(−)-Poly((*R*)-1-octen-3-ol sulfone): The ^{13}C-NMR Fine Structure of the First Partially Isotactic Poly(olefin sulfone) Prepared by a Free-Radical Mechanism

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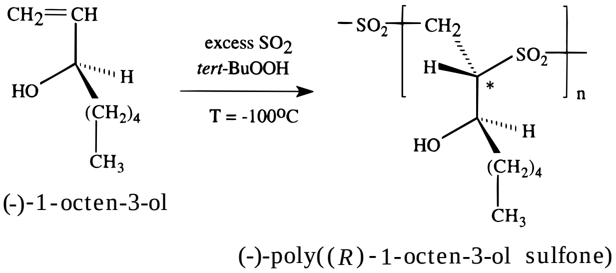
ABSTRACT: Poly(olefin sulfone)s have been prepared from (*R*)- and (*RS*)-1-octen-3-ol, in which the chiral centers are adjacent to the double bond. The ^{13}C-NMR spectra of the polymers have shown that the stereochemistry of the main chain methine carbon formed in the propagation reaction depended primarily upon that of the side chain chiral carbon within the same residue. The polysulfone of (*R*)-(−)-1-octen-3-ol is therefore the first partially isotactic polysulfone to be prepared by a free-radical polymerization. Large dispersions of chemical shift and well-resolved fine structure in the ^{13}C-NMR spectra have allowed assignments to be made of sequence and intraresidue effects in isotactic and atactic polymers at the main chain tetrad level.

Introduction

Poly(olefin sulfone)s (POS's), the alternating copolymers of an olefin and sulfur dioxide prepared directly from these two monomers by a free-radical mechanism, are atactic according to ^{13}C-NMR spectroscopy.[1−3] We wish to prepare tactic POS's for two reasons. First, atactic poly(eicosene sulfone) and poly(hexadecene sulfone) are known to adopt helical conformations in nonpolar solvents,[2,4] as well as when isolated upon a surface,[5] and to exhibit main chain liquid crystalline behavior in the bulk.[6] The stability of the helices may be enhanced by preparing tactic POS's,[7] as has been found for other polymers.[8−10] Second, despite the fact ^{13}C-NMR spectroscopy has been used routinely to probe the microstructure of POS's,[1−3,11−13] tacticity assignments have never been made for homopolysulfones beyond the main chain diad level,[1] a consequence of only being able to prepare atactic forms by the free-radical reaction. (The diad level assignments were made from the ^{13}C-NMR spectrum of an oxidized isotactic poly(propylene sulfide).) POS's having different stereoregularities should display differences in their ^{13}C-NMR signal intensities aiding tacticity assignments. These differences are indeed observed, as we report here for an atactic and isotactic poly(1-octen-3-ol sulfone).

The preparation of the isotactic polymer is shown in Scheme 1. The stereochemistry of the main chain methine carbon in the polymer may be controlled by that of the chiral methine carbon already present in the monomers (by an *asymmetric induction*), as we have reported previously for a range of racemic monomers.[12] A powerful influence of one backbone chiral center on another has been found in the formation of poly(but-2-ene sulfone): at ambient temperatures only meso residues form.[1,3,14] Since both chiral centers form in the same residue, this provides no control of backbone structure. Besides the conventional stereochemical relationships *m* and *r* between successive chiral centers in polymer main chains, the polymers of this study present a new issue in ^{13}C-NMR characterization, that of the stereochemical relationship between a chiral center in the side chain and one in the backbone within each residue, for which we have introduced the terms *m*′ and *r*′.

Scheme 1. Preparation of Partially Isotactic Poly((*R*)-1-octen-3-ol sulfone)[a]



[a] The residue has an *m*′ stereochemical relationship as the new chiral center, labeled with an asterisk, also has an *R* stereochemistry, following the Cahn−Ingold−Prelog rules.[15]

Experimental Section

Materials. *RS*-(±)-1-Octen-3-ol (98%) and *R*-(−)-1-octen-3-ol (99%, $[\alpha]_D^{20} = -25.4°$) were obtained from Acros. Sulfur dioxide was supplied by BOC. Dimethyl-d_6 sulfoxide (99.5+ atom % D) and *tert*-butyl hydroperoxide (70%) were obtained from Aldrich.

Poly(olefin sulfone) Preparation. Polysulfones of (*RS*)-1-octen-3-ol and (*R*)-1-octen-3-ol were prepared as follows: 1.0 g of the monomer and 5 g of liquid sulfur dioxide were placed in a thick-walled glass reaction tube maintained at −100 °C[16] (methanol/liquid N_2 slush bath). Eight drops of *tert*-butyl hydroperoxide were added at this temperature over a period of 20 min, and a white polymer was observed to precipitate out of solution. After 1 h the contents of the reaction vessel were filtered off and twice redissolved in chloroform and reprecipitated in hexane. The polymers were then dried in a vacuum oven at ambient temperature overnight. Polymer yields: 1.14 g of poly((*RS*)-1-octen-3-ol sulfone) (76%), 1.26 g of poly((*R*)-1-octen-3-ol sulfone) (84%).

^{1}H-NMR Spectroscopy. ^{1}H-NMR spectra were recorded on a General Electric QE 300 MHz instrument. Approximately 10 mg of the polymers was placed in a 5 mm NMR tube and dissolved in deuterated dimethyl sulfoxide. Sixteen transients were recorded. By adding one or two drops of trifluoroacetic acid to the NMR tube and hydroxyl signal was pushed downfield, revealing clearly the main chain resonances. Chemical shifts are reported in parts per million (δ) downfield of the internal standard tetramethylsilane (TMS).

^{13}C-NMR spectroscopy was performed on a General Electric GNΩ 500 MHz instrument operating at 125.8 MHz.

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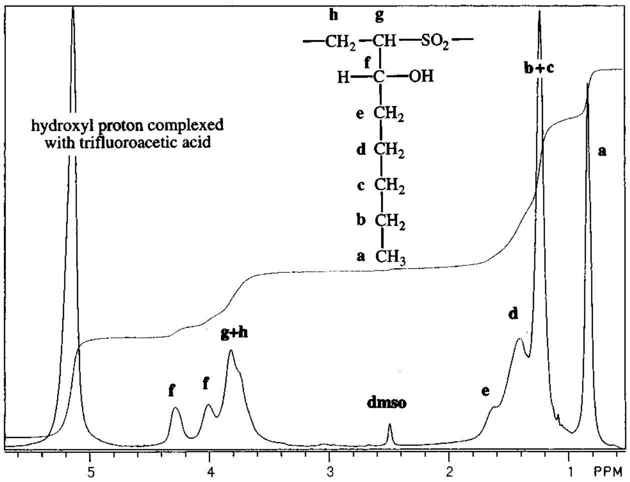


Figure 1. ^{1}H-NMR spectrum of (−)-poly((*R*)-1-octen-3-ol sulfone) at 300 MHz dmso-d_6 solvent at ambient temperature. NS = 16.

Approximately 200 mg of polymer were placed in a 5 mm NMR tube and dissolved in deuterated dimethyl sulfoxide. Either 40 000 or 100 000 transients were recorded at 100 °C. Other operating parameters are given in the figure captions. Chemical shifts are reported in parts per million (δ) downfield of TMS.

Optical rotation measurements for poly((*R*)-1-octen-3-ol sulfone) in acetone solution (230 mg in 10.0 mL) were made at 589 nm on a Perkin-Elmer 241 polarimeter.

Results

Poly((*R*)-1-octen-3-ol sulfone) showed a negative optical rotation, $[\alpha]_D^{20} = -4.77°$ ($c = 0.023$ g/mL in acetone). Poly((*RS*)-1-octen-3-ol sulfone) was optically inactive.

The ^{1}H-NMR spectrum of poly((*R*)-1-octen-3-ol sulfone) is presented in Figure 1 and was similar to that obtained for poly((*RS*)-1-octen-3-ol sulfone) which is not shown. Assignments were based on our knowledge of other polysulfones.[12,13,17,18] The three methyl a protons are found at 0.83 ppm, methylene protons b, c, d, and e between 1 and 2 ppm, and protons f, g, and h further downfield between 3.4 and 4.4 ppm. The region between 3.4 and 4.4 ppm showed three main signals and a shoulder. The two low field signals, with a downfield: upfield integral ratio of 0.7:0.3, were assigned to proton f, as for similar poly(olefin sulfone)s,[12,13] and reflect the sensitivity of proton f to the stereochemical relationships between chiral carbons f and g.

The ^{13}C-NMR spectra of the (*R*)- and (*RS*)-poly(1-octen-3-ol sulfone)s are presented in parts a and b of Figure 2, respectively, where eight sets of resonances are observed corresponding to the eight carbons of the residue. Assignments, which were made after allowing for the substitution of a hydroxyl group[19] at carbon f of poly(1-octene sulfone),[1] are entered in Table 1. Carbons a, b, and c show only single resonances, 13.7, 22.0, and 31.0 ppm respectively, as they are distant from the chiral carbons g and f. Carbon d shows more than one resonance in the spectrum of the (*R*)-polymer and is observed upfield of carbon c at 25.1 ppm, a consequence of a large γ-oxygen effect.[18] The side chain methylene carbon e shows a distinct doublet feature in both polymers (at 33.6 and 34.2 ppm), similar to that observed for proton f in the ^{1}H-NMR spectrum. However, the (*R*)-polymer, with only *R* configurations in the side chain and therefore fewer stereosequences, shows much greater resolution with three upfield and at least four downfield resonances that suggests sensitivity to a further two and three main chain chiral centers, respectively.

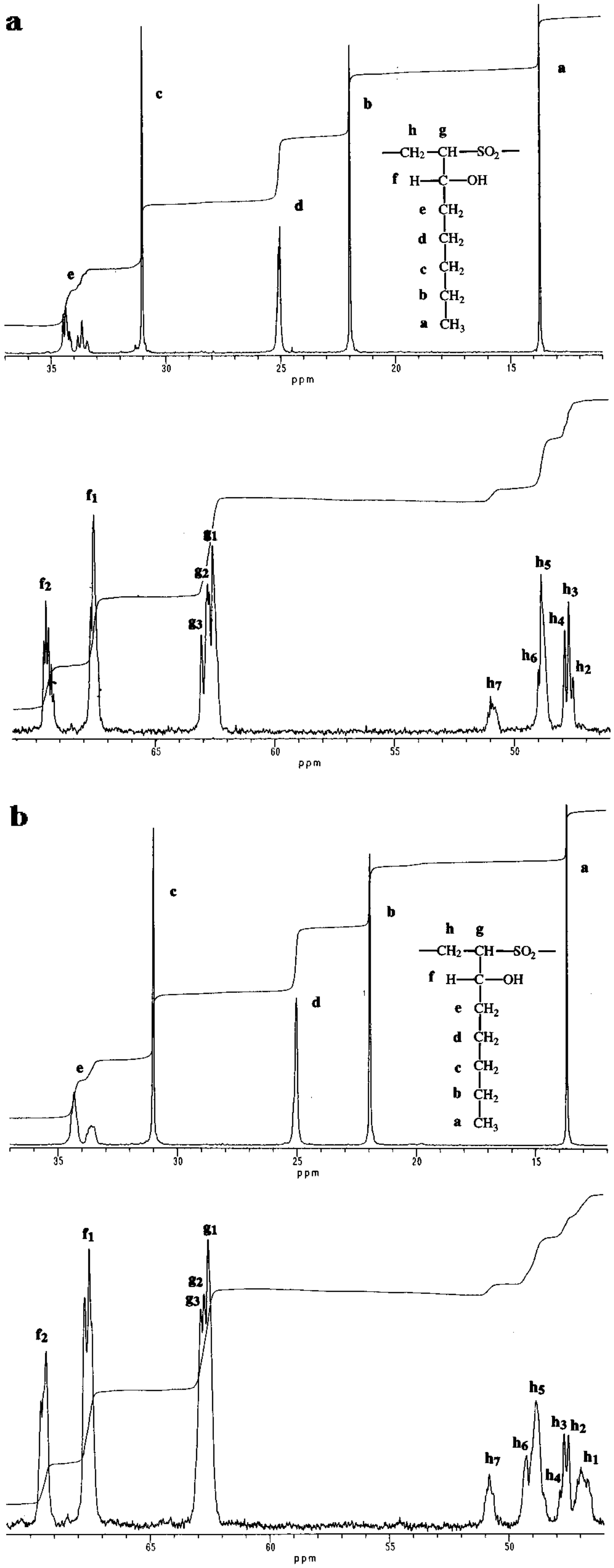


Figure 2. ^{13}C-NMR spectra of (a) (−)-poly((*R*)-1-octen-3-ol sulfone) and (b) (−)-poly((*RS*)-1-octen-3-ol sulfone) at 125.8 MHz in dmso-d_6 solvent at 100 °C. NS = 40 000, acquisition time = 1.08 s, spectral window = 30 303 Hz, and LB = 1 Hz.

The integral ratio of the two distinct groups of peaks for carbon e gives a second measure of the asymmetric induction for these polymers.[12,13] A similar doublet pattern is observed for carbon f at 67.5 and 69.5 ppm,

Table 1. Observed ^{13}C-NMR Chemical Shifts for Poly((*R*)-1-octen-3-ol sulfone) and Poly((*RS*)-1-octen-3-ol sulfone)

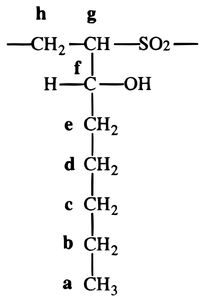
Polymer Repeat Unit		^{13}C-nmr chemical shifts, δ (ppm), in dmso-d_6 at 100°C	
		Polymer prepared from **R** monomer	Polymer prepared from **RS** monomer
	**a**	13.71	13.68
	b	21.97	21.96
	c	31.02	31.01
	d	25.01	25.02
	e	33.64, 34.33	33.60, 34.32
	f	67.55, 69.56	67.53, 69.43
	g	62.59	62.56
	h	47.89, 48.86, 50.98	46.99, 47.68, 48.85, 50.83

Table 2. The 16 Possible Stereoisomers in Pairs of Residues of Poly((*RS*)-1-octen-3-ol sulfone)

	Stereosequences	Designation	P		Stereosequences	Designation	P
(a)	$—\underset{R}{R}—SO_2—CH_2—\underset{R}{R}—$	m' m m' $R_b(R_s)\ R_b(R_s)$	$x^2.y^2$	(i) (h')	$—\underset{R}{R}—SO_2—CH_2—\underset{R}{S}—$	m' r r' $R_b(R_s)\ S_b(R_s)$	$x^2.y(1-y)$
(b)	$—\underset{S}{R}—SO_2—CH_2—\underset{R}{R}—$	r' m m' $R_b(S_s)\ R_b(R_s)$	$x(1-x).y(1-y)$	(j) (g')	$—\underset{S}{R}—SO_2—CH_2—\underset{R}{S}—$	r' r r' $R_b(S_s)\ S_b(R_s)$	$x(1-x).(1-y)^2$
(c)	$—\underset{R}{R}—SO_2—CH_2—\underset{S}{R}—$	m' m r' $R_b(R_s)\ R_b(S_s)$	$x(1-x).y(1-y)$	(k) (f')	$—\underset{R}{R}—SO_2—CH_2—\underset{S}{S}—$	m' r m' $R_b(R_s)\ S_b(S_s)$	$x(1-x).y^2$
(d)	$—\underset{S}{R}—SO_2—CH_2—\underset{S}{R}—$	r' m r' $R_b(S_s)\ R_b(S_s)$	$(1-x)^2.(1-y)^2$	(l) (e')	$—\underset{S}{R}—SO_2—CH_2—\underset{S}{S}—$	r' r m' $R_b(S_s)\ S_b(S_s)$	$(1-x)^2.y(1-y)$
(e)	$—\underset{R}{S}—SO_2—CH_2—\underset{R}{R}—$	r' r m' $S_b(R_s)\ R_b(R_s)$	$x^2.y(1-y)$	(m) (d')	$—\underset{R}{S}—SO_2—CH_2—\underset{R}{S}—$	r' m r' $S_b(R_s)\ S_b(R_s)$	$x^2. (1-y)^2$
(f)	$—\underset{S}{S}—SO_2—CH_2—\underset{R}{R}—$	m' r m' $S_b(S_s)\ R_b(R_s)$	$x(1-x).y^2$	(n) (c')	$—\underset{S}{S}—SO_2—CH_2—\underset{R}{S}—$	m' m r' $S_b(S_s)\ S_b(R_s)$	$x(1-x). y(1-y)$
(g)	$—\underset{R}{S}—SO_2—CH_2—\underset{S}{R}—$	r' r r' $S_b(R_s)\ R_b(S_s)$	$x(1-x).(1-y)^2$	(o) (b')	$—\underset{R}{S}—SO_2—CH_2—\underset{S}{S}—$	r' m m' $S_b(R_s)\ S_b(S_s)$	$x(1-x). y(1-y)$
(h)	$—\underset{S}{S}—SO_2—CH_2—\underset{S}{R}—$	m' r r' $S_b(S_s)\ R_b(S_s)$	$(1-x)^2.y(1-y)$	(p) (a')	$—\underset{S}{S}—SO_2—CH_2—\underset{S}{S}—$	m' m m' $S_b(S_s)\ S_b(S_s)$	$(1-x)^2. y^2$

[a] $x = P_{R_s}$, $y = P_{m'}$.

the order now being reversed. As for carbon e, further fine structure is observed within both components of the doublet of carbon f, being clearly better resolved for the (*R*)-polymer. The downfield component of carbon f is particularly well-resolved, showing five resonances and suggesting main chain tetrad sensitivity.

The main chain methine carbon g shows three main sets of peaks centered at 63 ppm and dispersed over 1 ppm for both polymers, while the main chain carbon h has three sets of peaks dispersed over 3.5 ppm for the (*R*)-polymer and four sets of resonances dispersed over nearly 4.5 ppm for the (*RS*)-polymer. We attribute the large dispersion of shifts of carbon h to the conformationally sensitive γ_{OH} effect[19] and to similar effects from the sulfone oxygens.[20] Further well-resolved fine structure, indicating sensitivity to longer main chain stereosequences, is also evident for carbon h. For example, three well-resolved resonances are found at 47.7 ppm in both polymers, their intensities being very different.

Discussion

Configurational Probabilities. In the polymer made from the racemic monomer each residue has a main and side chain chiral center, so there are four possible stereoisomers per residue. To understand and assign the fine structure, we initially considered main chain stereosequences of two polymer residues for which 16 stereoisomers are possible and give these in Table 2. We use the following terms to designate the structure and the stereochemical relationships: the subscripts b and s refer to backbone and side chain configurations, respectively; *m* and *r* indicate a conventional meso and racemic relationship of adjacent backbone chiral centers; *m′* and *r′* indicate a meso or racemic relationship between a side chain and backbone chiral center within the same residue.

Each of the first eight stereosequences in Table 2 is indistinguishable by NMR spectroscopy from one of the last eight as they are enantiomeric: e.g. stereosequence (p) is indistinguishable from (a). We have therefore also labeled (p) as (a′), and so on. A maximum of eight resonances at the main chain diad level might be observed in the spectrum of the (*RS*)-polymer if resolution were optimal, whereas only four might be found in the spectrum of the (*R*)-polymer.

We may be able to determine the preferred stereochemistry of carbon g relative to that of carbon f by considering the way in which the *γ*-gauche effect of Grant and Paul[22] (an upfield chemical shift) operates on the carbon atoms of the set of diastereomers within a residue. Chart 1 shows the three conformations of the two sets of stereoisomers, together with an indication of steric repulsions (***r***) between the side chain substituents and the main chain $-CH_2-$ and $-SO_2-$ groups. (A similar argument applies to the remaining two sets of stereoisomers which display the same shift effects.) The energies of conformations (A) **II**, (A) **III**, (B) **V**, and (B) **IV** are considered less favored than (A) **I**

Chart 1. γ and Steric Repulsion Interactions (*r*) Experienced by Main Chain Carbon h and Side Chain Methylene Carbon e[21] ($-CH_2-$), Where the Chiral Site Nearest the Eye is Carbon f

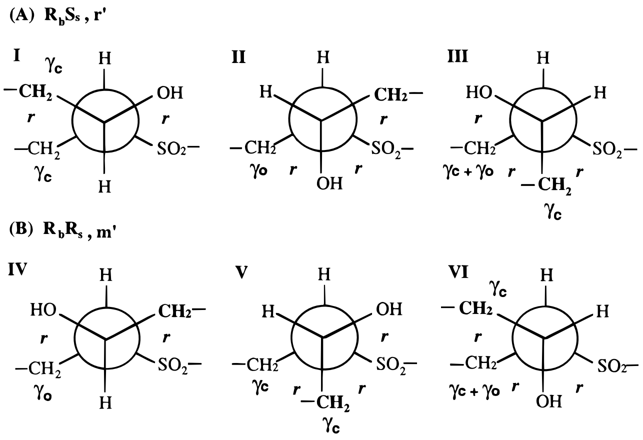


Table 3. Asymmetric Induction Ratios and Splittings for the Carbons in Poly((*R*)- and Poly((*RS*)-1-octen-3-ol sulfone)s Showing the Doublet Feature

carbon	downfield (%)	upfield (%)	splitting (ppm)
poly((*R*)-1-octen-3-ol sulfone)			
e	65.7	34.3	0.75
f	34.3	65.7	1.89
geom mean of $P_{m'}$:$P_{r'}$	65.7:34.3		
Poly((*RS*)-1-octen-3-ol sulfone)			
e	63.1	36.9	0.64
f	40.2	59.8	1.82
geom mean of $P_{m'}$:$P_{r'}$	61.4:38.5		

and (B) **IV** because they each experience an extra steric interaction, so we limit our discussion to (A) **I** and (B) **IV**. The γ-effect we identify is experienced by the side chain methylene carbon e (shown in bold type) when it is gauche with respect to the main chain methylene carbon h. The effect is present in conformation (A) **I**, but not in (B) **IV**, implying that the smaller upfield component of the doublet feature of carbon e corresponds to a R_bS_s residue (and its enantiomer S_bR_s) having an *r′* relationship.[12] (In fact, using similar arguments the $-CH_2-$ groups in (A) **II** and B (**VI**) have equivalent γ_c-effects.) Thus for these polymers, the larger downfield doublet component of carbon e suggests that when the backbone forms, carbon g prefers to adopt the *same* stereochemistry as that of carbon f,[12,13] i.e. the probability of an *m′* placement, $P_{m'}$, is greater than 0.5. (The complement of $P_{m'}$ is $P_{r'}$.) This type of analysis is supported by the consistency with which it interpreted fine structural features in the shifts of two carbons in the side chain of poly(3-methylpent-1-ene sulfone).[12] (If it is wrong then we have to reverse all our *m′* and *r′* assignments in what follows.) We have neglected a possible γ-gauche effect from the sulfur atom, as the steric compression mechanism[22,23] cannot act.

Table 4. Assignment of Fine Structure of Methylene Carbon h of Poly((*R*)-1-octen-3-ol sulfone) to Main Chain Diad Stereosequences as in Table 2 Using $P_{m'} = 0.614$

	h_7 50.9 ppm	$h_5 + h_6$ 48.9 ppm	h_2-h_4 47.7 ppm
relative intensity	0.13	0.50	0.38
probability term	$(1 - P_m)^2$	$2P_{m'}(1 - P_{m'})$	$(P_{m'})^2$
P	0.15	0.47	0.38
stereosequence assignment	(m)	(e) and (i)	(a)

The values for the asymmetric induction factor, measured at carbons e and f, are found in Table 3 for both polymers, along with a mean value. The poly((*R*)-1-octen-3-ol sulfone) has a lower side chain 1,2-asymmetric induction value ($P_{m'} = 0.614 \pm 0.017$) than has the racemic polymer ($P_{m'} = 0.657 \pm 0.009$) suggests that the main chain 1,4-asymmetric induction shows a barely significant preference for syndiotacticity. Our use of the side chain peaks to obtain $P_{m'}$ values has tacitly assumed that the nuclear Overhasuer enhancements for these carbons, which may well be less than 2.0,[1] are insensitive to main chain stereochemistry. This assumption is fortified by the probability that any fixed backbone configuration will have been destroyed by the use of high temperature and a polar solvent. The magnitude of the peak splittings for side chain carbons, also recorded in Table 3, was found to increase with proximity to the side chain chiral center, as has been observed previously in similar cases.[12]

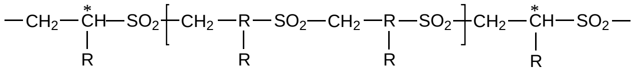
In the final column of Table 2 we enter for each stereosequence a probability product, *P*, to express the probability of each stereosequence being found. *P* has two components; one term which expresses the probability that two adjacent side chains will be of *R* stereochemistry and has values $(P_{R_s})^2$, $P_{R_s}(1 - P_{R_s})$ or $(1 - P_{R_s})^2$ depending on whether two, one or none of the side chains have *R* stereochemistry, respectively, and a second term which expresses the relative stereochemistry within a residue, and has values respectively of $(P_{m'})^2$, $P_{m'}(1 - P_{m'})$, or $(1 - P_{m'})^2$. In so defining *P*, we neglect any influence from the penultimate main chain chiral center, an influence which we have shown to be barely significant.

A Detailed Assignment and Comparison of the ^{13}C-NMR Fine Structure in Poly((*R*)- and Poly((*RS*)-1-octen-3-ol sulfone)s. We have made main chain diad assignments for the three groups of peaks of carbon h in the (*R*)-polymer by comparing the relative integrals with those predicted by the statistical model described in Table 2. For example, peak h_7 at 51 ppm contributes 13% of the integral for this carbon and is tabulated as 0.13 in Table 4. As $P_{R_s} = 1.0$ only sequences (a), (e), (i), and (m) are expected, and to make the assignments the *P* values are simply $(P_{m'})^2 = 0.38$, $P_{m'}(1 - P_{m'}) = 0.24$ and $(1 - P_{m'})^2 = 0.15$. As the later value corresponds most closely to that of 0.13 we assign peak h_7 to stereosequence (m). Similarly, the group of peaks h_2-h_4 at 47.7 ppm have an integral fraction of 38.0%, which is the same as the predicted value of $(P_{m'})^2 = 0.38$ for stereosequence (a). The remaining stereosequences, (e) and (i), must coincide at 49 ppm, verified by the similarity of the probability value $2P_{m'}(1 - P_{m'}) = 0.47$ and the observed integral fraction 0.50. These assignments are entered in Table 4. The ease of matching predicted and observed integrals for this main chain carbon suggests that nuclear Overhauser enhancements are independent of the chiral sequences present in the main chain under the conditions we have used to obtain the spectra. The stereosequence (m) $S_b(R_s)S_b(R_s)$, with two *r′* relationships, is therefore found furthest downfield, while (a) $R_b(R_s)R_b(R_s)$ having two *m′* relationships is found furthest upfield. As both these stereosequences have an *m* relationship (for their main chain configurations), a pattern is evident: *for the main chain methylene carbon, h, the stereochemical relationship within two adjacent residues has more effect on its chemical shift dispersion than the usual diad relationship between adjacent residues*. (This is consistent with the main chain methylene coming further upfield for the *m′* case, because the γ_o effect is bigger than the γ_c

Table 5. Assignment of Fine Structure of Methylene Carbon h of Poly((*RS*)-1-octen-3-ol sulfone) to Main Chain Diad Stereosequences (Table 2) Using the Mean Asymmetric Induction Ratio $P_{m'} = 0.658$ ($P_{R_s} = 0.50$)

	h_7 50.8 ppm	$h_5 + h_6$ 49.0 ppm	$h_2{-}h_4$ 47.7 ppm	h_1 47.0 ppm
relative intensity	0.10	0.46	0.21	0.23
probability term	$(1 - P_{m'})^2$	$2P_{m'}(1 - P_{m'})$	$(P_{m'})^2/2$	$(P_{m'})^2/2$
P	0.12	0.45	0.22	0.22
stereosequence assignments	(d) and (m) (g) and (j)	(e) and (l) (h) and (i) (b) and (o) (c) and (n)	(a) and (p)	(f) and (k)

Chart 2. Tetrad Structures Assigned to the Triplet at 47 ppm of Poly((*R*)-1-octen-3-ol sulfone) (See Table 3)[a]



$$-CH_2-\overset{*}{C}H(R)-SO_2-[CH_2-R-SO_2-CH_2-R-SO_2]-CH_2-\overset{*}{C}H(R)-SO_2-$$

[a] The bracketed structure is common to all four stereoisomers, but the chiral carbons, labeled with an asterisk may be *R* and *S*, with probabilities of $P_{m'}$ and $(1 - P_{m'})$

effect[20] when (A) **I** and (B) **IV** are compared in Chart 1.)

For the (*RS*)-polymer $P_{R_s} = 0.50$, the values of $(P_{R_s})^2$, $P_{R_s}(1 - P_{R_s})$ and $(1 - P_{R_s})^2$ are each $^1/_4$. The four main chain diad stereosequences (a), (e), (i), and (m) of the (*R*)-polymer are present together with 12 other stereosequences of Table 3, where it may be seen that four of these 12, (d), (h), (l), and (p), are enantiomeric with (a), (e), (i), and (m). For example, stereosequence (d), $R_b(S_s)$-$R_b(S_s)$, is enantiomeric with stereosequence (m), $S_b(R_s)$-$S_b(R_s)$, both being assigned to the peak at 51 ppm in the (*RS*)-polymer. We attempted to assign the remaining eight stereosequences by matching peak integrals to the probability model.

Stereosequences (f) and (k) each have the same probability $(P_{m'})^2/4$ factor as sequences (a) and (p): as they have two *m′* relationships they may have a similar chemical shift value. The group of signals h_1, which have yet to be assigned in the (*RS*)-polymer, have the same area as the group of neighboring peaks $h_2{-}h_4$ from (a) and (p), suggesting the assignment of h_1 to stereosequences (f) and (k), that have the same $P_{m'}$ term.

We now consider the peaks grouped at 51 ppm to which sequences (m) and (d) contribute about half the observed area. The remaining area is readily assigned to sequences (g) and its enantiomer (j) that have the same probability in the model as (m) and (d). The remaining four stereosequences (b), (c), (n) and (o) are assigned to the set of peaks h_6 centered at ~49 ppm. Confirmation of the assignments is made by comparing the integration and statistical probability values. All 16 main chain diad stereosequences of (*RS*)-polymer have now been assigned and are presented in Table 5.

The downfield peak in h_6 of the racemic polymer must be attributed solely to stereosequences containing *m* residues since the larger peak at 49.0 ppm was attributed to *r* residues only in the optically active polymer (Table 4). It is likely, from an estimation of the integrals, that there is also a contribution from *m* residues in the peak at 49.0 ppm in the racemic polymer's spectrum. Furthermore sequences (m) and (g) and sequences (d) and (j), each of which have two *r′* relationships and differ only in the main chain stereochemical relationship, are not readily resolved. However, when the internal relationships are all *m′*, as in the case for the more upfield peaks of carbon h, sequence (a) is resolved from (f) and sequence (p) is resolved from (k).

For both the (*R*)- and (*RS*)-polymers further fine structure was observed in several of the resonances of carbon h and allows us to distinguish longer stereosequences. The triplet splitting ($h_2{-}h_4$) of main chain diad stereosequence (a) at ~47.7 ppm in the spectrum of the (*R*)-polymer, suggesting tetrad sensitivity (Chart 2), is very well-resolved and allows integrals to be measured accurately. For example, the smallest peak h_2 has a relative area 0.17 which compares well with the value of $(1 - P_{m'})^2 = 0.15$. The stereosequences were thus assigned in a manner similar to that used for the main chain diad level and are entered in Table 6. The order of the lines at the main chain tetrad level is the reverse of that at the main chain diad level for this group of signals. It is likely, as found to be the case earlier,[12] that this reversal in the pattern of resonances is a further manifestation of the γ-gauche effect. A similar order to that seen at the diad level is observed for the triplet h_5 shoulder$-h_5-h_6$ in the spectrum of poly((*R*)-1-octen-3-ol sulfone) (the h_5 shoulder peak is considered to be the one of medium intensity, analogous to h_4 in the upfield triplet). Assignments are made in the same manner as for the $h_2{-}h_4$ triplet and are given in Table 7.

The $h_2{-}h_4$ resonances in the ^{13}C-NMR spectrum of the (*RS*)-polymer have different intensities from those found in the (*R*)-polymer. The peaks are not as well resolved for the (*RS*)-polymer, because of overlap of the 16 tetrad stereosequences, all having the bracketed diad structure of Chart 1, but the following relative integrals: h_2, 0.43; h_3, 0.45; h_4, 0.13. We will first assign the h_4

Table 6. Assignment of 47 ppm Triplet Fine Structure of Methylene Carbon h of Poly((*R*)-1-octen-3-ol sulfone) to Diastereomers of Main Chain Tetrads Using the Mean Asymmetric Induction Ratio $P_{m'} = 0.614$ Where the Bracketed Structure Is Common to All Stereosequences

	h_4 47.89 ppm	**h_3** 47.72 ppm	**h_2** 47.54 ppm
Rel.Intensity	0.36	0.47	0.17
Prob. term	$(\mathbf{P}_{m'})^2$	$2\mathbf{P}_{m'}(1-\mathbf{P}_{m'})$	$(1-\mathbf{P}_{m'})^2$
P	0.38	0.47	0.15
Diastereomers	m′ m m′ m m′ m m′ $\mathbf{R}_b(\mathbf{R}_s)[\mathbf{R}_b(\mathbf{R}_s)\mathbf{R}_b(\mathbf{R}_s)]\mathbf{R}_b(\mathbf{R}_s)$	m′ m m′ m m′ r r′ $\mathbf{R}_b(\mathbf{R}_s)[\mathbf{R}_b(\mathbf{R}_s)\mathbf{R}_b(\mathbf{R}_s)]\mathbf{S}_b(\mathbf{R}_s)$ r′ r m′ m m′ m m′ $\mathbf{S}_b(\mathbf{R}_s)[\mathbf{R}_b(\mathbf{R}_s)\mathbf{R}_b(\mathbf{R}_s)]\mathbf{R}_b(\mathbf{R}_s)$	r′ r m′ m m′ r r′ $\mathbf{S}_b(\mathbf{R}_s)[\mathbf{R}_b(\mathbf{R}_s)\mathbf{R}_b(\mathbf{R}_s)]\mathbf{S}_b(\mathbf{R}_s)$

Table 7. Assignment of 49 ppm Triplet Fine Structure of Methylene Carbon h of Poly((*R*)-1-octen-3-ol sulfone) to Diastereomers of Main Chain Tetrads Using the Mean Asymmetric Induction Ratio $P_{m'} = 0.614$ Where the Two Bracketed Structures Are Common to Four Stereosequences Each

	h_6	h_5	h_5 shoulder
Rel.Intensity	small	large	medium
Prob.term	$(1-P_{m'})^2$	$2P_{m'}(1-P_{m'})$	$(P_{m'})^2$
Diastereomer	r' r m' r r' m r' $S_b(R_s)[R_b(R_s)S_b(R_s)]S_b(R_s)$	m' m m' r r' m r' $R_b(R_s)[R_b(R_s)\,S_b(R_s)]S_b(R_s)$	m' m m' r r' r m' $R_b(R_s)[R_b(R_s)S_b(R_s)]R_b(R_s)$
		r' r m' r r' r m' $S_b(R_s)[R_b(R_s)\,S_b(R_s)]R_b(R_s)$	
	r' m r' r m' r r' $S_b(R_s)[S_b(R_s)R_b(R_s)]S_b(R_s)$	m' r r' r m' r r' $R_b(R_s)[S_b(R_s)\,R_b(R_s)]S_b(R_s)$	m' r r' r m' m m' $R_b(R_s)[S_b(R_s)R_b(R_s)]R_b(R_s)$
		r' m r' r m' m m' $S_b(R_s)[S_b(R_s)\,R_b(R_s)]R_b(R_s)$	

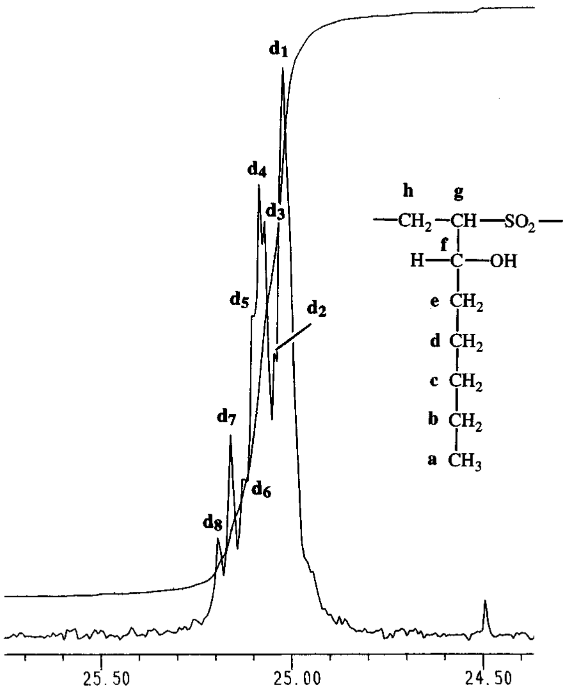


Figure 3. ^{13}C-NMR fine structure of the side chain methylene carbon d of (−)-poly((*R*)-1-octen-3-ol sulfone) at 125.8 MHz in dmso-d_6 solvent at 100 °C. NS = 100 000, acquisition time = 1.08 s, spectral window = 30 303 Hz, and LB = 0 Hz.

peak. In the (*R*)-polymer h_4 was assigned to the isotactic main chain tetrad $R_b(R_s)R_b(R_s)R_b(R_s)R_b(R_s)$ which, along with its enantiomer $S_b(S_s)S_b(S_s)S_b(S_s)S_b(S_s)$, must be assigned to the same signal in the (*RS*)-polymer. The predicted intensities for these tetrads in the (*RS*)-polymer are 0.11 and 0.03 respectively, whose sum (0.14) corresponds well to the measured intensity of 0.13. This peak is assigned to two of 256 possible octad stereosequences. We have not yet been able to assign particular stereosequences of peaks h_2 and h_3 in the (*RS*)-polymer.

The side chain methylene carbons d (~25 ppm) of the optically active polysulfone shows three well-resolved groups of eight peaks (Figure 3) which may be readily assigned initially at the main chain diad level, in the same manner as for the triplet of carbon h. The assignments, based upon the relative intensities obtained by cutting and weighing, are given in Table 8. It is interesting that the main chain diad stereosequence pattern for carbon d is not the same as that of carbon h, the more intense (e) and (i) resonances in the former found instead upfield of the (a) resonance. This suggests that for carbon d *the stereochemical relationship between adjacent residues has more effect on the chemical shift dispersion than the stereochemical relationship within a residue*, the opposite of that found at carbon h. Further fine structure within these three distinct groups of peaks indicates a sensitivity to one or more chiral center. For example, the doublet splitting of the $S_b(R_s)$-$S_b(R_s)$ at 25.15 ppm suggests triad sensitivity, the smaller downfield resonance being attributed to a further *r′* residue on one side of the diad label, $S_b(R_s)$-$S_b(R_s)S_b(R_s)$, and representing an isotactic triad of the unpreferred main chain *S* stereochemistry. The main chain methine carbon g in the (*R*)-polymer also shows three well-resolved groups of peaks (Figure 4) whose pattern and assignments (Table 8) are entirely similar to that of carbon d. The (*RS*)-polymer does not show the same degree of fine structure at carbons d or g as found in the (*R*)-polymer, and assignments are not attempted.

Table 8. Assignment of Fine Structure of Side-Chain Methylene Carbon d and Main Chain Carbon g of Poly((*R*)-1-octen-3-ol sulfone) to Main Chain Diad Stereosequences as in Table 2 Using $P_{m'} = 0.614$

probability term	$(1 - P_{m'})^2$	$(P_{m'})^2$	$2P_{m'}(1 - P_{m'})$
P	0.15	0.38	0.47
carbon d	$d_{7,8}$	d_{3-6}	$d_{1,2}$
	25.15 and 25.19 ppm	25.07 ppm	25.01 ppm
relative intensity	0.15	0.37	0.48
carbon g	g_3	g_2	g_1
	63.1 ppm	62.8 ppm	62.5 ppm
relative intensity	0.13	0.37	0.50
stereosequence assignment	(m)	(a)	(e) and (i)

For the (*R*)-polymer further fine structure is also observed (Figure 5) within the doublet splitting of carbon e. Both the upfield and downfield components of the doublet show three clearly resolved groups of peaks suggesting main chain triad sensitivity, with further fine structure in the downfield one indicating main chain tetrad sensitivity. The relative intensities of the signals are summarized on the first line of Table 9 for the peaks e_1 to e_7 of Figure 5, e_4 and e_5 being grouped together for the moment. Assignments may be made at the triad level, in a similar manner to those at the diad level, by using $P_{m'} = 0.614$ in the expressions $(P_{m'})^3$, $(P_{m'})^2(1 - P_{m'})$, $P_{m'}(1 - P_{m'})^2$ and $(1 - P_{m'})$, the values of which are entered in Table 9 under the appropriate diastereomer structure. Among the *m′*-

Table 9. Assignment of the Fine Structure of Carbon e of Poly((*R*)-1-octen-3-ol sulfone) to Diastereomers of Main Chain Traids Using the Mean Asymmetric Induction Ratio $P_{m'} = 0.614$

	e_7 34.46 ppm	e_6 34.2–34.4 ppm	e_5 and e_4 34.1– 34.2 ppm	e_3 ~33.8 ppm	e_2 ~33.6 ppm	e_1 ~33.4 ppm
Rel.Intensity	0.15	0.32	0.14	0.10	0.20	0.09
P	0.15	0.32	0.15	0.09	0.20	0.09
Diastereomers	*a* r’ r m’ m m’ $S_b(R_s)R_b(R_s)R_b(R_s)$	m’ m m’ m m’ $R_b(R_s)R_b(R_s)R_b(R_s)$	*a* m’ m m’ r r’ $R_b(R_s)R_b(R_s)S_b(R_s)$	*b* m’ r r’ m r’ $R_b(R_s)S_b(R_s)S_b(R_s)$	r’ m r’ m r’ $S_b(R_s)S_b(R_s)S_b(R_s)$	*b* r’ m r’ r m’ $S_b(R_s)S_b(R_s)R_b(R_s)$
Prob. terms	$(P_{m'})^2 (1-P_{m'}) = 0.15$	$(P_{m'})^3 = 0.23$	$(P_{m'})^2 (1-P_{m'}) = 0.15$	$(P_{m'})(1-P_{m'})^2 = 0.09$	$(1-P_{m'})^3 = 0.05$	$(P_{m'})(1-P_{m'})^2 = 0.09$
		r’ r m’ r r’ $S_b(R_s)R_b(R_s)S_b(R_s)$			m’ r r’ r m’ $R_b(R_s)S_b(R_s)R_b(R_s)$	
		$(P_{m'})(1-P_{m'})^2 = 0.09$			$(P_{m'})^2 (1-P_{m'}) = 0.15$	

a,b each pair of *a* or *b* diastereomers are interchangeable.

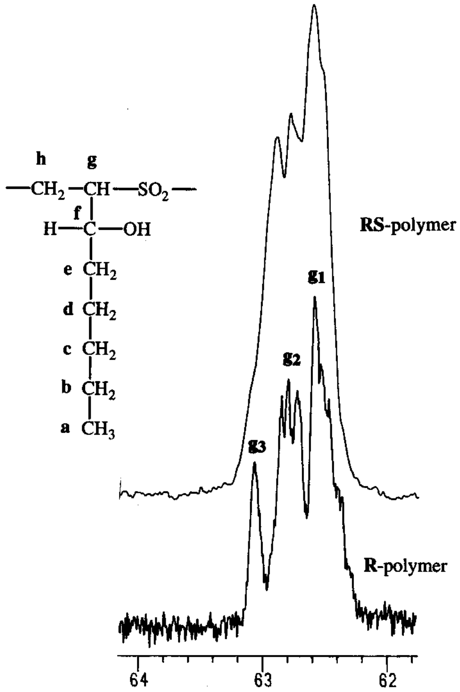


Figure 4. ^{13}C-NMR fine structure of the main chain methine carbon g of both poly((*R*)- and (−)-poly((*RS*)-1-octen-3-ol sulfone) at 125.8 MHz. Solvent and spectral parameters are as for Figure 3.

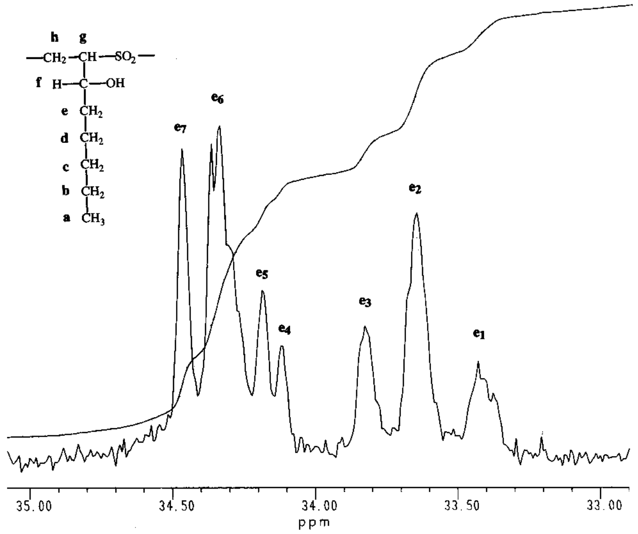


Figure 5. ^{13}C-NMR fine structure of the side chain methylene carbon e of optically active poly((*R*)-(−)-1-octen-3-ol sulfone) at 125.8 MHz. Solvent and spectral parameters are as for Figure 3.

centered structures, the intensity of peak e_6 can be obtained only from a $(P_{m'})^3 + (P_{m'})^2(1 - P_{m'})$ term, leaving e_7 and $e_4 + e_5$ to the remaining two *m*′-centered structures. Peaks e_4 and e_5 have a relative intensity of $(1 - P_{m'}):P_{m'}$ which indicates that it is sensitive to one further chiral center but we cannot tell whether this is in the head or tail direction. In a similar way the *r*′-centered structures have been allocated. In the spectrum of the (*RS*)-polymer, the smaller upfield component of the e doublet shows at least five peaks and the downfield component three, but the larger number of stereosequences causes chemical shift overlap, and integrals cannot be measured accurately.

Conclusions

Both ^{1}H- and ^{13}C-NMR spectroscopy on poly(1-octen-3-ol sulfone) in solution show that the stereochemistry of the methine carbon that forms in the backbone depends on that of C_3, which bears the alcohol. Considerations expressed in Chart 1 suggest that the line order of carbon e is consistent with an *R* side chain inducing an *R* backbone preferentially. The preference is barely significantly higher for the (*RS*)-polymer, $P_{m'} = 0.658 \pm 0.009$, than for the (*R*)-polymer, $P_{m'} = 0.614 \pm 0.017$), which indicates a slight tendency toward a syndiotactic placement in the backbone chiral centers: the effect over one bond within the residue is much greater than any over four bonds along the main chain. Because the (*R*)-polymer has only one type of side chain stereochemistry, it contains fewer stereosequences within a given number of residues and has a correspondingly simpler ^{13}C spectrum, an effect particularly apparent in the shifts of the side chain methylene carbon h, as seen in Figure 2. The h carbon shifts were first assigned at the main chain diad level, and then certain features were assigned at the main chain tetrad level for both optically active and racemic polymers, to sequences that involve eight chiral centers.

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