NMR Determination of the Microstructure of Poly(vinyl chloride sulfone). I. ^{1}H Spectra

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ABSTRACT: ^{1}H NMR spectra of poly(vinyl chloride-β,β-d_2 sulfone)'s with different compositions discriminated effects on the methine proton resonance due to (i) the proximity of the SO_2 group at each end of the SV_nS sequence, (ii) the proximity of SO_2 groups at the ends of neighboring sequences, (iii) the "internal" diad tacticity in SV_nS sequences with $n \geqslant 2$, and (iv) the "across SO_2" diad tacticity in VSV comonomer triads (V = -CHCl-CH$_2$-, S = -SO$_2$-). Copolymers prepared above 0 °C contained few SVS sequences, and those below 0 °C few SVVVS sequences, whereas copolymers prepared at 0 °C contained >95% of SVVS sequences. The internal stereoregularity in SVVS sequences increased with copolymerization temperature. The ^{1}H NMR spectra of the fully protonated copolymers were complex due to the additional effects of the methylene proton resonances and vicinal and geminal spin–spin coupling. Four resonance areas could be assigned to VV (methylene), VV (methine), VS (methylene), and SV (methine) comonomer diads. Dehydrochlorination, which occurred during radiation-initiated polymerization, or in DMSO solutions, produced a low-field resonance due to SE diads (E = -CH=CH-). Vicinal coupling in SVS sequences indicated a predominantly trans conformation in acetone solutions.

Vinyl chloride (VC) and sulfur dioxide copolymerize by a free radical mechanism to form poly(vinyl chloride sulfone) in which the average macroscopic composition, expressed by the ratio $\bar{n}$ of VC to SO_2 units in the chain, is variable.[1–3] The value of $\bar{n}$ depends on the polymerization temperature and the comonomer composition. This is in contrast to poly(olefin sulfone)'s, which have regularly alternating structures with $n = 1.0$,[4] with the exception of poly(ethylene sulfone) prepared in the gas phase.[5]

The relationship between copolymer and comonomer compositions does not obey first-order Markoff statistics (Lewis-Mayo copolymerization model) at any temperature above −78 °C.[6] The copolymerization therefore follows a more complex mechanism, which may include participation of comonomer complexes, depropagation, or penultimate unit effects. Several of these models have been suggested for the copolymerization of styrene with SO_2 in the formation of a variable-composition copolymer.[7–10]

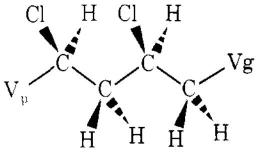
The relationship between macroscopic copolymer composition and comonomer composition cannot always be used to unambiguously distinguish between the various models. Several authors[11–13] have pointed out that additional information could be provided by analyses of monomer sequence distributions. The experimental determination of monomer sequence distributions is often difficult, although a number of techniques, including hydrolysis,[14] pyrolysis gas chromatography,[15] mass spectrometry,[16] infrared[17] and uv[18] spectroscopy, dipole moments,[19] and NMR[20–22] have been used for suitable copolymers. Recently, increasing success has been achieved with NMR by using high fields[23] or partially deuterated monomers.[24]

NMR also provides information on the stereochemistry of the copolymers. If an asymmetric or pseudo-asymmetric center is present, then there will also be a distribution of configurational sequences. This distribution will depend on the copolymerization mechanism and may have a strong influence on the properties of the copolymer.

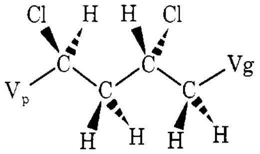
NMR studies have been made of the microstructure of 1:1 alternating poly(olefin sulfones)'s, of the analogous poly(olefin sulfide)'s, and of poly(ethylene sulfone)'s and poly(styrene sulfone)'s with various macroscopic compositions. Ivin and Navratil[24] reported the first detailed NMR investigation of a poly(olefin sulfone). They found that the methylene protons in partially deuterated poly(propylene sulfone) were sensitive to triad stereosequences. Similar behavior was observed in poly(propylene sulfide).[25,26] Ivin et al.[27] have also reported the ^{1}H NMR spectra of six poly(olefin sulfone)'s. Ovenall et al.[23] have measured the sequence distribution in poly(ethylene sulfone) by ^{1}H NMR. The lack of configurational isomerism in this copolymer enabled the ^{1}H NMR spectrum to be readily interpreted. Iino et al.[28] have obtained some monomer sequence information for poly(styrene-β,β-d_2 sulfone) by ^{1}H NMR, although this differs from limited pyrolysis–mass spectrometry results of Hummel and Schüdemage.[16]

Poly(vinyl chloride sulfone)'s will have comonomer distributions in which SO_2 groups are always isolated, since SO_2 does not homopropagate, and blocks of vinyl chloride units will always be capped at both ends by SO_2, except at chain ends. Thus, we can represent the comonomer distribution of a particular copolymer by the number fractions of SVS, SV_2S, . . . , SV_nS sequences (S = SO_2, V = VC), which we will represent by N(1), N(2), etc.

The resultant stereochemical possibilities are complex. Vinyl chloride sequences of sufficient length will contain sites of steric isomerism which are effectively pseudo-asymmetric and analogous to those in poly(vinyl chloride). We can therefore define meso (m) and racemic (r) relative configurational placements for pairs of vinyl chloride units in these sequences.



m



r

However, in short vinyl chloride sequences, or at the ends of long sequences, the effects of the SO_2 capping groups must be considered, as they cause adjacent methine carbons to be genuinely asymmetric and nonequivalent. The designation of relative configurational placements between two such asymmetric centers by m and r is not appropriate, and the R, S nomenclature will be used.

Thus for SVVS sequences, the two nonequivalent, configurational combinations may be represented by S,R and S,S (related to m and r, respectively, in infinite V sequences). Each copolymer chain will be a racemic modification of the two chiralities, so that there will always be corresponding amounts of the R,S and R,R mirror-image configurational placements. It is important to note that mirror-image placements cannot be distinguished by NMR in

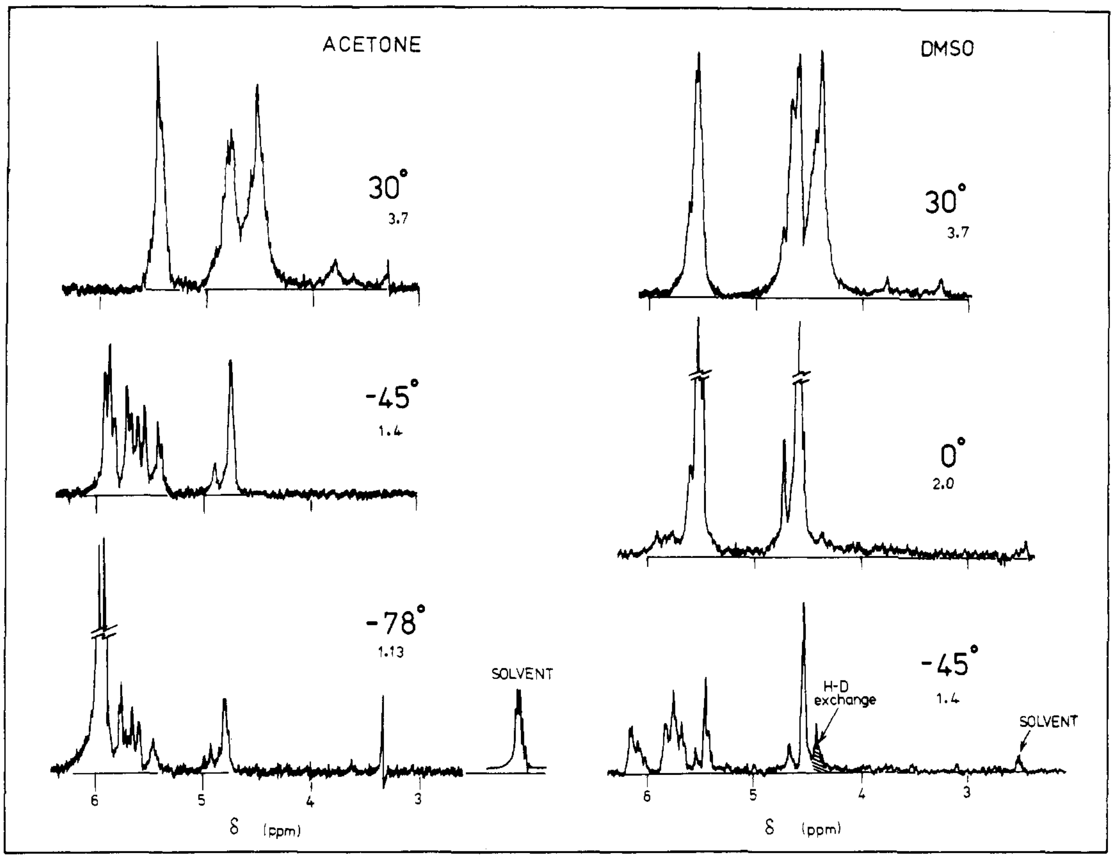
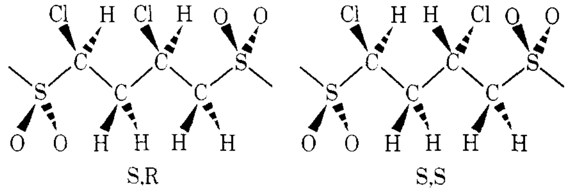


Figure 1. ^1H NMR spectra of poly(vinyl-β,β-d_2 chloride sulfone)'s at 100 MHz in acetone and DMSO. Polymerization temperatures (T_p) and copolymer compositions ($\bar{n}$ values) as indicated.

an achiral solvent. However, considering SVVS sequences for example, we can distinguish S,R from S,S (R,S from R,R), but not S,R from R,S and S,S from R,R.

SVVS



The structures above represent "internal" diad tacticities. We can also distinguish the relative configurational placements across SO_2 groups in VSV sequences for which we will use the notation S/R (not distinguishable from R/S) and S/S (R/R). The poly(vinyl chloride sulfone) chains are directional. Therefore R/R/S (S/S/R) triad stereo sequences are, in principle, distinguishable from S/R/R (R/S/S) stereo sequences. It is important to distinguish between comonomer and stereo sequences, in the sense that although VSV is a comonomer triad, it defines a vinyl chloride diad stereo sequence. The abbreviated formulas, e.g., SVS, used to represent the comonomer sequences are also directional in that V represents -CHCl-CH_2-.

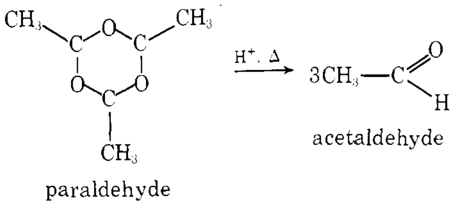
We have investigated the microstructure of poly(vinyl chloride sulfone)'s by ^1H NMR in an endeavor to elucidate the monomer sequence distributions in sufficient detail to enable us to distinguish between different possible models for the copolymerization mechanism. These models are not satisfactorily distinguished by the comonomer–copolymer composition relationships. Poly(vinyl chloride sulfone)'s were prepared with a range of $\bar{n}$ values from 1.03 to 4.1 by using polymerization temperatures from −95 to +46 °C and various comonomer compositions. Copolymers were prepared from vinyl-β,β-d_2 chloride in order to aid the interpretation of the NMR spectra. The spectra of the deuterated copolymers showed that the chemical shift of the methine proton depended on the proximity of up to four SO_2 groups (i.e., nearest and next-nearest pairs) and on diad and triad configurational distributions.

The spectra of the undeuterated copolymers were more complex on account of the methylene resonances and vicinal and geminal proton couplings. However, the vicinal coupling enabled the conformation of the chain about the C–C bond in SVS sequences to be determined.

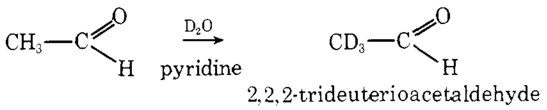
Experimental Section

Vinyl chloride (polymerization grade, inhibitor-free) was provided by ICI Australia Ltd. Water was removed by 3A molecular sieves and no other impurities were detected above 10 ppm by gas chromatography. SO_2 (Matheson Co.) was dried over molecular sieves and P_2O_5.

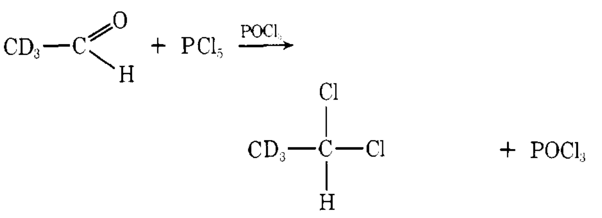
Vinyl-β,β-d_2 Chloride. 1-Chloro-2,2-dideuterioethene (vinyl-β,β-d_2 chloride) was prepared by the reaction sequence in eq 1–4.



(1)

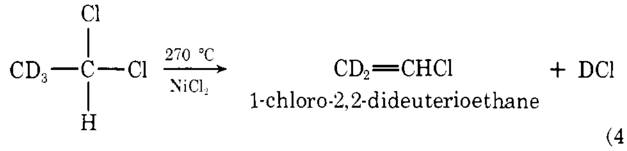


(2)



$$\mathrm{CD_3CHO} + \mathrm{PCl_5} \xrightarrow{\mathrm{POCl_3}} \mathrm{CD_3CCl_2H} + \mathrm{POCl_3} \qquad (3)$$

1,1-dichloro-2,2,2-trideuterioethane



$$\mathrm{CD_3CCl_2H} \xrightarrow[\mathrm{NiCl_2}]{270\ ^\circ\mathrm{C}} \mathrm{CD_2{=}CHCl} + \mathrm{DCl} \qquad (4)$$

1-chloro-2,2-dideuterioethane

All procedures were carried out under a nitrogen atmosphere. The overall yield was 4.1%.

Step 1. Paraldehyde (Unilab laboratory reagent) was dried over Na_2SO_4 and then heated at 42 °C for 4 h with 0.5 mol % of *p*-toluenesulfonic acid as catalyst.[29] Acetaldehyde was collected in a condenser at −10 °C.

Step 2. D_2O (99.75%), 73 ml, acetaldehyde, 12.5 g, and pyridine, 2.28 ml, were degassed at −85 °C and sealed in a glass ampule.[30] The exchange was allowed to proceed at 50 °C for 20 h. Partially deuterated acetaldehyde (70% yield, 77% D in methyl group) was obtained by fractional distillation and collected in D_2O. The exchange was repeated twice to give 98% deuterium substitution. Crotonaldehyde was the main product if the exchange was carried out at 100 °C, resulting from dehydration of the aldol condensation product, β-hydroxybutyraldehyde.

Step 3. The chlorination flask contained 94 g of PCl_5 and 30 ml of $POCl_3$ (included to ensure that the initial reaction was homogeneous) and was immersed in an ice-water bath.[31] Acetaldehyde was added over a 2-h period and the temperature maintained below 5 °C. The CD_3CHCl_2 was isolated (20% yield) by distillation and washed free of HCl and $POCl_3$ by ice-water. The ^1H NMR spectrum in $CDCl_3$ showed a sharp singlet at 5.9 ppm (CH) and a very weak multiplet at 1.24 ppm (CD_2H); the relative areas indicated ≥98% substitution.

Step 4. The dehydrochlorination was carried out by passing the CD_3CHCl_2 in the vapor phase at 270 °C over $NiCl_2$ (32 g) absorbed on alumina powder (200 mesh, 200 g).[32] Unreacted CD_3CHCl_2 was collected at −10 °C and $CD_2{=}CHCl$ at −78 °C. The efficiency of the catalyst deteriorated rapidly due to carbon formation.

Copolymerization. Comonomer mixtures were prepared on a vacuum line by successively condensing measured pressures of SO_2 and VC from a calibrated bulb at 30 °C into glass ampules, which were then sealed under vacuum. ^{60}Co γ irradiations were carried out at ≈0.5 Mrad h^{-1} in the pond facility of the Australian Atomic Energy Commission or in a Gammacell. The unreacted comonomer mixture containing vinyl-β,β-d_2 chloride was recovered by distillation on a vacuum line.

For chemical initiation, 3–5 vol % of a 1:4 *tert*-butyl hydroperoxide (Koch-Light; 70%) solution in methanol was freeze-thaw degassed and sealed in a compartment separated from the comonomer mixture in the ampule by a thin glass membrane. After temperature equilibration, the glass membrane was broken and the initiator and comonomer solutions mixed by shaking. This procedure was necessary because the copolymerization was very rapid at low temperatures and appreciable polymer was formed during thawing and warming of a frozen mixture of the comonomers and initiator. Polymerization was stopped by opening the ampule at the polymerization temperature and transferring the contents into excess methanol.

The copolymer precipitated as a white solid during all polymerizations. After washing with methanol, the copolymers were dried in a vacuum oven at 30 °C. Copolymers with high SO_2 content were susceptible to thermal degradation at relatively low temperatures. Macroscopic compositions of the copolymers were determined by microanalysis for C, H, S, and Cl.

NMR Spectra. The ^1H NMR spectra were recorded at 100 MHz with tetramethylsilane (TMS) as internal standard using a JEOL JNM-MH-100 spectrometer. The NMR solvents were perdeuterated acetone, tetrahydrofuran (THF), or DMSO and the probe temperature was 50 °C. This was the optimum temperature for high resolution without serious decomposition of the copolymers, especially for $\bar{n} < 2.0$.

Table I
Details of Preparation of Poly(vinyl-β,β-d_2 chloride sulfone)

No.	x_{VC} comonomer	Copolym temp, °C	Yield, wt %	Initiation method	$\bar{n}$
1	0.33	−78	7.0	*t*-BuOOH	1.13
2	0.44	−45	3.5	*t*-BuOOH	1.4
3	0.40	0	21.0	γ	2.0
4	0.35	30	7.0	γ	3.7

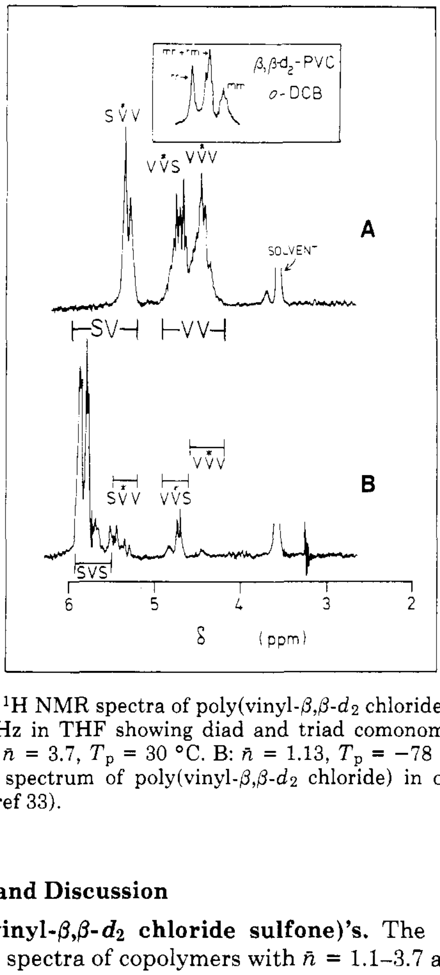


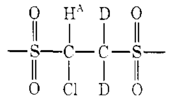
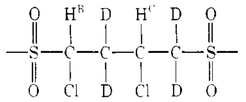
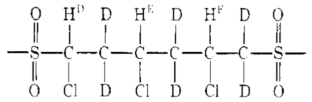
Figure 2. ^1H NMR spectra of poly(vinyl-β,β-d_2 chloride sulfone)'s at 100 MHz in THF showing diad and triad comonomer assignments. A: $\bar{n}$ = 3.7, T_p = 30 °C. B: $\bar{n}$ = 1.13, T_p = −78 °C. Insert: ^1H NMR spectrum of poly(vinyl-β,β-d_2 chloride) in o-dichlorobenzene (ref 33).

Results and Discussion

Poly(vinyl-β,β-d_2 chloride sulfone)'s. The 100-MHz ^1H NMR spectra of copolymers with $\bar{n}$ = 1.1–3.7 are shown in Figure 1. Dehydrochlorination was negligible for the solutions in acetone and only serious in DMSO for $\bar{n}$ = 1.4. Peaks due to TMS, solvent, and HCl–H_2O in DMSO have been omitted for clarity. The HCl–H_2O peak was readily assigned by recording a second spectrum of the sample ≈15 min after the first, when a downfield shift was observed due to further dideuteriochlorination and proton exchange. The details of the preparation of these copolymers are given in Table I.

Assignment of Diad Monomer Sequences. The assignments of the resonance areas to diad monomer sequences are shown in Figure 2A. The high-field resonance area (5.0–4.2 ppm) can be assigned to VV diads (arising from VV*S and SVV* triads and longer VC blocks with the methine proton situated ≥β from SO_2, by comparison with the spectrum of poly(vinyl-β,β-d_2 chloride)).[33] The asterisk indicates the monomer unit in which the proton under observation is located, α, β, etc., refers to the proximity of the carbon atom, to which the methine proton is bonded, to the S atom, as shown in Table II, and V represents a vinyl chloride unit in the direction -CHCl–CH_2-. The low-field resonance area (6.2–5.4 ppm) is then assigned to SV diads, i.e., α-sulfonyl methine protons, which will comprise SVS,

Table II
Proximity of Methine Proton to $>SO_2$ in Various Monomer Sequences in Poly(vinyl-β,β-d_2 chloride sulfone)

SVS	 $-SO_2-CH^{A}Cl-CD_2-SO_2-$	A = α, β
SVVS	 $-SO_2-CH^{B}Cl-CD_2-CH^{C}Cl-CD_2-SO_2-$	B = α, δ C = β, γ
SVVVS	 $-SO_2-CH^{D}Cl-CD_2-CH^{E}Cl-CD_2-CH^{F}Cl-CD_2-SO_2-$	D = α, ϕ E = γ, δ F = β, ϵ

SV*VS and sequences with longer VC blocks, i.e., all SV*V_mS with $m \geq 0$.

The VV diad resonance area in Figure 2A can be further divided into two major peaks (5.0–4.6 and 4.6–4.2 ppm). The low-field peak can be assigned to VS diads, arising from SVV*S and similar sequences (SV_mV*S with $m \geq 1$), i.e., the β-sulfonyl methine proton. The high-field peak is then due to methine protons situated $\geq\gamma$ from SO_2.

The effect of the proximity of the SO_2 group is clearly shown by the increasing upfield chemical shift of the methine proton $\alpha \rightarrow \beta \rightarrow \geq \gamma$ (relative to SO_2).

Assignment of Triad Monomer Sequences. The resonances due to different triad monomer sequences can be assigned by considering the relative intensities of the various peaks in the VS, SV, and VV diad areas as a function of $\bar{n}$.

VV Region. In the copolymer with $\bar{n}$ = 1.13, shown in Figure 2B, SVS sequences must predominate. VVV sequences should be very infrequent; therefore, the resonances in the VV diad region in Figure 2B are assigned to the β-sulfonyl methine protons in VV*S triads. Furthermore, this triad must be derived from SVV*S tetrad sequences in this copolymer.

In the copolymer with $\bar{n}$ = 3.7, VVV triad sequences should be most frequent among the comonomer triads. The low-field peak in the VV region is assigned to VV*S triads as before and the high-field peak to VVV triads as indicated above. The relevant protons are shown in Table II.

SV Region. The α-sulfonyl methine resonance in SV diads also shows the difference in shielding between the positions β and $\geq\delta$ with respect to the second neighboring SO_2 groups. In the copolymer with $\bar{n}$ = 1.13, the most intense resonance area (and furthest downfield) is assigned to SVS triads in which the methine proton is α to one SO_2 and β to the other. This assignment is extended to the high-field side of the intense pair of doublets to include the weak resonances shown; these will be assigned later to higher comonomer sequences.

The copolymer with $\bar{n}$ = 3.7 does not contain any SVS sequences (further evidence for this is given later), therefore the SV diad resonances in this copolymer are due to SV*V triads. Consequently, the high-field peaks in the SV diad region of the copolymer with $\bar{n}$ = 1.13, having the same chemical shift as those in the copolymer with $\bar{n}$ = 3.7, must also be due to SV*V triads.

Fine Structure of Resonance Derived from VV Diads. VV*S Triads. $\bar{n}$ < 2. The VV*S triad region of the copolymers with $\bar{n}$ = 1.13 and 1.4 is shown on an expanded scale in Figure 3. A solvent effect on the chemical shifts and on the resolution was observed, the best resolution being obtained in THF. The VV*S triad corresponds to an SVV*S tetrad in the copolymer with $\bar{n}$ = 1.13, because the proportion of VC blocks >2 must be almost negligible in this nearly alternating structure. Therefore, it is necessary to explain the multiplet resonance of the β-sulfonyl methine proton in SVV*S tetrads.

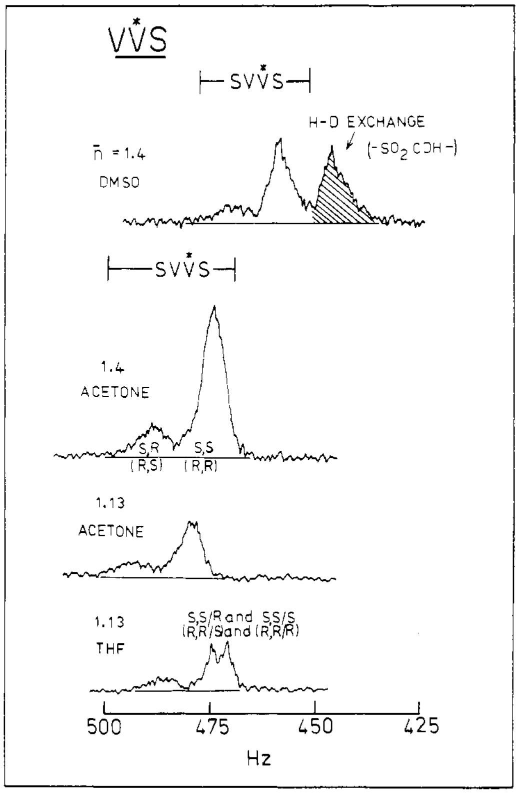


Figure 3. Resonances of β-sulfonyl methine protons in poly(vinyl-β,β-d_2 chloride sulfone)'s with $\bar{n}$ = 1.13 and 1.4. Comonomer compositions, solvents, and assignments as indicated.

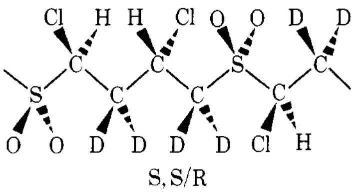
The most reasonable explanation of the observed 0.13 ppm difference between the low-field peak and the more-intense high-field peak (which is a doublet in THF and shows incipient splitting in acetone) is tacticity. It is unlikely to be the effect of neighboring sequence lengths in the copolymer with $\bar{n}$ = 1.13, since the SVV*S sequences should be distributed at random and each have single VC neighbors, i.e., –SV*SVVS*VS–. Furthermore, the nearest SO_2 unit outside the SVV sequence is ≥5 main-chain bonds distant from the methine proton under consideration so that the chemical shift difference between SVV*SVS and SVV*SVVS should be negligible.

It is therefore proposed that "internal" VV diad configurational sequences, S,R (R,S) and S,S (R,R), are being resolved.

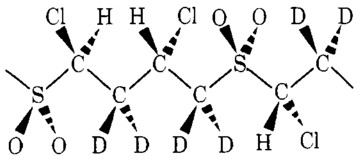
The diad assignment S,R (R,S) or S,S (R,R) to each resonance cannot be made unambiguously without a study of the appropriate model compounds of known stereochemistry. An analogy with PVC, where the methine proton resonance derived from the r diad (related to S,S and R,R) appears at lower field than that in the m diad, cannot be used, as the highly anisotropic sulfone group will play a major role in determining the chemical shifts of the protons. A tentative assignment can be made by considering steric interactions in the copolymer. Molecular models indicate that the S,S (R,R) diad in SVVS sequences should have appreciably less steric hindrance than the S,R (R,S) diad. Therefore, the most intense peak, which occurs at higher field, is likely to be due to the S,S (R,R) diad. The intensities of the peaks in the copolymer with $\bar{n}$ = 1.13 (prepared at −78 °C) gave S,S (R,R):S,R (R,S) = 2.3, whereas the copolymer with $\bar{n}$ = 1.4 (prepared at −45 °C) showed the same splitting, but the intensity ratio had increased to 3.6, suggesting that the S,S (R,R) placement became more favored with increasing copolymerization temperature. This surprising result is in contrast to the usual effect of increasing temperature in favoring more random stereosequence placements.

The doublet splitting on the upfield peak in Figure 3 observed for the copolymer with $\bar{n}$ = 1.13 in THF (3.7 Hz) can also be explained by a tacticity effect. This splitting is less than between "internal" S,R (R,S) and S,S (R,R) diads. We therefore propose that it arises from "across-SO_2" stereoisomeric placements, since the nearest asymmetric center is then three main-chain bonds distant (compared with two for the inner placement). The doublet can be assigned to:

SVV*SV



S,S/R



S,S/S

(including the corresponding mirror-image pairs R,R/S and R,R/R) although which stereoisomer corresponds to which peak cannot be determined from the present evidence. It is unlikely that the splitting arises from R/S,S (S/R,R) and S/S,S (R/R,R) stereosequences in VSVV*S comonomer sequences, since five main-chain bonds separate the asymmetric centers in this case. The low-field resonance assigned to the S,R (R,S) diad did not appear to be sensitive to this "triad" tacticity.

$\bar{n}$ = 2. The VV*S triad region in copolymers with $\bar{n}$ = 2.0 and 3.7 is shown in Figure 4 (the copolymer with $\bar{n}$ = 1.4 is included for comparison). There is an upfield shift in the VV*S triad resonance in DMSO ($\bar{n}$ = 2) compared to the spectrum in acetone ($\bar{n}$ = 1.4), DMSO was the only suitable solvent for the copolymer with $\bar{n}$ = 2. A later analysis of the SVS triad region shows that the proportion of these sequences in the 2:1 copolymer is almost negligible; consequently, for the composition to be 2:1 (verified by microanalysis) the proportion of SVVVS sequences will also be very small. Hence, the remarkable spectrum of the 2:1 copolymer in the VV*S region must be due to SVV*S tetrad sequences.

We propose that two "internal" tactic diads are again being resolved. The ratio of the two peaks (S,S (R,R):S,R (R,S)) is 5.9, confirming an increasing trend in this ratio with the increasing copolymerization temperature. The more intense peak, assigned to S,S (R,R) VV diads in SVV*S sequences, showed incipient splitting (*ca.* 0.5 Hz) which is most likely due to vicinal deuterium coupling. This could also be due to S,S/R (R,R/S) and S,S/S (R,R/R) "triad" stereosequences, which only appear to be well resolved in THF (the 2:1 copolymer does not dissolve in this solvent). Broad-band deuterium irradiation would have removed all vicinal deuterium coupling and enabled this point to be resolved, but this facility was not available to us. The very weak peak at high field (4.37 ppm) can be assigned to VV*V triad monomer sequences, to be discussed later.

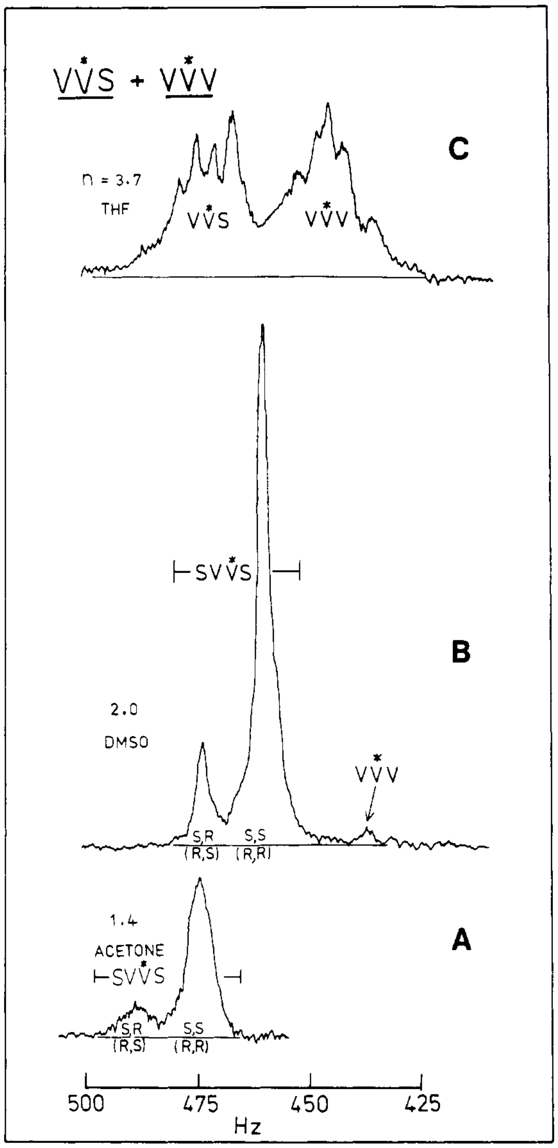


Figure 4. Resonances of β-sulfonyl and further removed methine protons in poly(vinyl-β,β-d_2 chloride sulfone)'s with $\bar{n}$ = 2.0 and 3.7. Copolymer compositions, solvents, and assignments as indicated.

$\bar{n}$ > 2. The VV*S triad resonance in the copolymer with $\bar{n}$ = 3.7 is complex. The multiplet nature of the peak indicates that there are several overlapping resonances due to higher monomer sequences, which are split by the large "internal" tacticity effect. However, it was not possible to discriminate different VC block lengths at 100 MHz for this copolymer.

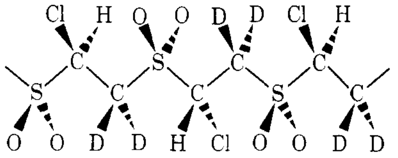
VV*V Triads. The VV*V triad sequence gives a strong resonance in the spectrum of the copolymer with $\bar{n}$ = 3.7. This resonance (like that from β-sulfonyl methine protons in VV*S triads) is complex, due to the overlap of chemical shifts due to different comonomer and stereo sequences. By analogy with PVC, triad stereosequences should be resolved and these could be assigned (in order of increasing field) to rr, rm (mr), and mm, as in PVC[33] (Figure 3). Triad rm and mr stereo sequences will be equivalent in long sequences of VC units. Thus three main peaks should be observed for VV*V resonances; the fact that four were observed indicates that effects due to tetrad monomer sequences need to be considered.

Fine Structure of Resonance Derived from SV Diads. The α-sulfonyl methine proton in SV diads showed the greatest sensitivity to monomer sequence length distribution and "across-SO$_2$" tacticity. Figure 5 shows the resonances derived from SV diads in copolymers with $\bar{n}$ = 1.13 and 1.4.

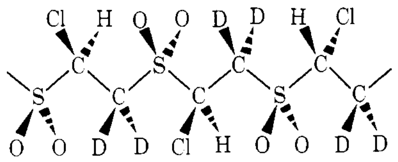
SVS Triads. In the spectrum of the copolymer with $\bar{n}$ = 1.13, the intense low-field doublet can be assigned to SVS triads (as discussed previously). Furthermore, since the composition of this copolymer is almost 1:1, this triad must correspond to SV*SVS*VS heptad comonomer sequences. Both the position and resolution of this doublet were solvent dependent. The resonance was at higher field and the resolution was better in THF than in acetone. The doublet splitting (6 Hz in THF, 4.5 Hz in acetone) can be assigned to S/S (R/R) and S/R (R/S) "across-SO$_2$" diad stereosequences.

However, triad stereosequences (in the pentad comonomer sequence VSV*SV) should be considered, as the asymmetric center in the central SVS sequences is equidistant from the asymmetric center to the left and to the right. The "triad" stereosequences are:

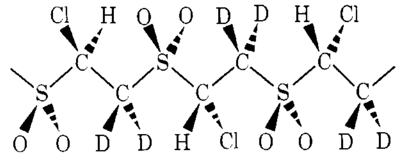
VSV*SV



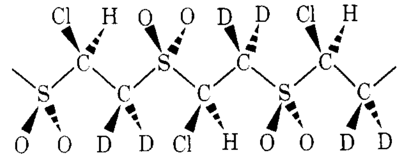
S/S/S



S/R/R



S/S/R



S/R/S

and the corresponding indistinguishable mirror-image sequences R/R/R, R/S/S, R/R/S, and R/S/R. Because the chain is directional, S/R/R is not equivalent to R/R/S, for example (although this nonequivalence may not be resolvable). Therefore, these four triad stereosequences could be expected to give rise to four peaks in the ^{1}H NMR spectrum. In THF, the two main peaks of the SVS resonance were each split by 1 to 2 Hz. However this is most likely due to vicinal deuterium coupling (the vicinal proton coupling constant is ≈14 Hz for the fully protonated copolymer), which could be confirmed by decoupling the deuterium atoms.

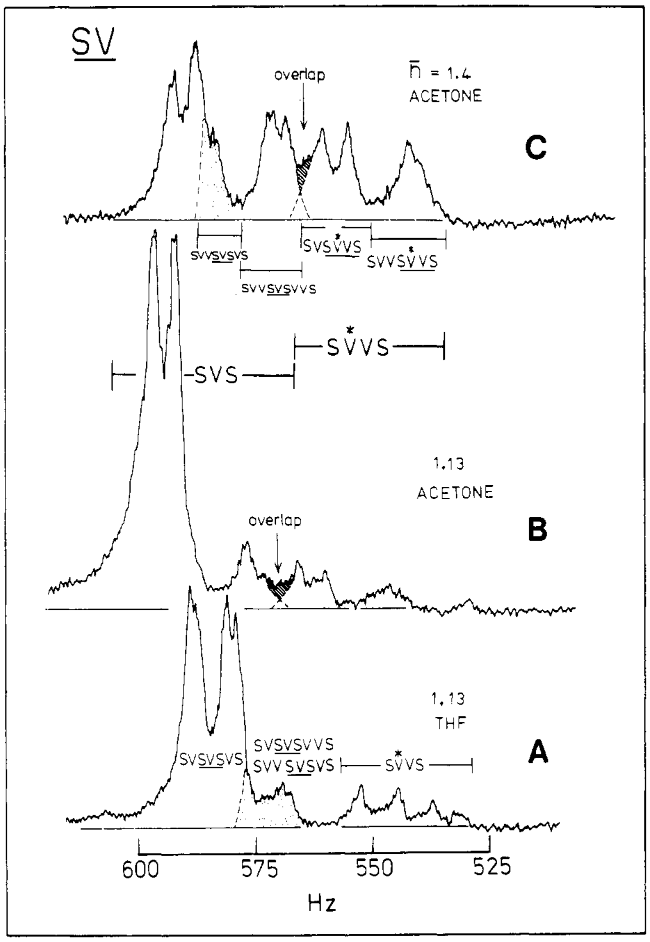
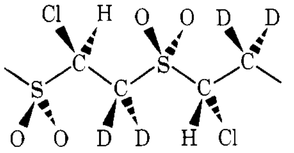


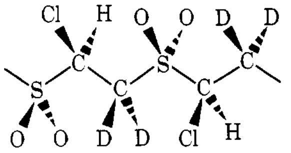
Figure 5. Resonances of α-sulfonyl methine protons in poly(vinyl-β,β-d_2 chloride sulfone)'s with $\bar{n}$ = 1.13 and 1.4. Copolymer compositions, solvents, and assignments as indicated.

It is therefore most probable that the methine proton in SVS sequences is sensitive to the configuration relative to only one of the neighboring asymmetric centers, i.e., to diad stereosequences. A similar observation was reported for the methine-^{13}C resonance in poly(propylene sulfide).[34] In the present case, it appears that the SVS methine proton is sensitive to the asymmetric center to the right. This conclusion is based on the observation that the β-sulfonyl methine proton in the S,S (R,R) "internal" diad of SVV*S was split into a doublet in the ^{1}H NMR spectrum of the copolymer with $\bar{n}$ = 1.13 in THF (Figure 3). This was previously assigned to S,S/R (R,R/S) and S,S/S (R,R/R) triad stereosequences in SVV*SVS hexad comonomer sequences (4 Hz splitting), since the asymmetric center to the right was closer than the one to the left. The diad stereo sequences leading to the doublet splitting of the SVS resonance are therefore assigned to:

SV*SV



S/S



S/R

and the corresponding mirror-image pairs R/R and R/S. This contrasts with the report by Boileau et al.[35] that the methine-^{13}C resonance in poly(propylene sulfide) is sensitive to diad structure with the asymmetric center to the left. In the present case a definite assignment requires a study of the appropriate model compounds.

The ratio of the S/S (R/R) and S/R (R/S) diad peaks was 1.3 (in both acetone and THF). The low-field resonance was more intense due to its broader shoulder and allowance for the partial overlap of the high-field resonance with the peak later assigned to SVV*SVS*VS and SV*SVS*VVS sequences. This ratio shows that S/S (R/R) and S/R (R/S) placements are not equally probable in the copolymer prepared at −78 °C. When poly(propylene sulfone) was prepared by free-radical catalysts, the probabilities of S/S (R/R) and S/R (R/S) diads were equal[24] although the S/S (R/R) placement was more favored with $CdCO_3$ or $ZnCO_3$ initiation of propylene sulfide polymerization.[25]

Higher Monomer Sequences Derived from SVS Triads. The changes in relative peak areas in the SV diad region with $\bar{n}$ show that the SVS resonance is sensitive to higher comonomer sequences. The doublet at low field has already been assigned to SV*SVS*VS heptad comonomer sequences, and its intensity diminishes as expected with increasing $\bar{n}$. This doublet is partially overlapped by a peak (indicated by the light shading in Figure 5) on its high-field side, giving the appearance of a triplet in the copolymer with $\bar{n}$ = 1.4. The area of this high-field shoulder on the SV*SVS*VS doublet resonance increased with $\bar{n}$, showing that it was sensitive to the number of VV sequences. The solvent effect (cf. spectra of the copolymer with $\bar{n}$ = 1.13 in the THF and acetone) indicates that this shoulder is derived from SVS sequences. It can therefore be assigned to SVS triads with an adjacent VV sequence: SVV*SVS*VS and SV*SVS*VVS. The area of the resonance from these sequences must correspond to twice the area of SVVS sequences in the copolymer with $\bar{n}$ = 1.13 since SVV*SVS*VVS sequences will be negligible in this sample. This enabled the peak to be assigned to the lightly shaded area in Figure 5.

In the copolymer with $\bar{n}$ = 1.4, SVS and SVVS sequences occur with almost equal probability, enabling the highest-field peak in the SVS region (in Figure 5C) to be assigned to SVV*SVS*VVS comonomer sequences (this peak also shows the S/S (R/R) and S/R (R/S) stereosequence diad splitting). The upfield shift of this peak relative to the SV*SVS*VS and SVV*SVS*VS peaks can be attributed to the further distance of sulfone units outside the SVS triad.

These distances (in terms of the number of intervening main-chain bonds) for the three possible SVS sequences with VV neighbors are:

4 7 6 7 6 5
SV*SVS*VVS SVV*SVS*VVS SVV*SVS*VS

and for the sequence with two VS neighbors: S^4VSVSV^5S. It therefore seems reasonable that the methine resonance (in the central *SVS* sequence) which is "4, 5" to the next-nearest sulfone unit should appear at lowest field, while that which is "6, 7" is at highest field in the indicated SVS region. Methine protons which are even further removed from neighboring sulfone units need not be considered for the copolymers with $\bar{n}$ = 1.13 and 1.4, since there is a negligible proportion of VVV sequences in these copolymers. Later results from the spectra of copolymers with $\bar{n} \geqslant 2$ show that "6, 7" and further removed SVS methine resonances are not distinguished. It also appears that the spectra do not discriminate "6, 5" and "4, 7" methine resonances, both of which are assigned to the lightly shaded area in Figure 5.

SV*V Triads. The α-sulfonyl methine resonances for SV*V triads (H = α, $\geqslant\delta$) occur at higher field than for SVS triads (H = α, β). Furthermore, for copolymers with $\bar{n} < 2$, the almost negligible proportion of VVV sequences allows the SV*V region to be assigned to SV*VS tetrad sequences (H = α, δ, Figure 5). The sensitivity of the α-sulfonyl methine proton in SVS triads to the sequence length of adjacent units can be attributed to the lack of "internal" tacticity effects smearing the resonances. However, this will not be the case for the α-sulfonyl methine resonances in SV*V sequences, which should be sensitive to this tacticity as well as the proximity of the next-nearest sulfone unit to the left (the next nearest to the right being removed by at least seven main-chain bonds and consequently having little effect).

$\bar{n}$ < 2. Figure 5 shows that the resonances assigned to the α-sulfonyl methine proton in SV*VS sequences are weak for the copolymer with $\bar{n}$ = 1.13, as to be expected from its composition. The resonances appear as a pair of doublets in THF. The low-field doublet can be assigned to SVS*V*VS* sequences and the high-field doublet to SVVS*V*VS* sequences. The chemical shift difference (≈15 Hz) reflects the effect of the distance to the next-nearest sulfone unit to the left (4 vs. 6 main-chain bonds). This shift is the same as that between SV*SVS* and SVV*SVS* resonances in THF, supporting the assignment. The doublet splitting on each resonance can be assigned to S,S (R,R) and S,R (R,S) "internal" stereo sequence diads. A reliable intensity ratio cannot be obtained from these weak resonances in the copolymer with $\bar{n}$ = 1.13. Previous results showed that the α-sulfonyl methine proton was not sensitive to "across-SO_2" tacticity with the asymmetric center to the left.

The SV*VS resonances are more intense in the copolymer with $\bar{n}$ = 1.4 (Figure 5C), since SVS and SVVS sequences are almost equally probable for this composition. Two main peaks are again observed and assigned to SVS*V*VS* (low field) and SVVS*V*VS* (high field) sequences. The high-field resonance does not show the proposed "internal" diad stereo sequence splitting in acetone, although the low-field resonance does. The overlap of the SVS*V*VS* resonance with the peak due to SVV*SVS*VVS sequences (as indicated in Figure 5C) does not allow a reliable intensity ratio to be determined, although the β-sulfonyl methine resonance from the same sequence (Figure 3) indicated that the S,S (R,R) diad predominates in this copolymer. The tacticity splitting is 5.5 Hz for the *SV*VS* α-sulfonyl methine proton (cf. 5 Hz for *VSVS* in acetone), although this may be due to an overlapping combination of "internal" and "across-SO_2" placements.

$\bar{n} \geqslant 2$. Figure 6 shows the SV diad region in copolymers with $\bar{n}$ = 2.0 and 3.7. Comparing the spectra (in acetone) of the copolymers with $\bar{n}$ = 1.4 and 3.7 supports the assignment of the high-field SV*VS resonance in the copolymer with $\bar{n}$ = 1.4 to SVVS*V*VS* sequences. The proportion of SVS*V*VS* sequences in the copolymer with $\bar{n}$ = 3.7 is zero, since no peaks are observed in the SVS triad region. Therefore SVVS sequences in this copolymer are derived from sequences of the type:

$$S(V)_pSVVS(V)_qS$$

with p, $q \geqslant 2$. The low-field peak in the SV diad resonance area for the copolymer with $\bar{n}$ = 3.7 may be assigned to the sequence with $p = q = 2$ by comparison with Figure 6A. However, there is considerable overlap with resonances from sequences with higher p and q values. Consequently, VC sequences of length 2 and 3 (and higher) cannot be discriminated quantitatively by the α-sulfonyl methine resonance in SV diads at 100 MHz, as was the case with the β-sulfonyl methine resonance in VS diads. The α-sulfonyl methine proton in SV*V sequences is not split by "internal" tactic placements to the extent observed for the corresponding β-sulfonyl methine in VV*S sequences. This reduced sensitivity may be ascribed to the dominant effect of the SO_2 unit on the α position.

The copolymer with $\bar{n}$ = 2.0 again shows a remarkable ^1H NMR spectrum (Figure 6B). The intense singlet from the α-sulfonyl methine proton is assigned to "internal" S,S (R,R) stereosequence diads in SV*VS sequences. The weak low-field peaks are assigned to SVV*SVS*VVS and

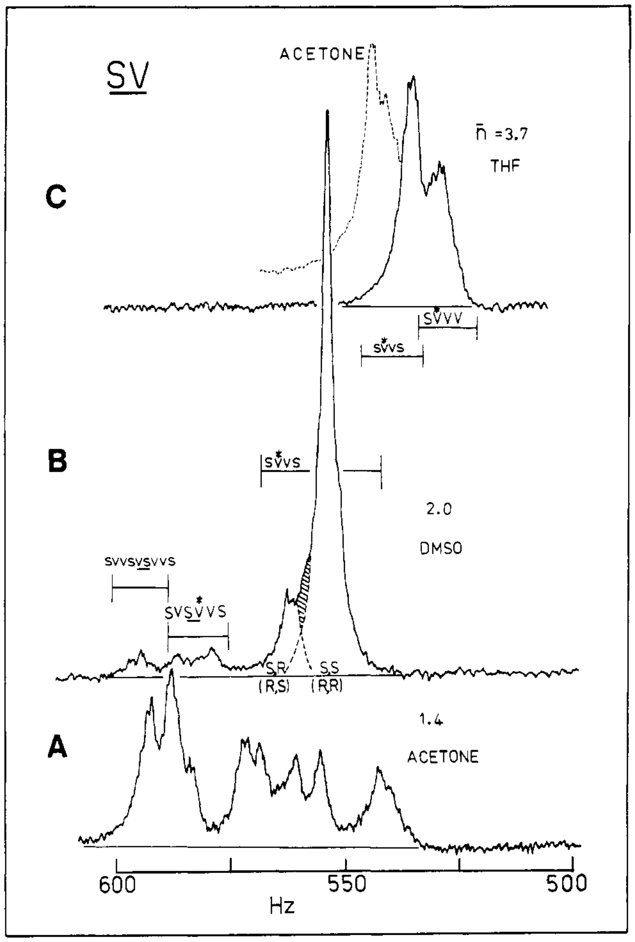


Figure 6. Resonances of α-sulfonyl methine protons in poly(vinyl-β,β-d_2 chloride sulfone)'s with $\bar{n}$ = 2.0 and 3.7. Copolymer compositions, solvents, and assignments as indicated.

SVSV*VS sequences as shown, in accord with previous assignments in the SV diad region. The small proportion of SVS sequences shows that the copolymer consists of 95% SVVS sequences. This also allows the small peak noted in Figure 4B on the high-field side of the main peak to be assigned to VVV sequences. There must be a small proportion of these for the composition to be precisely 2.0:1 (confirmed by microanalysis), given the presence of some SVS sequences.

Figure 6B shows a small low-field shoulder on the α-sulfonyl methine resonance in S,S (R,R) SV*VS sequences. This peak cannot be due to the effect of neighboring VC sequence lengths, since almost all sequences are SVVS. It is therefore assigned to the S,R (R,S) "internal" stereosequence diad, as for the β-sulfonyl resonance. The diad splitting is 8 Hz for the α-sulfonyl methine, which may be compared with 14 Hz for the β-sulfonyl methine (Figure 4). The ratio of S,S (R,R):S,R (R,S) diads is 5.8 from the α-sulfonyl methine resonances, and 5.9 from the β-sulfonyl methine resonances, which confirms the remarkable stereo and monomer sequence regularity of the 2:1 copolymer. This regularity was also observed in the ^{13}C {^{1}H} NMR spectrum of this copolymer.[6]

The apparent shoulder on the high-field side of the resonance from the S,S (R,R) SV*VS sequence may be due to vicinal deuterium coupling, as previous results indicated that this methine proton was not sensitive to tacticity "across-SO$_2$" with the asymmetric center to the left.

Evidence Supporting Peak Assignments. The peak assignments could be made unambiguously for copolymers with $\bar{n}$ = 1.13, 2.0, and 3.7. However, there was a degree of overlap in the spectrum of the copolymer with $\bar{n}$ = 1.4, arising from the almost equal proportions of SVS and SVVS sequences. The composition of the copolymer was known to be $\bar{n}$ = 1.4 by ^{1}H NMR analysis using the relative areas of the clearly resolved SV, VS, and VV diad resonances and by microanalysis of samples prepared under identical conditions with undeuterated VC. The total area A of α-sulfonyl methine protons in Figure 5C in sequences of all lengths is 1452 (arbitrary units). Based on the assignments shown in Figure 5 and allowing for the overlap as indicated, $A_{\mathrm{SVS}} = 929$, $A_{\mathrm{SVVS}} = 523$, and $A_{\mathrm{VVV}} = 0$. Therefore $\bar{n} = (A_{\mathrm{SVS}} + 2A_{\mathrm{SVVS}})/(A_{\mathrm{SVS}} + A_{\mathrm{SVVS}}) = 1.36$. This excellent agreement with the known value of 1.4 supports the assignments to SVS and SVVS sequences.

The "internal" tacticity of the SVVSV*VS resonance of the copolymer with $\bar{n}$ = 1.4 was resolved in DMSO (this was not the case in acetone, Figure 5C). The splitting was 12 Hz, which may be compared with the 8-Hz splitting in the copolymer with $\bar{n}$ = 2.0 (Figure 6B). This difference may be due to the presence of olefinic units in the copolymer with $\bar{n}$ = 1.4. The S,S (R,R):S,R (R,S) ratio is 4.5, in reasonable agreement with the value of 3.6 determined from the corresponding β-sulfonyl methine resonance in SVVS tetrads (Figure 4A).

Conclusions

1. The α-sulfonyl methine proton in SVS sequences was sensitive to the proximity of SO$_2$ in neighboring sequences, and the effect of these SO$_2$ units was observed up to six main-chain bonds distant. This allowed SVSVSVS, SVSVSVVS/SVVSVSVS, and SVVSVSVVS sequences to be discriminated.
2. The β-sulfonyl methine proton in VS diads was sensitive "across-SO$_2$" to the configuration of the asymmetric center to the right. However this effect was less than the splitting from "internal" diad tacticity, which arose in S(V)$_n$S sequences, with $n \geq 2$. The α-sulfonyl methine in these sequences was less sensitive to the "internal" tacticity, and showed no splitting due to diad configuration with the "across-SO$_2$" asymmetric center to the right.
3. SVVS and SVVVS sequences could not be discriminated at 100 MHz for $\bar{n} > 2$. However, it was clearly established that copolymers prepared above 0 °C did not contain SVS sequences, while those prepared below 0 °C contained only a very small proportion of VVV sequences.
4. The copolymer prepared at 0 °C was highly regular, both in monomer and stereo sequence distribution. It is proposed that the most probable "internal" diad stereo sequence is S,S (R,R). The S,S (R,R):S,R (R,S) ratio increased with copolymerization temperature and was 2.3 at −78 °C, 3.6 at −45 °C, and 5.8 at 0 °C.
5. "Across-SO$_2$" diad placements with respect to the asymmetric center to the right for the SVS methine proton were not equally probable in the copolymer with $\bar{n}$ = 1.1. The ratio was 1.3:1, although it could not be deduced which stereoisomer was most probable. This ratio could not be reliably measured for the copolymer with $\bar{n}$ = 1.4 due to overlap in the spectrum.

Poly(vinyl chloride sulfone). The 100-MHz ^{1}H NMR spectra of full-protonated copolymers with different values of $\bar{n}$ (1.03 and 4.1) are shown in Figure 7. The spectra are generally complex and show only broad resonance envelopes due to geminal and vicinal proton coupling adding to comonomer and configurational sequence effects observed for the copolymers from vinyl-β,β-d_2 chloride. However, the magnitudes of the two vicinal coupling constants will indicate the predominant chain conformation about the C–C bond.

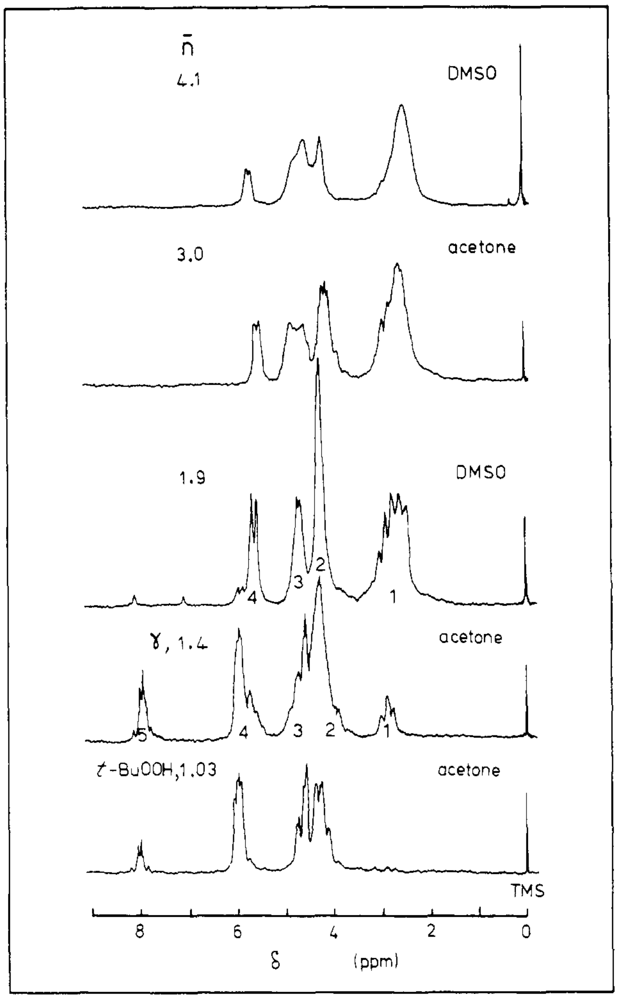


Figure 7. ^{1}H NMR spectra at 100 MHz of poly(vinyl chloride sulfones)'s with various compositions.

Table III
^{1}H NMR Diad Assignments for Poly(vinyl chloride sulfone)

No.	Chem shift	Diad sequence	Abbreviation	Proton type
1	2.0—3.0	$-CHCl-\mathit{CH}_2-$ $CHCl-CH_2$	VV	PVC methylene
2	3.6—4.4	$-CHCl-\mathit{CH}_2-$ SO_2-	VS	α-Sulfonyl-methylene
3	4.4—4.8	$-CHCl-CH_2-$ $\mathit{CH}Cl-CH_2-$	VV	PVC methine
4	5.4—6.2	$-SO_2-\mathit{CH}Cl-$ CH_2	SV	α-Sulfonyl methine
5	7.8—8.2	$-SO_2-CH{=}CH-$ $-CH{=}CH-SO_2-$	SE ES	α-Sulfonyl olefinic

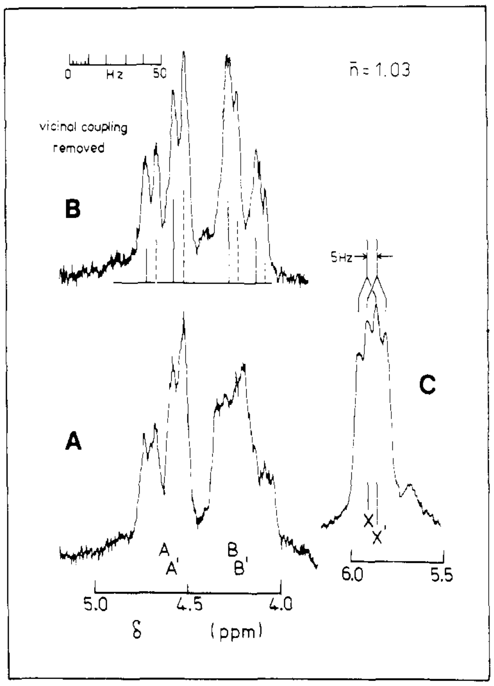


Figure 8. ^{1}H NMR spectra at 100 MHz of poly(vinyl chloride sulfone) with $\bar{n}$ = 1.03. A: α-sulfonyl methylene (AB) resonances; B: resonances in A with irradiation of methine (X); C: α-sulfonyl methine resonances (X).

By comparison with the ^{1}H NMR spectra of poly(vinyl-β,β-d_2 chloride sulfone)'s shown in Figures 1–6 two methylene resonances areas can be identified, due to VV and VS diad comonomer sequences. The assignments for these two methylene diads and for the VV and SV methine diads (VS methine is included with VV) are given in Table III and also shown in Figure 7.

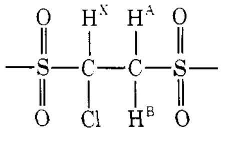
The composition of poly(vinyl chloride sulfone) can be determined rapidly and accurately from the relative areas (A) of these resonances using any of the formulas

$$\bar{n} = 1 + A_1/A_2 = 1 + A_3/A_4 = 1 + A_1/2A_4 = 1 + 2A_3/A_2$$

Resonances 1 and 4 are normally well resolved and give the most reliable results.

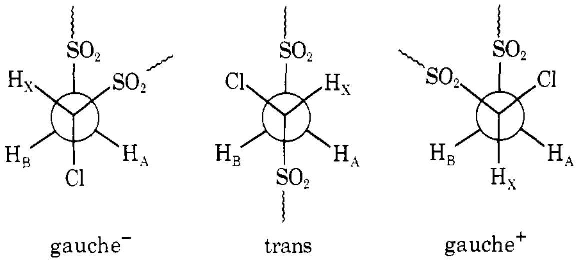
Copolymer with $\bar{n} \approx 1$. The simplest copolymer spectrum in which to measure the coupling constants is that with $\bar{n} \approx 1.0$, where the loss of resolution due to overlapping of resonances from different monomer sequence lengths will be negligible. Figure 8 shows the 100-MHz ^{1}H NMR spectrum of the methylene and methine protons in a copolymer with $\bar{n}$ = 1.03 (i.e., SVVS sequences can be effectively ignored). The spin system closely approximates ABX at 100 MHz. Figure 8A shows the AB system coupled to X (the methine proton) and Figure 8B shows the same region on irradiation of the X proton, i.e., with all vicinal coupling removed.

It is clear that two AB quartets are being resolved (AB and A′B′), arising from the S/S (R/R) and S/R (R/S) "across-SO2" stereo sequence diads. Figure 8B shows that $|J_{AB}| = |J_{A'B'}|$ = 14 Hz and that the chemical shift difference $\nu_{AB} = \nu_{A'B'}$ = 42 Hz. The diad chemical shifts are δ_B = 4.23 and $\delta_{B'}$ = 4.18 ppm. The splitting between these two (5 Hz) compares with the 4.5-Hz splitting of the methine proton resonance observed in the spectrum of the partially deuterated copolymer with $\bar{n}$ = 1.13 with acetone as solvent.



$$-\overset{\overset{\large O}{\|}}{\underset{\underset{\large O}{\|}}{S}}-\overset{\overset{\large H^X}{|}}{\underset{\underset{\large Cl}{|}}{C}}-\overset{\overset{\large H^A}{|}}{\underset{\underset{\large H^B}{|}}{C}}-\overset{\overset{\large O}{\|}}{\underset{\underset{\large O}{\|}}{S}}-$$

The geminal coupling constant may be assigned a negative value, by analogy with other geminal coupling constants. By comparing the upper and lower spectra, it is seen that the A resonances are not changed significantly by irradiation of the X proton, unlike the B resonances. Consequently $J_{AX} \ll J_{BX}$, which leads to the conclusion that with acetone as solvent, the preferred conformation about the main-chain C–C bonds must be trans. These three possible conformers are shown in the Newman projections below:



For ethane derivatives, $J_{trans} \approx 12$ Hz and $J_{gauche} \approx 4$ Hz. The magnitude of J_{BX} can be found by considering the spectrum of the X proton.

The X resonance shown in Figure 8C is clearly a quartet and, since $J_{AX} \approx 0$, this can be attributed to BX vicinal coupling splitting X and X′ by 9–10 Hz. This will closely approximate the value of J_{BX}. The chemical shift difference between X and X′ is 5 Hz, in good agreement with the value measured in the spectrum of the deuterated copolymer, and is attributed, as for the methylene protons, to S/S (R/R) and S/R (R/S) stereo sequence diads. The value of $J_{BX} \approx 10$ Hz further supports the predominance of *trans* conformations about the C–C main-chain bonds, as has been observed for poly(propylene sulfone)[24] and poly(propylene sulfide).[25]

The broadening of the A and X resonances indicates that $J_{AX} \neq 0$ on average, but nevertheless its value is small ($\leqslant 2$ Hz) compared with J_{BX}. Thus, the essential features of this spin system (superposition of ABX and A′B′X′) can be resolved.

The possibility of a solvent effect on the preferred chain conformation of the essentially 1:1 copolymer was examined by recording the spectrum at 220 MHz in DMSO as solvent (Figure 9). At this frequency, the spectrum approximates that for an AMX spin system. The central peak at 5 ppm is due to HCl and its spinning side bands are marked as shown. The copolymer contained 21% –CH=CH– units,[6] which led to further smearing of the resonances due to adjacent unsaturation. Consequently, there are probably more than the expected two overlapping AMX spin-system resonances. Furthermore, the overlap at 220 MHz appears to be greater than at 100 MHz. However, the principal splitting is similar to that in acetone, i.e., $J_{AX} \ll J_{MX}$ and $J_{MX} \approx 8$–9 Hz. It would therefore seem likely that the *trans* conformation is also preferred in DMSO.

Copolymers with $\bar{n} > 1$. The spectra in Figure 7 for the copolymers with $\bar{n} = 4.1$ and 3.0 show the broadening of resonances due to the effects discussed above. This broadening would also be expected in the copolymer with $\bar{n} = 1.9$, but in fact the line widths are remarkably narrow. This supports the previous evidence for the high monomer and stereo sequence regularity in this copolymer. The α-sulfonyl methine proton resonance in the SVVS tetrad (peak 4) is seen to be a sharp doublet (the small low-field doublet is due to SVSVVS sequences). This doublet is collapsed by irradiation of the β-sulfonyl methylene protons (peak 1, centered at 2.8 ppm), indicating that the splitting is due to vicinal coupling only, as expected from the spectra of the partially deuterated copolymer with $\bar{n} = 2.0$.

The β-sulfonyl methylene protons of the SVVS sequences show a sharp triplet resonance in the spectrum of the copolymer with $\bar{n} = 1.9$. They are also clearly resolved in the spectrum of the copolymer with $\bar{n} = 1.4$ in acetone. These methylenes couple to two adjacent methine protons (M and X):

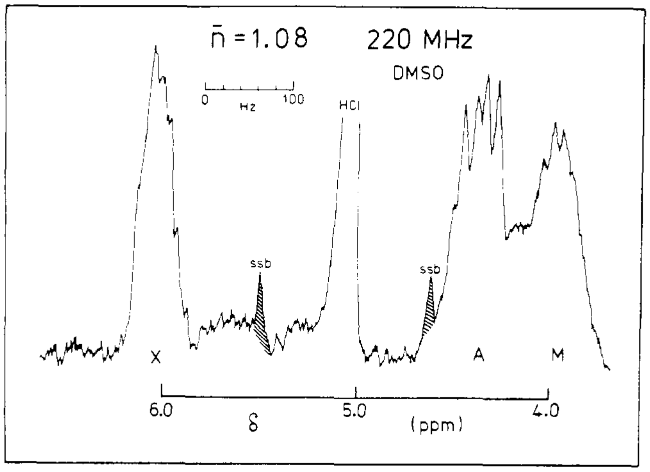
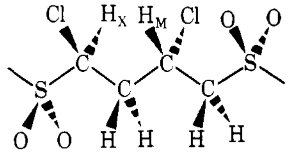


Figure 9. ^{1}H NMR spectrum at 220 MHz of poly(vinyl chloride sulfone) with $\bar{n} = 1.08$.



S, S diad

In the S,S diad shown above as well as in the R,R diad the methylenes should be nearly homosteric, since the immediate environment is symmetrical.

On a simple first-order basis, the S,S (R,R) diad should give a spin system closely approximating AA′MX, while the S,R (R,S) diad should give an ABMX spin system. Therefore the S,R (R,S) diad should give a more complex spectrum than the S,S (R,R) diad. However, a definite assignment cannot be made without a study of model compounds of known stereochemistry.

Dehydrochlorination. The sulfone group was found to catalyze the elimination of HCl from vinyl chloride units in the copolymers under a variety of conditions,[6] including γ irradiation during polymerization and solution in DMSO. This dehydrochlorination occurred readily in SVS sequences, hence copolymers prepared below 0 °C were particularly unstable. In the ^{1}H NMR spectra of dehydrochlorinated copolymers a peak was observed at 7.8–8.2 ppm, which was assigned to olefinic protons in the residual double bond, i.e., in SES sequences (E = ethene = –CH=C·H–). This resonance (peak 5) is shown in Figure 7 for copolymers with $\bar{n} = 1.03$ and 1.4. The peak also occurred in *poly(vinyl-β,β-d_2 chloride sulfone)'s which had undergone* dehydrochlorination. The DCl liberated underwent isotopic exchange with H_2O in the system to form HCl, which was observed as a peak of variable position. H–D exchange also occurred with the $-CD_2-SO_2-$ protons to form $-CDH-SO_2-$ which gave a resonance at 4.35 ppm as shown in Figure 3.

The small peak at 7.1 ppm in the spectrum of the copolymer with $\bar{n} = 1.9$ in Figure 7 is attributed to a small proportion of SEVS (or SVES) sequences.

Conclusions. 1. The mean, macroscopic composition of any sample of poly(vinyl chloride sulfone) can be readily determined from the relative areas of appropriate diad comonomer resonances.

2. Dehydrochlorination occurs during γ irradiation initiated polymerization and in solution in DMSO. The HCl is eliminated preferentially from SVS sequences and the extent *of dehydrochlorination can be quantitatively deter-*

mined from the area of the $-SO_2—CH{=}CH—SO_2-$ resonance.

3. The copolymer with $\bar{n} \approx 1.0$ approximates to ABX at 100 MHz and AMX at 220 MHz. $J_{AB} \approx -14$ Hz, $J_{BX} \approx 10$ Hz, J_{AX} or $J_{MX} \approx 2$ Hz. Therefore, the conformation is predominantly trans in acetone and DMSO solutions.

4. The copolymer with $\bar{n} \approx 2$ has remarkably narrow resonance peaks attributed to high monomer and stereo sequence regularity. The predominant internal configuration is tentatively assigned to the S,S (R,R) diad.

Comonomer Sequence Distributions. The mechanism of copolymerization of vinyl chloride and sulfur dioxide is complex and cannot be elucidated solely from the average, macroscopic compositions of the copolymers. The NMR investigation of the microstructure of poly(vinyl chloride sulfone) reported in this paper enables the comonomer sequence distributions to be determined, at least over a limited range of $\bar{n}$. The comonomer sequence distributions in poly(vinyl chloride sulfone)'s, prepared at different temperatures and from a range of comonomer concentrations, will be used in a subsequent paper as evidence in assigning the copolymerization mechanism.

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Note Added in Proof: Proton NMR spectra of poly(vinyl-β,β-d_2 chloride sulfone) with $\bar{n} = 1.13$ have recently been obtained at 270 MHz for a 10% w/v solution in THF-d_8. Two spectra were recorded, each in the FT mode (100 scans, 16K data points for the free induction decay, 3600 Hz spectral window, ca. 90° pulse), with and without broadband deuterium decoupling. The higher observing field strength and improved signal-to-noise ratio obtained for these spectra, in comparison with their 100 MHz counterparts, allowed the following conclusions to be made: 1. The doublet splitting on each of the two main peaks at 5.8 and 5.9 ppm was 6.7 and 2.5 Hz, respectively (cf. 2.5 and 1.1 Hz at 100 MHz), proving that this splitting was not due to vicinal deuterium coupling. The quartet structure of the resonance can therefore be assigned to the four distinct stereosequences in the $VS\overset{*}{V}SV$ comonomer pentad, S/S/S (R/R/R), S/S/R (R/R/S), S/R/S (R/S/R), and S/R/R (R/S/S). 2. There was no observable difference between the deuterium coupled and uncoupled spectra, indicating that deuterium coupling made a negligible contribution to the observed line width at 270 MHz. 3. A doublet splitting of 12 Hz was resolved on the S,R $V\overset{*}{V}S$ resonance centered at 4.85 ppm, thereby discriminating S,R/R (R,S/S) and S,R/S (R,S/R) stereosequences.

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