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Microstructure of Poly(but-2-ene sulfone) and the Role of the SO_2–Olefin Charge-Transfer Complex in the Polymerization Reaction[1]

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ABSTRACT: Two model compounds for the poly(but-2-ene sulfone) chain have been prepared and characterized by IR and NMR spectroscopy, and the crystal structure of one of these, *meso*-2,3-bis(isopropylsulfonyl)butane, has been established. Similarities in the infrared and ^{13}C NMR spectra of the models and of the polymer chains allowed us to identify *meso*-but-2-ene and *rac*-but-2-ene residues within the polymers, and the influence of other microstructural features upon the fine structure of the ^{13}C NMR spectra has been observed. While the polymer derived from *cis*-olefin has racemic residues irrespective of the preparation temperature, the polymer derived from the *trans*-olefin has an increasing proportion of *meso*-alkene structures as the temperature is lowered. This we interpret as proving that the charge-transfer complex is the main reacting species at low temperatures.

Introduction

There has been a long debate over the role of the charge-transfer complexes that form from olefins and sulfur dioxide in the reaction scheme for the formation of the 1:1 alternating copolymers, the poly(olefin sulfone)s.[2-5] A proof that the complex itself is a reacting species in the free-radical chain reaction has not previously been offered. This we attempt to do, by showing a relationship between the structure of the olefinic monomer and the microstructure of the poly(but-2-ene sulfone) chain with the aid of ^{13}C NMR spectroscopy. This chain is extremely simple in structure, as there are only achiral sulfonyl and chiral methylmethylene units present, the latter being found as pairs: $-SO_2-$ alternating with $-CH(CH_3)-CH(CH_3)-$.

The existence of the charge-transfer complexes in mixtures of olefins and SO_2 has been demonstrated by a number of methods; with styrene, they have a straw yellow color,[3] but more often they are detected in the UV spectrum[3,4] or by monitoring the ^{1}H NMR shifts as a function of the composition.[5,6] The phase diagram of mixtures of SO_2 and 2,3-dimethylbut-2-ene shows a temperature maximum at a 1:1 proportion,[5] as do mixtures of SO_2 and vinyl chloride.[6] By the same measure isobutene forms a 2:1 complex with SO_2[7] and vinyl chloride also forms a 1:2 complex.[6] (In that case the second SO_2 molecule is probably coordinated through the chlorine atom.) Typically, if a 1:1 complex is assumed, for 10:1 mixtures of SO_2 and olefin, at least 40% of the olefin might be in the complexed form,[2,5] so the reaction must be influenced by their presence. It is not possible to argue from the 1:1 copolymer composition that a 1:1 complex is a reacting species; the composition may simply reflect the ability of the radical of one monomer to react only with the free form of the other monomer.[4,8-10] Computer simulations have shown that the formation of the variable composition poly(vinyl chloride sulfone) might involve the complex at a low temperature, but there were other explanations.[11] In terpolymerizations with acrylonitrile or with *n*-butyl acrylate, the increase in polymer content of 1-butene and sulfonyl residues upon UV irradiation has been attributed to the activation for propagation of the olefin–SO_2 charge-transfer complex by a quantum of light.[12,13] Here we develop new arguments, based upon the stereochemistry of the residues derived from *cis*- and *trans*-but-2-enes in the polysulfones, that point to the charge-transfer complex being a reacting species at low temperatures.

According to the infrared spectra, identical polysulfones were obtained from the cis and trans isomers of but-2-ene when these were first examined.[14,15] However ^{13}C NMR spectroscopy later found a new type of residue, that formed from the *trans*-olefin when the preparation temperature was lowered to near −78 °C.[16] Structural assignments were then made on the basis of the γ carbon effect of Grant and Paul[17] coupled with an assumption that the preferred conformation of the C–C bond was trans, but the possible interference of a larger conformationally sensitive γ effect from the two oxygen atoms of the sulfone group[18] was neglected.

To check these assumptions, we have prepared and characterized two model compounds for the polymer chain. They contain *meso*-2,3-bis(alkylsulfonyl)butane and *rac*-2,3-bis(alkylsulfonyl)butane structures, the alkyl groups being isopropyl groups. Thus they represent one alkylene residue of the polymer flanked on each side by a sulfone group and a unit equivalent to half an alkylene residue:

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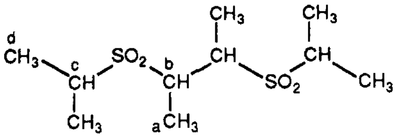


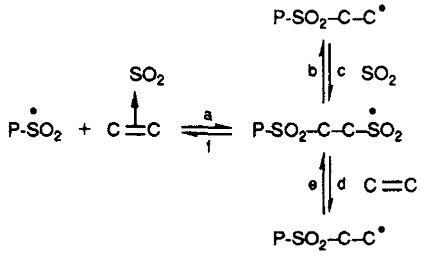
I

For the higher melting point α form, which was more readily obtained pure, we have determined the crystal structure, to establish for certain the relationship between the central chiral centers and to explore conformationally sensitive γ-shift effects. (We show that the preferred conformation of the central bond in one model in solution is not trans.) The infrared spectra of the two crystalline solids and the ^{13}C NMR solution shifts of the central methyl and methine carbons have been measured for comparison with the corresponding polymer spectra. The ^{13}C NMR spectra of several of these poly(but-2-ene sulfone)s are now reported at a higher resolution than before. Correspondences between the IR spectra and the ^{13}C NMR shifts of the disulfone models and of the polymers have been found, and the microstructure of the latter has been identified. The fine structure seen in the ^{13}C NMR spectrum is discussed in terms of the chain microstructure, the main feature of which—the relative chiralities of the two methine groups within an alkylene residue—is shown to be dependent upon the type of olefin used as well as the temperature of preparation. Fine structure from longer range interactions is also present and is discussed.

Reaction Mechanism

For the formation of the backbone of alternating sulfone and alkylene residues, the simplest free-radical mechanisms would have each monomer radical reacting only with the other monomer; in Lewis–Mayo terms, $r_1 = r_2 = 0$, and the charge-transfer complex is incidental. Within the comprehensive reaction scheme shown below, only steps c and d would be used, and these would be followed alternately. They are shown vertically down on the reaction scheme. On the other hand, and with equal simplicity, the charge-transfer complex reacts, as only it is susceptible to attack by the propagating polymer radical: the horizontal path from left to right (a) is taken, and the other reactions are not involved.

Scheme I

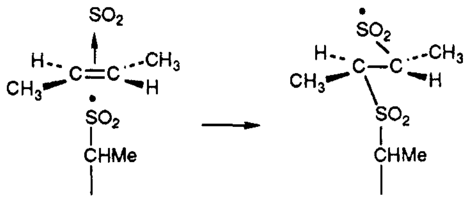


The issue is certainly more elaborate than either of these propositions; for example, depropagation steps have been demonstrated during polysulfone formation from but-2-ene[4,14] as well as from styrene,[19] the evidence being stereochemical isomerization of the double bonds in samples of recovered hydrocarbon (the styrene monomer was partly deuterated). Moreover, both sulfonyl and alkyl radicals have been observed by electron spin resonance during the initiation of the copolymerization of isobutene with SO_2,[20,21] and, curiously, in the case of the polymerization of methyl methacrylate in SO_2 the ESR signal came entirely from a sulfonyl radical, yet the polymer contained no sulfone groups.[22] Furthermore, the microstructure of the 2:1 polysulfones from styrene and vinyl chloride has been explained with the aid of depropagation processes.[23,24] We therefore include the SO_2 radical dissociation step (b) and the alkyl radical dissociation step (e) in the general reaction (Scheme I). From competition studies involving ethylene, propylene, and isobutene, that is, using olefins with an increasing proportion of alkyl substitution, it has been deduced that the attacking radical is electrophilic.[25] Thus the rate-determining step involves the attack of a sulfonyl radical upon a carbon atom; this step may be either a or d.

In contrast to earlier assumptions,[16] we suppose that the alkyl radical is planar or nearly so, as others have suggested,[26,27] and that there is a rapid rotation about the terminal $-C-C^{\bullet}$ bond: the low values of the β-hydrogen coupling constants in, for example, the ESR spectra of the $-SO_2$–alkyl radicals of styrene, isobutene, and α-methylstyrene[21] resemble the values for $RSC-C^{\bullet}$ radicals, which were shown to be consistent with a rapid rotation about the C–C bond.[28] After this internal rotation the addition of a sulfur dioxide molecule (in step c) fixes the configuration of the but-2-ene residue in a manner that is independent of the type of alkylene. Within the reaction scheme shown above, isomerization of but-2-ene[4] occurs as follows: after the formation of an alkyl radical by either stages b or d, the radicals formed may initially depend upon the type of precursor olefin, but equilibration of the two radical types is obtained by rapid rotation about the terminal $-C-C^{\bullet}$ bond. If a depropagation by stages e and f releases the olefin, then it has a structure independent of the precursor.

In stage a of this mechanism, when the charge-transfer complex is the species attacked by the sulfonyl radical, we suppose that it opens up in a concerted process, with a retention of the configuration that the two olefinic carbons have in the charge-transfer complex itself. Thus the *trans*-olefin gives the racemic structure (Scheme II) and the *cis*-olefin would give the meso structure. A similar mechanism was invoked by Olson and Butler[29] for another copolymerization.

Scheme II



In summary, we hope to be able to deduce which reaction pathway is used during the polymerization from the configuration of the polymer chain: we suppose that if the propagation reaction shown horizontally is used, there will be a retention of the configuration of the alkenes, but if the reaction involves the routes shown vertically, the structure of the polymer produced will be independent of the starting materials.

Experimental Section

Preparation of α- and β-2,3-Bis(isopropylsulfonyl)butane. Propane-2-thiol (65 g) was dissolved in dimethylformamide (300 mL) containing sodium hydroxide with stirring under nitrogen. 2,3-Dichlorobutane (55 g) was added in portions, and after 2 days, water was added to retain the DMF, while the dithioether was extracted with chloroform. These extracts were

Table I
Preparation Conditions for But-2-ene Polysulfones[a]

prepn no.	olefin,[b] mL	SO_2, mL	*T* prepn, °C	yield, g	m_c, %
SCH/7	10.5 t	38	-95^c	3.5	63.8
SCH/8	4.5 t	55	-95^c	2.0	63
SCH/2	8 t	28	−78	1	40.1
U27	15 t	15	−63	4.3	23.2
U23	5 c	10	−84	0.5	12.1
SCH/1	29 c	36	−78	5.0	7
U101	15 c	15	−30	1.0	2.4
SCH/34	25 c	30	−25	2.5	2.1

[a] 30 mL of toluene was also present. [b] t and c for trans and cis isomers, respectively. [c] Toluene slush bath.

oxidized with hydrogen peroxide in glacial acetic acid, and, after neutralization and extraction with chloroform, 1.3 g of a solid was obtained following removal of the chloroform and cooling to −20 °C.[30] At room temperature the pasty mass was treated with ether, and after filtration a small quantity of crystals was obtained. After recrystallization from a chloroform–ether mixture, this fraction weighed 0.34 g and sublimed at 133 °C. ^1H NMR spectroscopy showed that the sample was a pure isomer, which we termed the α form. Two further fractions of total weight 0.093 g of the same material were obtained similarly by cooling the ether solution. However, after the solution in ether was heated, a little petroleum ether was added, and the solution was cooled to room temperature, a crop of new crystals was obtained (0.10 g). They had a melting point of 63 °C, and according to their ^1H NMR spectrum were 92% pure β form.

Preparation of the Poly(but-2-ene sulfones). The copolymers were prepared from feeds of the olefin and SO_2 made miscible at low temperatures by the presence of the solvent toluene that was cooled within slush baths formed with liquid nitrogen, as is summarized in Table I. Initiation of the free-radical reaction was performed in open tubes with the slow addition of *tert*-butyl hydroperoxide (10%) in toluene at temperatures above −50 °C. The reaction was performed at lower temperatures within a sealed tube by means of UV irradiation of azobis(isobutyronitrile). This initiator had been released into the feed within the sealed reaction tube by breaking open a small glass tube at the temperature of the polymerization. The reaction was terminated by freezing the feed, followed by the addition of cold acidified methanol containing a free-radical scavenger, resorcinol,[31,32] to prevent any further polymerization before precipitation. For purification, polymers were reprecipitated from chloroform.

Infrared spectra were obtained on a Perkin-Elmer 598 spectrometer that was calibrated with a polystyrene film. NMR spectra were recorded on a GEC QE 300, a Bruker WM250, or a Bruker WH 400-MHz instrument.

Crystal data for α- or *meso*-2,3-bis(isopropylsulfonyl)butane: $C_{10}H_{22}S_2O_4$; monoclinic; a = 6.055 (6), b = 12.372 (12), c = 9.150 (9) Å; β = 91.2 (1)°; U = 685.2 Å^3; space group $P2_1/n$ [alternative $P2_1/c$ (No. 14)]; Z = 2, D = 1.31 g cm^{-3}; $F(000)$ = 292; clear colorless, elongated, flat plates; crystal dimensions 0.15 × 0.20 × 1.0 mm; λ(Mo Kα) = 0.710 69 Å, μ(Mo Kα) = 3.35 cm^{-1}.

Data Collection and Processing. The lattice was characterized from oscillation and Weissenberg photographs using Cu Kα radiation (λ = 1.5418 Å). Diffraction data were recorded on a Stöe STADI-2 two-circle diffractometer using the background–ω scan–background mode with graphite-monochromated Mo Kα radiation, scan width 1.5°, scan speed 1.5° min^{-1}, $3° < \theta < 30°$. A total of 771 independent data with $I > 3\sigma(I)$ were deemed to be observed. These were corrected for Lorentz and polarization factors and were used in the subsequent analysis and refinement. No absorption corrections were applied.

Structure Analysis and Refinement. The structure was solved by the direct phasing methods of MULTAN[33] and refined by least squares using SHELX.[34] Anisotropic vibrations were allowed for non-hydrogen atoms. Hydrogen atoms were located in a difference Fourier synthesis and were included in the refinement with individual isotropic temperature factors. The final conventional R was 0.044. The weighting scheme used was $w = 3.21/[\sigma^2(F) + 0.00088F^2]$. The final fractional coordinates are listed in Table II, and bond lengths and angles and torsional angles are in Table III. Full results are given as supplementary material.

Table II
Fractional Atomic Coordinates for *meso*-2,3-Bis(isopropylsulfonyl)butane

atom	*x*	*y*	*z*
S	0.64608 (13)	0.16196 (6)	0.51919 (8)
O_1	0.6931 (5)	0.1889 (2)	0.3699 (3)
O_2	0.8284 (5)	0.1293 (2)	0.6138 (3)
C_1	0.4430 (6)	0.0527 (2)	0.5241 (3)
C_2	0.3432 (8)	0.0489 (3)	0.6770 (4)
C_3	0.5152 (6)	0.2793 (3)	0.5957 (4)
C_4	0.3097 (9)	0.3109 (4)	0.5068 (5)
C_5	0.6912 (9)	0.3674 (4)	0.6044 (6)
H_1	0.337 (5)	0.074 (2)	0.455 (3)
H_{21}	0.235 (7)	−0.011 (4)	0.689 (4)
H_{22}	0.278 (7)	0.111 (4)	0.697 (4)
H_{23}	0.444 (9)	0.029 (4)	0.744 (5)
H_3	0.479 (6)	0.259 (3)	0.679 (4)
H_{41}	0.365 (7)	0.325 (3)	0.414 (4)
H_{42}	0.201 (8)	0.254 (4)	0.508 (4)
H_{43}	0.259 (8)	0.373 (5)	0.540 (5)
H_{51}	0.646 (7)	0.423 (4)	0.646 (4)
H_{52}	0.731 (8)	0.390 (4)	0.511 (5)
H_{53}	0.828 (10)	0.339 (4)	0.659 (6)

Table III
Bond Lengths and Angles for *meso*-2,3-Bis(isopropylsulfonyl)butane (Atoms Numbered as in Figure 1b)

(a) Bond Lengths, Å			
$S-O_1$	1.440 (2)	$S-O_2$	1.446 (3)
$S-C_1$	1.829 (3)	$S-C_3$	1.802 (3)
C_1-C_2	1.537 (5)	$C_1-C_{1'}$	1.543 (6)
C_3-C_4	1.523 (6)	C_3-C_5	1.525 (5)
(b) Bond Angles, deg			
O_1-S-O_2	118.0 (2)	C_1-S-O_1	109.9 (1)
C_1-S-O_2	106.5 (2)	C_3-S-O_1	106.2 (2)
C_3-S-O_2	109.2 (2)	C_3-S-C_1	106.5 (2)
C_2-C_1-S	108.8 (2)	$C_{1'}-C_1-S$	108.2 (3)
$C_{1'}-C_1-C_2$	114.9 (4)	C_4-C_3-S	111.1 (3)
C_5-C_3-S	106.5 (3)	$C_5-C_3-C_4$	114.0 (4)
(c) Torsion Angles for Heavy Atoms,[a] deg			
$O_1-S_1-C_3-C_5$	112.1	$O_1-S_1-C_3-C_4$	−123.2
$O_1-S_1-C_1-C_2$	17.2	$O_1-S_1-C_1-C_{1'}$	−108.3
$O_2-S_1-C_3-C_5$	−119.7	$O_2-S_1-C_3-C_4$	5.0
$O_2-S_1-C_1-C_2$	−111.7	$O_2-S_1-C_1-C_{1'}$	122.8
$C_{1'}-C_1-S_1-C_3$	6.4	$C_2-C_1-S_1-C_3$	131.9
$C_1-S_1-C_3-C_4$	119.6	$C_1-S_1-C_3-C_5$	−5.0

[a] For this table the convention is that the torsion angle for the trans conformation has the value of 0°.[35]

Results and Discussion

The addition to a solution of the β form in chloroform of a little Eu(fod)$_3$ caused the three methyl doublets to appear as six doublets in the proton spectrum, showing that it has the racemic structure. The preliminary inspection of the X-ray scattering pattern of the α form as well as the detailed unit cell structure we found, as is described below, confirmed that the α form has a center of inversion and that the central methine carbons have a meso relationship.

We first describe and discuss the structure of the α-2,3-bis(isopropylsulfonyl)butane molecule in the crystal, before contrasting its IR and ^1H and ^{13}C NMR spectra with those of the β molecule. These two molecules have, respectively, meso and racemic relationships of their internal chiral methine centers. A comparison of their spectra with those of the polymers allows us to identify the meso and racemic residues present in the polysulfone chains.

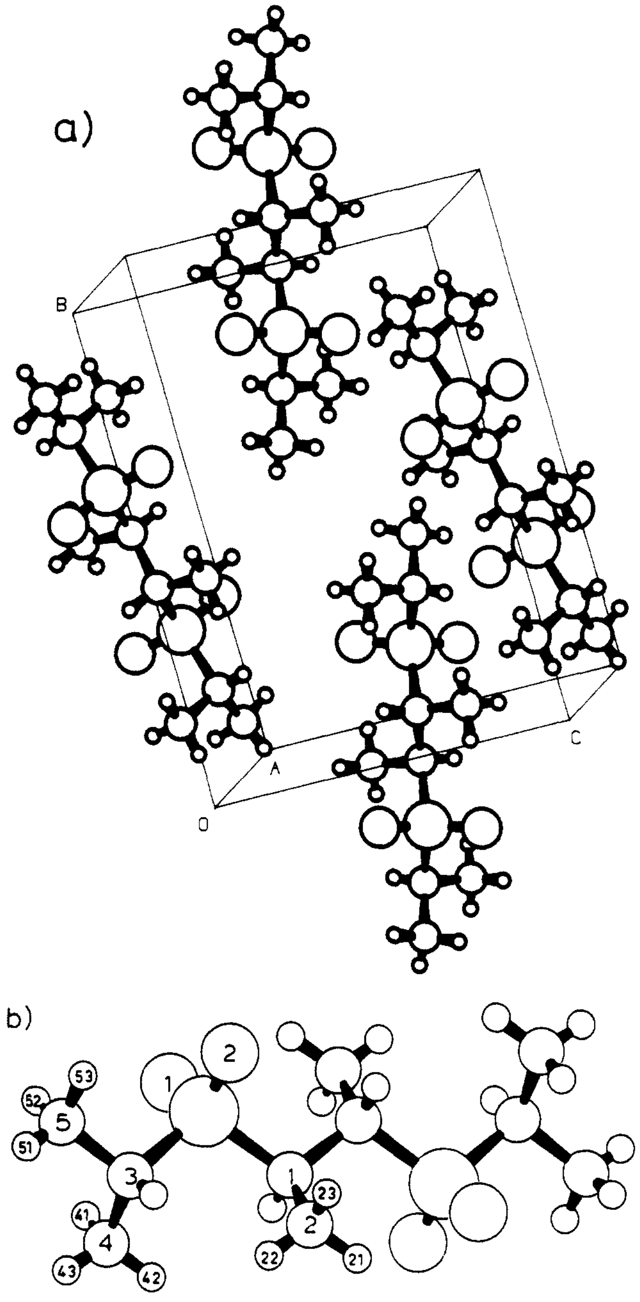


Figure 1. Crystal structure of α-2,3-bis(isopropylsulfonyl)butane: (a) the unit cell, (b) a projection from the side of the isolated molecule. The centrosymmetric structure of the molecule is apparent in the solid state, in which all the interior bonds have the trans conformation. Note also how the isopropyl groups are positioned so that methyl groups are not juxtaposed across a sulfonyl group. (The numbering scheme of Figure 1b corresponds to the entries of Table III.)

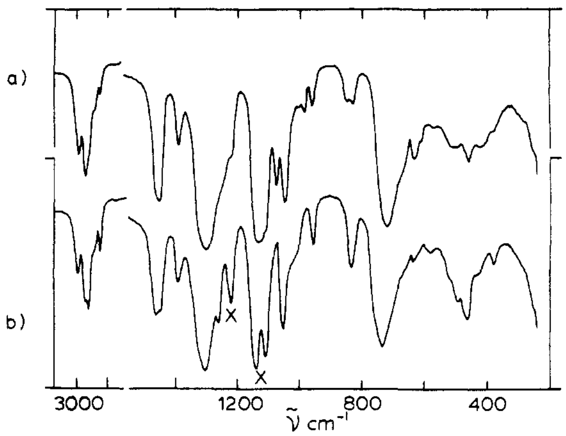


Figure 2. Infrared spectra of two poly(but-2-ene sulfone)s: (a) sample SCH/7 was prepared from *trans*-olefin at −84 °C; and (b) sample SCH/34 was prepared from *cis*-olefin at −34 °C. The absence of the band at 1220 cm^{-1} from a and the splitting of the band at 1100 cm^{-1} in b, at the points marked with an X are indicative that polymer a contains *meso*-but-2-ene units and that polymer b contains racemic but-2-ene units. The ^{13}C NMR spectra showed that the polymer of a contained 64% meso units and that the polymer of b contained 98% racemic units.

A. X-ray Crystal Structure of α-2,3-Bis(isopropylsulfonyl)butane. We show in Figure 1a for α-2,3-bis(isopropylsulfonyl)butane the X-ray determined unit cell, which is seen to contain two molecules. The fractional atomic coordinates for half of one molecule are recorded in Table II. In part b of Figure 1 a projection of the molecule is shown, and from the two views a centrosymmetric structure is apparent for the single molecule. The bond lengths and angles that are entered in Table III have similar values to those for the same structures present in dimethyl sulfone and in another arylalkyl disulfone.[36,37] Within this molecule the two sulfone dipoles are antiparallel. The bonds adopt simple trans and gauche conformations, as in the other less substituted disulfone,[37] though here the rotational angles deviate on average about 7° from the conventional 0°, ±120° values because of the lack of symmetry of the substitution pattern of the C–C and the C–S bonds. The central methyl groups are disposed in a trans relationship to each other (so that if the configuration were adopted in solution, they would lack the γ gauche interaction and the chemical shift would correspondingly be downfield by about 6 ppm[17], and the terminal isopropyl groups are disposed so that there is no severe steric interaction between methyl groups linked through the S atoms by five bonds: the left-hand methine hydrogen, for example, is orientated nearly parallel to the methyl group across the C–S–C link, and the methine hydrogen on the next carbon is oriented nearly parallel to a methyl group of the terminal isopropyl group. (These methyl groups and hydrogen atoms are thus staggered, in the manner previously assumed for the secondary alkyl units of dialkyl sulfones when interpreting ^{13}C shift differences for conformational energies,[18,38] and when treating the configurational statistics of the poly(cyclohexene sulfone) chain.[39] We discuss the solution conformations of the molecule below in connection with the NMR spectroscopy results.

B. A Comparison of the IR and ^{13}C NMR Spectra of the Models and of the Copolymers. We show in Figure 2 the infrared spectra of copolymers prepared at −78 °C from *trans*-olefin (part a) and from *cis*-olefin (part b), the SO_2 stretch bands at 1100 and 1300 cm^{-1} being the most prominent bands. The latter spectrum resembles those reported earlier by others.[14,15] The two IR spectra differ clearly in many places, confirming that the polymerization at −78 °C is stereospecific,[16] which is contrary to the finding of the earliest studies with IR spectroscopy.[14,15] There are significant differences near 1050 cm^{-1} in the C–C stretch region, at 950 cm^{-1} in the methyl group deformation region,[41,42] and at 850 cm^{-1}, where a methine C–H bend mode probably lies, as well as minor differences in the C–H stretch region near 3000 cm^{-1} and below 700 cm^{-1} (particularly at 633 cm^{-1}) where the sulfone group bending modes are;[41,42] we have marked with an X two regions of the spectra where there are major differences between the spectra of the two polymers and will return to these once the features have been discussed in the spectra of the models.

In Figure 3a we show IR spectra of the meso (α) and

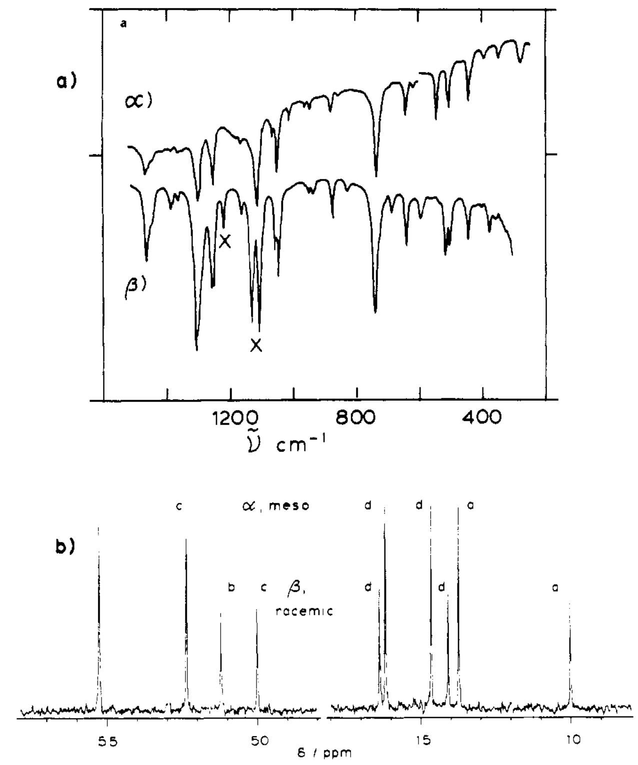


Figure 3. (a) Infrared spectra of α- and β-2,3-bis(isopropylsulfonyl)butane, showing that the two molecules have different spectra. The points X mark features that differ in the spectra of these two model molecules and where differences are also seen in the spectra of the two polymers (Figure 2). (b) ^{13}C NMR spectrum at 75 MHz of a mixture of α- and β-2,3-bis(isopropylsulfonyl)butane, in approximately 2:1 proportions, showing 10 distinct peaks from the chloroform solution (64 scans, LB = 0.2 Hz, 300 mg in 1 mL of CDCl$_3$). The peaks are labeled with their assignments, according to I.

of the racemic (β) forms of the model molecule. These spectra also differ in several places; most interestingly only the β form has the moderately strong band at 1221 cm^{-1} (Raman shift 1218 cm^{-1} [38]), which probably corresponds to a methine C–H bending mode[41,42] that is again sensitive to the configuration of the central methine groups. (This band, which is labeled with an X, has also been found in the spectra of two other small racemic disulfones containing the RSO$_2$CHMeCHMeSO$_2$R structure.[38]) Another notable feature, also marked with an X, is that there are two strong SO$_2$ symmetrical stretch IR bands[41,42] at 1109 and 1131 cm^{-1} in the spectrum of the β form but only one (at 1113 cm^{-1}) for the centrosymmetric α form. (The Raman spectra have shifts close to each of these frequencies.[38]) The other differences between the spectra of the two molecules lie in the methyl rock region near 1050 cm^{-1} and below 700 cm^{-1} where none of the C–SO$_2$–C unit vibrational modes are common in the two spectra: the latter result is expected, as in this region the frequencies of the corresponding vibration modes of MeSO$_2$Et are conformation sensitive.[41]

According to the ^{13}C NMR spectrum, as is discussed below, the polymer of Figure 2a has a 37% proportion of racemic residues. Bands characteristic of these racemic residues are present in that spectrum at 1050, 946, and 833 cm^{-1}, close to bands at, respectively, 1078, 988, and 850 cm^{-1} from the meso residues; and from the small proportion of racemic residues there also are shoulders at 1220 cm^{-1} and at 1112 cm^{-1} on the major bands of the predominantly meso polymer.

Table IV
^{1}H and ^{13}C NMR Shifts of α (Meso) and β (Racemic) 2,3-Bis(isopropylsulfonyl)butane in CDCl$_3$ at Ambient Temperatures

		position of atom in I			
isomer	atom	a	b	c	d
α (meso)	^{1}H	1.41	3.38	2.91	1.86, 1.09
	^{13}C	13.74	55.20	52.36	14.65, 16.18[a]
β (racemic)	^{1}H	1.35	3.95	2.55	0.82, 1.01[b]
	^{13}C	10.01	51.20	50.00	14.09, 16.37

[a] When the temperature was lowered[38] only this pair of peaks showed the expected[18] increase in their separation.[40] [b] Extra peaks show in the presence of Eu(fod)$_3$, indicating this is the racemic isomer.

We have not attempted to assign all of the bands to particular vibrations, as there are many modes in both the polymers and the model compounds. What we find useful is that the two X features—the splitting of the SO$_2$ symmetrical stretch band and the smaller C–H bend mode at 1223 cm^{-1}—are present in both the spectrum of the racemic molecule and of the polymer prepared from the *cis*-olefin and are absent from the spectra of the meso molecule and from the spectrum of the polymer prepared from the *trans*-olefin (except for the remnants noted above). This is one indication that in the polymer prepared from the *cis*-olefin the alkene residues are predominantly racemic, and the polymer prepared from the *trans*-olefin contains meso structures. A second indication is provided by the ^{13}C NMR spectra.

Assigning the shifts (Table IV) of the three methyl carbons in the spectrum of the racemic isomer shown in Figure 3b was straightforward, for that at about 10 ppm from the central methyl group is distinct from the other two, which have typical shifts near 15 ppm for the methyl carbons of an isopropylsulfonyl group.[18] The difference between the two methyl shifts (2.2 ppm) derives from the upfield γ effect of the sulfone oxygen atoms[18] and the inequality of the populations of the conformational states of the C–S bond that is caused by the chirality of the methine carbon on the other side of the sulfone group and is much larger than the difference for the methyl carbons of the isopropyl group of isopropyl-2-butyl sulfone (0.6 ppm[38]); the bulk of the interior groups of the model disulfone molecule thus causes larger differences in conformational energies for the SO$_2$–isopropyl bond than does the 2-butyl group in the latter molecule.

The shifts of the methyl carbons of the meso isomer are less readily assigned, for the central methyl carbon and the two isopropyl carbons are all found within a range of 2.5 ppm (see Figure 3b). However, from the temperature dependence of their shifts the upfield peak is assigned to the central methyl group and the other two are assigned to the methyl groups of the isopropyl group,[40] C$_5$ being upfield of C$_4$ (Figure 1b). We expect that shift differences will increase as the temperature is lowered and the most stable conformer is more weighted.[18] The difference in conformational energies of the isopropyl groups in the meso molecule, as measured by the difference of the chemical shift of their methyl carbons ~ 1.5 ppm, is thus intermediate between the values for the isopropyl-2-butyl sulfone and the racemic disulfone. The methine carbons were assigned as shown, when it was found that lowering the proton decoupler irradiation frequency from the equivalent of 2.0 to 4.0 ppm, where the protons of the interior methine group are found, caused the upfield peak (50 ppm) to fall in height relative to that of the peak at 51 ppm.

In the solid state the central bond of the meso molecule has the trans conformation, as is consistent with the simple conformation theory of disulfones.[39] However, the

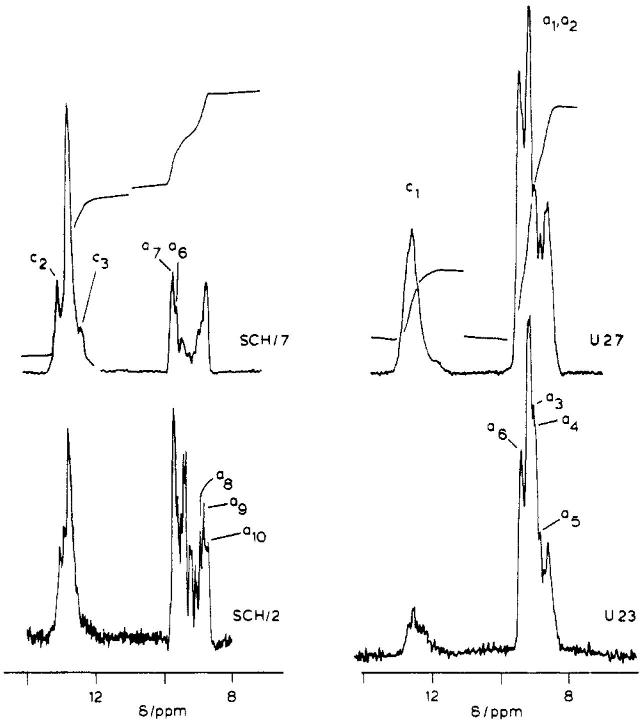


Figure 4. 100.6-MHz ^{13}C NMR spectra of the methyl groups of four samples of poly(but-2-ene sulfone) recorded in dimethyl sulfoxide solvent at 70 °C. The spectra are labeled with the sample code on the figure. For the typical sample U27, the spectrometer settings were as follows: NS, 67 241; SW, 25 000; AQ, 0.6554; PW, 13.0 μs. The Fourier transform was performed with an LB of −10.0 and a GB of 0.15.

theory is inadequate for the molecule in solution, as its ^{1}H NMR spectrum displays an unexpected result: the coupling constant between the central methine protons is only 4.6 Hz. This value is much less than that for a normal trans coupling constant (we have found a value of 11.6 Hz for a trans coupling constant in a cyclic disulfone in a fixed conformation[38]), though the value is greater than the 1.9 Hz shown by the β form, in which the two protons must thus be disposed in a gauche relationship. In solution, the central C–C bond of the α or meso form cannot be entirely or even be predominantly in the conformation found in the solid state. This surprising finding justifies our caution in deciding the type of alkyl residue present on the basis of an assumed bond conformation and the γ gauche shift effect between carbon atoms.

Once the stereochemistries of the two models has been established, it is apparent that both the methyl and the methine carbon shifts of these groups at the center of the meso form are downfield of the corresponding shifts of the racemic form, the differences being 3.7 and 2.4 ppm, respectively, for the two types of carbons. These observations support the earlier assignments[16] of the signals in the low-resolution spectra of the polysulfones to meso and racemic hydrocarbon residues, which have the same line order for the methyl and methine carbon shifts. We are able to measure the proportion of meso structures in a poly(but-2-ene sulfone) by measuring the proportion of methyl group signal that is located at 13 ppm and by assuming that the nuclear Overhauser enhancements are the same for each type of residue. Integrals we obtained for this purpose are drawn in the upper two parts of Figure 4, where the ^{13}C NMR spectra of the methyl groups of four polysulfones are shown.

C. High-Resolution ^{13}C NMR Spectra of the Polymers. (a) Methyl Region. The ^{13}C NMR resonances in the methyl region of four of the polysulfones are shown in Figure 4. Resolution enhancement was obtained for these spectra by using a negative line broadening factor, −10 Hz, when performing the Fourier transform. It may be seen that the signal in the region of 13 ppm from the meso residues becomes more intense in the order of samples U23, U27, SCH/2, and SCH/7 and that there are progressive changes in the appearance of the fine structures in the two parts of the spectrum, particularly in the upfield portion, where there is much detail present.

Table V
Shifts and Sequence Assignments for the Methyl Region of the Polymer ^{13}C NMR Spectra[a]

label	shift, ppm	sequence
a_1	9.421	$r_c\mathrm{m_s r_c}$
a_2	9.357	$r_c\mathrm{m_s r_c}$
a_3	9.234	$r_c\mathrm{r_s r_c}$
a_4	9.175	$r_c\mathrm{r_s r_c}$
a_5	9.077	$r_c\mathrm{r_s r_c}$
a_6	9.584	$r_c\mathrm{m_s m_c}$
a_7	9.711	$r_c\mathrm{m_s m_c}$
a_8	8.939	$r_c\mathrm{r_s m_c}$
a_9	8.835	$r_c\mathrm{r_s m_c}$
a_{10}	8.707	$r_c\mathrm{r_s m_c}$
c_1	12.80	$\mathrm{r_c}m_c\mathrm{r_c}$
c_2	13.08	$m_c\mathrm{m_s m_c}$
c_3	12.42	$m_c\mathrm{r_s m_c}$

[a] Shifts from the spectrum of sample SCH/2.

Table VI
Shifts and Sequence Assignments for the Methine Region of the Polymer ^{13}C NMR Spectra[a]

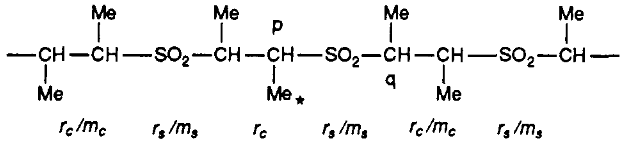
label	shift, ppm	sequence
b_1	53.53	$\mathrm{m_s}r_c\mathrm{m_s}$
b_2	51.42	$\mathrm{m_s}r_c\mathrm{r_s}$
b_3	53.8	$\mathrm{m_s}r_c\mathrm{r_s}$
b_4	52.47	$\mathrm{r_s}r_c\mathrm{r_s}$
b_5	55.22	$\mathrm{r_c}r_c\mathrm{m_c}$
b_6	53.30	$\mathrm{r_c}r_c\mathrm{m_c}$
b_7	55.00	$\mathrm{m_c}r_c\mathrm{m_c}$
b_8	52.96	$\mathrm{m_c}r_c\mathrm{m_c}$
b_9	53.8	$\mathrm{m_c}r_c\mathrm{m_c}$
b_{10}	53.8	$\mathrm{m_c}r_c\mathrm{m_c}$
d_1	56.66	$\mathrm{m_s}m_c\mathrm{m_s}$
d_2	57.50	$\mathrm{m_s}m_c\mathrm{m_s}$
d_3	57.95	$\mathrm{m_s}m_c\mathrm{m_s}$
d_4	58.32	$\mathrm{m_s}m_c\mathrm{m_s}$
d_5	58.02	$\mathrm{m_s}m_c\mathrm{m_s}$

[a] Taken from the spectrum of SCH/7.

In the r_c region near 9 ppm we have identified 10 shifts, each being present either as distinct peaks or shoulders in at least three of the four spectra; see Tables V and VI. A prominent line or pair of lines, a_1 and a_2, near the middle of the multiplet and three smaller lines upfield, a_3, a_4, and a_5, apparently fall in intensity as the m_c content rises. A second set of lines, a_6 to a_{10}, that are spaced on each side of the first set, grow in intensity relative to the first set of lines as m_c content rises, but they eventually diminish as a proportion of the total area of the methyl region. The first set is assigned to methyl carbons within r_c-centered residues that are adjacent to a second r_c-centered residue; i.e., the lines arise from the two interior methyl groups in an r_cr_c sequence. The second set of lines is assigned to the single methyl carbons in r_c-centered residues that are next to m_c-centered residues: i.e., one methyl carbon in an $\mathrm{r_c}m_c$ sequence and one in an $\mathrm{m_c}r_c$ sequence.

The major source of splitting of the peaks in this $\mathrm{r_c}$ region is associated with the γ effect of the two sulfone group oxygens, whose influences vary in intensity, depending upon the statistical weights of the C–S bond rotational states.[18,38] We have noted above an illustration of this effect, that the two methyl carbons of the isopropyl groups have shift differences of 1.4 and 2.2 ppm for the α and β models, respectively. Their nonequivalence derives from the influence of the shape of the central part of the molecules, which, particularly in the latter case, creates a difference in populations of the two low-energy isopropyl C–S bond conformations. For 2-butyl-isopropyl sulfone the corresponding differences in shift are only 0.5 ppm, reflecting the reduced influence of the smaller ethyl group, which causes an energy difference of about 300 J/mol.[38] For the polymers, di-2-butene sulfone is a better analogy: in that case the signal from the β-methyl group of the meso molecule is upfield by about 0.5 ppm of the shift of the racemic molecule;[18] in the latter case the two doglegged conformations of the molecule have equal energy, and in the former case the conformation that has the two ethyl groups brought close together has an excess energy of about 700 J/mol[38] above the alternative conformation in which the two groups are extended away from each other.[18] The minor splittings in the r_c region (e.g., between a_1 (r_s) and a_5 (m_s), 0.34 ppm) and the major splittings (e.g., between a_6 (r_s) and a_{10} (m_s), 1.00 ppm) correspond to conformational energy differences of about 300 and 500 J/mol, respectively. These estimates for the polymers are approximate, as conformational entropy differences may not be insignificant: values of 700 to −450 J/deg·mol have been found by studying the splittings in small molecules as a function of temperature.[18,38]

That there are five shifts in the r_c region in each type of sequence we have recognized leads us to consider further how these may arise. The lines (a_1,a_2) are found with roughly the same intensity in each spectrum, and together they have the same intensity as do lines a_3, a_4, and a_5 taken together in the spectra of samples U23 and U27, though in samples SCH/2 and SCH/7 the former pair of lines have a greater intensity than does the combined intensity of the latter. Referring to II, the shift of Me* causes lines a_1 and a_2 if the C_p and the C_q form an r_s diad, but the lines a_3, a_4, and a_5 are caused by an m_s diad of these two carbons. The simplest explanation of the splitting between lines a_1 and a_2 is that it arises from r_s/m_s effects at the sulfone group to the left. One of the splittings of the triplet of lines a_3, a_4, and a_5 has the same origin, but the other splitting probably derives from the r_s/m_s structures at the sulfone group to the right. Thus the Me* shift is sensitive to the chirality of five neighboring methine carbons.



$$\text{—CH(Me)—CH(Me)—SO}_2\text{—CH(Me)—CH}_p\text{(Me*)—SO}_2\text{—CH}_q\text{(Me)—CH(Me)—SO}_2\text{—CH(Me)—}$$

II

The second set of five lines in the region—those that grow in intensity as the m_c content rises—also have a large splitting between (a_6,a_7) and (a_8,a_9,a_{10}) from the r_s/m_s effect. The lines a_7 and a_{10} do not appear immediately as m_c content rises, which suggests that they are caused by the presence of a second neighboring m_c group to the left-hand side.

(b) Methine Region. We show in Figure 5 the 100.6-MHz spectrum near 50 ppm of four poly(but-2-ene sulfone)s, which in the order (a) U23, (b) U27, (c) SCH/2, and (d) SCH/7 have, respectively, a 0.121, 0.232, 0.401, and 0.638 proportion of m_c-centered sequences. Polymers such as U101, which were made at ambient temperatures, had the four peaks b_1, b_2, b_3, and b_4, which have previously been assigned to the methine carbons of r_c-centered diads in a chain containing only these structures,[16] that is, as $r_cr_cr_c$-centered sequence triads. The four methine lines are created by the m_s/r_s diad relationship of the methine carbons on each side of the two sulfone groups linked directly to the r_c but-2-ene residue:[16] b_1, $m_sr_cm_s$; b_2 and b_3, $m_sr_cr_s$; b_4, $r_sr_cr_s$. (A similar effect has been noted in the spectra of the two models, in the shifts of the methyl groups of the terminal isopropyl groups; see Table IV.) The splitting of peaks b_3 and b_4 in the 100.6-MHz spectra of samples U23 and U101[43] we associate with the next variable chiral feature along the chain, which is the m_s/r_s diad relationship of the methine carbons on the further side of the nearest r_c residue to the carbon concerned: the splitting, of the order of 0.11 ppm, is caused by the chirality of the carbon five bonds along the chain.

As the proportion of m_c-centered peaks increases from sample U23 to sample SCH/7, the spectra become modified progressively: the relative intensities of the b_1 to b_4 peaks fall, though not in concert, so new structures may have shifts that coincide in these places: for example, the downfield b_3 peak is more prominent in proportion to the upfield b_1 peak in the spectrum of sample SCH/7 than it is in the spectrum of sample U23. New peaks appear both above 55.8 ppm and below that, down to about 60 ppm. The shifts of the central methines of the two models were the following: meso, 52.5 ppm; racemic, 50.2 ppm (Table IV), which is the same order as the meso and racemic residues of the copolymers, but these model compound shifts are not helpful in assigning the new peaks in detail. If for the copolymers U101, U23, U27, SCH/2, and SCH/7, which have, respectively, 2.4%, 12.1%, 23.2%, 40.1%, and 63.8% m_c structures, the areas of the methine region down to 55.8 ppm are 2.5%, 11.6%, 23.9%, 38.2%, and 61.0%, then the areas of the region between 55.8 and 53.5 ppm are, respectively, 3.3%, 3.9%, 4.5%, 6.5%, and 10.0%. It is clear that the first two sets of figures are in good correspondence and that the latter region derives from r_c structures that are not flanked by two other r_c sequences. It is possible to assign new peaks that appear in the region above 55.8 ppm to two types of r_c structure, those in sequences of $r_cr_cm_c$ or $m_cr_cr_c$ and those in $m_cr_cm_c$ sequences. As the proportion of m_c residues rises, shifts from the first type of three residue sequence should appear and rise more quickly than shifts of the second type. In the former category are the peaks we have labeled b_5 and b_6: they are clearly seen in the spectrum of U23, but the second category of b peaks appear only in the spectrum of U27, where b_7, b_8, and b_9 appear. A further peak, b_{10}, appears in the spectrum of sample SCH/7.

Peaks from the methine carbons of m_c-centered sequences first appear at 55.66 ppm (d_1) and at 57.50 ppm (d_2); the latter peak grows relative to the former as m_c residue content rises and sequences of m_cm_c and $m_cm_cm_c$ develop. The signal maximum comes further down at 57.95 ppm (d_3) in the spectrum of sample U27 and develops shoulders, which become resolved as peaks in the spectrum of sample SCH/7, at 58.02 ppm (d_5) and 58.32 ppm (d_4). The changes in relative areas of the two main peaks and the minor changes in their positions are the consequence of sequence effects. In the spectra of the three polymers U27, SCH/2, and SCH/7 the upfield d component is, respectively, 64%, 47%, and 30% of the total area of the d peaks, which compares quite well with

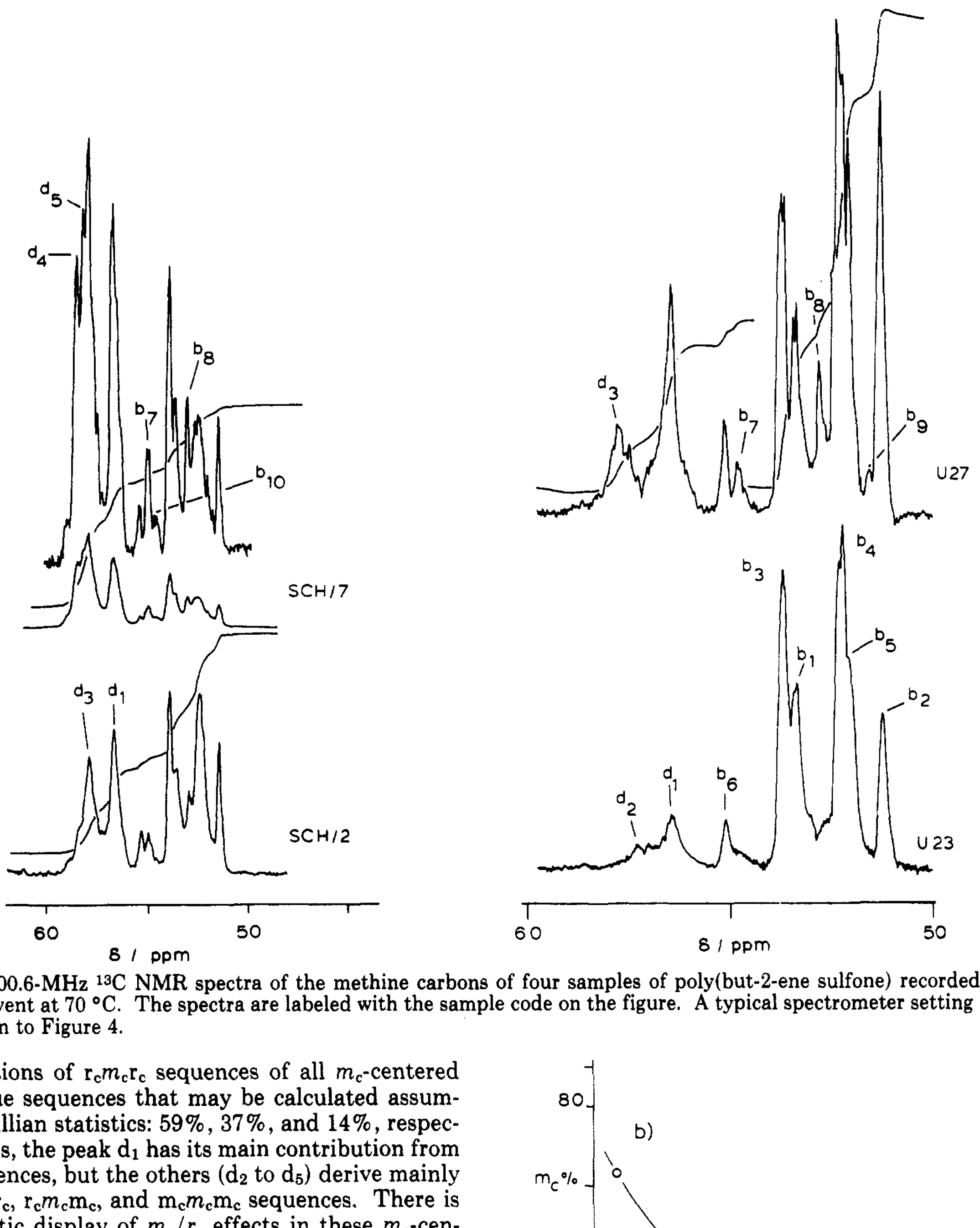


Figure 5. 100.6-MHz ^{13}C NMR spectra of the methine carbons of four samples of poly(but-2-ene sulfone) recorded in dimethyl sulfoxide solvent at 70 °C. The spectra are labeled with the sample code on the figure. A typical spectrometer setting used is given in the caption to Figure 4.

the proportions of $r_cm_cr_c$ sequences of all m_c-centered triad residue sequences that may be calculated assuming Bernouillian statistics: 59%, 37%, and 14%, respectively. Thus, the peak d_1 has its main contribution from $r_cm_cr_c$ sequences, but the others (d_2 to d_5) derive mainly from $m_cm_cr_c$, $r_cm_cm_c$, and $m_cm_cm_c$ sequences. There is no systematic display of m_s/r_s effects in these m_c-centered structures.

The spread of shifts for the r_c-centered structures, 3.8 ppm, is much greater than the spread for the m_c-centered structures, 1.4 ppm. Each methine carbon is placed β in the chain with respect to a sulfone group, whose anisotropy permits shift influences of the order of up to 9.4 ppm, depending on the conformation of the S–C bond.[18] Insofar as the dispersion of shifts that we have observed is associated with the γ shift term of the sulfone oxygens, we may conclude that C–S bond conformations in the r_c-centered residues, particularly, those adjacent to one m_c residue, are more biased toward one particular conformation than are the conformations of the r_c-centered residues.

D. Reaction Mechanism. For the two series of polysulfones obtained from *cis*- and *trans*-but-2-enes we plot in Figure 6 against the temperature of preparation the mole fraction of m_c residues, measured from the methyl region of the ^{13}C NMR spectrum. The value of 63% m_c obtained for the two polymers prepared from *trans*-olefin at −95 °C compares well with the value of 55% found at that temperature when a terpolysulfone of but-1-ene and *trans*-but-2-ene was made at the same temperature.[31] It is clear that if the temperature of preparation is below −60 °C, there are two distinct types of polymer, but if the preparation temperature is above that value, the chains contain predominantly r_c units, irrespective of which olefin was the precursor. Only when

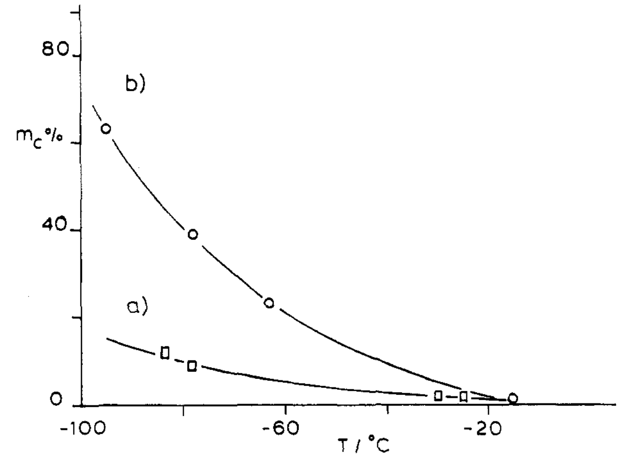


Figure 6. Plots of meso residue content against temperature of preparation, for the series of poly(but-2-ene sulfone) polymers prepared from *cis*- and *trans*-but-2-ene, curves a and b, respectively.

prepared at the low temperatures do the alkene residues in the polymer chains have structures that depend on the structure of the olefin used.

During reactions in the high-temperature range when alkyl radicals terminate the growing polymer chain, they are present long enough before the formation of the next C–S bond for an equilibrium species to form by bond rotations. Apparently from the equilibrium species the r_c structures almost invariably form, perhaps because the planar radical is attacked from one side only. In Scheme I, steps b and c may be followed successively, or if the charge-transfer complex is involved, step a must then be followed in nearly every case by a dissociation (b) and radical equilibration before (c) and then another (a) step takes place.

For reactions at low temperatures we conclude that the charge-transfer complex is involved, as the polymer structure is directly related to which olefin is used in the manner of Scheme II. While the horizontal step a predominates when the *trans*-olefin is the precursor to the m_c residues, there is a small fraction of r_c residues also obtained, but we cannot decide whether this is because step a is regularly followed by step b, a radical equilibration, and then step c, or because step a may sometimes be followed by steps d and c. When the *cis*-olefin is the precursor the chain is predominantly r_c, but there is an increasing tendency for the m_c structure to form: evidently then the radical equilibration tends a little toward the precursor for the m_c structure.

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Supplementary Material Available: Full details of the crystal structure determination including tables of fractional atomic coordinates, anisotropic and isotropic thermal parameters, bond lengths, and bond angles for *meso*-2,3-bis(isopropylsulfonyl)butane (5 pages); listing of observed and calculated structure factors for *meso*-2,3-bis(isopropylsulfonyl)butane (9 pages). Ordering information is given on any current masthead page.

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Registry No. *meso*-I, 125330-28-1; *rac*-I, 125330-29-2; SO$_2$, 7446-09-5; propane-2-thiol, 75-33-2; 2,3-dichlorobutane, 7581-97-7; (*cis*-2-butene)(SO$_2$) (copolymer), 34903-08-7; (*trans*-2-butene)(SO$_2$) (copolymer), 34903-09-8; *cis*-but-2-ene, 590-18-1; *trans*-but-2-ene, 624-64-6.