

polymer papers

The first sample of synthetic rubber made by William Tilden in 1892—modern work reveals a mystery

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(Received 3 January 1997)

A sample of 'Artificial Rubber', made in 1892 by Sir William Tilden at the Mason College of Science (precursor of the University of Birmingham), has come to light, and has been found to still possess remarkably good rubbery properties. It has been investigated by pyrolysis-g.c.-m.s. and by n.m.r. spectroscopy in order to characterize its structure. © 1997 Elsevier Science Ltd.

(Keywords: rubber; methyl rubber; polyisoprene)

INTRODUCTION

Two samples from the archives of the School of Chemistry in the University of Birmingham are labelled on the bottles as 'Isoprene' and 'Artificial Rubber'. The latter is captioned as 'The original specimen of synthetic rubber first made from isoprene by Sir William Tilden in the University of Birmingham, 1892–4'. This rubber sample is the subject of the present investigation.

In 1880 William Tilden was appointed to be the first Professor of Chemistry at the new Mason College of Science (the precursor of the University of Birmingham), where he continued his work on isoprenoid compounds and terpenes which he had previously studied at Clifton College¹. In that same year, 1880, he published his *Introduction to the Study of Chemical Philosophy*², in which he noted that terpenes are the chief ingredients of the essential oils of turpentine, lemon, orange, and bergamot, and have the formula $C_{10}H_{16}$. He proposed that the differences in their properties are due to changes in their molecular structure. On the same page he introduces the subject of 'Polymerides', but at that stage does not associate terpenes with rubber polymers.

However, some research he performed at the Mason College in Birmingham in the 1880s laid the foundations for this. It began with his studies of the thermal decomposition of the terpenes. As early as 1884 he was performing what might now be called 'hydrocarbon cracking' experiments, in which he found that when the vapour of turpentine oil is passed through a heated iron tube on which redness is just visible in darkness (this would correspond to a temperature of about 550°C), hydrocarbons such as dipentene, *p*-cymene, colophene, small amounts of aromatics, and most importantly, isoprene, C_5H_8 , are evolved and can be condensed.

Tilden was aware that isoprene is one of the products obtainable by the dry distillation of natural rubber, so this led him to realize that there could be a 'spontaneous conversion of isoprene to caoutchouc' [caoutchouc, natural rubber, and India-rubber were all terms used for the same material at that time]. In 1891 he reported³ his observation that isoprene yielded a rubber-like mass as a result of the action of heat and hydrochloric acid. In 1892 he presented a paper on this subject to the Philosophical Society of Birmingham⁴, in which he recalls first that isoprene can be converted into a tough elastic solid when it is brought into contact with strong acids, but then goes on to report a new phenomenon:

'Specimens of isoprene were made from several terpenes in the course of my work on these compounds, and some of them I have preserved. I was surprised a few weeks ago at finding the contents of the bottles containing isoprene from turpentine entirely changed in appearance. In place of a limpid colourless liquid, the bottle contained a dense syrup in which was floating several large masses of a solid of a yellowish colour. Upon examination, this turned out to be India-rubber.'

Thus by using isoprene obtained from the cracking of turpentine, Tilden could justly claim to have synthesized rubber by a route that did not correspond to its reconstitution from isoprene obtained as a rubber decomposition product.

By present-day standards, Tilden had few techniques available for comparing the structure of the polymer with that of natural rubber, the structure of which itself was then unknown. In his paper⁴ he quotes the following rather circumstantial evidence for the correspondence between the two:

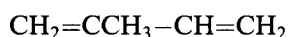
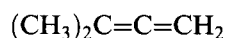
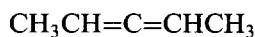
(a) A solution of the artificial rubber in benzene

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leaves on evaporation a residue which agrees in all characters with a similar preparation from 'Pararubber' (not defined).

- (b) The artificial rubber unites with sulfur in the same way as 'ordinary rubber', forming a tough elastic compound.
- (c) The artificial rubber, like natural rubber, appears to consist of two substances, one of which is more soluble in benzene or carbon bisulfide than the other.

Tilden wondered whether the reaction might have been promoted by the presence of traces of formic or acetic acid which had in some way been formed by oxidation due to the presence of air. He realized that a combination process had occurred, but could hardly speculate on the chemistry involved, or on the structure of rubber, because the isoprene structure was unknown at that time. He simply lists the following possibilities for isoprene structure in his paper:



and notes that such double-bonded structures can obviously polymerize in a variety of ways. (At that time, however, the word 'polymerize' did not have the present meaning 'form a macromolecule', but simply implied combination to form any larger structure with the same empirical formula. The concept of *high* polymers had to await the vision of Staudinger in the 1920s.)

Tilden left Birmingham in 1894 to take the chemistry chair at (what was later called) Imperial College. He was devoted to the Chemical Society, and was awarded a knighthood in 1909. He died in retirement in 1926.

TILDEN'S SAMPLES

The sample labelled 'Isoprene' is no longer a mobile liquid, but consists of a yellowish transparent polymer set to a glass in the lower part of the bottle. The contents whilst liquid had previously penetrated into the surfaces of the ground-glass stopper, as a result of which the bottle became completely sealed. Its contents must therefore have been totally protected from air for about a century, which explains the absence of oxidative colouration in the sample. Since it was found to be impossible to remove the stopper, no particle of this sample could be removed for investigation.

The other sample, labelled 'Artificial Rubber' is a lump of material of approximate volume 3 cm³, contained in a bottle sealed with a cork lined with tissue paper. In view of this more imperfect seal, it is not surprising that the sample is now strongly discoloured to dark brown, and is covered with a powdery crust (0.5–1-mm deep). When attempting to pull off a small particle for analysis from beneath the crust at the edge of the sample, the whole mass proved to display remarkably good elasticity, so to remove the particle it was finally necessary to cut it off with a scalpel. This rubbery sample

was examined by pyrolysis-g.c., pyrolysis-g.c.-m.s., and n.m.r. spectroscopy. In addition, a sample of the crust material was also examined by n.m.r.

A modern sample of polyisoprene, obtained from T.A.R.R.C., the Malaysian Rubber Producers' Research Association, was used for comparison analysis.

INVESTIGATION OF THE SAMPLES

Pyrolysis-gas-chromatography

A 10 µg sample of the Tilden Artificial Rubber was subjected to pyrolysis-g.c. analysis by depositing it from chloroform solution on to a microthermocouple-controlled resistive filament⁵ to take the sample to 500°C for 6 s. The volatile products were separated using a 30 m semi-polar capillary column, i.d. 0.25 mm. The temperature programme for the g.c. analysis was as follows: 2 min at 40°C, then 10°C min⁻¹ ramp to 300°C, then 2 min at 300°C. The detector was an FID.

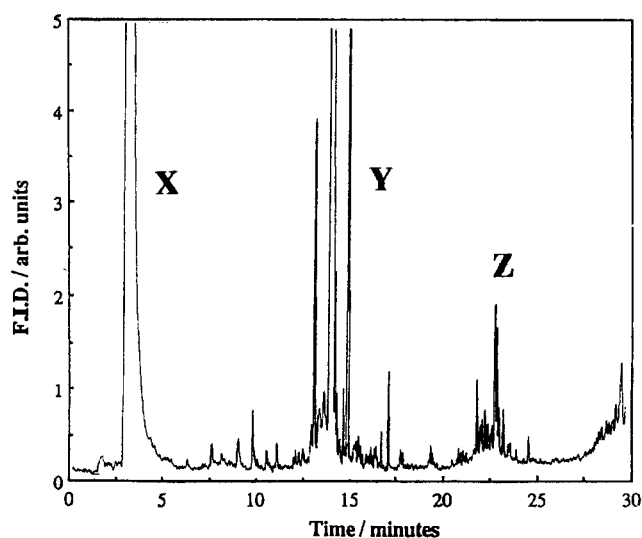


Figure 1 Pyrolysis-g.c. of Tilden's sample of rubber. Pyrolysis conditions: 500°C for 6 s

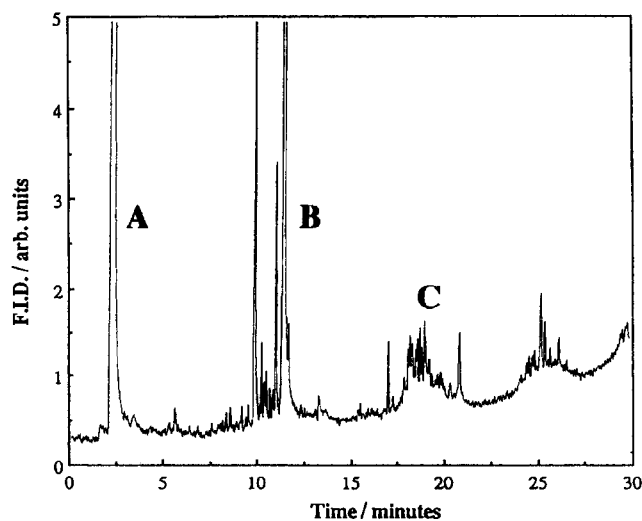


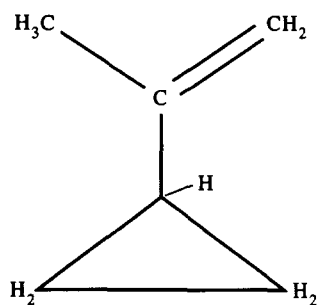
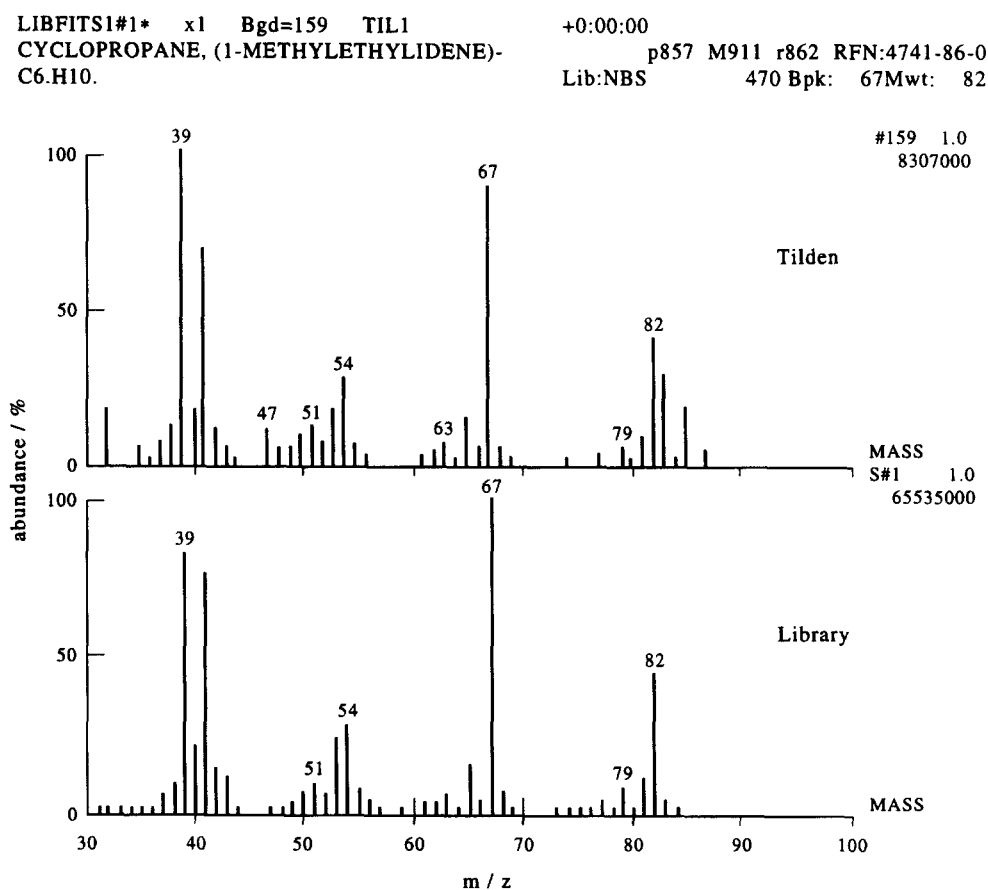
Figure 2 Pyrolysis-g.c. of reference sample of synthetic poly(isoprene). Pyrolysis conditions: 500°C for 6 s

An identical procedure was then used to examine the modern reference sample of synthetic polyisoprene.

The pyrogram of the Tilden sample is shown as *Figure 1* and that for the reference polyisoprene as *Figure 2*. The two chromatograms are placed with the time axes in correspondence for ease of comparison. Although there is a slight similarity between the general patterns of the two pyrograms (and also with that for natural rubber⁶), it is clear that the Tilden sample cannot be of identical structure to polyisoprene, because the retention times of the volatiles are so different.

In the polyisoprene pyrogram, peaks A are shown to be monomeric, peaks B to be dimeric, and peaks C to be

trimeric⁶. On this basis, it could be postulated that in the pyrogram of the Tilden sample, peaks X, Y, and Z could similarly correspond to monomeric, dimeric, and trimeric species in which the repeating unit is larger and less volatile than isoprene. This could mean either that the original Tilden polymer is not polyisoprene, or that if the polymer had originally possessed the polyisoprene structure, it has aged or oxidized in some way so that virtually every repeating unit has become modified. The pyrolysis products were therefore characterized by pyrolysis-g.c.-m.s., and the sample itself was also analysed by n.m.r. spectroscopy, in order to ascertain which of these proposals could be true.



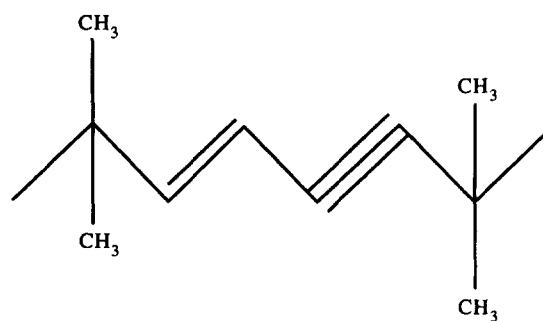
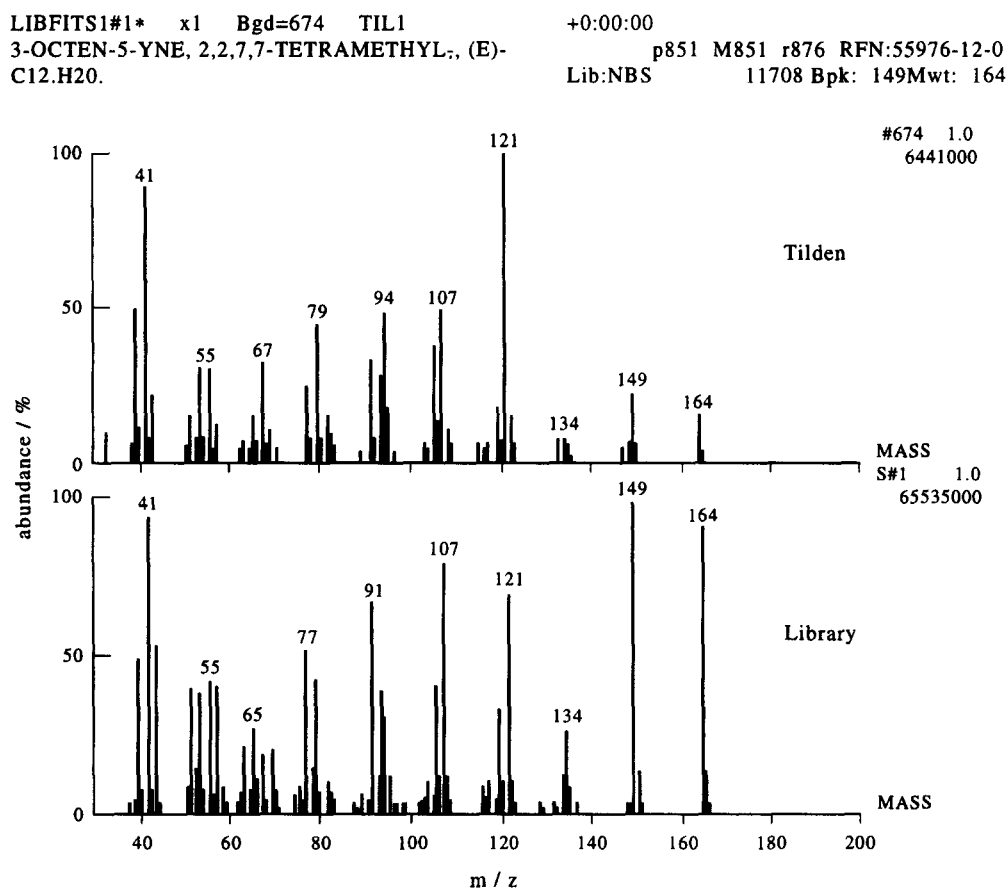
cyclopropane, (1-methylethylidene)
(C₆H₁₀ MW 82)

Figure 3 Mass spectrum (upper) of one of the principal monomer peaks in the total ion current chromatogram of the pyrolysis products from Tilden's sample. The lower mass spectrum corresponds to the best fit from the mass spectral library

Pyrolysis-g.c.-m.s.

The Tilden rubber was pyrolysed using similar pyrolysis and chromatographic conditions to those above, and the g.c. effluent was passed directly in to the source of a VG TS250 trisector mass spectrometer, operating in electron impact mode. The total ion current chromatogram was very similar to that previously obtained (Figure 1), and attempts were made to characterize the principal chromatographic peaks from their mass spectra stored in the data-handling unit of the mass spectrometer. Those corresponding to the assumed monomeric g.c. peaks were consistent with a molecular ion of $m/z = 82$ (see, for example, Figure 3), which

corresponds to C_6H_{10} , equivalent to isoprene plus a methyl group. The dimeric peaks were consistent with a molecular ion peak of 164 (see, for example Figure 4), corresponding to $C_{12}H_{20}$, i.e. the dimer of the above species. Similarly the trimeric peaks showed a molecular ion peak at $m/z = 246$. The best-fit cracking patterns are shown as the lower mass spectrum in each of Figures 3 and 4, and correspond to the structures indicated. However, the library fits are by no means perfect, and in view of the strong susceptibility of isoprenoid and terpenoid structures to rearrange and isomerize at elevated temperatures, it must not be assumed that the indicated pyrolysis product structures correspond to those of the monomer or sections of the chain. Nevertheless



3-octen-5-yne, 2,2,7,7-tetramethyl-, (E)-
 ($C_{12}H_{20}$)

Figure 4 Mass spectrum (upper) of one of the principal dimer peaks in the total ion current chromatogram of the pyrolysis products from Tilden's sample. The lower mass spectrum corresponds to the best fit from the mass spectral library

Table 1

Group	¹ H n.m.r.		¹³ C n.m.r.	
	Lit./ppm	Found/ppm	Lit./ppm <i>cis/trans</i>	Found/ppm
CH ₂	2.08	2.04	33.9, 33.60	34.09, 33.62, 33.39, 32.96
C=C	—	—	122.8, 125.8	128.4
CH ₃	1.59	1.65, 1.67	18.7, 18.4	18.24, 18.69

there is little doubt from this pyrolysis-g.c.-m.s. work that the repeating unit in the Tilden rubber is not isoprene but a structure commensurate with a methyl-substituted isoprene. Further structural characterization may be more appropriately obtained by n.m.r. spectroscopy.

Nuclear magnetic resonance spectroscopy

The Tilden rubbery sample and its outer crust here both examined by ¹H n.m.r. spectroscopy in *d*-chloroform. The spectra showed essentially identical characteristics: two singlets at 1.67/1.65 ppm, a band at 2.04 ppm with fine splitting, two minor bands at 4.81/4.69 ppm, and another minor band at 2.71 ppm. There were other minor bands in the 2.4 to 1 ppm region.

A very significant finding is that the absence of any *cis* olefin band at 5.05 ppm rules out the possibility that either of the samples could have the *cis*-1,4-polyisoprene structure. The two bands at 4.81 and 4.69 ppm could be olefinic CH= or CH₂=, but they are minor components in comparison to the alkyl region. The major bands at 2.04/1.67 + 1.65 showed a ratio of 4/6, which is the ratio expected for poly(2,3-dimethyl butadiene). Both ¹H and ¹³C n.m.r. spectroscopic data have been published by Wharry and Yeh for this polymer⁷. ¹³C n.m.r. spectroscopy was therefore also performed by the present authors on the Tilden rubber sample, and all of our results are compared with the literature values in Table 1.

The literature spectra of Wharry and Yeh were obtained in trichlorobenzene at 125°C, so some differences in chemical shift could be expected between their data and our results. In particular, they find two chemical shifts for each carbon, assigning them to *cis* and *trans* isomers. We find only one olefin carbon band but four methylene carbon bands. It is reasonable to assume that this can be attributed to the different conditions we used. In all other respects, the chemical shifts of the samples are sufficiently close to the literature values to be reasonably certain of confirming the identity of both of the Tilden samples to be poly(2,3-dimethyl butadiene).

CONCLUSION AND COMMENT

Both the pyrolysis-g.c.-m.s. and the n.m.r. spectroscopy investigations lead to the conclusion that the Tilden Artificial Rubber sample is not polyisoprene, as its caption stated, but that it is poly(2,3-dimethyl butadiene).

Such material has been known as a rubber for some time; indeed the ability of 2,3-dimethyl butadiene to undergo polymerization to a rubber-like product was first reported in 1901 by Kondakov⁸. The monomer may be obtained from acetone via pinacol⁹, and the polymeric product was developed in Germany during the first

world war as 'methyl rubber', a substitute for natural rubber. About 2350 tons of it were manufactured for this purpose at Leverkusen, and at the end of that war there were in course of erection two additional plants for the methyl rubber manufacture with a joint capacity of 8000 tons per year¹⁰. This project was abandoned in 1918 and the polymerization not further exploited¹¹, despite receiving the attention in the early 1920s of several workers, including Hofmann¹². Interest in the polymer revived ten years later in Canada, where both the polymerization¹³ and the vulcanization of the product¹⁰ were studied in order to compare the overall behaviour and properties with those of isoprene and polyisoprene. Perhaps one paragraph by two of these authors, Whitby and Crozier¹³ could be especially relevant to the present discussion:

'At room temperature, dimethylbutadiene undergoes polymerization far more readily than isoprene. Samples of the former were generally observed to undergo complete polymerization to typical, white, cauliflower masses when kept for a year or two. Kondakov found it [dimethylbutadiene polymerization] to be complete in 1 year, whereas a sample of isoprene kept for 4½ years showed no separation of solid polymer and only about 16% polymerization to rubber. Even when considerably diluted, samples of dimethylbutadiene were observed by Macallum and Whitby to undergo, on keeping, conversion to the solid polymer after 2 or 3 years'.

So, returning to the present Tilden sample, we are left with the interesting question: *did William Tilden believe this particular sample of his to be polyisoprene, or did some early curator of the University of Birmingham Chemical Society Museum jump to conclusions when assembling the exhibit?* There is no one alive today who can provide an answer to this, so it must remain an open question. It's still a very good rubber!

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