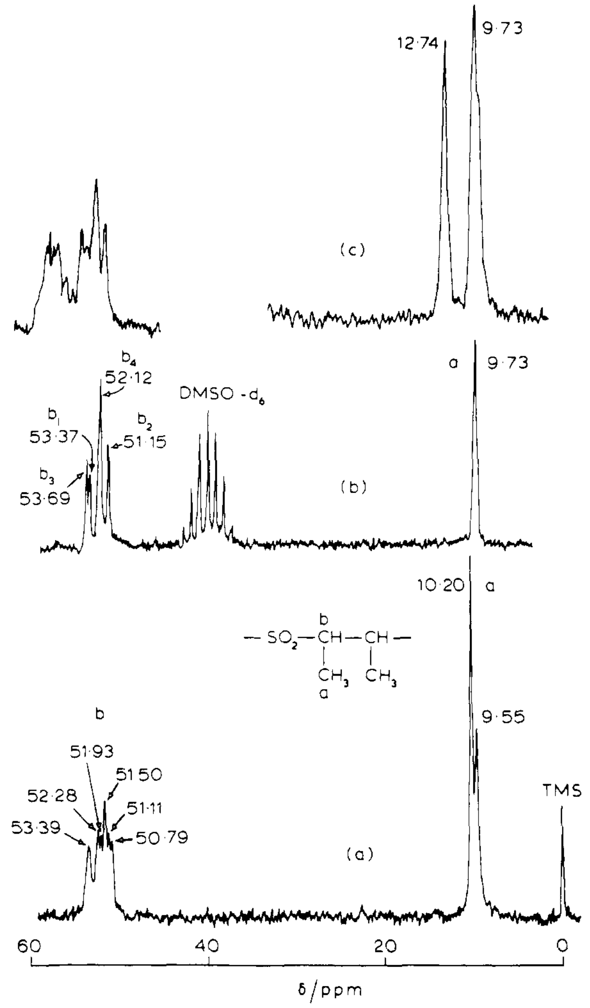


Figure 4. ^{13}C-{^{1}H} NMR spectrum of poly(but-2-ene sulfone). (a) Polymer made from *trans*-but-2-ene at −15 °C, solvent CDCl$_3$/30 °C, 2500 pulses, 24 μs width, repetition time 2.0 s, spectral window 3012 Hz. (b) Polymer made from *cis*-but-2-ene at 0 °C, solvent DMSO-d_6/60 °C, 34 000 pulses, 14 μs width, repetition time 1.7 s, spectral window 2500 Hz. Assignment is to the structures shown in Figure 6; see text. (c) Polymer made from *trans*-but-2-ene at −78 °C, solvent DMSO-d_6/30 °C, 4096 pulses, 7 μs width, repetition time 0.7 s, spectral window 6024 Hz.

Poly(2-methylpent-1-ene sulfone). The shift for the quaternary carbon (f) is about 2 ppm downfield from the position to be expected from 1(c) or 3(e) by applying rule (1). However, the α substitution parameter for substitution leading to quaternary carbons tends to be higher than the value for rule (1)[8] so that this difference is not significant. Of the three carbons which are β with respect to the sulfone group attached to the quaternary carbon, d and e are both upfield from their expected positions (by 2–4 ppm) while c is about in the position expected, and only d is sensitive to tacticity. Had the conformation about the SO$_2$–CMePr bond been the only factor one would have expected an upfield shift of one β carbon to be counterbalanced by a downfield shift of at least one of the other β carbons, together with another tacticity-sensitive carbon, as in di-*sec*-butyl sulfone;[8] perhaps the γ-sulfone group also exerts a significant influence. It seems reasonable to suppose that the presence of the α-methyl group leads to a greater population of conformers in which either d or e lies in the median plane of the $\angle$OSO bisector.

Poly(but-2-ene sulfone). The first question to be answered is the origin of the additional peaks in the spectrum of polymer made from *trans*-but-2-ene at −78 °C. It is well known that radical reactions of alkenes may be stereospecific

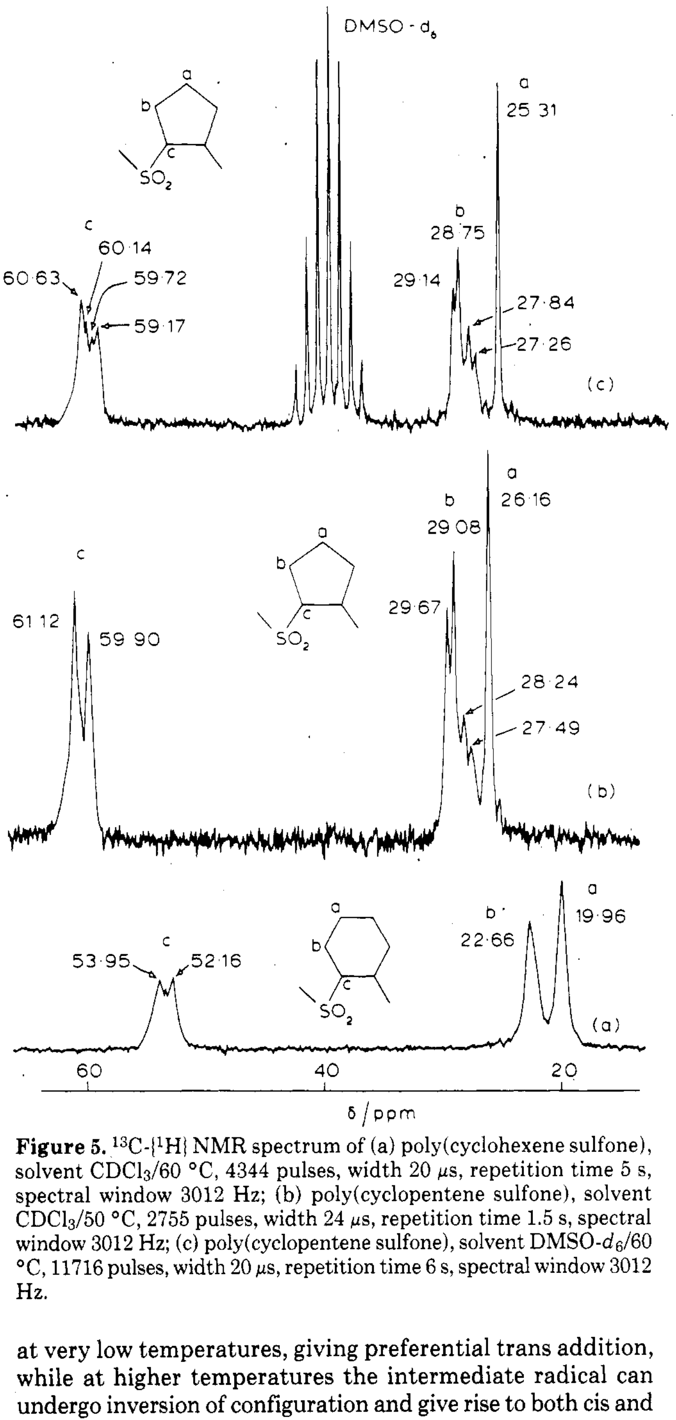
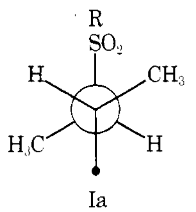
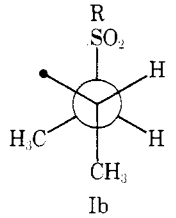


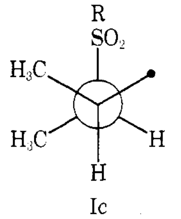
Figure 5. ^{13}C-{^{1}H} NMR spectrum of (a) poly(cyclohexene sulfone), solvent CDCl$_3$/60 °C, 4344 pulses, width 20 μs, repetition time 5 s, spectral window 3012 Hz; (b) poly(cyclopentene sulfone), solvent CDCl$_3$/50 °C, 2755 pulses, width 24 μs, repetition time 1.5 s, spectral window 3012 Hz; (c) poly(cyclopentene sulfone), solvent DMSO-d_6/60 °C, 11716 pulses, width 20 μs, repetition time 6 s, spectral window 3012 Hz.



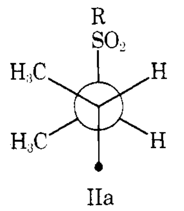
Ia



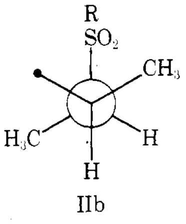
Ib



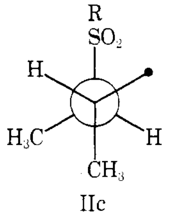
Ic



IIa



IIb



IIc

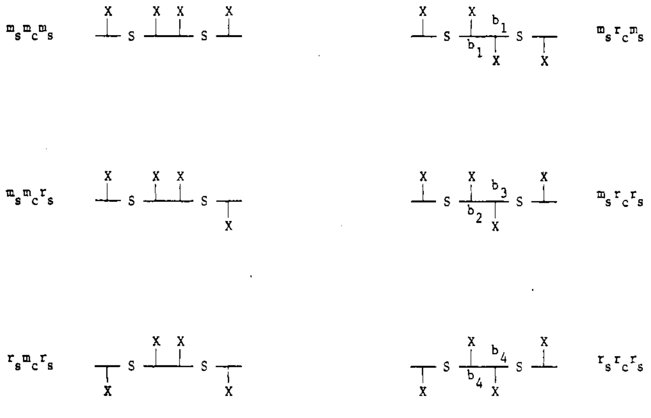


Figure 6. The six possible "tetrad" structures involving two sulfone groups and a central but-2-ene unit. X denotes a methyl group. m, r denote the dyad structure appropriate to each pair of neighboring chiral centers.

at very low temperatures, giving preferential trans addition, while at higher temperatures the intermediate radical can undergo inversion of configuration and give rise to both cis and trans addition products.[14] Indeed this effect has been reported[2] in the copolymerization of sulfur dioxide with *cis*-propene-*1,2*-d_2. The present case is different in that it appears that one product is much preferred (98%) at temperatures above −78 °C, namely the structure formed by trans addition to *cis*-but-2-ene, which is equivalent to cis addition to *trans*-but-2-ene. Thus we postulate that the radical initially formed from *trans*-but-2-ene has the structure Ia and can rotate to other conformations Ib and Ic without loss of configuration, but that given time it will invert almost entirely to the radical II, having possible conformations IIa, IIb, and IIc. (A similar argument can be developed if the radical is written with a planar, instead of pyramidal, structure.) We may suppose that the interactions of the bulky groups lead to Ia and Ib being preferred to Ic and to IIb and IIc being preferred to IIa. Overlap between the orbital of the free electron and the vacant π orbitals of the sulfone group may be an additional factor. This can occur equally for IIb, IIc, and Ib but not for Ia and may be responsible for tipping the balance in favor of radical II. The temperature range required for transition from preferential trans addition on the one hand to equilibrium attainment of I $\rightleftharpoons$ II on the other depends on the activation energy for inversion of configuration compared with that for addition of the next molecule of SO$_2$. In the propene system[2] this is relatively small (11 kJ mol^{-1}) and the temperature range is fairly wide (−78 to 0 °C). In the but-2-ene system the temperature range appears to be much shorter, suggestive of a rather higher activation energy for the inversion process, although still occurring very rapidly at −78 °C. On this basis the peaks in Figures 4a and 4b are assigned to the r_c-centered structures shown diagrammatically in Figure 6, while the additional peaks in Figure 4c are assigned to the m_c-centered structures; m_c and r_c units are formed by trans addition to *trans*- and *cis*-but-2-ene, respectively.

Next we consider the general positions of these peaks compared with those which may be estimated by application of rules (1) and (2) to poly(propene sulfone), using data obtained with DMSO as solvent. Taking average shifts for each carbon in **1** we find that for **8** we may expect *C*H$_3$ at 10.1 ± 0.6 ppm (obsd 8.7, 9.7, 12.7; av 10.4) and *C*H at 55.6 ± 1.0 ppm (average of two values estimated from 1(c) and 1(b) separately), (obsd 54.8; average of upfield and downfield groups centered on 57.2 and 52.4 ppm). Thus the average positions of all the peaks in Figure 4c are as expected, but if we take the m_c- and r_c-centered structures separately then the former have *C*H and *C*H$_3$ peaks downfield from the expected positions and the latter have *C*H and *C*H$_3$ peaks upfield from the expected positions. In CDCl$_3$ as solvent the peaks seem to be generally upfield from the positions expected, even ignoring a probable solvent effect of about 1 ppm (cf. spectra for **2** and **3** in both DMSO and CDCl$_3$).

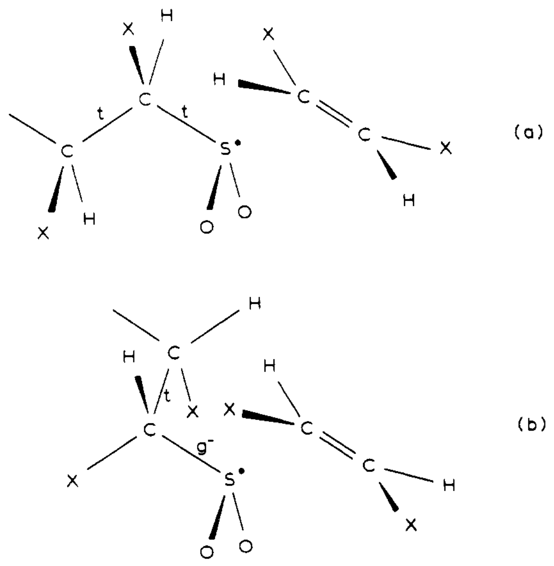


Figure 7. Possible modes of addition of *cis*-but-2-ene to $RSO_2CH(CH_3)CH(CH_3)\dot{S}O_2$ to form (a) an r_s structure and (b) an m_s structure ($X = CH_3$).

In order to explain the upfield shift for *C*H in r_c structures one may examine the possible gauche interactions on both sides of a given *C*H. On the one side it may interact with a methyl carbon and this effect should have been allowed for by the γ_s parameter, rule (1). On the other side it can interact with two oxygens as well as another *C*H. The upfield shift, in conjunction with rule (3), suggests that in r_c units there is an increased tendency for the C–S bonds to take up a trans conformation compared with **1;** the reverse situation would have to hold for m_c units. The corollary of this is that *C*H$_3$ in r_c units should tend to occupy more of the gauche positions relative to the sulfone group and so experience a downfield shift. However, one must also take account of the gauche interaction between *C*H$_3$ groups on adjacent carbon atoms. Dielectric measurements on polymer which almost certainly contained only r_c units (since no special steps were taken to keep the preparation temperature at −78 °C) showed no sign of a dispersion in dioxane as solvent[15] indicating a predominance of trans main-chain C–C conformations in r_c units; elsewhere we have discussed[12] the interpretation of this observation. Here it suffices to note that this will place all methyl carbons in a gauche position with respect to the next nearest methyl group and the dominance of this effect accounts for the observed upfield shift.

The splitting of the methyl signal in Figure 4a, and part of the fine structure for the methine carbon, may be accounted for in the same way as for the splitting of the β-*C*H$_2$ and β-*C*H$_3$ signals in di-*sec*-butyl sulfone.[8] For the r_s structures the preferred conformations about the two adjacent C–S bonds are expected to be tg$^+$ and g$^-$t, with equal probability; for the m_s structures tt and g$^+$g$^+$ are preferred, but with tt having greater weight. The predicted line order is as for di-*sec*-butyl sulfone, namely (downfield to upfield) *C*H m_s, r_s; *C*H$_3$ r_s, m_s, and the magnitude of the splitting for *C*H$_3$ (0.65 ppm) is very similar to that for β-*C*H$_3$ in di-*sec*-butyl sulfone (0.57 ppm in CDCl$_3$). The intensities of the *C*H$_3$ lines indicate about 65% r_s structures and 35% m_s. This may be understood as a preference for the but-2-ene to add to an $R\dot{S}O_2$ radical with the free electron occupying the trans position rather than the gauche position, as shown in Figure 7. The proportion of m_s structures is independent of the starting compound and is not very dependent on temperature.

So far as the *C*H peaks are concerned the observed intensity distribution is generally consistent with the predicted m_s, r_s line order, with r_s having the greater intensity, but there is subsplitting both in DMSO and in CDCl$_3$; Figures 4a and 4b. Before pursuing the interpretation of this subsplitting we must note with some surprise that the splitting of the methyl resonance is not observed in DMSO for polymer containing only r_c units, although for di-*sec*-butyl sulfone the splitting is essentially the same in DMSO and CDCl$_3$. Close inspection of an expanded version of Figure 4b did in fact reveal a slight upfield shoulder. The other differences in the appearance of the spectra in the two solvents, relatively minor for r_c-centered units, but major for m_c-centered units (the 12.74 ppm peak of Figure 4c is not seen in CDCl$_3$ as solvent), are indicative of some profound difference in conformational populations about the main-chain bonds in the polymer in the two solvents. Thus it would appear that whereas r_c-centered units have a predominantly trans C–C bond in all solvents, m_c-centered units have a much lower proportion of trans C–C bonds in CDCl$_3$ (so leading to similar methyl–methyl gauche interactions in both r_c and m_c structures) than in DMSO where the downfield shift to 12.74 ppm suggests mainly trans methyl–methyl interactions. One would predict therefore that the polymer containing m_c-centered units would show a dielectric dispersion in dioxane. The upfield shoulder which develops on the side of the 9.73 ppm *C*H$_3$ peak in DMSO as the m_c content increases appears not to originate from *C*H$_3$ in m_c units but from *C*H$_3$ in r_c units with m_c neighbors.

Finally we consider the assignment of the four lines in the fine structure of the *C*H signal in Figure 4b to the four types of carbon atom labeled b_1 to b_4 in Figure 6. The origin of the secondary splitting of the carbons adjacent to m_s units (b_1 and b_3) and of the carbons adjacent to r_s units (b_2 and b_4) is not clear. The atom concerned in each case is α with respect to the sulfone group of the next unit; in di-*sec*-butyl sulfone such a carbon shows only very slight sensitivity to m_s/r_s structure[8] (0.015 ppm). However the factor responsible for eliminating the sensitivity of the *C*H$_3$ peak to m_s/r_s tacticity (in DMSO as solvent) may also be the cause of the enhanced sensitivity of the *C*H carbons.

We have already concluded that there are about 65% r_s structures and 35% m_s structures, so that, allowing for the equal probability of $m_sr_cr_s$ and $r_sr_cm_s$ structures, we can expect the intensity ratio for b_1:b_2:b_3:b_4 to be approximately 12:23:23:42. On this basis we assign the strongest peak (52.12 ppm) to b_4 and the weakest (53.37 ppm) to b_1. The other two peaks are then assigned to b_3 (53.69 ppm) and b_2 (51.15 ppm) on the grounds that they are for carbons β with respect to m_s and r_s units respectively. This gives the line order $b_3b_1b_4b_2$. The resolution of the *C*H peaks in the m_c-centered units in DMSO is not good enough to warrant an attempt at assignment. In CDCl$_3$ there is additional splitting of two of the *C*H peaks (b_1 and b_2 if the line order is as in DMSO), which suggests sensitivity to "hexad" structure: $r_sr_cm_sr_cm_s$ and $m_sr_cm_sr_cm_s$ in the case of b_1; $r_sr_cm_sr_cr_s$ and $m_sr_cm_sr_cr_s$ in the case of b_2. However, the intensity pattern is not entirely consistent with such an interpretation and further work is needed.

Poly(cyclopentene sulfone) and Poly(cyclohexene sulfone). These two polymers provide an interesting comparison with 8 for we have seen that in 8 the r_c units adopt a mainly trans conformation in which the methyl groups are in a gauche relationship. The corresponding carbons in the cyclohexene polymer are necessarily in a gauche relationship while those in the cyclopentene polymer must be in a similar relationship in view of the absence of a dipole moment.[15] It is possible that a small variation of the dihedral angle about the main-chain C–C bond is in some way responsible for the increasing sensitivity of the side-chain α-*C* shift to tacticity as one proceeds through the series cyclohexene, but-2-ene, and cyclopentene polysulfones (1, 2, 4 lines, respectively, in CDCl$_3$; 0, 1, 4 lines, respectively, in DMSO).

The intensity pattern for α-*C*H$_2$ of 14 in DMSO is similar to that for CH_3 of **8** in $CDCl_3$ (stronger line downfield) but is reversed for the CH lines (stronger line downfield in **14**, upfield in **8**). It is therefore not possible to make any firm assignments to the fine structure in **14**. All one can say is that the proportions of m_s and r_s in **14** are approximately 60:40 or 40:60. In **15** they are near to 50:50.

Relaxation Times. In all cases except poly(but-2-ene sulfone) (**8**) T_1 values of 75 ± 10 ms are observed for main-chain CH carbons and 43 ± 8 ms for main-chain CH_2 carbons. The uniformity of relaxation data suggests that the dominant magnetic relaxation process of main-chain nuclei is a segmental motion which in no case involves rotation about the C–C bond. If C–C rotation were significant, one would expect the relaxation times in **14** and **15**, where this motion is not possible, to be very different from the other polymers. In surprising contradistinction, it has been found[4] that dielectric relaxation of poly(hex-1-ene sulfone) is molecular weight dependent and therefore proceeds via whole molecule rotation. The very different origin of magnetic and dielectric relaxation is emphasized by a calculation of the relaxation times expected if the chain were as rigid as dielectric relaxation indicates. Assuming that the dynamics of poly(cyclohexene sulfone) (**14**) are the same as poly(hex-1-ene sulfone),[4] the overall tumbling correlation times at 25 °C estimated[4] for the samples of molecular weight 2.4×10^5 and 4.5×10^4 would produce ^{13}CH relaxation times of 30 and 2.5 s, respectively. It would reasonably be expected that a segmental motion rapid enough to dominate magnetic relaxation would also lead to dipole reorientation since the major dipole moment component is perpendicular to the chain. A resolution of this anomaly is suggested in the adjoining papers.[5,6]

Nuclei in side groups generally have longer relaxation times due to side-group rotation. Methyl groups at the end of ethyl or propyl chains are especially free ($T_1 \sim 400$ ms, **2** and **7**). Methyls directly attached to the backbone are more restricted (**1**, **7**, and **8**), probably due to steric interaction with groups in the backbone. The relaxation times of both types of CH_2 in **15** are equal, and comparable to the values measured for main-chain CH_2 in other polymers. The cyclohexene ring must be effectively rigid which accords with the previous conclusion[15] that the sulfone groups have a strong preference for a 1,2-diaxial structure. However, the cyclopentene ring in **14** evidently undergoes a ring-puckering motion, since the β-CH_2 relaxation time (a) is significantly longer than that of the α-CH_2 (b).

Measurements of the main-chain carbon relaxation times for poly(but-1-ene sulfone) in $CDCl_3$ over a limited temperature range (10 to 50°C) showed that T_1 decreases with increasing temperature, indicating that the condition $\omega_o \tau_c > 1$ is fulfilled.[11] The correlation time for segmental motion in this temperature range must be $\gtrsim 10^{-8}$ s. If the correlation functions for C–H bond orientation were exponential, the Overhauser factors η for correlation times of this magnitude would be <0.2.[11] The measured values are much greater, so the correlation functions must be nonexponential. A realistic model for polymer motion which gives such a correlation function is that due to Valeur et al.,[16] who combined conformational jumps (correlation time τ_D) with overall rotational diffusion (correlation time τ_o). This model has been used successfully to interpret ^{19}F, ^{13}C, and ^1H relaxation times[17-19] and fluorescence depolarization[20] measurements of polymers in solution. Using the results of calculations presented earlier,[18] it is found that values of $\eta \geqslant 0.6$ are consistent with values of $\tau_D \geqslant 10^{-8}$ s when $\tau_D/\tau_o \lesssim 0.1$. If the jump model is correct, the NMR data alone show therefore that segmental motion is faster than overall tumbling, in agreement with the qualitative comparison of NMR and dielectric results discussed above. The fact that the T_1 of main-chain CH carbons is close to double the T_1 of CH_2 carbons indicates that both groups experience essentially the same dynamics. In view of the fact that ^{13}C relaxation data alone are incapable of discriminating clearly between different forms of the correlation function,[14] a complete test of the applicability of the jump model to poly(alkene sulfones), and hence accurate values of τ_D and τ_o, must await the accumulation of further relaxation data, in particular proton relaxation times[19] or spin–spin relaxation times.

Acknowledgments. We thank the Science Research Council for financial assistance in the purchase of the F.T. spectrometers.

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