

Cis-trans Isomerisation of Natural Rubber by Treatment with Sulphur Dioxide. I. Sequence Distribution of Isomeric Structures

ZAINUL ABDIN BIN MAIDUNNY AND SIDEK BIN DULNGALI

Natural rubber in the form of a crumb biscuit obtained after drying the wet crumbs was isomerised by the treatment of sulphur dioxide gas at 100°C. The various isomeric diad structures, namely cis-cis, cis-trans, trans-cis and trans-trans, were precisely quantified by ¹³Carbon Nuclear Magnetic Resonance technique. The distributions of the diad structures were statistically analysed and were found to be randomly distributed.

Natural rubber (NR), 100% head-to-tail *cis* 1,4-polyisoprene, can be isomerised by treating the rubber with sulphur dioxide gas at 100°C, the ceiling temperature, or above¹⁻⁵. The rate of crystallisation of NR at low temperature is relatively fast, e.g. crystallisation half life, $t_{1/2}$, at -26°C is 480 min^{1, 5}. *Cis-trans* isomerisation greatly retards the low temperature crystallisation¹; e.g. isomerised NR containing 6% *trans* double bonds had $t_{1/2}$ of several hundred times slower. The physical properties including the vulcanisate properties have been reported to be affected by *cis-trans* isomerisation^{4,5}. The changes in properties depend on the extent of isomerisation and are affected by the sequence distributions of the *cis* and *trans* units along the polyisoprene chain.

The sequence distribution of the isomeric diad structures of polyisoprene can be analysed by ¹³Carbon Nuclear

Magnetic Resonance Spectroscopy (¹³C-NMR)⁶⁻⁸. ¹³C-NMR spectroscopy can also be used to determine the level of *trans* structure in 1,4-polyisoprene accurately even at low levels⁹. Analysis of the sequence distribution of the isomeric structures could bring further understanding of the mode of the isomerisation reaction.

In this work, we have investigated the sequence distribution of the *cis-trans* diads in NR isomerised at various levels and checked the randomness of the isomerisation reaction.

EXPERIMENTAL

Material

Dry NR in the form of crumb biscuits was prepared from fresh field latex by the standard procedures used in preparing block rubber to the technical specification

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of SMR 5. Liquified sulphur dioxide (BDH) and oxygen-free nitrogen were used directly from the suppliers without further purification or treatments.

Isomerisation Method

The dry rubber as it emerged from the dryer was in the form of a crumb biscuit loosely knit together and having a substantial void volume. The biscuit was placed in a vacuum oven and heated to a constant temperature of 100°C. Once the temperature of 100°C was reached the chamber was evacuated, followed by the introduction of nitrogen gas to atmospheric pressure and then re-evacuated. Sulphur dioxide gas was then introduced into the oven until the atmospheric pressure was attained. Reaction times ranging from 2 h to 24 h were employed. At the end of the reaction time, the sulphur dioxide gas was flushed out and bubbled through sodium hydroxide solution.

NMR Measurement

The ^{13}C -NMR spectra of the isomerised rubbers were recorded on a JEOL FX 100 using 25% (weight/volume) solutions in deuterated chloroform (CDCl_3) with tetramethylsilane (TMS) as internal reference. Measurements were made at 28°C. The spectra were taken by a pulse Fourier transform method using a gated proton decoupling, without nuclear Overhauser enhancement (NOE) at a pulse repetition time of 4 s. Generally, 3000 scans were collected for each sample, using a sweep width of 3500 Hz in 16K of memory. The pulse width was 5.5 μs , corresponding to a flip angle of 30°. Quantitative measurements of peaks were made by computer integration.

The levels of *trans* structures (i.e. the degree of isomerisation) were calculated from the peak areas of the methyl resonances of the *cis* and *trans* isomeric units.

RESULTS AND DISCUSSION

The ^{13}C -NMR spectra of NR and partially isomerised NR are shown in *Figures 1* and *2* respectively giving peak assignments for the various carbon atoms. In addition to the five characteristic singlet peaks (peaks 1 to 5) of NR (*Figure 1*), five more signals (peaks 6 to 10), three of which are split signals, are shown in the spectra of the partially isomerised NR (*Figure 2*). The triplet at 77.0 p.p.m. is due to the solvent, CDCl_3 . The assignments of the signals of NR and the isomerised NR⁶⁻¹⁰ are given in *Table 1*.

The *cis* and *trans* structures of 1,4-polyisoprene (*Figure 3*) are easily identified by methyl carbon C(5) at 23.44 p.p.m. and C(10) at 15.96 p.p.m. respectively, the methylene carbon C(1) at 32.22 p.p.m. and C(6) at 40.06 p.p.m., and the methine carbon C(3) at 125.04 p.p.m. and C(8) at 124.23 p.p.m. As shown in *Figure 2* the singlet signal due to the methyl carbon of both configurations i.e. C(5) and C(10), are well separated enabling precise determination of *trans* content in the isomerised NR. The doublet signal of C(1) and C(6) are actually resonances from the *cis-trans* and *trans-cis* diad linkages, similarly, the quadruplet signals due to C(2), C(7) and C(4), C(9) are due to the *cis-trans* linkages. Chicle polyisoprene which contains both *cis*- and *trans*-1,4-polyisoprenes; gutta-percha, a 100% *trans*-1,4-polyisoprene; and synthetic high *cis*-1,

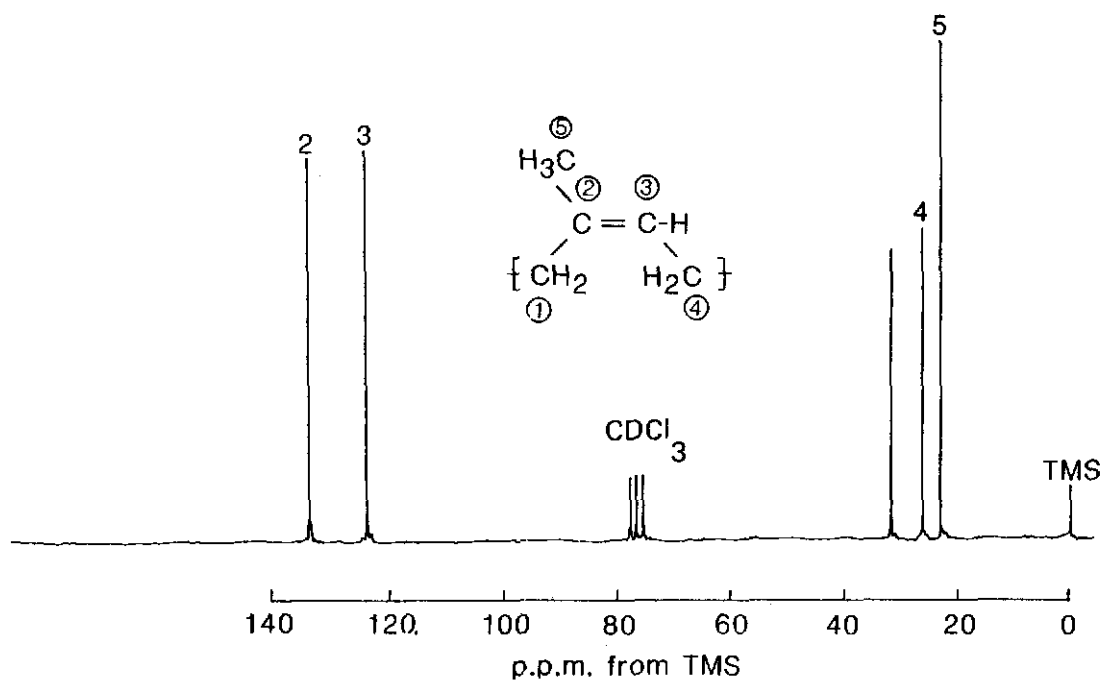


Figure 1. ^{13}C -NMR spectrum of natural rubber.

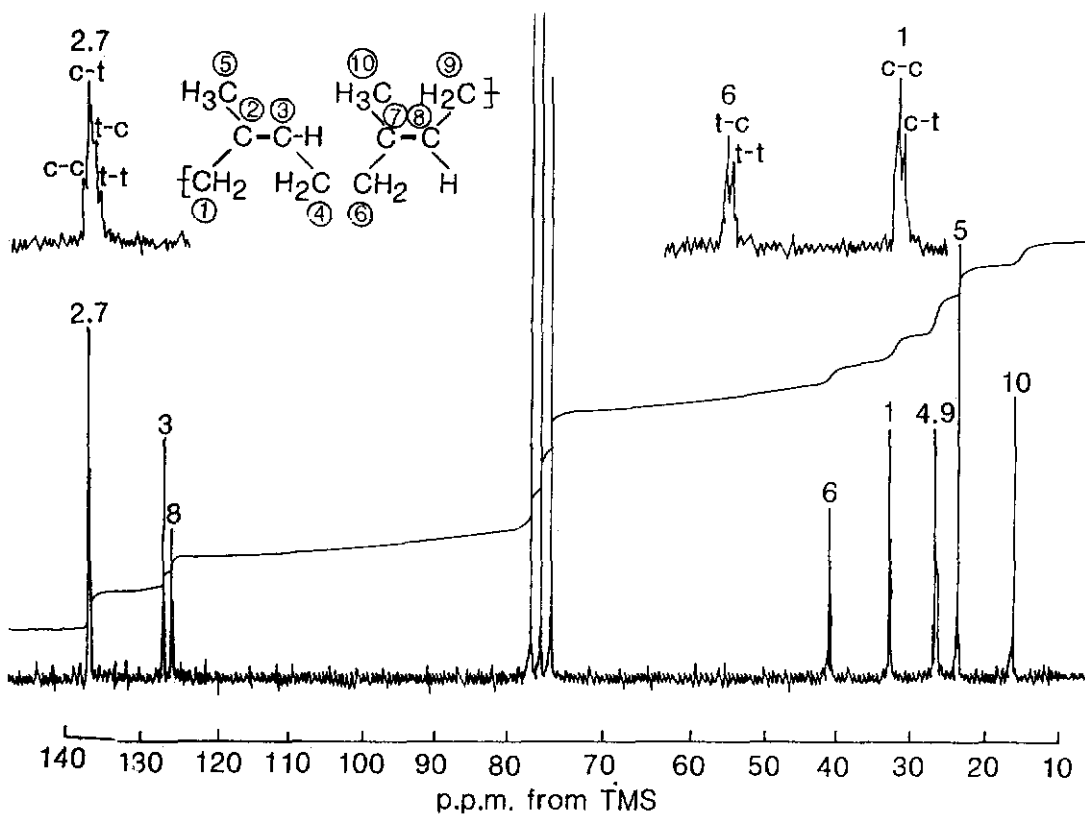
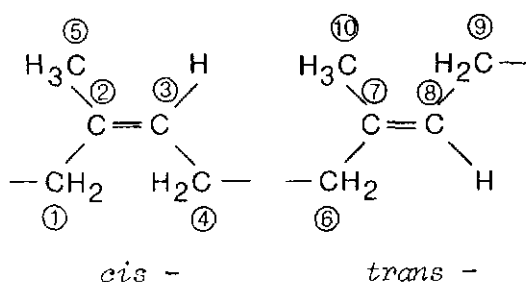


Figure 2. ^{13}C -NMR spectrum of cis-trans isomerised natural rubber.

TABLE 1. ^{13}C CHEMICAL SHIFT DATA OF 1,4-POLYISOPRENE

Carbon	Chemical shift from TMS (p.p.m)	
	<i>cis</i>	<i>trans</i>
C (1)	32.22	—
C (2)	135.20	—
C (3)	125.04	—
C (4)	26.42	—
C (5)	23.44	—
C (6)	—	40.06
C (7)	—	135.00
C (8)	—	124.23
C (9)	—	26.66
C (10)	—	15.96

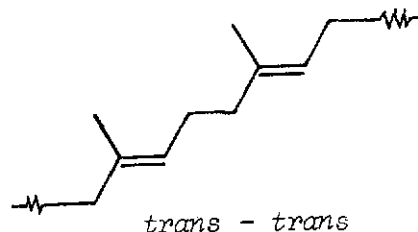
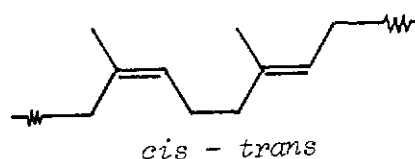
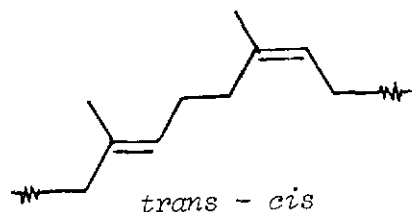
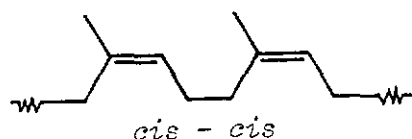
Figure 3. *Cis and trans structures of 1, 4-polyisoprene.*

4-polyisoprene did not give such signals⁷. Other signals were absent which indicated that the isomerisation occurs without any detectable side reactions particularly cyclisation. Similarly, Cunneen *et al.*¹¹, by means of infra-red spectrophotometric method, concluded that when NR was treated with sulphur dioxide, *cis-trans* isomerisation solely occurred without any movement of the double bond.

Sequence Distribution of Isomeric Structures

The isomerisation of NR from *cis* to *trans* structures produced the *cis-trans*

diad linkages and consequently other diad sequences. There are four types of diad sequences as shown below:



The diad sequences are identified from the signals due to C (1), C (2), C (4), C (6), C (7) and C (9) as assigned ^{7,8} in Table 2.

TABLE 2. SIGNALS ASSIGNMENT ^a FOR DIAD SEQUENCES IN ISOMERISED NATURAL RUBBER

Carbon	Chemical shift (p.p.m. from TMS)			
	<i>cis-cis</i>	<i>cis-trans</i>	<i>trans-cis</i>	<i>trans-trans</i>
C (1)	32.22	32.00	—	—
C (6)	—	—	40.03	39.77
C (2), C (7)	135.34	135.20	135.08	134.98
C (4), C (9)	26.42	26.51	26.66	26.73

^a After Tanaka *et al.*⁷ and Tanaka and Sato⁸

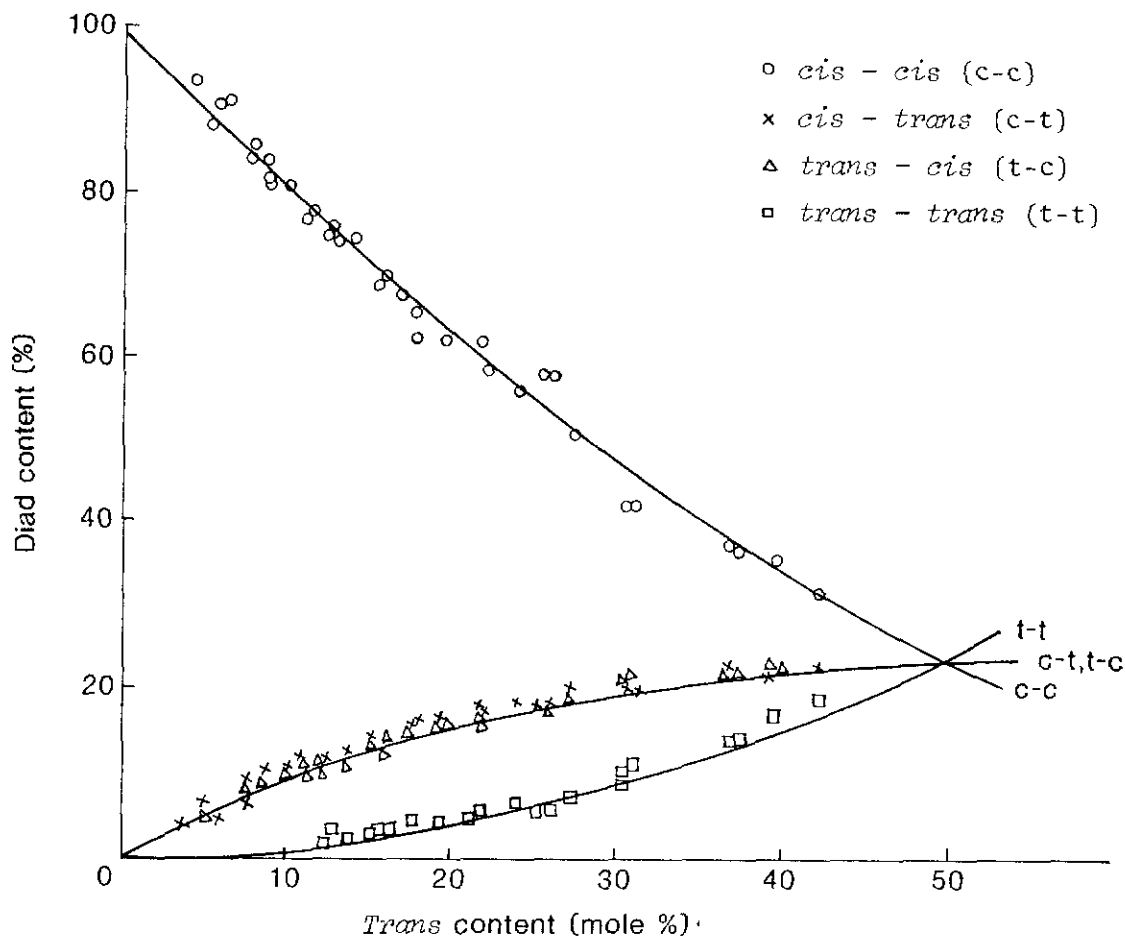


Figure 4. Content of various diad isomeric structures at different trans content. (Lines in full are theoretical curves assuming random distribution.)

The proportions of the diad sequences were determined from the relative intensities of the two signals of C (1) carbon and two signals of C(6) carbon. In Figure 4, the mole percentage of each diad sequence was plotted against the trans content in the partially isomerised NR.

By statistical analysis using the chi-square distribution test (confidence limit 96%) as shown in Table 3, it was found that the experimental data agree very well

TABLE 3. THE CHI-SQUARE FOR THE DIAD DISTRIBUTIONS

Linkages	Chi square
<i>cis-cis</i>	4.18
<i>cis-trans</i>	8.50
<i>trans-cis</i>	2.80
<i>trans-trans</i>	15.70
Table value ($n = 41, \alpha = 0.05$)	56.93

with the theoretical data. The results indicate that the distribution of the various diad sequences follows the expected ran-

dom distribution. The validity of signal assignment and the theoretical assumption of random distribution were characterised not only by the remarkable agreement between the theoretical and experimental values but also by the identical distribution of the *cis-trans* and *trans-cis* linkages (Figure 4).

CONCLUSION

The sequence distribution of isomeric structures of the *cis-trans* isomerised NR obtained by treating NR with sulphur dioxide was found to be randomly distributed and in accordance with the theoretical random distribution.

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