

Copolymerization of chloroprene with elemental sulphur. ^1H n.m.r. study on the stereochemistry of the chloroprene unit adjacent to the sulphur unit

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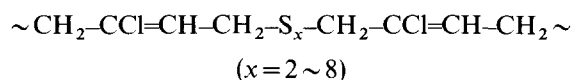
Free radical copolymerization of chloroprene (Cp) with elemental sulphur (S_8) was studied in a range of temperatures from 20 to 100°C as a function of total monomer concentration. The stereochemistry of the Cp unit adjacent to the sulphur unit has been examined by the reduction of polysulphide linkages to thiol and by observing ^1H nuclear magnetic resonance (n.m.r.) spectra of the methylene group directly bonded to the thiol. Two-dimensional n.m.r. spectroscopy has been applied to the stereochemical assignments of $-\text{CH}_2-\text{SH}$. The effect of total monomer concentration and polymerization temperature on the directional isomerism was explained by a mechanism including the depropagation of growing polymer radical $\sim\text{S}_x-\text{Cp}\cdot$. It was found that the population of 1,4 addition of the polysulphenyl radicals decreases with decreasing total monomer concentration or with increasing polymerization temperature. It was also found that the *cis* configuration is preferentially formed in the Cp unit which is arranged by the 4,1 addition of the polysulphenyl radicals. It has been suggested that the incorporated sulphur unit clearly shows the penultimate unit effect on the *cis/trans* isomerism for this Cp unit.

(Keywords: copolymerization; chloroprene; elemental sulphur; stereochemistry; ^1H n.m.r.)

INTRODUCTION

There are very few studies on the direct copolymerization of organic monomers with elemental sulphur (S_8). It is well known that most radical polymerizations are inhibited or strongly retarded by the presence of S_8 (refs 1-4). Chloroprene (Cp) and S_8 , on the contrary, copolymerize readily by a free-radical mechanism^{5,6}. Although the Cp- S_8 copolymer is one of the well-known synthetic rubbers, very little is known about its copolymerization mechanism.

Recently⁷, we have demonstrated the potentiality of ^1H n.m.r. in resolving the detailed microstructure of the Cp- S_8 copolymer, which has, in part, the following structure:



The major sulphur unit in the copolymer is octasulphide, the next is disulphide and the least common are the other polysulphides with three to seven sulphur atoms. It was also evidenced that stereochemistry of the Cp unit adjacent to the sulphur unit ($-\text{Cp}-\text{S}_x-$) is different from that found in the Cp homosequence. The effects of total monomer concentration and polymerization temperature on the copolymer composition and the length of polysulphide linkages have been explained by the depropagation process involving both carbon-sulphur and sulphur-sulphur bond scissions⁸.

As the polymerization of Cp can produce structures having geometrical and directional isomerism, information on the structural characteristics of polymers has been very useful in studies on polymerization mechanism. In the present work, the effect of

polymerization conditions on the stereochemistry of $-\text{Cp}-\text{S}_x-$ was investigated to obtain further insight into the copolymerization mechanism of Cp with S_8 . The reduction of polysulphide linkages in the copolymer to thiol provides detailed information on the stereochemistry of $-\text{Cp}-\text{S}_x-$, which was obtained by observing ^1H n.m.r. spectra of the methylene group directly bonded to the thiol group. Furthermore, the stereochemistry of $\text{Cp}-\text{S}_x-$ was compared with that of the Cp units bonded to n-dodecylthio and trichloromethyl groups with respect to the penultimate unit effect.

EXPERIMENTAL

Polymerization

The procedure for Cp- S_8 copolymerizations has been described elsewhere⁸. Copolymerization details are given in Table 1. The effect of polymerization conditions, i.e., total monomer concentration (samples A-E) and polymerization temperature (samples F, C, G, H and I) on the copolymer structure is investigated. Polymerization conditions were restricted by the solubility of S_8 in Cp/diluent mixture. In order to eliminate the effect of Cp conversion, the conversions were controlled to be almost constant (about 20%) for all copolymerizations.

Two kinds of Cp homopolymers were prepared in the presence of chain transfer agents, n-dodecylmercaptan (n-DDM) and bromotrichloromethane (BrCCl_3), respectively. Polymerization was carried out at 40°C in the emulsion system based on the well-known method⁹. Cp conversions were 50%. After polymerization, the emulsion was poured into a large amount of methanol

Table 1 Polymerization data for Cp-S₈ copolymers^a

Sample	Monomer conc. in feed [Cp] (mol l ⁻¹)	Polym. temperature (°C)	Initiator conc. (mol l ⁻¹)	Polym. time (h)	Cp conversion (%)
A	5.7	40	0.025	7.5	21
B	4.1	40	0.018	7.5	22
C	3.1	40	0.014	10.0	20
D	2.2	40	0.010	13.0	19
E	1.2	40	0.005	16.0	18
F	3.1	20	0.220	15.0	15
G	3.1	60	0.006	3.0	20
H	3.1	80	0.008	1.3	28
I	3.1	100	0.007	0.7	18

^a [S₈]/[Cp] molar ratio in feed is 0.069 for all copolymerizations.

Initiator: A-G, 2,2'-Azobis(2,4-dimethylvaleronitrile); H, 2,2'-Azobisisobutyronitrile; I, 1,1'-Azobis(cyclohexane-1-carbonitrile)

Diluent: A-G, carbon disulphide; H, I, toluene

containing a trace of antioxidant, 2,6-di-tertbutyl-4-methylphenol. The polymer was purified by reprecipitation from benzene/methanol and then freeze-dried from benzene solution.

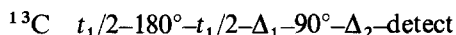
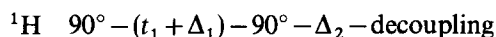
Reduction

The Cp-S₈ copolymer (10.0 g) was dissolved in benzene (70 cm³) and methanol (15 cm³) was added to the solution. Zinc powder (2.25 times molar quantity of sulphur in the copolymer) was suspended in the solution at 40°C under vigorous stirring. Hydrochloric acid (12 mol l⁻¹, 2.5 times molar quantity of zinc powder) was added dropwise to the solution. After 8 h at 40°C, the reaction mixture was left overnight at 0°C. The reduced copolymer was recovered from benzene layer by freeze drying.

Characterization

¹H n.m.r. spectra were observed in deuteriochloroform (CDCl₃) at 27°C using a Jeol GX-400 spectrometer operated at 400 MHz. Polymer concentrations were about 0.20 g cm⁻³ for all samples. Tetramethylsilane (TMS) was used as an internal standard for chemical shifts. Thirty-two transients were accumulated by using a 45° pulse and a pulse interval of 7 s. Peak intensities of well-separated signals in the spectra were determined by the standard software package for integration attached to the spectrometer.

The two-dimensional ¹³C-¹H heteronuclear shift-correlated experiment was performed with the following standard pulse sequence:



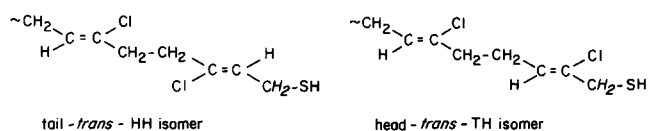
A total of 96 scans was accumulated for each t_1 value with a repetition time of 1.1 s. The delay times, Δ_1 and Δ_2 , were set to 3.6 and 1.8 ms, respectively. The data matrix was 16 000 Hz (2048 data points) in the ¹³C dimension and 2000 Hz (256 t_1 values) in the ¹H dimension.

The proton two-dimensional long range *J*-correlated experiment was performed with the standard 90°- Δ - t_1 -90°- Δ - t_2 pulse sequence. A total of 16 scans was accumulated for each t_1 value with a repetition time of 2.0 s. The delay time, Δ , was set to 200 ms. The data matrix consisted of 240 spectra of 1024 data points each and was zero filled to 512 by 1024 points covering 2500 Hz in both dimensions.

RESULTS AND DISCUSSION

Stereochemical assignments

In order to obtain the information on the stereochemistry of -Cp-S_x-, the contribution of the length of polysulphide linkages to chemical shifts of methylenic protons was eliminated by the reduction of polysulphides to thiol. In Figure 1 is shown the expansion of the -CH₂-SH resonances for sample I. We have reported previously⁷ that the Cp unit adjacent to the sulphur unit is in the 1,4 configuration, and that the discernible stereochemistry in this spectrum can be explained by three factors: head/tail arrangement to the thiol group, *cis/trans* isomerism and directionality of the neighbouring Cp unit (-Cp-Cp-S_x-). The directionality of -Cp-Cp-S_x- results in tail-to-tail (TT) and tail-to-head (TH) linkages for the head arrangement, and head-to-head (HH) and head-to-tail (HT) linkages for the tail arrangement. Typical stereochemical isomers are as follows.



Considering these three kinds of factors, eight kinds of stereochemical isomers should be distinguished in the ¹H n.m.r. spectrum. Two doublets and three triplets are observed in Figure 1. Resonances 2, 3, 4 and 5 were assigned to -CH₂-SH in the head arrangement, and tail-trans-HT, tail-trans-HH and tail-cis isomers, respectively⁷. Resonance 1 was assigned to -CH₂-SH in another head arrangement. In order to accomplish complete resonance assignments, a 2D ¹³C-¹H heteronuclear shift-correlated spectrum and a 2D long range *J*-correlated spectrum were observed.

As the carbon resonance of the methylene group in the Cp homosequence is more sensitive to the *cis/trans* isomerism than the proton resonance, the configurational assignments of resonances 1 and 2 were achieved with the aid of the ¹³C n.m.r. spectrum. Carbon resonances of -CH₂-SH can be assigned on the basis of the heteronuclear chemical shift correlation. Figure 2 shows the contour plot of the 2D ¹³C-¹H heteronuclear shift-correlated spectrum of sample I. The 2D ¹³C-¹H correlated spectrum maps each proton resonance to the carbon resonance of the corresponding directly attached

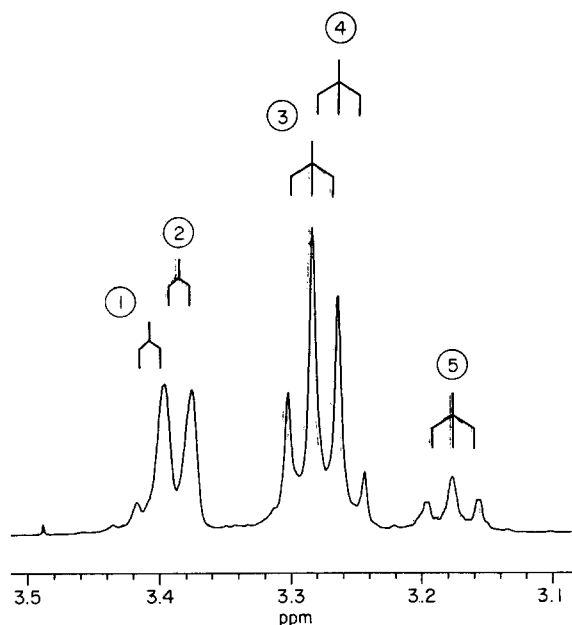


Figure 1 Expanded ^1H n.m.r. spectrum of sample I in the region of $-\text{CH}_2\text{-SH}$ resonance

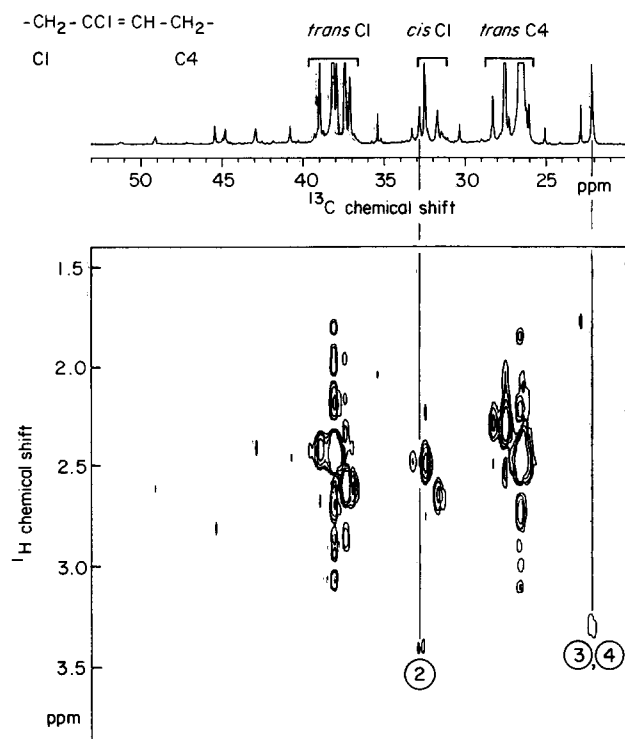


Figure 2 Contour plot of the 2D ^{13}C - ^1H heteronuclear shift-correlated spectrum of sample I. The x and y axes correspond to the carbon and proton chemical shifts, respectively, and the projection of the carbon spectrum is given on the former

carbon. The crosspeaks corresponding to resonances 2, 3 and 4 are observed. Corresponding carbon resonances are observed at 33 and 22 ppm in the normal spectrum.

Coleman *et al.*¹⁰ have reported that the methylene carbon resonance patterns of the Cp homosequence can be roughly divided into three groups assigned to *trans* C1, *cis* C1 and *trans* C4 from the lower to higher field. Further splittings have been accounted for by postulating a distribution of triad sequence isomers. The crosspeak maps proton resonances 3 and 4 to the carbon resonance

at 22 ppm. As proton resonances 3 and 4 correspond to the tail-*trans* isomer, the carbon resonance at 22 ppm corresponds to the *trans* C4. Therefore, the carbon resonance of $-\text{CH}_2\text{-SH}$ should appear in a higher field than that of the stereochemically corresponding methylene group in the Cp homosequence for more than 4 ppm. On the other hand, the crosspeak maps proton resonance 2 to the carbon resonance at 33 ppm. As proton resonance 2 corresponds to the head isomer, the carbon resonance at 33 ppm corresponds to C1. Therefore, proton resonance 2 is assigned to $-\text{CH}_2\text{-SH}$ in the head-*trans* isomer on the basis of chemical shift additivity rules.

The digital resolution and sensitivity of the 2D spectrum are not sufficient to detect a unique crosspeak for resonance 1. However, resonance 1 is also assigned to $-\text{CH}_2\text{-SH}$ in the head-*trans* isomer, since the small chemical shift between resonances 1 and 2 (0.02 ppm) cannot be explained by the *cis/trans* isomerism. Although the signal corresponding to the head-*cis* isomer is not detectable in Figure 1 because of the small peak intensity, the effect of *cis/trans* isomerism on the chemical shift of $-\text{CH}_2\text{-SH}$ in the head isomer is expected to be larger. It has been reported that the chemical shift between $-\text{CH}_2\text{-S}_8-$ in the head-*trans* isomer and that in the head-*cis* isomer is 0.11 ppm⁷. As will be seen in Figure 3, the chemical shift between two singlets assigned to $=\text{CCl}-\text{CH}_2\text{-SC}_{12}\text{H}_{25}$ is 0.07 ppm and that between two singlets assigned to $=\text{CCl}-\text{CH}_2\text{-CCl}_3$ is 0.11 ppm. These chemical shifts between two singlets are supposed to be induced by

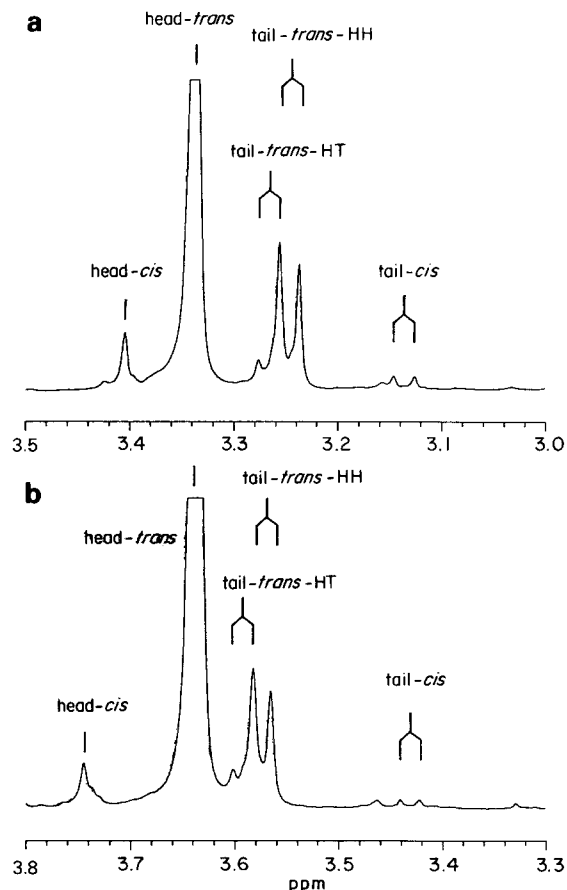


Figure 3 ^1H n.m.r. spectra of methylene groups at the polymer terminals. $-\text{CH}_2\text{-S-C}_{12}\text{H}_{25}$ (a) and $-\text{CH}_2\text{-CCl}_3$ (b), of two Cp homopolymers prepared with chain transfer agents, *n*-DDM and BrCCl_3 , respectively

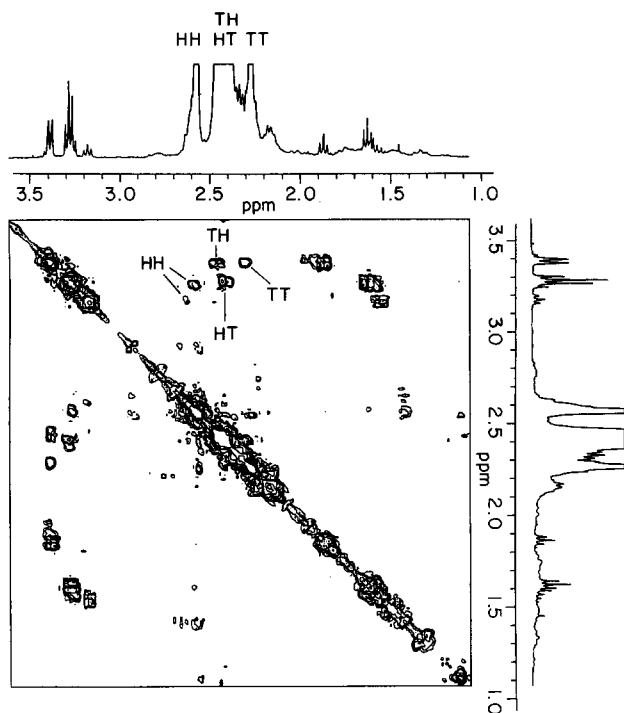


Figure 4 Contour plot of the 2D long range J -correlated spectrum of sample I. The normal spectrum is contained along the diagonal, and crosspeaks connect protons which are J -coupled

cis/trans isomerism. The chemical shift between resonances 1 and 2 may be attributed to the directionality of $-Cp-Cp-S_x-$ as shown below.

In order to determine the directionality of $-Cp-Cp-S_x-$, the long range coupling network was investigated. In *Figure 4* is shown the expanded 2D long range J -correlated spectrum of sample I. Inserting a fixed delay, Δ , after each pulse increases the relative intensity of signals due to small coupling¹¹. Thus, we can observe the long range couplings such as 5J . Two kinds of crosspeaks are observed for the resonances of $-CH_2-SH$, i.e., 3J couplings with thiol proton and 5J couplings with other methylenic protons in the same Cp unit. From the chemical shift of these methylenic protons, we can determine the directionality of $-Cp-Cp-S_x-$.

It has been suggested that the major features of the methylene resonances of the Cp homosequence can be satisfactorily accounted for only by postulating a distribution of dyad sequence isomers, HH, HT (TH) and TT¹². Three blocks of main methylene resonances were assigned to two equivalent methylene groups directly bonded with each other in the HH isomer, two non-equivalent ones in the HT isomer, and two equivalent ones in the TT isomer from the lower to higher field.

From these assignments and the crosspeaks of 5J coupling in *Figure 4*, resonance 2 corresponding to the intense crosspeak is assigned to $-CH_2-SH$ in the head-*trans*-TH isomer and resonance 1 corresponding to the weak crosspeak to the head-*trans*-TT isomer. It is confirmed that resonances 3 and 4 are assigned to the tail-*trans*-HT and tail-*trans*-HH isomers, respectively. Resonance 5 is assigned to the tail-*cis*-HH isomer, because it has been postulated that the methylene resonance patterns of the Cp homosequence are slightly affected by *cis/trans* isomerism¹². Surprisingly, the signal corresponding to the tail-*cis*-HT isomer cannot be detected in *Figure 1*. This signal is expected to appear

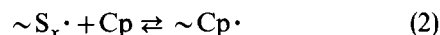
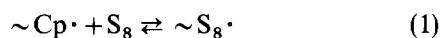
0.02 ppm downfield from resonance 5 analogous to the chemical shifts of tail-*trans* isomers.

Copolymerization mechanism

Now that the stereochemical assignments of $-CH_2-SH$ have been established, we can obtain detailed information on the stereochemistry of $-Cp-S_x-$. As can be seen in *Figure 1*, the total intensity of head isomer peaks is different from that of tail peaks. If the sulphur units are only incorporated into the polymer chain by the usual propagation mechanism, the population of head isomers should be equal to that of tail isomers. *Figure 1* shows that the *cis* configuration exists only in the Cp unit of the tail-HH arrangement. In order to elucidate the origin of these observations, the influence of the polymerization conditions on the stereochemistry of $-Cp-S_x-$ was investigated.

Quantitative results derived from corresponding resonance areas are summarized in *Table 2*. The relative intensity of $-CH_2-SH$ to all methylenic protons of the Cp unit is approximately equal to that of $-CH_2-S_x-$ in the original copolymer. This equality suggests that the information on the stereochemistry derived from the reduced copolymer is accurately reflected by the stereochemistry of $-Cp-S_x-$ in the original copolymer. With decreasing total monomer concentration, in the sample order A-E, the relative intensity of the head isomer peaks decreases. With increasing polymerization temperature, in the sample order F, C, G, H and I, the relative intensity of the head isomer peaks also decreases.

Both results suggest that the depropagation step is highly relevant to the directionality of $-Cp-S_x-$. For the copolymerization of Cp with S_8 , the following propagation and depropagation steps can be assumed to be taking place:



Recently, we have demonstrated the evidence for the occurrence of the depropagation of the growing polysulphenyl radical, expressed by equation (1), from the investigation of copolymer composition⁸. As both 1, 4 and 4, 1 additions take place in the Cp polymerization, additional insight into the depropagation step can be gained by observing the directionality of $-Cp-S_x-$.

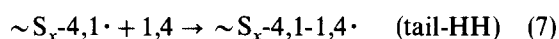
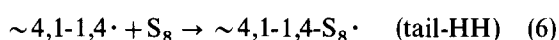
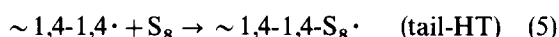
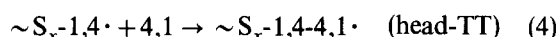
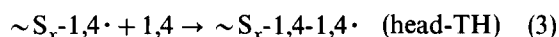
Table 2 Stereochemistry of the Cp unit adjacent to the sulphur unit in the $Cp-S_8$ copolymers determined from the 1H n.m.r. spectra of the reduced copolymers

Sample	Relative intensity of $-CH_2-S_x^a$ (%)	Relative intensity of $-CH_2-SH^b$ (%)	Relative intensity		Cis Content (%)
			Head	Tail	
A	2.40	2.38	0.37	0.63	8.8
B	2.29	2.08	0.37	0.63	8.1
C	2.13	2.05	0.36	0.64	8.7
D	1.92	1.80	0.35	0.65	9.1
E	1.79	1.69	0.33	0.67	10.0
F	1.68	1.44	0.39	0.61	5.9
G	2.52	2.58	0.34	0.66	11.5
H	4.74	4.76	0.33	0.67	11.7
I	5.06	5.04	0.33	0.67	12.3

^a Relative intensity of $-CH_2-S_x-$ to all methylenic protons of Cp unit, cited from ref. 8

^b Relative intensity of $-CH_2-SH$ to all methylenic protons of Cp unit

It is well known that 1,4 addition is predominant in the free radical homopolymerization of Cp. It has been reported that the concentration of the *trans*-1,4 unit is 82% and that of the inverted one is 9% for the homopolymer prepared at 40°C¹³. The predominance of 1,4 addition results in mainly the tail isomer via the reaction given by equation (1), and in mainly the head isomer as given by equation (2) unless the depropagation leads to the decrease of the head isomer, indicating the preferential loss of 1,4 addition and the compensatory enhancement of 4,1 addition in equation (2). Further evidence for the enhancement of 4,1 addition by equation (2) can be gained from the directionality of $-Cp-Cp-S_x-$. The direction of propagation and the resulting directional isomers are depicted as follows:



In the above equations, 1,4 and 4,1 represent the directionality of the Cp unit and Cp monomer. The predominance of 1,4 addition should govern the directionality of $-Cp-Cp-S_x-$, since the radical $\sim Cp-Cp\cdot$ does not depropagate under the present conditions, and inversions of 1,4 units have been found to occur at random in the Cp homosequence¹⁴. Therefore, the propagations expressed by equations (3) and (5) are predominant relative to those expressed by equations (4) and (6), respectively. In Figure 1, the smaller intensity of the head-TT isomer peak relative to the head-TH peak is reasonable with regard to the predominance of equation (3) relative to equation (4). On the other hand, the comparable intensity of the tail-HH isomer peaks relative to the tail-HT peak is inconsistent with the predominance of equation (5) relative to equation (6). The radical $\sim S_x-4,1\cdot$ formed in equation (2) reacts with a second molecule of Cp by the predominant 1,4 addition (eq. (7)) and results in the tail-HH isomer. Therefore, the comparable intensity of the tail-HH isomer peaks is rationalized by the enhancement of 4,1 addition in equation (2). In conclusion, these observations are the evidence for the occurrence of the depropagation expressed by equation (2). The depropagation step causes the preferential loss of the terminal Cp units which have added to the polysulphenyl radicals at C1 rather than C4. It is not clear what kind of interaction causes the selectivity on the depropagation of terminal Cp units. The decrease of the population of head isomer with increasing polymerization temperature is similar to the case of Cp-sulphur dioxide copolymerization¹⁵.

The *cis* configuration exists only in the tail-HH arrangement, indicating that the preferential formation of the *cis* isomer takes place only via the reaction shown in equation (7). The resonances corresponding to the *cis* configuration in other arrangements are not detectable in Figure 1. About one-third of the tail-HH isomer is in the *cis* configuration. The *cis* isomer content (Table 2) is quite large compared with that in the Cp homosequence. The content of *cis* isomer has been reported to be 5.2% for the homopolymer prepared at 40°C and 7.8% at 90°C¹³. These observations suggest a significant difference in the

cis/trans isomerism between the Cp unit which is arranged by the 4,1 addition of the polysulphenyl radicals and that in the homosequence. Therefore, it is concluded that the incorporated sulphur unit shows the penultimate unit effect on the *cis/trans* isomerism for this Cp unit. On the other hand, the same effect is absent for the Cp unit which is arranged by the 1,4 addition of the polysulphenyl radicals. Although there are many studies on the microstructure of the diene copolymers prepared by a free-radical polymerization, there is little indication of the penultimate unit effect on the *cis/trans* isomerism^{16,17}.

The *cis* isomer content shown in Table 2 does not provide the origin of the penultimate unit effect on the *cis/trans* isomerism. The increase of *cis* isomer with increasing polymerization temperature is consistent with the usual observation in the radical polymerization of Cp. In order to examine further the characteristic of this type of penultimate unit effect, the stereochemistry of the Cp units bonded to $-SC_{12}H_{25}$ and $-CCl_3$ groups was investigated.

Figure 3 shows the expanded ¹H n.m.r. spectra of methylene groups at the polymer terminals, i.e., $-CH_2-SC_{12}H_{25}$ and $-CH_2-CCl_3$, for the Cp homopolymers prepared with chain transfer agents, n-DDM and BrCCl₃, respectively. In both spectra, there are three kinds of doublets which are assigned to the respective methylene resonances in the tail-*trans*-HT, tail-*trans*-HH and tail-*cis* isomers from the lower to higher field with reference to the stereochemical assignments of $-CH_2-SH$. Two singlets are assigned to the respective methylene resonances in the head-*cis* and head-*trans* isomers. The resonance intensity of the tail-*trans*-HT isomer is smaller than that of the tail-*trans*-HH isomer, indicating that most of the tail isomers are derived from the 4,1 addition of $\cdot SC_{12}H_{25}$ and $\cdot CCl_3$. The radicals formed by the 4,1 addition of $\cdot SC_{12}H_{25}$ and $\cdot CCl_3$ to Cp react with a second molecule of Cp by the predominant 1,4 addition. The 4,1 addition of $\cdot SC_{12}H_{25}$ and $\cdot CCl_3$ results in mainly the tail-HH isomer. The resonance intensity of the tail-*cis* isomer is extremely weak compared with that of the tail-*trans* isomers. There is no significant difference in the *cis/trans* isomerism between the terminal Cp units bonded to $-SC_{12}H_{25}$ and $-CCl_3$ groups, and the Cp unit in the homosequence. Therefore, these spectra indicate that $-SC_{12}H_{25}$ and $-CCl_3$ groups do not show the penultimate unit effect on the *cis/trans* isomerism for the Cp unit. Consequently, this effect is the characteristic inherent in polysulphides.

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