Nuclear Magnetic Resonance Analysis of the Microstructure of Poly(chloroprene sulfone)

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ABSTRACT: Poly(chloroprene sulfone)s containing 48–16 mol % sulfur dioxide were prepared by free-radical copolymerization at temperatures from −78 to 100 °C. Their microstructures were examined by 90.52-MHz ^{13}C and 360-MHz ^1H NMR spectroscopy. Resonances were assigned to the monomer sequence triads MMM, MMS, SMM, and SMS (S = sulfone; M = chloroprene), and the effect of copolymerization temperature on the compositional sequence distribution was explained by a model involving depropagation reactions. The penultimate sulfone unit in the sequence –SMS· did not enhance the likelihood of depropagation of the terminal sulfonyl radical, which showed that adjacent sulfones do not interact unfavorably when separated by five backbone bonds. At −78 °C 99% of the chloroprene units were trans-1,4, but other isomers became more probable with increasing temperature, to the extent of 13% cis-1,4 and 3% 1,2 at 100 °C. Well resolved fine structure in the ^{13}C spectra was indicative of directional isomerism of the chloroprene unit, which could enter the growing chain in a head-tail (1,4) or tail-head (4,1) orientation. The effect of temperature on directional isomerism in the sequence MSM was consistent with a lower ceiling temperature for 1,4 addition compared to 4,1 addition of chloroprene to the sulfonyl radical.

Sulfur dioxide and 2-chloro-1,3-butadiene (chloroprene) copolymerize readily by a free-radical mechanism over a wide temperature range.[1-4] The product is a poly(chloroprene sulfone) with variable composition. Specifically, the macroscopic copolymer composition, which may be expressed as the ratio R of chloroprene to sulfur dioxide, is a function of the copolymerization temperature, monomer feed ratio, and concentration. In this respect chloroprene is unique as it is the only 1,3-diene known to form a variable composition polysulfone.

Polysulfones from other 1,3-dienes[5,6] and most monoolefins[7] always have an equimolar composition with a strictly alternating monomer sequence structure. However, it is still debatable whether this structure results exclusively from cross-propagation steps involving discrete monomer molecules (the Lewis–Mayo model with $r_1 = r_2 = 0$) or "homopolymerization" of a 1:1 molecular association complex between unsaturated hydrocarbon (donor) and sulfur dioxide (acceptor).[8]

Additional insight into propagation step mechanisms can be gained from variable composition polysulfones by observing the effect of copolymerization parameters on monomer sequence distibutions. Chloroprene is especially interesting in this regard because of its potential for structural isomerism not inherent in vinyl comonomers. Thus, in addition to the primary consideration of monomer sequences, the following structures can be anticipated: *cis*-1,4-, *trans*-1,4-, 1,2-, and 3,4-chloroprene units, directional isomers (head-to-tail vs. head-to-head placements), and stereochemical relationships between asymmetric centers in 1,2 and 3,4 units.

Recently, Brame et al. have demonstrated the power of ^{13}C NMR in resolving the detailed microstructure of chloroprene homopolymers[9] and copolymers,[10,11] but little is known concerning the microstructure of poly(chloroprene sulfone)s. Stannett et al.[2] concluded from IR analysis that the chloroprene units were mainly 1,2. This was not substantiated by Matsuda and Hara,[4] who performed ^1H NMR as well as IR measurements. They found a majority of trans-1,4 isomers, with some cis-1,4 and 3,4 isomers and proposed a model involving depropagation reactions. Mechanisms which featured either Lewis–Mayo behavior or molecular complexes were disallowed. The monomer sequence distributions, however, were not characterized by either group.

We have shown previously that NMR can be used to determine monomer sequence distributions in variable composition polysulfones, namely those from vinyl chloride,[12] styrene,[13] and acrylamide.[14] The work described in the present paper forms a continuation of this series. A clear distinction by NMR between structural isomers is possible with the field from a superconducting magnet (8.3 *T*). The monomer sequence distribution is revealed at the triad level by ^{13}C and ^1H NMR, and its dependence on temperature is considered in terms of a copolymerization model.

Only ^{13}C NMR analysis could provide detailed information on geometrical and directional isomerism of the chloroprene unit. A novel observation concerning the latter isomerism provides evidence for selective depropagation of terminal chloroprene units, namely those bonded to a penultimate sulfone unit.

Experimental Section

Materials. Chloroprene was obtained from Pfaltz and Bauer Inc. as a 50% solution in xylene. The mixture was distilled in argon at reduced pressure, and the fraction collected at 18.3 °C and 22.3 kPa was retained for copolymerizations. This fraction was better than 99.5% pure according to ^{13}C NMR analysis (the chemical shifts for $C(1)H_2{=}C(2)Cl{-}C(3)H{=}C(4)H_2$, in acetone-$d_6$ (0.5 g/cm^3) at 33 °C, reference internal Me_4Si, were: $\delta(C_1)$ 118.58, $\delta(C_2)$ 139.61, $\delta(C_3)$ 134.47, and $\delta(C_4)$ 116.56). Chloroprene was used as soon as possible after distillation because it polymerized slowly during storage, even at low temperature.

Sulfur dioxide and 2,2′-azobis(isobutyronitrile) were purified as described previously.[13] Commercial silver nitrate, *tert*-butyl hydroperoxide, toluene, and 1,1′-azobis(1-cyclohexanenitrile) were used as received. Perdeuterio solvents for NMR studies were purchased from Merck and Co. Inc.

Copolymerizations. Copolymerizations took place without the use of diluents in 100-cm^3 spherical flasks. The initial monomer mixture always contained 50 mol % sulfur dioxide. A typical procedure was as follows. The required amount of solid initiator was weighed into a flask, and chloroprene (30 cm^3, 29 g, 0.33 mol) was added by a pipet. The flask was attached immediately to a vacuum manifold, and its contents were frozen with a liquid nitrogen bath. Traces of air were pumped out during repeated freeze–thaw cycles. Sulfur dioxide (21 g, 0.33 mol; determined by its gas pressure in a calibrated volume) was distilled from a reservoir into the flask, which was then sealed under vacuum. The monomers were thawed and mixed thoroughly before the flask was placed in a constant temperature bath. After a suitable polymerization time had elapsed, the contents were frozen in liquid nitrogen, removed from the flask, and transferred to a large excess of chilled methanol, which contained several drops of concentrated hydrochloric acid to promote coagulation.

This procedure was duplicated for reactions which employed *tert*-butyl hydroperoxide as an initiator component, with the following exception. A side arm, sealed by a septum, was attached

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Table I
Conditions for the Bulk Polymerizations of Equimolar Mixtures of Chloroprene with Sulfur Dioxide

sample no.	temp, °C	polym time, h	initiator	[init.], mol %	yield, wt %	$\overline{R}$[a]
1	−78	17.25	*t*-BuOOH	0.46	9.8	1.12
2	−45	1.67	*t*-BuOOH	0.46	14.0	1.13
3	−17	6.25	*t*-BuOOH	0.46	15.4	1.28
4	0	14.83	$AgNO_3$	0.02	22.6	1.11
5	25	4.67	$AgNO_3$	0.02	22.3	1.33
6	40	6.32	AIBN	0.05	22.1	1.63
7	60	3.30	AIBN	0.05	32.1	2.14
8	100	1.03	ACHCN[b]	0.05	15.4	5.08

[a] $\overline{R}$ = the average chloroprene/SO_2 molar ratio in copolymer from analysis for C, Cl, S, and O. [b] ACHCN = 1,1′-azobis(1-cyclohexanenitrile).

to the polymerization flask which was subsequently charged with the monomer mixture in the usual manner. The flask was allowed to thermally equilibrate at the desired temperature, and then 0.6 cm^3 of a 1:1 mixture (by volume) of the hydroperoxide with toluene was injected through the septum to initiate copolymerization.

The copolymers were recovered from methanol, washed several times with fresh methanol on a filter flask, and finely divided in a high-speed blender. All volatiles were then removed by continuous evacuation under 0.13 Pa at ambient termperature for approximately 15 h. No antioxidant was added to the copolymers, which were stored at -40 °C in a nitrogen atmosphere prior to spectroscopic examination. In selected cases the methanol washings were collected and evaporated to yield crystals of 3-chloro-2,5-dihydrothiophene 1,1-dioxide.

Characterizations. Elemental analyses were performed by Childers Laboratories, Milford, N.J. IR spectra were obtained with a Perkin-Elmer Model 620 grating spectrometer operated under standard conditions. The samples were either cast as films or pressed into disks with potassium bromide.

NMR spectra were recorded exclusively in the FT mode with natural abundance samples. A Bruker HX 360, Varian XL 100, and Bruker WH 90 provided field strengths of 8.3, 2.3, and 2.1 *T*, respectively, corresponding to ^{13}C resonance frequencies of 90.52, 25.16, and 22.62 MHz. Solutions were prepared in dimethyl-d_6 sulfoxide and, where possible, methylene-d_2 chloride. Concentrations were 0.20 and 0.10 g/cm^3 for ^{13}C and ^1H NMR studies, respectively. Observation temperatures ranged from 30 to 70 °C. At more elevated temperatures, the solution viscosity slowly changed during the course of data acquisition when the solvent was dimethyl sulfoxide. However, it was verified by ^{13}C NMR that minor chain scission or cross-linking never entailed detectable alteration of the copolymer sequence structure.

Results and Discussion

1. Copolymerizations. Details pertaining to the copolymerizations are given in Table I. A significant trend is the increase in chloroprene content (and hence the *R* value) of the copolymers with increasing temperature. This trend has a parallel in other variable composition polysulfone systems.[12-14] However, the change in composition of poly(chloroprene sulfone) with temperature is not as marked as that for the polysulfones from vinyl chloride and styrene, although all three systems form nearly equimolar copolymers at −78 °C. The dependence of *R* on temperature will be considered further in section 4.

Poly(chloroprene sulfone)s with *R* less than 2 dissolved completely in dimethyl sulfoxide and dimethylformamide, but they were insoluble in hot benzene, toluene, chloroform, dioxane, and acetone. Some light cross-linking took place during copolymerizations above 40 °C, and about 50% by weight of samples 7 and 8 could not be extracted with chloroform. Their gel fractions swelled in the above-mentioned solvents, and they exhibited high-resolution ^{13}C NMR spectra identical with those from the respective sol fractions.

Sample 3 was used in another test for compositonal heterogeneity. This material was extracted overnight with refluxing chloroform. During concentration of the chloroform washings at room temperature, a precipitate formed which could be redissolved in acetone. The total extract represented 2% by weight of the copolymer, and it yielded two nearly equal portions, according to their solubility characteristics in cold chloroform. These extracts were examined by IR and ^1H NMR spectroscopy. Both were poly(chloroprene sulfone)s. The chloroform soluble fraction had an *R* value close to 3 whereas the acetone soluble fraction had the same composition as the parent material. However, the latter fraction also had a very low degree of polymerization (reflected by narrow NMR line widths), accounting for its solubility in acetone.

Evidently, concurrent homopolymerization of chloroprene in liquid sulfur dioxide is not a significant source of heterogeneity in sample composition. The extraction test showed additionally that, when prepared under present conditions, poly(chloroprene sulfone) is reasonably monodisperse in composition.

An increase in copolymerization temperature also resulted in a greater yield of a methanol-soluble crystalline compound, which melted from 99.1 to 100.3 °C. Elemental analysis revealed an equimolar ratio of chloroprene to sulfur dioxide. Anal. Calcd for $C_4H_5ClO_2S$: C, 31.48; H, 3.30; S, 21.01; Cl, 23.23; O, 20.97. Found: C, 31.27; H, 3.31; S, 20.91; Cl, 23.69; and O, 20.82. Therefore the compound is the cyclic sulfone, 3-chloro-2,5-dihydrothiophene 1,1-dioxide, which has been described by Backer and Blaas[15] (reported mp 100.5–101.0 °C). Its NMR chemical shifts, obtained at 33 °C in dimethyl sulfoxide (40 mg/cm^3), reference internal Me_4Si, are: $\delta(C_2)$ 58.04, $\delta(C_3)$ 124.35, $\delta(C_4)$ 122.07, and $\delta(C_5)$ 57.72. The 90-MHz ^1H NMR spectrum, observed under the same conditions, is fairly complex owing to an appreciable four-bond coupling across the ring. The chemical shifts and multiplicities are: $\delta(H_2)$ 4.15 (quartet), $\delta(H_4)$ 6.30 (nonet), and $\delta(H_5)$ 4.03 (pentuplet).

2. NMR Spectra. The ^{13}C NMR spectra of poly(chloroprene sulfone)s will be considered first, since they reveal more structural detail than ^1H NMR spectra.

As there was a significant improvement in resolution for spectra recorded at 8.3 *T* compared to 2.3 and 2.1 *T*, only the high-field spectra will be presented here. However, many preliminary studies and several dynamic ^{13}C NMR experiments were done at the lower field strengths to aid interpretation, and these will be discussed where appropriate.

a. ^{13}C NMR Spectra. Figure 1 shows the complete spectrum of sample 6, which exhibits most structural features found in this series of poly(chloroprene sulfone)s. Each chemical shift is diagnostic of one of the four carbon *types* (here designated as C_1, C_2, C_3, or C_4, in keeping with the monomeric notation) and its particular structural environment. For convenience, the spectrum is divided into two regions, one at low field from 113 to 144 ppm and one at high field from 25 to 62 ppm. These regions will be considered separately.

Assignment of Carbon Type. By virtue of their chemical shift ranges, it is obvious that low-field resonances arise from olefinic carbons whereas high-field resonances arise from saturated carbons. The actual assignments to carbon type, shown in Figure 1, were made according to the results from several experiments. These involved the observation of ^1H-coupled ^{13}C spectra, the measurement of ^{13}C spin–lattice relaxation times (T_1's), the selective single-frequency irradiation of ^1H while observing ^{13}C, and

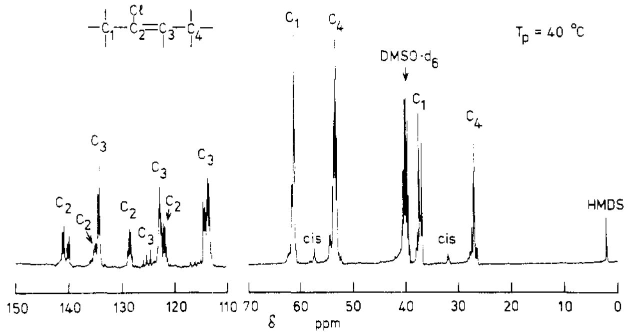


Figure 1. Basic assignments to carbon type in the 90.52-MHz ^{13}C spectrum of poly(chloroprene sufone) prepared at a polymerization temperature (T_p) of 40 °C (sample 6). The observation conditions are: temperature, 60 °C; number of transients added, 3000; sweep width, 15.151 kHz; data points (FID), 32K; pulse flip angle, 90°; pulse interval, 3.0 s; solvent, dimethyl-d_6 sulfoxide (DMSO-d_6); concentration, 0.20 g/cm^3; internal reference, hexamethyldisiloxane (HMDS) at 2.00 ppm.

Table II
Selected Parameters for the ^{13}C Resonances of Sample 3 Observed at 60 °C in $(CD_3)_2SO$ Solution (0.2 g/cm^3) and at 2.1 *T* Magnetic Field Strength

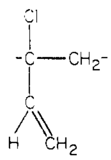
δ,[a] ppm	mult[b]	$^1J_{^{13}C-^1H}$, Hz	T_1 ± 10%, ms	NOE ± 20%	monomer sequence assignment[c]
141.0	s	0	nd[d]	nd	C_2(M*M*S)
134.5	d	164	240	nd	C_3(S*M*M)
128.7	s	0	2710	2.4	C_2(S*M*S)
123.2	d	166	250	2.7	C_3(S*M*S)
122.2	s	0	nd	nd	C_2(S*M*M)
114.3	d	168	250	nd	C_3(M*M*S)
61.3	t	142	140	2.6	C_1(S*M*)
53.4	t	142	120	2.9	C_4(*M*S)
37.2	t	126	160	nd	C_1(M*M*)
26.8	t	130	120	nd	C_4(*M*M)

[a] Approximate multiplet center. [b] Multiplicity from ^1H coupling: s = singlet, d = doublet, t = triplet. [c] Refer to text. [d] Not determined.

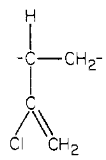
the comparison of chemical shifts with those from model compounds. Some pertinent results are shown in Table II.

It was possible to make most assignments based on the multiplicities of ^{13}C resonances when subject to one-bond ^1H coupling. Zero or doublet splitting in the low-field region identified C_2 and C_3 carbons, respectively. All high-field resonances became triplets, showing they originated from methylene carbons only.

These observations, combined with the fact that no triplets resulted from low-field resonances, indicate that the major structural isomer of the chloroprene unit is 1,4. Detectable amounts of 1,2 and 3,4 isomers are formed at elevated copolymerization temperatures only.



1,2



3,4

An alternative approach confirmed the C_2 and C_3 assignments. A partially-relaxed, pulsed-NMR experiment (with ^1H noise decoupling restored) was designed to exploit the tenfold greater T_1 of C_2 compared to that of C_3 (Table II). Accordingly, a 22.62-MHz ^{13}C spectrum of sample 3 was obtained at 60 °C with an accumulation of 1500 π–t–$\pi/2$–T pulse sequences (a π pulse was 26.0 μs, and T was 2.00 s). By choosing 0.35 s for t, all C_2 signals remained inverted whereas all C_3 signals had recovered to positive intensities. The resulting "up-down" contrast highlighted four distinct positions for each olefinic carbon resonance; the assignments in this region (Figure 1) are as follows: C_2 at 141, 136, 128, and 122 ppm, and C_3 at 134, 126, 123, and 114 ppm.

Methylene carbons in the high-field region were identified by the following means. The pair at 37 and 27 ppm match the reported chemical shifts for C_1 and C_4, respectively, in polychloroprene.[9] They were assigned on this basis. The pair at 61 and 53 ppm have no precedent in the polychloroprene spectrum, however, since they are associated with sulfone groups. They were assigned by a different strategy, which involved recourse to sample 1 and an accurate determination of its methylene proton resonance frequencies.

The methylene protons on C_1 and C_4 can be differentiated clearly in the ^1H spectrum of sample 1 because the latter pair are spin coupled to the olefinic proton whereas the former pair experience no three-bond homonuclear coupling (section b). They were identified by appropriate single-frequency (coherent) decoupling (at 360 MHz the resonance frequency of H_1 was 108 Hz greater than that of H_4).

Next, the ^{13}C spectrum (Figure 3a) was observed under identical conditions, but with coherent irradiation (power = 0.9 W) centered at either of the two methylene ^1H frequencies measured above. In both cases $^1J_{^{13}C-^1H}$ was reduced to zero for C_1 *and* C_4 (owing to the small frequency difference between their protons),[16] but full restoration of the nuclear Overhauser enhancement (NOE) was specific to the carbon with irradiated protons. This experiment showed that C_1 resonated at lower field than C_4 (61 compared to 53 ppm). These assignments are also consistent with the fact that C_1 is in the β position to chlorine whereas C_4 is in the γ position.[17]

Now that major resonances have each been identified with one of the four carbon *types*, it is necessary to account for their extensive multiplicities in terms of structural dissimilarities caused by the sequence environment. The effect of copolymerization temperature (and hence *R*) on resonance intensities shows the influence of compositional isomerism, which is discussed next.

Monomer Sequence Assignments. The low-field region will be considered first, and Figure 2 shows the 90.52-MHz ^{13}C spectra of olefinic carbons in samples 1, 3, 6, and 8. As noted above, there are four dissimilar environments which substantially influence the resonance positions of C_2 and C_3. These environments must result from triad monomer sequence structure because other isomerism (e.g., involving 1,2, 3,4, and cis-1,4 units) is too infrequent to account for the observed intensities. More subtle environmental differences cause the fine structure of each resonance and these will be discussed later. For the present, the monomer sequences in question are SMS, SMM, MMS, and MMM, where M represents a chloroprene unit and S represents a sulfone unit.[18]

Poly(chloroprene sulfone)s cannot contain contiguous sulfone units, because sulfur dioxide does not add to sulfonyl radicals during copolymerization.[7] A polysulfone with an *R* value of unity must then necessarily have the sequence structure $(\text{-SM-})_n$. Sample 1 closely approximates this structure, which results in its relatively simple spectrum (Figure 2a), allowing identification of the major peaks at 128.7 and 123.2 ppm with C_2(S*M*S) and C_3(S*M*S),

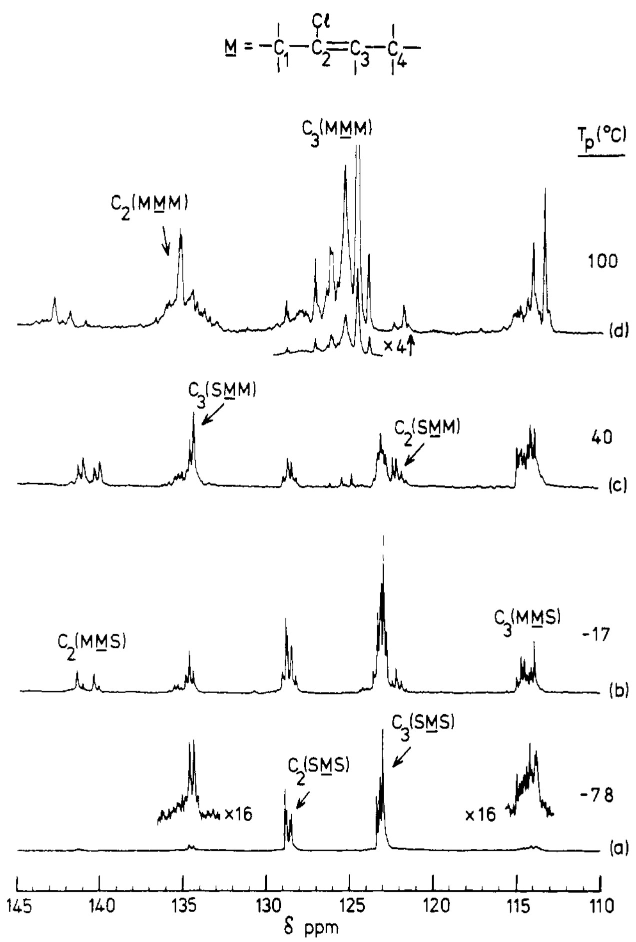


Figure 2. Assignments to compositional sequence triads in the olefinic region of 90.52-MHz ^{13}C spectra of poly(chloroprene sulfone) samples 1, 3, 6, and 8 (spectra a, b, c, and d, respectively). The sequence notation is explained in the text. The observation conditions are the same as those given in the caption to Figure 1, with the following exceptions: spectra a and b, 6000 transients each; spectrum d, 5000 transients at 30 °C with methylene-d_2 chloride as solvent.

respectively. Sample 8 tends to the other end of the composition range, and its spectrum indicates that a good proportion of carbon nuclei exists in a "polychloroprene-like" environment. Its major peaks at 136 and 126 ppm therefore correspond to C$_2$(M*M*M) and C$_3$(M*M*M).

Assignments to SMM and MMS sequences are not so straightforward. However, these were accomplished by consideration of some empirical chemical shift rules, which were deduced as follows. An examination of the olefinic carbons already assigned, i.e., those in SMS and MMM sequences, suggests the following *specific* rules: (i) a sulfone in the β position to an olefinic carbon shields it by −12 ppm; and (ii) a sulfone in the γ position to an olefinic carbon deshields it by +8 ppm. It follows that C$_2$(M*M*S) should be 12 ppm downfield from C$_2$(S*M*S) and that C$_3$(M*M*S) should be 8 ppm upfield from C$_3$(S*M*S). The peaks at 141 and 114 ppm are within 1 ppm of the predicted positions for C$_2$(M*M*S) and C$_3$(M*M*S), respectively, which established these assignments. Two unassigned peaks remain which, by elimination, must be C$_2$(S*M*M) at 122 ppm and C$_3$(S*M*M) at 134 ppm. These positions also conform with the above chemical shift rules.

Examination of the high-field or methylene carbon resonances (Figure 3) shows that C$_1$ and C$_4$ discern only two major structural differences. This makes assignments very simple, since compositional dyads (MM, MS, and SM) are involved. One dyad induces the same shifts as polychloroprene,[9] so it must be the structure where C$_1$ and C$_4$ are flanked by carbons, i.e., the MM dyad. The relevant assignments are C$_1$(M*M*) at 37 ppm and C$_4$(*M*M) at 27 ppm. The other dyad induces a substantial deshielding of methylene carbons (by about 25 ppm), so here C$_1$ and C$_4$ must be bonded directly to a sulfone group. Likewise the sulfone inductive effect causes the 9% increase in $^{1}J_{^{13}\text{C}-^{1}\text{H}}$ for these methylenes compared to those in the MM dyad (Table II). The respective assignments are C$_1$(S*M*) and C$_4$(*M*S) at 61 and 53 ppm.

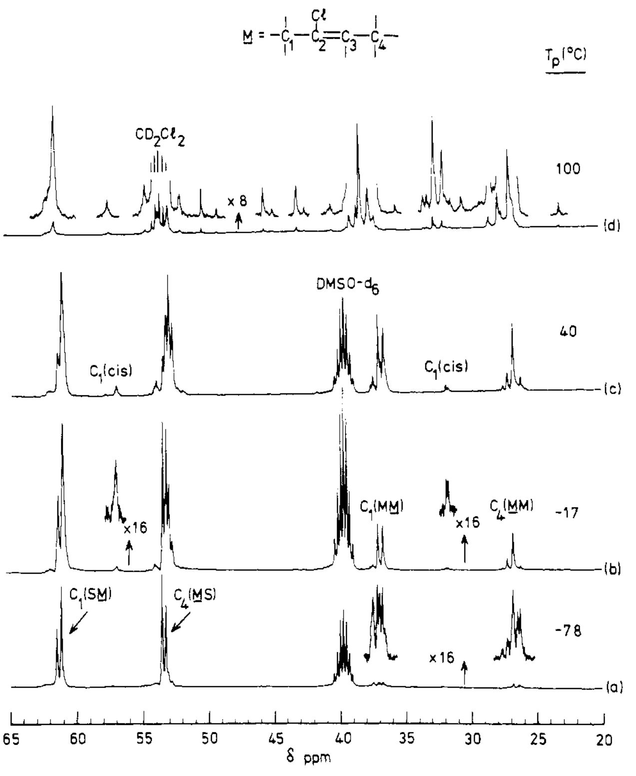
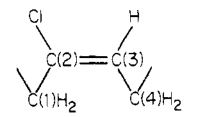
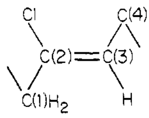


Figure 3. Assignments to compositional sequence dyads in the methylene region of 90.52-MHz ^{13}C spectra of poly(chloroprene sulfone) samples 1, 3, 6, and 8 (spectra a, b, c, and d, respectively). The relevant conditions are given in the caption to Figure 2.

Assignments of Cis and Trans Isomers. Throughout the above discussion it has been implicit that 1,4-chloroprene units are trans. This can be verified here by consideration of C$_1$ resonance positions. In both dyads C$_1$ resonances are split, but typically by little more than 1 ppm, which is too small to be due to cis- vs. trans-1,4 isomerism. In general, the ^{13}C NMR spectra of 1,4-polydienes show that methylene carbons in the cis structure can be shielded by as much as 8 ppm from those in the trans structure. The former structure has eclipised carbon-carbon bonds, which results in the shielding of C$_1$ and C$_4$ by an effect analogous to that for the well-known gauche interaction of γ carbon substituents.[20]



cis



trans

In polychloroprene, however, C$_4$ experiences similar shifts for cis and trans structures, because in both it encounters a bulky group across the double bond (i.e., C$_1$ or Cl, respectively). This is not so for C$_1$, which is eclipsed by a smaller substitutent (hydrogen) in the trans structure. An analogous situation exists for the methylene carbons in 1,4-polyisoprene.[21,22]

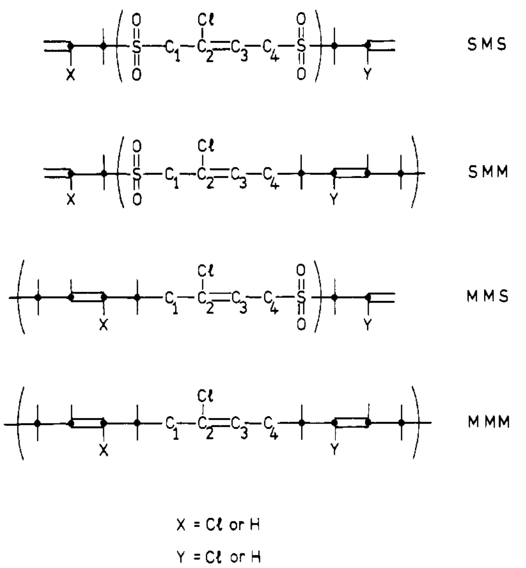


Figure 4. Schematic representation of directional isomerism involving M units in the four M-centered compositional triads.

Figures 1 and 3 show a minor peak at 32 ppm, which is assigned to C_1 in a cis-1,4 unit of an M*M* dyad.[9] There is a counterpart resonance at 57 ppm for C_1(*cis*-1,4-S*M*). In both cases the shielding, $\delta(C_1 \text{ trans}) - \delta(C_1 \text{ cis})$, amounts to about 5 ppm, as reported for α carbons in corresponding structures involving simple alkenes.[23]

Several poly(chloroprene sulfone)s were examined by IR spectroscopy, which corroborated NMR evidence for the preponderance of trans-1,4 structures. The major C=C stretching frequency was 1660 cm^{-1} (trans), with a minor shoulder at 1652 cm^{-1} (cis).[24,25]

Now that the principal assignments to carbon type, their compositional environment, and the chloroprene unit structure are established, an interpretation is required for the fine structure on each major resonance and the appearance of new resonances, particularly at higher copolymerization temperatures.

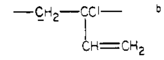
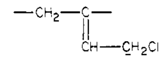
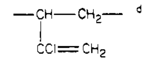
Directional Isomers, Higher Order Compositional Sequences, and Minor Irregularities. Most fine structure is caused by directional isomerism, a feature of polymers from unsymmetrically substituted dienes like chloroprene. This becomes apparent on examination of the spectrum of sample 1 (Figures 2a and 3a), where each of the four main resonances is a well-resolved multiplet. The only logical explanation invokes directional isomerism, because otherwise the structural environment is very regular, being to a good approximation $(-trans\text{-}1{,}4\text{-MS}-)_n$.

Directional isomers from three chloroprene units in or adjoining each of the four compositional triads are shown schematically in Figure 4. By present convention, central (observed) units are always oriented in the 1,4 sense, but flanking chloroprene units can be 1,4 (X = H; Y = Cl), 4,1 (X = Cl; Y = H), or some permutation. Altogether there are four permutations for each sequence shown, with chloroprene units oriented (from left to right): 1,4-1,4-1,4; 1,4-1,4-4,1; 4,1-1,4-1,4; and 4,1-1,4-4,1.[26]

Inspection of the ^{13}C spectra shows that C_1 and C_4 are sensitive mainly to directional dyads (doublet fine structure) and that C_2 and C_3 are sensitive to directional triads (quartet fine structure). This is not surprising in view of the abilities of methylene and olefinic carbons to sense compositional dyads and triads, respectively.

With the present data the strategy for obtaining reasonable assignments involved several assumptions and observations. First, the polymer is treated as a ternary system consisting of isolated S units and *trans*-1,4- and *trans*-4,1-M units. Next, the frequencies of *cis*-1,4-, 1,2-, isomerized 1,2-, and 3,4-M units are low enough that the probability of their juxtaposition can be ignored. Then, the variation of the fine structure with changing *R* allows the differentiation of compositional isomerism from directional isomerism, and in selected cases the relative intensities within a given spectrum point to conclusive directional assignments. Finally, substitutent effects on chemical shift often provide a rule for assignments, as was the case for olefinic resonances from different compositional isomers.

Table III
Chemical Shifts and Assignments for the Methylene Carbon Resonances in Poly(chloroprene sulfone)

C type and primary structure	resolved sequence	δ ppm ± 0.05 in $(CD_3)_2$SO at 60 °C	in CD_2Cl_2 at 30 °C
C_1(S*M*)	*cis*-1,4-1,4-MS*M*	61.98	62.28
	4,1-1,4-MS*M*	61.42	62.21
	1,4-1,4-MS*M*	61.10	61.84
	1,4-*cis*-1,4-MS*M*	57.06	57.61
C_4(*M*S)	*cis*-1,4-*M*S	54.09	54.78
	1,4-1,4-S*M*SM	53.53	nd[a]
	1,4-4,1-S*M*SM	53.26	54.30
	1,4+4,1-1,4-1,4-M*M*SM	53.02	53.78
	1,4+4,1-1,4-4,1-M*M*SM	52.77	53.08
 [b]	1,4-1,2-1,4-M*M*M	44.29	45.79
 [c]	*i*-1,2-1,4-*M*M	41.70	43.23
 [d]	1,4-3,4-1,4-M*M*M	nd	40.64
C_1(M*M*)	*cis*-1,4-1,4-M*M*	37.70	39.30
	1,4-1,4-1,4+4,1-M*M*M	37.43	38.37
	1,4-1,4-M*M*S	37.09	37.88
	4,1-1,4-1,4+4,1-M*M*M	36.94	37.57
	4,1-1,4-M*M*S	36.70	37.21
	1,4-*cis*-1,4-M*M*	31.85	32.81
	4,1-*cis*-1,4-M*M*	31.69	32.09
C_4(*M*M)	*cis*-1,4-1,4-*M*M	27.53	28.56
	1,4+4,1-1,4-4,1-M*M*M	27.19	27.86
	1,4-4,1-S*M*M	27.21	27.65
	1,4-1,4-S*M*M	26.75	27.13
	1,4+4,1-1,4-1,4-M*M*M	26.18	27.02

[a] nd = not determined. [b] 1,2-Chloroprene unit. [c] Isomerized 1,2-chloroprene unit. [d] 3,4-Chloroprene unit.

These considerations led to the assignments for the relatively simple fine structure from the methylene resonances, which are summarized in Table III.

In the spectrum of sample 1 (Figure 3a), C_1(S*M*) and C_4(*M*S) are doublets from directional dyads in the sequence MSM. With increasing copolymerization temperature, the C_1(S*M*) doublet does not exhibit further splitting from increasing *R*, but its low-field component decreases in intensity relative to its high-field component. This means that, contrary to normal expectation, directional isomerism in the sequence MSM becomes *more* regular with increasing temperature. An explanation for this significant observation will be offered in section 4. For the present, consideration of relative intensities of C_1(M*M*) and C_4(*M*M) demonstrates that the preferred isomer involves head-to-tail placement across the sulfone unit. This will be proven shortly. Accordingly, the low-field component is assigned to C_1(4,1-1,4-MS*M*), and the high-field component to C_1(1,4-1,4-MS*M*).

In contrast with C_1(S*M*), C_4(*M*S) develops fine structure which reflects increasing *R*. The simple doublet from

C_4(1,4-1,4-S*M*SM) and C_4(1,4-4,1-S*M*SM), observed in order of increasing field in Figure 3a, becomes overlapped by two new peaks in spectra of copolymers prepared at higher temperatures. These new peaks are displaced slightly to higher field and arise from the compositional triad MMS. An additional weak peak, most likely from C_4(*cis*-1,4-*M*S), appears at low field from the main resonance.

The quartet derived from C_4(*M*S) therefore corresponds to the two directional isomers from MSM in both compositional sequences SMSM and MMSM. Sample 8 gives a somewhat simpler spectrum in this region, owing to few SMS sequences. A broad doublet is observed (Figure 3d), from 1,4+4,1-1,4-1,4-M*M*SM and 1,4+4,1-1,4-4,1-M*M*SM, with overlap by the sharp solvent pentuplet (CD_2Cl_2). Note that although C_4(*M*) can distinguish whether its preceding unit is S or M, it apparently does not distinguish the directional sense of the latter unit. This is indicated by the notation 1,4+4,1 to include both possibilities.

Some interesting conclusions can be drawn also from the high-field pair of methylene resonances, which pertain to the MM sequence or "polychloroprene-like" environment.

Few such sequences form at −78 °C, accounting for the low intensity in the region under consideration in Figure 3a. However, with 16-fold vertical expansion C_1(M*M*) and C_4(*M*M) resonances can be discerned, but they are unusually complex in comparison with the spectrum of sample 3 (Figure 3b). This complexity is incompatible with the structural regularity expected at −78 °C, but it can be explained by minor contamination with material having *R* close to 3 (section 1).

The spectra show that C_1 and C_4 within the MM dyad can discern compositional triads and directional dyads. In other words C_1(M*M*M) is distinguishable from C_1(M*M*S), and C_4(M*M*M) is distinguishable from C_4(S*M*M). Resonances due to contamination of the above kind are most apparent in the spectrum of sample 1, where their intensities are then comparable to those from the few SMMS sequences in authentic material.

Insofar as the extent of compositional heterogeneity is minor, MMM is rarely observed in copolymers prepared below 40 °C, so that most MM dyads in these samples must be flanked by sulfone units. This circumstance permits identification of the predominant directional dyad in the sequence MSM. Conclusive evidence can be obtained from the spectrum of sample 3 (Figure 3b), where C_1(SM*M*S) has nearly twice the intensity of C_4(S*M*MS). A necessary conclusion is that more C_4's are bonded to sulfone than C_1's, so that 4,1-1,4-MSM must be less likely than either 1,4-1,4-(= 4,1-4,1-) or 1,4-4,1-MSM. Only in two idealized cases can C_1(S*M*) and C_4(*M*S) be equiprobable. These are for a poly(chloroprene sulfone) with no directional isomerism or with *R* exactly unity.

At 100 °C the copolymer incorporates little sulfur dioxide, so its major high-field methylene resonances (Figure 3d) are derived from the MMM sequence. Their directional fine structure was assigned according to Brame et al.[9] The perturbation induced by sulfone units is apparent only from minor intrusion of C_1(M*M*S) and C_4(S*M*M) resonances. Directional dyad splitting is imposed, as well as splitting from cis-1,4 neighbors, which can no longer be ignored.

The positional effect of chlorine substituents on the chemical shift of methylene carbons in different directional isomers can be formulated from the assignments for MMM and MSM sequences, which have been established above. Thus a γ chlorine instead of hydrogen shields a methylene carbon by about −0.4 to −0.5 ppm (see MMM assignments), and a δ chlorine instead of hydrogen deshields a methylene carbon by about +0.3 ppm (see MSM assignments). This rule was used to complete directional assignments in Table III.

Table IV
Chemical Shifts and Assignments for the Olefinic Carbon Resonances in Poly(chloroprene sulfone)

C type and primary structure	resolved sequence	δ ppm ± 0.05 in $(CD_3)_2SO$ at 60 °C	δ ppm ± 0.05 in CD_2Cl_2 at 30 °C
C_2(M*M*S)	1,4-1,4-1,4-M*M*SM	140.83	142.14
	1,4-1,4-4,1-M*M*SM	140.50	141.75
	4,1-1,4-1,4-M*M*SM	139.85	140.98
	4,1-1,4-4,1-M*M*SM	139.55	140.62
C_2(M*M*M)	1,4-1,4-1,4-M*M*M	134.54	135.03
	4,1-1,4-1,4-M*M*M	nd	134.46
	1,4-1,4-4,1-M*M*M	nd	133.78
	4,1-1,4-4,1-M*M*M	nd	133.45
C_3(S*M*M)	4,1-1,4-4,1-MS*M*M	134.84	135.42
	1,4-1,4-4,1-MS*M*M	134.59	nd
	4,1-1,4-1,4-MS*M*M	134.12	134.72
	1,4-1,4-1,4-MS*M*M	133.87	nd
C_2(S*M*S)	1,4-1,4-1,4-MS*M*SM	128.23	nd
	1,4-1,4-4,1-MS*M*SM	128.16	128.85
	4,1-1,4-1,4-MS*M*SM	127.97	nd
	4,1-1,4-4,1-MS*M*SM	127.88	nd
C_3(M*M*M)	1,4-*cis*-1,4-1,4-M*M*M	nd	127.09
	4,1-1,4-4,1-M*M*M	125.62	126.21
	1,4-1,4-4,1-M*M*M	124.88	125.41
	4,1-1,4-1,4-M*M*M	124.88	125.41
	1,4-1,4-1,4-M*M*M	124.25	124.55
C_3(S*M*S)	4,1-1,4-4,1-MS*M*SM	122.78	nd
	1,4-1,4-4,1-MS*M*SM	122.62	123.85
	4,1-1,4-1,4-MS*M*SM	122.55	nd
	1,4-1,4-1,4-MS*M*SM	122.41	nd
C_2(S*M*M)	1,4-1,4-1,4-MS*M*M	121.88	122.38
	4,1-1,4-1,4-MS*M*M	121.61	nd
	1,4-1,4-4,1-MS*M*M	121.32	121.79
	4,1-1,4-4,1-MS*M*M	121.04	nd
C_3(M*M*S)	4,1-1,4-4,1-M*M*SM	114.12	114.85
	4,1-1,4-1,4-M*M*SM	113.97	114.40
	1,4-1,4-4,1-M*M*SM	113.63	114.09
	1,4-1,4-1,4-M*M*SM	113.34	113.40

Minor irregularities have characteristic resonances in the methylene region. The probabilities of 1,2 and 3,4 structures increase with increasing polymerization temperature, so their resonances are seen best in the spectrum of sample 8 (Figure 3d). Assignments for 1,2-, isomerized 1,2-, and 3,4-M units were made according to the data reported by Brame et al. from model compounds.[9] The respective peaks are at 45.79, 43.23, and 40.64 ppm (observed in CD_2Cl_2). The weak intensities show that the above structures are infrequent, so it is quite unlikely that their pseudoasymmetric centers will be adjacent and present different tacticities. Note however that *cis*-1,4-M units are sufficiently numerous in sample 8 that their resonances show directional dyad splitting. For example, the peaks at 32.81 and 32.09 ppm are due to C_1(1,4-*cis*-1,4-M*M*) and C_1(4,1-*cis*-1,4-M*M*), respectively.

More structural detail is revealed by the olefinic resonances. Both C_2 and C_3 resonances from each of the four compositional triads are at least quartets, indicating a minimum sensitivity to directional triads therein. These are assigned in Table IV. This table is not exhaustive, however (it lists 33 peaks whereas some 62 peaks were resolved at 90.52 MHz), as it contains only those assignments which could be derived with some confidence according to the strategy outlined previously. Several factors prevented completion of the assignments for the intricate fine structure, namely, spurious resonances due to compositional heterogeneity, overlap of multiplets from different compositional isomers (over the regions 133–135 and 121–123 ppm), nonquantitative intensities (section 3), and the lack of model compound data.

The tabulated directional assignments are internally consistent with chemical shift rules, which assume that, for a given compositional triad, C_2 and C_3 are affected by their positional relationships to the two chlorines in the closest pair of adjoining M units (Figure 4). In the M*M*M sequence, for example, C_2 in *M* has these chlorines in the following substituent positions for the four directional isomers: 1,4-1,4-1,4, $\epsilon + \epsilon'$; 1,4-1,4-4,1, $\epsilon + \zeta'$; 4,1-1,4-1,4, $\delta + \epsilon'$; and 4,1-1,4-4,1, $\delta + \zeta'$. The corresponding positions with respect to C_3 are $\zeta' + \delta$, $\zeta' + \epsilon$, $\epsilon' + \delta$, and $\epsilon' + \epsilon$ (the prime distinguishes those chlorines which are sensed through the double bond of the observed carbon). Numerical values for these substituent effects were obtained from the chemical shifts for *trans*-4-chloro-4-octene (—CCl═, 134.8 ppm; ═CH—, 125.5 ppm), which provides the base values, and for polychloroprene.[9] They are: δ, −1,4; ϵ, -0.8; ϵ', +1.0; and ζ', +0.05 (a minus signifies shielding, a plus signifies deshielding).

Four additional substituent parameters are required to describe the chlorine neighbor effects on C_2 and C_3 in the six compositional triads incorporating sulfone. They are ϵ_S, ζ_S, ζ'_S, and η'_S (the subscript S distinguishes those chlorines sensed through a sulfone unit). Base chemical shifts were derived from the *trans*-4-chloro-4-octene values[9] by allowing β sulfone effects of −12.6 ppm for C_2 and −11.2 ppm for C_3 and γ sulfone effects of +6.3 ppm for C_2 and +9.3 ppm for C_3. The appropriate base ppm values are: C_2(S*M*S), 129.2; C_3(S*M*S), 123.6; C_2(S*M*M), 122.2; C_3(S*M*M), 134.8; C_2(M*M*S), 141.1; and C_3(M*M*S), 114.3. Then, the assignments for C_2(S*M*S) and C_3(S*M*S) in Table IV were made according to the intensity distribution observed in Figure 2a among their directional isomers and the corresponding probabilities for 1,4-1,4-, 1,4-4,1-, and 4,1-1,4-MSM, which were established previously from C_1 and C_4 resonances. An initial set of substituent parameters was obtained as a result.

The initial parameter set was used with the base chemical shifts to predict the remaining assignments, and it was refined by an iterative procedure to reproduce the experimental chemical shifts as closely as possible. The final values are: ϵ_S, −1.37; ζ_S, −1.12; ζ'_S, +0.56; and η'_S, +0.30. These parameters are necessarily approximate, because of the assumption that each has the same value for C_2 as it does for C_3. The refined values for the β and γ sulfone effects above were obtained without such an assumption.

Long-range effects like those with chlorine above are manifest only insofar as they influence the probabilities of *gauche* interactions of the observed carbon with its γ substituents.[27] It is interesting to note that when the γ substituent is a sulfone oxygen, then the effect of long-range chlorine is substantially greater then when it involves a carbon (e.g., compare ϵ_S with ϵ). Another interesting observation is the reversal in sign of a given effect when the particular chlorine substituent is sensed through the double bond of the observed carbon.

Table IV accounts completely for quartet fine structure of the olefinic resonances from each compositional triad, although partial to complete resolution of an octet is possible for sequences which have the observed carbon β to sulfone. Higher order compositional sequences are differentiated in these instances (the intensity patterns preclude involvement of minor irregularities). They are most likely C_2(*M*M*SM), C_3(MS*M*M*), C_2(*MS*M*SM), C_3(MS*M*SM*), C_2(*MS*M*M), and C_3(M*M*SM*), where * can be S or M, thereby doubling the four peaks from the directional triads for an overall octet. The position * is at most a η_S substituent for the observed carbon, and sensitivity of this order was noted for certain directional triads. It is again significant that a β sulfone, and hence a γ oxygen, is necessary for such long-range sensitivity. Complete resonance octet assignments were not possible for the reason given previously.

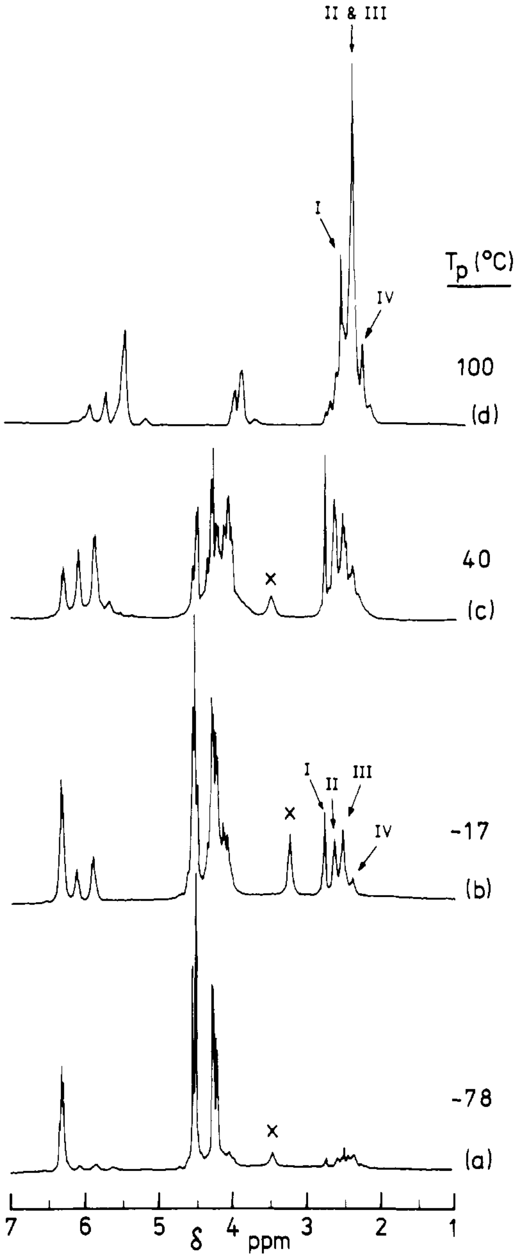


Figure 5. ^{1}H spectra (360 MHz) of poly(chloroprene sulfone) samples 1, 3, 6, and 8 (spectra a, b, c, and d, respectively). The observation conditions for spectra a, b, and c are: temperature, 70 °C; transients, 40; sweep width, 3.623 KHz; data points (FID), 16K; pulse flip angle, 90°; pulse interval, 4.0 s; solvent, DMSO-d_6; concentration, 0.10 g/cm^3. Spectrum d was obtained under the same conditions, except for the solvent (chloroform-*d*) and observation temperature (50 °C). Peaks I–IV are explained in the text and Figure 6, and peak X (variable position and intensity) is due to water.

b. ^{1}H NMR Spectra. From a structural point of view, 90-MHz ^{1}H NMR spectra are not particularly revealing, owing to vicinal homonuclear spin–spin coupling which obscures the chemical shift dispersion induced by all sequence isomers, except compositional dyads. This is not true at 360 MHz, as is apparent from Figure 5, which shows the spectra from poly(chloroprene sulfone) samples 1, 3,

Table V
Chemical Shifts and Assignments for the Proton Resonances in Poly(chloroprene sulfone)

		δ ppm ± 0.05	
proton type	resolved sequence	in $(CD_3)_2$-SO at 60 °C	in $CDCl_3$ at 50 °C
$=\overset{H}{C_3}-$	S*M*S	6.28	6.15
	S*M*M	6.04	5.94
	M*M*S	5.80	5.72
	M*M*M	5.58	5.45
$-\overset{H}{\underset{H}{C_1}}-$	4,1-1,4-MS*M*S	4.51	nd
	1,4-1,4-MS*M*S	4.48	nd
	4,1-1,4-1,4+4,1-MS*M*M	4.31	3.96
	1,4-1,4-1,4+4,1-MS*M*M	4.27	
$-\overset{H}{\underset{H}{C_4}}-$	1,4-1,4-S*M*SM	4.24	nd
	1,4-4,1-S*M*SM	4.19	nd
	1,4+4,1-1,4-1,4-M*M*SM	4.09	3.87
	1,4+4,1-1,4-4,1-M*M*SM	4.03	
$-\overset{H}{\underset{H}{C_1}}-$ (I)	4,1-1,4-M*M*	2.73	2.53
(II)	1,4-1,4-M*M*	2.59	2.39
$-\overset{H}{\underset{H}{C_4}}-$ (III)	1,4-1,4-*M*M	2.48	2.39
(IV)	1,4-4,1-*M*M	2.35	2.23

6, and 8. Three resonance regions are distinguished, corresponding to the olefinic proton from 6.3 to 5.5 ppm, methylene protons β to sulfone (i.e., in SM and MS dyads) from 4.6 to 3.8 ppm, and methylene protons like those in polychloroprene (i.e., in the MM dyad) from 2.8 to 2.2 ppm. Their detailed assignments are given in Table V.

Resonances from the olefinic proton are more sensitive to structure, and they distinguish the compositional isomers SMS, SMM, MMS, and MMM, in order of decreasing chemical shift. Sample 1 contains the most SMS triads whereas MMM triads predominate in sample 8, so those assignments were made by reference to the appropriate spectra. The MMM assignment is comparable to the literature value of 5.4 ppm for the olefinic proton in *trans*-1,4-polychloroprene.[28,29]

Assignments for SMM and MMS are not so obvious. The latter sequence must have a more intense resonance, however, since it was established by ^{13}C NMR that *M*S is more probable than S*M* (recall that *M* is 1,4 by convention). The compositional triad assignments were therefore completed in the order above by an inspection of the intensities in Figure 5.

Methylene protons β to sulfone are differentiated most readily in the spectrum of sample 1, where homonuclear coupling is clearly observed. The sequence SMS allows vicinal coupling only between the olefinic proton and the methylene protons bonded to C_4. An A_2X spin system is observed (even at 90 MHz), and single frequency homonuclear decoupling proved that methylene protons on C_4 are 0.3 ppm upfield from those on C_1 (this result was used previously to help assign C_1 and C_4 resonances). The dyad assignments are S*M* at 4.5 ppm and *M*S at 4.2 ppm.

The above dyad assignments actually correspond to the compositional triad SMS, because new resonances appear at higher field (as far as 3.8 ppm) with increasing *R*, owing to S*M*M and M*M*S sequences. Splitting from directional isomerism and homonuclear spin coupling causes considerable overlap in this region, however, rendering it less informative than the olefinic region with regard to compositional sequences.

The C_1 and C_4 methylene proton resonances from sample 1 are sensitive to directional dyads, which are responsible for splittings of 0.033 and 0.056 ppm, respectively. Here the splitting is clearly resolved owing to the absence of compositional isomerism. An additional splitting of 7.2 Hz is imposed on C_4 methylene protons by the vicinal coupling discussed above.

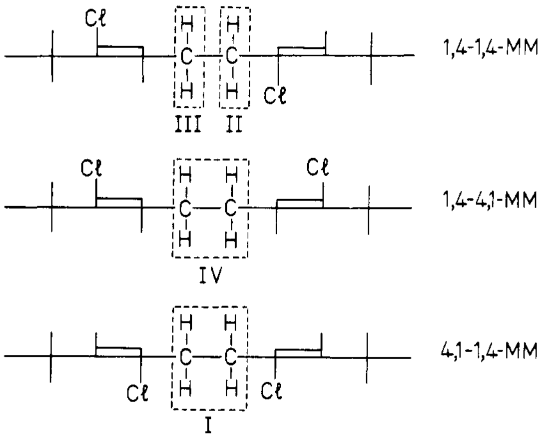


Figure 6. The four types of methylene protons from the three nonequivalent directional isomers of the MM compositional dyad.

Methylene protons in the MM dyad are insensitive to higher order compositional sequences, but they are resolved into four main peaks, which correspond to directional dyads. The relevant structures are shown in Figure 6. Assignments were made with regard to the spin coupling multiplicity and the proximity of chlorines to the observed protons.

By virtue of their symmetrical environments, the four protons designated type I are equivalent, as are type IV. In the region being considered they give the least and most shielded resonances, respectively, in accord with their distances from the nearest chlorines. Furthermore, protons I give a singlet resonance, because no vicinal coupling with olefinic protons is possible in the head-to-head (4,1-1,4) dyad. The existence of such coupling in the tail-to-tail (1,4-4,1) dyad results in the broader resonance from protons IV.

Proton pairs II and III are nonequivalent. The former, being γ to chlorine, are deshielded with respect to the latter, which are δ to flanking chlorines. Protons II also have a narrower and less structured resonance than protons III, to which they are coupled, because the latter experience additional vicinal coupling with an olefinic proton. Interestingly, type II and type III resonances coalesce in the spectrum of sample 8. The nonequivalent methylene pairs in the head-to-tail dyad of polychloroprene cannot be differentiated by ^1H NMR either.[28] Nearby sulfone units may accentuate the magnetic nonequivalence of these protons in the copolymer, or their resolution may depend on solvent.

Although the ^1H spectra do not reveal structure in such detail as the ^{13}C spectra, they supplement the latter with conformational information, which is inherent in the magnitude of certain spin coupling constants. Thus, the vicinal coupling constant of 7.2 Hz, observed for the C_4 methylene protons in sample 1, indicates that the C_3–C_4 bond in the SMS sequence prefers a *skew* conformation (Figure 7) on average. One dihedral angle between vicinal protons is 180° and the other is 60°, which accounts for the observed coupling according to Karplus' equations.[30] Energy calculations also show that this rotational isomeric state is the most likely.[31]

3. Quantitative Analysis of the Microstructure. The probabilities of the various microstructures discriminated in poly(chloroprene sulfone) by NMR are derived

Table VI
Unconditional Probabilities of Various Microstructures in Poly(chloroprene sulfone) as Determined by NMR Analysis

	triad compositional sequences[a]					MSM directional isomers			M structural isomers			
sample no.	SMS	SMM -- MMS	MMM	MSM	R[b]	4,1-1,4	1,4-1,4 +4,1-4,1	1,4-4,1	trans-1,4	cis-1,4	1,2	3,4
1	0.435	0.040	0.009	0.475	1.09	0.18	0.64	0.18	0.99	0.002	nd[c]	nd
2	0.457	0.024	0.014	0.481	1.08	0.15	0.60	0.25	0.98	0.02	nd	nd
3	0.341	0.106	0.000	0.447	1.24	0.12	0.66	0.22	0.98	0.02	nd	nd
4	0.390	0.072	0.004	0.462	1.17	0.10	0.71	0.18	0.98	0.02	nd	nd
5	0.240	0.166	0.022	0.406	1.46	0.07	0.65	0.28	0.97	0.03	nd	nd
6	0.157	0.220	0.028	0.376	1.66	0.08	0.62	0.30	0.93	0.05	0.02	nd
7	0.068	0.246	0.126	0.314	2.19	0.04	0.55	0.41	0.92	0.06	0.02	nd
8	0.035	0.133	0.532	0.168	4.96	0.05	0.53	0.42	0.84	0.13	0.026	0.004

[a] S = sulfone unit, M = chloroprene unit without regard to directional sense or isomeric form. [b] Calculated according to eq 4 in text. [c] Not determined; less than 0.001.

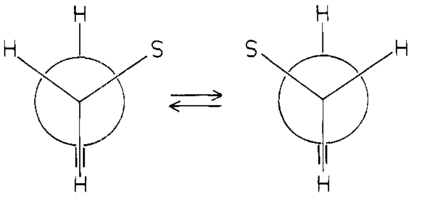


Figure 7. The two *skew* conformations of the C_3-C_4 bond in the MS sequence.

from the corresponding resonance areas. These areas were measured by a planimeter and by weighing peaks which had been traced and cut out. Both methods gave identical results, and they proved more reliable than using the intensities computed by the standard software package on the spectrometer.

Due consideration must be given to T_1 and NOE values, however, to decide whether resonance area bears the same correspondence to structural probability for all carbons. The T_1 and NOE values for a particular carbon type are determined by the local segmental reorientation rate, which in turn depends on the local microstructure. Furthermore, T_1 varies inversely as the number of protons on each carbon type, so C_3 carbons will have T_1 values twice the size of those for C_1 and C_4 carbons in a given microstructure (Table II). A necessary condition for direct comparison of resonance areas from carbons whose T_1 values differ owing to these factors is that the delay period between pulses during the NMR experiment is at least three times the maximum T_1 value. Then the magnetization of all nuclei will have recovered to at least 95% of their equilibrium values.

The above condition still does not validate the direct comparison of resonance areas because the NOE values of the contributing carbons may vary. One way of avoiding this complication is through quenching the NOE by addition of small amounts of a paramagnetic relaxation agent. This is rarely necessary for rubbery polymers, however, owing to their rapid segmental motions in solution which ensure that all carbons have the same NOE, namely the maximum value of 2.99.

The segmental mobility of poly(chloroprene sulfone) depends on its sulfone content. Increasing proportions of the sulfone unit hinder segmental motion, as evidenced qualitatively by the state of the copolymer at room temperature, which varied from rubbery (samples 8 and 7), to leathery (samples 6 and 5), to glassy (samples 4–1). This trend is verified quantitatively by the T_1 values from the polymers which exhibit the two extremes of dynamic behavior in the present series, namely *trans*-1,4-polychloroprene (rubber) and sample 1 (glass). The recent T_1 data of Coleman and Brame[32] for the former polymer show that its segmental reorientational frequency at 28 °C is about 5.0 GHz. Relaxation measurements in the present study reveal a frequency at 60 °C of about 0.8 GHz for the glassy samples 1–4.

The above motional frequencies are appropriate for maximum NOE values from carbons in all copolymer samples when observed at field strengths of 2.1 and 2.3 *T*. These values will be reduced slightly, to about 2.7, for the glassy copolymers when they are observed at 8.3 *T*. Fortunately, NOE values in this range are insensitive to small differences in motional frequency, and it is safe to assume that within experimental error, they will not vary with microstructure in a given copolymer. This assumption proved reasonable, since the microstructural probabilities derived from independent ^{13}C and ^{1}H data were consistent.

The delay period between pulses during accumulation of ^{13}C NMR data was greater than at leasst three times the longest T_1 value for protonated carbons. It was impractical to wait suitable periods for C_2, however, since it relaxes inefficiently without an attached proton and has a T_1 value of around 3 s. The time required to avoid suppression of C_2 resonance areas through incomplete relaxation was therefore prohibitive, and they were not employed in this work for quantitative purposes.

The triad compositional sequence distribution is defined by the set of unconditional probabilities p(MMM), p(MMS), p(SMM), p(MSM), and p(SMS). Here M simply denotes a chloroprene unit, without regard to its directional sense or isomeric form, so p(SMM) will be equal to p(MMS) in accord with the principle of sequence reversibility. Each unconditional probability of M-centered triads was obtained for the individual samples by dividing the appropriate C_3 resonance area by the total of the C_3 resonance areas. This was done for spectra recorded at 90.52 and 25.16 MHz and also for olefinic proton spectra at 360 MHz. The results from the three independent sets of data were in good agreement, as noted above.

Once the triad compositional sequence distribution is known, the dyad and monad distributions are prescribed, according to eq 1–3. As a test of the NMR assignments

$$p(\mathrm{MM}) = p(\mathrm{MMS}) + p(\mathrm{MMM}) \qquad (1)$$

$$p(\mathrm{SM}) = p(\mathrm{MS}) = p(\mathrm{MMS}) + p(\mathrm{SMS}) \qquad (2)$$

$$p(\mathrm{M}) = 1 - p(\mathrm{S}) = p(\mathrm{MM}) + p(\mathrm{MS}) \qquad (3)$$

and quantitative reliability of the data, compositional dyads were also measured from C_1 and C_4 resonances at 90.52 and 25.16 MHz and from methylene proton resonances at 360 MHz. All results were consistent to within 5% on a relative basis.

Table VI gives the unconditional probabilities of those microstructures which could be measured accurately for all samples. The macroscopic compositions R, calculated according to eq 4, compare very favorably with those determined by elemental analyses (Table I). This agreement

$$R = p(\mathrm{M})/p(\mathrm{S}) \qquad (4)$$

provides another substantiation of the preceding NMR analyses.

The probabilties of the different M isomers at various temperatures agree closely with those determined by ^{13}C NMR of polychloroprene,[32] except for 3,4 isomers, which are an order of magnitude less likely. Agreement is not so good with the results of Matsuda and Hara,[4] which indicate significantly higher proportions of *cis*-1,4- and 3,4-M units in poly(chloroprene sulfone) at comparable temperatures. These conclusions were based on IR and 60-MHz ^{1}H NMR measurements, however, which are not as reliable as ^{13}C NMR in determining the above structures. Nevertheless, their results and the present work show unequivocally that poly(chloroprene sulfone) is not predominantly 1,2, as believed by Stannett et al.[2]

It appears that the double bond in poly(chloroprene sulfone) is resistant to further attack by sulfur dioxide under present conditions. Whereas exposure to sulfur dioxide can isomerize natural rubber to its equilibrium content of about 60% trans double bonds[33] and cause addition to pairs of double bonds in polybutadiene to form cyclic structures,[34] no similar structural changes were detected for poly(chloroprene sulfone).

4. Copolymerization Mechanism. Poly(chloroprene sulfone) is a binary copolymer from a monomer-based viewpoint, but in the preceding analyses three major structural units were distinguished, namely, S, *trans*-1,4-M, and *trans*-4,1-M. From a structural and mechanistic viewpoint, therefore, it is a terpolymer.

Our previous studies on variable-composition polysulfones[12-14] have shown that depropagation reactions and the penultimate unit from the growing chain end are highly relevant to the copolymerization mechanism. A general terpolymerization scheme with penultimate unit effects is described by 27 equations, but a reduction to 22 is possible in the present case, because SS sequences are not formed. In order to greatly simplify the discussion, however, the directionality of M will be ignored for the time being, in which case only eq 5–9 need be considered.

$$\sim\mathrm{SM}\cdot + \mathrm{S} \underset{k_\mathrm{d}(\mathrm{SMS})}{\overset{k_\mathrm{p}(\mathrm{SMS})}{\rightleftharpoons}} \sim\mathrm{MS}\cdot \qquad (5)$$

$$\sim\mathrm{SM}\cdot + \mathrm{M} \underset{k_\mathrm{d}(\mathrm{SMM})}{\overset{k_\mathrm{p}(\mathrm{SMM})}{\rightleftharpoons}} \sim\mathrm{MM}\cdot \qquad (6)$$

$$\sim\mathrm{MS}\cdot + \mathrm{M} \underset{k_\mathrm{d}(\mathrm{MSM})}{\overset{k_\mathrm{p}(\mathrm{MSM})}{\rightleftharpoons}} \sim\mathrm{SM}\cdot \qquad (7)$$

$$\sim\mathrm{MM}\cdot + \mathrm{S} \underset{k_\mathrm{d}(\mathrm{MMS})}{\overset{k_\mathrm{p}(\mathrm{MMS})}{\rightleftharpoons}} \sim\mathrm{MS}\cdot \qquad (8)$$

$$\sim\mathrm{MM}\cdot + \mathrm{M} \underset{k_\mathrm{d}(\mathrm{MMM})}{\overset{k_\mathrm{p}(\mathrm{MMM})}{\rightleftharpoons}} \sim\mathrm{MM}\cdot \qquad (9)$$

The rate coefficients for propagation and depropagation of a particular sequence are given by the respective k_p and k_d values, which increase with temperature according to the usual Arrhenius type expression. Their relative values characterize the compositional behavior of the system.

The formation of a nearly alternating 1:1 copolymer at −78 °C indicates that only k_p(SMS), k_p(MMS), and k_p(MSM) have appreciable values at this temperature. The homopropagation rate coefficients k_p(MMM) and k_p(SMM) are not significant by comparison, even when the temperature is raised to 0 °C. Although a few MMM sequences were observed in samples 1–4, they have random probabilities since they are associated with traces of the adventitious material discussed previously.

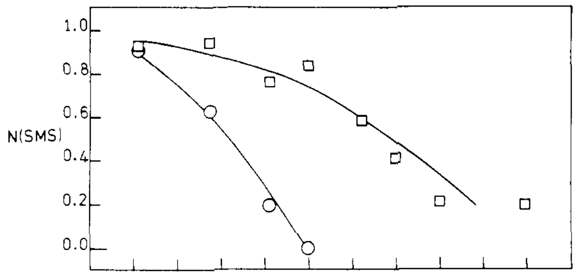


Figure 8. A comparison of the effect of polymerization temperature on the number fractions of SMS compositional triads, N(SMS), for poly(chloroprene sulfone) and poly(vinyl chloride sulfone): (○) M = vinyl chloride, see R. E. Cais and J. H. O'Donnell, *J. Polym. Sci., Polym. Lett. Ed.*, 15, 659–669 (1977); (□) M = chloroprene, this work. Here $N(\mathrm{SMS}) = p(\mathrm{SMS})/p(\mathrm{SMS}) + p(\mathrm{MMS})$, and this number fraction is one indication of the difference in probability that sulfur dioxide adds to a sequence with a penultimate sulfone unit compared to one without.

When the temperature is raised even further to 100 °C, however, the MMM compositional triad clearly becomes the most probable. Depropagation reactions must be invoked to explain this fact, since all propagation rate coefficients attain comparable values at this temperature. The net rate of inclusion of S in the copolymer becomes slower than that of M because k_d(SMS) and k_d(MMS) have increased substantially, unlike k_d(MMM) and k_d(SMM), which are still negligible. As expected, the relatively weak carbon-sulfur bonds are much more susceptible to homolysis by depropagation than carbon-carbon bonds.

The above scheme applied just as well to those copolymerizations of sulfur dioxide where M is vinyl chloride,[12] styrene,[13] or acrylamide.[14] However, these systems are characterized by intermediate temperatures, from 0 to 40 °C, above which p(SMS) is zero, even though p(MMS) is appreciable. It was concluded that the probability of depropagation of a sulfonyl radical was enhanced when its monomer sequence contained a pen-penultimate sulfone unit, i.e., $k_\mathrm{d}(\mathrm{SMS}) > k_\mathrm{d}(\mathrm{MMS})$.

In contrast, the present results give no indication of such an enhancement when M is chloroprene. The number fraction of SMS sequences falls to zero much more gradually with increasing temperature than when M is vinyl chloride, for example, as shown in Figure 8.

The most significant difference involves the number of backbone bonds which separate sulfone units in the SMS sequence, namely, five in 1,4-poly(chloroprene sulfone) and three in all polysulfones from mono olefins like vinyl chloride. In the latter systems the sulfone units repel each other in most conformations owing to unfavorable Coulombic and steric interactions.[35] The additional separation of sulfones by two more bonds when M is chloroprene eliminates these interactions to the extent that k_d(SMS) will no longer be measurably greater than k_d(MMS), as anticipated in an earlier publication.[14]

Carbon-13 NMR relaxation studies of polysulfones provide another source of evidence for the onset of unfavorable interactions between sulfone units when their intrachain spacing decreases from five to three backbone bonds. This decrease reduces the frequency of segmental motion by at least an order of magnitude, owing to an increase in bond torsional potential energies from the interactions described previously.[36]

The present results show that there is also a structural effect on the probability of depropagation of the −M· radical. Over the temperature range examined here this radical will be susceptible to depropagation provided that a carbon-sulfur bond is broken in the process, confining attention to the –MSM· terminal sequence. Evidence for the depropagation of this sequence is obtained when the directional isomerism of M is examined.

There are three directional isomers of the sequence MSM: 1,4-1,4-, 1,4-4,1-, and 4,1-1,4-. The probabilities in Table VI show that these conform to Bernoullian statistics at −78 °C, with $p(1,4) = 0.76$ (hence $p(4,1) = 0.24$). At more elevated temperatures, however, the inequality between $p(4,1\text{-}1,4)$ and $p(1,4\text{-}4,1)$ indicates that Bernoullian statistics no longer apply. More interestingly, the bias in the distribution of directional isomers is not reduced by raising temperature, but rather the 4,1-1,4-MSM isomer becomes increasingly unlikely, to the point of virtual exclusion at 100 °C.

These observations are suggestive of depropagation steps which cause the preferential loss of those chloroprene units which have added to the sulfonyl radical at C_1 rather than C_4. The former addition places chlorine closer to the sulfone unit than the latter and therefore may involve energetically less favorable interactions. An analogy is found in the terpolymerization of sulfur dioxide with a pair of olefins having different ceiling temperatures for the formation of their respective binary polysulfones. If the lower ceiling temperature corresponds to olefin M_1, for example, then the compositional triad M_1SM_1 becomes less likely than M_2SM_2 with increasing temperature, and the M_1/M_2 ratio becomes vanishingly small between the ceiling temperatures.[37]

In the case of the reaction of chloroprene with the sulfonyl radical, the ceiling temperature for 1,4 addition is lower than that for 4,1 addition. The analogy with the olefin pair does not carry over completely, however, because chloroprene reacts with its own radical (eq 9). If this were not the case, the limiting copolymer sequence structure at high temperatures would be $(-4,1\text{-SM}-)_n$. The direction of addition of M to –M· may be described by first-order Markov statistics, as its probability is conditional on the direction of the terminal unit.[32] Furthermore, because the radical –MM· does not depropagate under present conditions, the distribution of directional isomers in the sequences MMS, SMM, and MMM follows the more usual trends of becoming increasingly irregular as temperature is raised.

The monomers vinyl chloride, styrene, or acrylamide add unidirectionally during their copolymerizations with sulfur dioxide,[12-14] and fail to present a similar opportunity of observing structural changes with temperature which could be attributed directly to their depropagation. Recently, however, by monitoring cis-trans isomerization of the double bond in deuterium labeled monomer,[38] Iino et al. have proved that styrene adds reversibly to the sulfonyl radical.

Conclusions

There can be little doubt now concerning the central role of depropagation steps in a rational model for the copolymerization of sulfur dioxide with unsaturated monomers. Studies of the variable composition systems have brought to light the dependence of depropagation rate constants on monomer sequence structure as well as temperature, and the chloroprene system has allowed a consolidation of these findings by presenting new forms of sequence and structural isomerism. High-field ^{13}C NMR has been a particularly valuable probe in discerning many of the subtle structural differences encountered. It seems highly improbable that the present results would be consistent with a model which placed great significance on equimolar molecular association complexes between chloroprene and sulfur dioxide as propagating entities.

Compositional sequences and directional isomers are presently two examples of polymer structure which may be influenced by depropagation reactions. Under suitable conditions other forms of isomerism in addition polymers may be affected similarly, for example, stereoisomerism in homopolymers prepared near their ceiling temperatures.

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and thereby indistinguishable from it in the "infinite" chain. For example, C_3(1,4-1,4-1,4-M*M*M) is equivalent to C_3(4,1-4,1-4,1-M*M*M), C_2(1,4-1,4-4,1-MS*M*M) is equivalent to C_2(1,4-4,1-4,1-M*M*SM), and so on.
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Dynamics of Polymer Solutions. 1. Theory for an Instrument

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ABSTRACT: We present the theory for an instrument which can measure several parameters of the viscoelasticity of dilute solutions of very large polymer molecules. In previous work on solutions of large DNA molecules, we used retardation times, measured by creep recovery, to get the molecular weight of the largest such molecules in solution. We have now added the capability to measure stress relaxations, the theory for which is described here. In the following paper, we show that by combining creep-recovery and strain-relaxation measurements it is possible to get information about the molecular-weight distribution of large polymer molecules in the solution.

The viscoelastic behavior of dilute polymer solutions gives much information about the sizes of the polymer molecules and their distribution. With very large molecules the relaxation times are long and viscoelasticity is easy to measure; such is the case with large DNA. Herein we describe the theory for an instrument which can make a variety of viscoelastic measurements on dilute DNA solutions. We believe it will be of value to both biologists and rheologists. For example, with a simpler instrument our lab and others have measured one viscoelastic parameter—the longest retardation time—and used it for getting information about the size and structure of chromosomal DNA in viruses,[1] bacteria,[2] and eukaryotes.[3] Those experiments, called creep-recovery experiments, give primarily information about the largest molecules in the solution. Here, and in the following paper, we show that by adding the capability to measure shear-stress relaxation as well it is possible to get information about the distribution of sizes of those molecules. This now allows us to study natural populations of DNA sizes, biological mechanisms of DNA damage, and physical mechanisms of damage such as radiation or shear degradation in flow. For rheological studies, DNA is in some ways an ideal polymer. Each molecule is biologically synthesized to have the same molecular weight. Therefore, in physical studies of solutions of DNA from an appropriate source, molecular-weight distribution need not complicate the rheology. Here we present the theory for a general rheological instrument for DNA solutions with which we can measure specific viscosity, creep recovery, and shear-stress-relaxation dynamics on the same solution. With it we can study viscoelastic properties and molecular-weight distributions of DNA solutions. Elsewhere we present a detailed description of the instrument[4] and experimental results.[5]

Instrument Description

The DNA solution is in a cylindrical glass chamber. Concentric with the cylindrical chamber and suspended in the solution is a plastic rotor containing a metal ring at the bottom. An external electromagnetic field produces eddy currents in the ring which turn the rotor, thus applying a shear stress to the solution. This "windup" of the rotor prepares for either of two kinds of experiment (see Figure 1). Also during this windup, the applied stress is fixed and we can measure the strain rate, so that we can get the solution viscosity. Some of the applied energy is stored in the "elastic" entropy of the molecules as they are stretched from their equilibrium configuration by the shear. So now at the time we call $t = 0$, the molecules are allowed to relax, causing either (1) a relaxation of the strain in the solution or (2) a relaxation of the shear stress in the solution. Relaxation of the strain—a creep-recovery experiment—is accomplished by turning off the externally-applied drive field, allowing the rotor to be governed by the solution dynamics alone. The molecules relax, pulling the rotor in the reverse direction. The angular velocity of the rotor decays exponentially, which we follow with an optical system. In the relaxation of the shear stress—a stress relaxation—the rotor angular position, $\theta(t)$, as monitored by the optical system, is held fixed at θ_0 by servo electronics which apply a restoring torque, $T = -k(\theta(t) - \theta_0)$, to the rotor if the angular position deviates from θ_0. As the molecules relax, the shear stress in the solution, and the electromagnetically-applied torque which balances it, decay exponentially to zero. It is this torque that we measure in this case.

Theory

The dynamical behavior of the DNA solution acting on the rotor can be described by the Rouse–Zimm beads–springs theory,[6] in which it is assumed that the friction of each polymer molecule with the solvent is localized at beads along the chain, and that springs, which model the configurational entropy of the chain, connect the beads. To treat the complete dynamics of the instrument, we must include rotor inertia, and we consider a solution

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