CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND GEOLOGY,
CASE WESTERN RESERVE UNIVERSITY, CLEVELAND, OHIO 44106

An Inherently Fibrous Polymer[1]

BY S. E. FRAZIER, J. A. BEDFORD, J. HOWER, AND M. E. KENNEY

Received March 23, 1967

The reaction of chrysotile with hydrochloric acid and chlorotrimethylsilane has yielded a stable polymer having a silicon–oxygen sheet framework with trimethylsiloxy groups pendant on one side only. When dry, the polymer sheets are curled up into fibers similar in size to those of chrysotile. Exposure of the fiber rolls to organic solvents causes them to uncoil.

Introduction

For a polymer to be inherently fibrous, it must be composed of molecules or tight molecular aggregations which are much longer in one dimension than in the other two; *i.e.*, it must be composed of units which are in the form of slender ribbons, laths, rods, tubes, or other similar shapes. A further requirement is that these units must exert, at most, only relatively weak attractive forces on each other and, hence, be easily separable. It is also desirable that they be fairly rigid so that they cannot become easily knotted.

In view of these requirements it is apparent that tubular units are particularly well suited for the formation of fibrous polymers. Such units have inherently high structural integrity and stiffness and, in addition, can have, at most, only little contact with their neighbors, and hence can exert only weak attractive forces on them. Rods are also obviously quite suitable. Laths and ribbons are less suitable because their flat surfaces naturally lead to large interunit contacts and hence easily to nonfibrous massive superunits.

A good example of an inherently fibrous inorganic polymer based on tubular units is the form of serpentine known as chrysotile.[2] This mineral is a silicate with the idealized formula $Mg_3(OH)_4Si_2O_5$.[3] Like so many of the important silicates (*e.g.*, the clays and micas) it is derived from the $Si_2O_5^{2-}$ sheet, a portion of which is shown in Figure 1. In chrysotile this sheet occurs in long, narrow ribbons. These are condensed with $Mg(OH)_2$ or brucite layers to form long, narrow neutral ribbons. Because comparable segments of the brucite layer and the silicate layer do not quite match, the brucite segment being larger, the ribbons are strained. Relief from this strain is gained from a curl of the ribbons along their long axes with the brucite layer on the outside.[4] Ultimately in ordinary chrysotile or clinochrysotile, tubes with a dozen or so layers in their walls are formed. Usually these tubes are several hundred angstroms in outside diameter[5–7] and thousands of angstroms long.

On the basis of evidence in the literature it is not clear whether the tubes are composed of complete concentric cylinders, partial concentric cylinders, rolls, or a combination of these possibilities.[8] Also uncertain is the nature of the material inside and between the tubes.[9,10] Further complicating the situation are the polymorphism of chrysotile[11] and the curious tube within a tube arrangement which is sometimes observed.[6]

However, in spite of these uncertainties, the over-all multiwalled tube construction of chrysotile is clear and this suggests that it ought to be possible to synthesize organic or organometallic multiwalled tubes. While at first glance this seems a very difficult proposition, the possibility of converting the ribbons of chrysotile into ribbons which have pendant organic or organometallic groups and which have sufficient and proper strain to lead to curling does exit.

The basis for one practical approach to the synthesis of such sheet polymers is provided in work reported by Lentz.[12,13] In this work Lentz showed that under the proper conditions the silicate ions of simple silicates such as olivine, $(Mg,Fe)_2SiO_4$, and the silicate units of aluminosilicates such as natrolite, $Na_2Al_2Si_3O_{10}\cdot 2H_2O$, could be converted in good yield into the corresponding trimethylsilyl derivatives (*e.g.*, $((CH_3)_3SiO)_4Si$ and $((CH_3)_3SiO)_3SiOSi(OSi(CH_3)_3)_2OSi(OSi(CH_3)_3)_3$ in the cases of olivine and natrolite). This suggests that chrysotile and other sheet silicates could, under similar conditions, yield neutral sheet polymers with pendant trimethylsiloxy groups. Steric hindrance between the substituted groups and oxygen cross-linking of silicon atoms within the sheet provide potential sources for the needed strain.

Experimental Section

The crysotile used in this work was obtained through Ward's Natural Science Establishment, Rochester, N. Y. and was from Quebec. As received it consisted of grayish blocks of cross-grain silky fiber.

---

[1] This research was supported by the Office of Naval Research under Contract No. Nonr 1141(18).

[2] Most commercial asbestos is chrysotile.

[3] Collected and correlated analyses for several chrysotile specimens are given in W. A. Deere, R. A. Howie, and J. Zussman, "Rock Forming Minerals," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1962, p 176.

[4] This suggestion originated with L. Pauling, *Proc. Natl. Acad. Sci. U. S.*, **16**, 578 (1930).

[5] T. F. Bates and J. J. Comer, *Proc. Natl. Conf. Clays Clay Minerals*, **6**, 237 (1959).

[6] M. Maser, R. V. Rice, and H. P. Klug, *Am. Mineralogist*, **45**, 680 (1960).

[7] This diameter is much smaller than the diameter of any fiber produced by spinning or drawing procedures.

[8] E. J. W. Whittaker, *Acta Cryst.*, **10**, 149 (1957).

[9] A. W. Naumann and W. H. Dresher, *Am. Mineralogist*, **51**, 711 (1966).

[10] E. Martinez and J. J. Comer, *ibid.*, **49**, 153 (1964).

[11] E. J. W. Whittaker, *Acta Cryst.*, **9**, 855, 862, 865 (1956).

[12] C. W. Lentz, *Inorg. Chem.*, **3**, 574 (1964).

[13] For earlier work on the conversion of sheet silicates into organosilicon compounds see, for example, Y. I. Skorik, E. V. Kukharskaya, A. D. Fedoseev, and K. P. Klimova, *Zh. Prikl. Khim.*, **38**, 510 (1965).

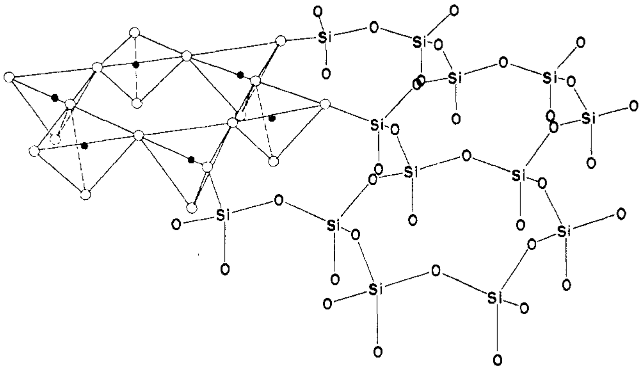

Figure 1.—The silicate sheet of chrysotile.

This chrysotile was treated with a variety of reagent mixtures similar to those used by Lentz.[12] In a typical reaction small pieces of the mineral were broken from the block material and twisted by hand until well opened. A 5.03-g portion of this opened chrysotile was then placed in a flask along with 2-propanol (250 ml), concentrated hydrochloric acid (50 ml), and chlorotrimethylsilane (100 ml) and refluxed for 1 day. An additional 50 ml of chlorotrimethylsilane was then added, and the mixture was refluxed for 7 more days. The product was washed with water, aqueous acetone, and acetone and dried at 110° for 2.5 hr (3.00 g).

At the start of the reaction the chrysotile was hydrophilic and was at the bottom of the reaction mixture, but within about 5 hr it had become hydrophobic and had risen to the top of the mixture. After about 1 day it had become visibly swollen and gelatinous, and by the end of the reaction it was highly swollen.

During the acetone washes, the final product swelled to a voluminous, transparent, colorless, fluid jelly. This jelly collapsed to a compact white mass when washed with water or when dried.

The washed product, when completely dry, was very much like a piece of filter paper—white and obviously fibrous. Microscopic examination of it with polarized light showed that it consisted of fiber bundles which extinguished approximately parallel to the plane of the polarized light. When wetted with organic solvents, the fiber bundles became nearly isotropic.

The sodium chloride region infrared spectrum (Beckman IR-8 infrared spectrophotometer) of a thin mat of the product on a salt plate showed absorptions characteristic of trimethylsiloxy and silanol groups.[14]

A portion of this product (1.49 g) was refluxed with stirring with a mixture of chlorotrimethylsilane (125 ml) and pyridine (15 ml) for 2 days, washed with water, aqueous acetone, acetone, and carbon tetrachloride, and dried at 110° for 2.5 hr (1.50 g). The resultant product was no longer fibrous in appearance but still swelled markedly in organic solvents. Microscopic examination showed that it was anisotropic and became much less so on swelling, but that well-defined fiber bundles were rare. Apparently the stirring broke up the bundles.

When this same step was run without stirring on an analogous starting material, the final product was still visibly fibrous. However, this product was somewhat contaminated with black decomposition products (from the pyridine). Most of these were removable with washing and hand sorting.

The infrared spectra of the two products were the same and very little changed from that of the initial product. The observed absorptions (cm^{-1}) were: 3472, w, b, 2967 m, 2907 sh, 1255 m, 1176 sh, 1075 s, b, 969 w, sh, 864 sh, 845 s, 756 m.

The X-ray diffraction traces (General Electric XRD-6 diffractometer, Ni-filtered Cu Kα radiation) of mats of the fibers on glass plates showed strong peaks corresponding to d spacings of 15.0 and 15.1 A. No other peaks were found in the region scanned (3–15°, 2θ).

The diffraction tracing of a mat of the (unstirred) product swelled with 2-butanone showed no 15-A peak but did show a weaker broad peak centered at about 13.6 A. The trace of this mat, upon evaporation of the solvent, was identical with its initial tracing.

A *p*-nitrobenzeneazoresorcinol magnesium test[15] on the stirred sample was negative. Quantitative elemental analyses of the stirred and unstirred samples gave, respectively: C, 16.2; H, 4.5; Si, 42.0; and C, 17.3; H, 4.5. These data correspond approximately to those calculated on the assumption that the $Si_2O_5^{2-}$ sheet was extracted from the chrysotile intact and that half the sheet silicon atoms were substituted by trimethylsiloxy groups and the remainder were cross-linked by oxygen bridges, *i.e.*, with 17.9% C, 4.5% H, and 41.7% Si.

That the agreement is only approximate is to be expected for at least two reasons. One is that the level of substitution is known to be variable from many other experiments and certainly is not exactly 50%. The other is that the product is known, on the basis of the infrared data, to contain some silanol OH groups.

Electron micrographs (Hitachi HU-11A) of the product were obtained from a sample (unstirred) which had been ground, swelled with chloroform, and deposited on a carbon-coated copper grid. Figure 2 is typical of those obtained. Micrographs of a sample (unstirred) which had been partially swelled in propylene oxide, embedded in Araldite resin, and cross-sectioned (Servall Porter-Blum M-1 microtome equipped with a diamond knife, approximately 700-A sections) were also obtained; see Figure 3.

Discussion

The electron micrographs reproduced in Figures 2 and 3 show that the polymer is fibrous and that the fibers are constructed of rolled up ribbons. They also show that the fibers are very similar to the parent chrysotile fibers in length to diameter ratio and in size.

The micrographs do not, however, make clear whether the cores of the fibers have any special complexity associated with them and whether, as a consequence, the ribbons making up the rolls have a uniqueness to their inner edges. One puzzling feature to the micrographs, in this regard, is the pair of black lines seen running down the center of many of the fibers when viewed sideways (see for example the fiber marked a in Figure 2).

The path followed in the formation of the ribbons observed in the micrographs is suggested in part by earlier streaming potential work on chrysotile.[16] This work shows that the isoelectric pH of chrysotile is high, a value of 11.8 having been obtained, and leads to the conclusion that the external brucite layer is completely stripped off the fiber when the pH is lowered to 2, leaving a silanol layer in its place.

This conclusion appears sound and suggests that the formation of the trimethylsiloxy-substituted ribbons is a multistage process, the first stage being the removal of the magnesium and hydroxyl ions from the surface of the chrysotile fibers and the substitution of silanol OH groups in their place. It then seems probable that substitution of this silanol layer takes place as a second step and that, when sufficient substitution has occurred, peeling of the layer takes place as a third step. Because peeling of the layer simultaneously exposes a fresh set of magnesium and hydroxyl ions,

---

(14) A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).

(15) F. Feigl, "Spot Tests," Elsevier Publishing Co., New York, N. Y., 1954, p 407.

(16) E. Martinez and G. L. Zucker, *J. Phys. Chem.*, **64**, 924 (1960).

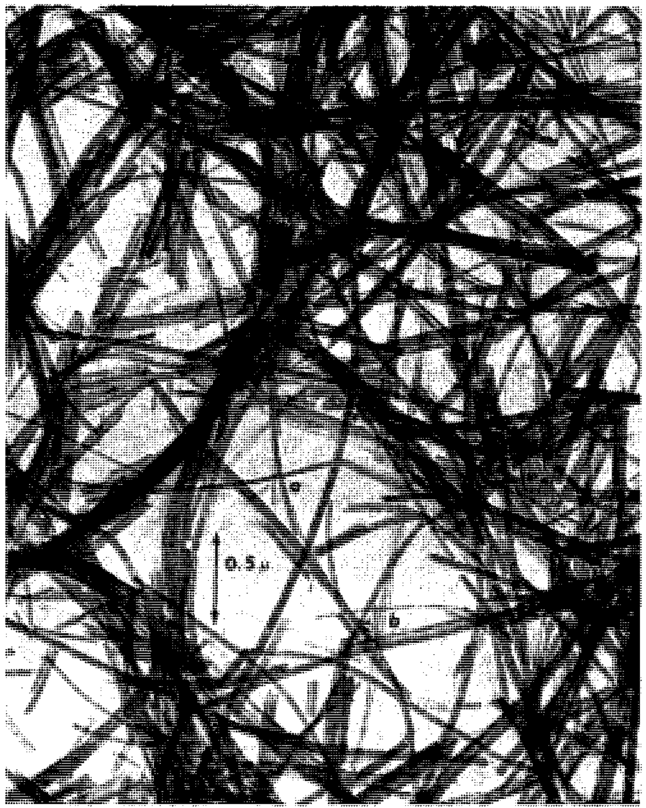

Figure 2.—Electron micrograph of fibers deposited from chloroform gel.

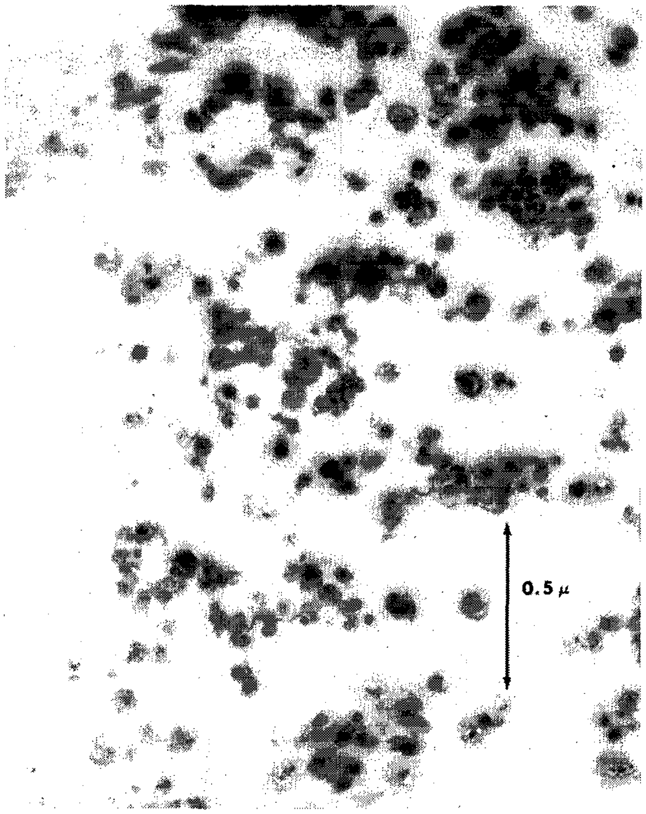

Figure 3.—Electron micrograph of a cross section of fibers embedded in Araldite resin.

the three stages must take place at the same time on a given tube. The fact that substantial substitution is achieved in the over-all process suggests that the rate of the substitution process is reasonably well matched to the leaching and peeling processes, for, if these latter processes were too fast, comparatively poor substitution would be expected.

Since all of the substitution must take place on the same side of the sheet, the question of the maximum attainable level of substitution arises. While this cannot be ascertained unequivocally by models or calculation because of the number of variables involved, models do suggest that the attainable level is considerably short of complete substitution—perhaps being about half of this. The experimental evidence obtained so far is in agreement with this conclusion, the usual level of substitution being around 50% (neglecting any differences in composition attributable to the fiber cores) and the maximum about 60% (in some room-temperature reactions).

Because the final product shows only a moderate infrared OH absorption, it appears that relatively few of the sheet silicon atoms of the final product carry silanol groups, and it can be concluded that a number of them are cross-linked to other sheet silicon atoms by added oxygen bridges. In view of the conditions under which the leaching and substitution occur and the unsymmetrical geometry of the ribbon itself, it is certain that all of this cross-linking is within a given ribbon.

Many patterns and combinations of patterns appear possible for this cross-linking, but those involving cross-linking between nearest, next nearest, and third nearest neighbor silicon atoms, *i.e.* 1,3 or 1,5 or 1,7 cross-linking, seem most reasonable. Since 1,3 cross-linking involves the formation of four-membered rings, and since such rings probably are strained, this type of cross-linking can be largely discounted. On the other hand, cross-links of the 1,5 and 1,7 type lead to the formation of six- and eight-membered rings, both of which are probably fairly strain free (eight-membered rings are among the favored rings in silicate chemistry[17]). Accordingly it is reasonable to conclude that either or both types of cross-links occur in the final ribbon. Whether this cross-linking is the cause of the curl of the ribbons or whether steric crowding is the cause is not yet clear.

The very pronounced 15-A *d* spacing which the X-ray work shows to be present can be attributed to the interlayer spacing, just as the 7.36-A *d* spacing of chrysotile is attributed to the interlayer spacing in this mineral. Substantiation of this assignment is found in the loss of this *d* spacing in the swollen product and its return in the redried product. The absence of strong reflections corresponding to other *d* spacings can be ascribed in part to an orientation effect (all fibers being oriented perpendicularly to the X-ray beam in the experiment performed) and in part to randomness in the substitution and cross-linking patterns.

What is perhaps surprising is the apparent ease with which the curling up, *i.e.*, ordering, of the ribbons takes

(17) T. Zoltai and M. J. Buerger, *Z. Krist.*, **114**, 1 (1960).

place upon solvent removal. While a few of what may be partially curled ribbons can be found in the micrographs (Figure 2, fiber marked b), most are apparently fully curled. Evidently very strong forces are at work here.

The method of synthesis of the polymer points up its general inertness.[18] The source of this inertness is, no doubt, attributable partly to the structure of the backbone of the polymer since the fission of it into even just two pieces requires the rupture of many bonds. However, also important must be the elemental composition of the polymer—fully 75% of the total being silicon and oxygen.

The fact that the ribbon comes out intact as a unit of substantial dimensions, perhaps a tenth of a micron by several microns, judging from the electron micrographs, leads to the conclusion that the molecular weight of the polymer is many millions. That an ordered product of such high molecular weight is obtained points up just how directed the polymerization process which leads to the formation of the $Si_2O_5^{2-}$ sheet of chrysotile is. Further, the ordered nature of the product brings out the advantages of making ordered organo polymers, as has been done here, by the substitution of polymeric frameworks formed as an integral part of a crystallization process and hence formed in circumstances where the orienting forces are very high. Now, while chrysotile is particularly suited for use in this approach because it has a robust and accessible framework and because the configuration of the framework is such as to tend to prevent intersheet cross-linking (the pendant oxygens are all on one side of the sheet), it is clear that the approach can be used to advantage on other natural and synthetic silicate and nonsilicate crystals containing suitable frameworks.

The Structure of Chrysotile.—In view of the results obtained, it appears that the closed concentric cylinder concept for the structure of chrysotile can be ruled out. The conversion of such cylinders into ribbons would require a lengthwise splitting of the cylinders and this seems most unlikely.

Acknowledgment.—The help of Drs. P. H. Geil, A. G. Walton, J. J. B. P. Blais, and Mr. A. Schwartz in the electron microscope work is gratefully acknowledged.

[18] Linear siloxane polymers rearrange under the type of conditions used.

Contribution No. 1300 from the Central Research Department,
Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Chemistry of Boranes. XXIX.[1] Thia- and Azaboranes

By W. R. HERTLER, F. KLANBERG, and E. L. MUETTERTIES

Received March 17, 1967

Reaction of decaborane(14) with aqueous ammonium polysulfide gives the thiaborane ion, $B_9H_{12}S$, in essentially quantitative yield. Dehydration of the hydrated conjugate acid of $B_9H_{12}S^-$ gives $B_9H_{11}S$ which in turn reacts with a variety of Lewis bases (L) to give complexes $L \cdot B_9H_{11}S$. Pyrolysis of $CsB_9H_{12}S$ gives the ion $B_{10}H_{11}S^-$, which on acidification is converted to the weak acid $B_{10}H_{12}S$. Treatment of $B_{10}H_{11}S^-$ or $B_{10}H_{12}S$ with strong base affords $B_{10}H_{10}S^{2-}$, which reacts with phenyldichloroborane to give icosahedral $C_6H_5B_{11}H_{10}S$. Reaction of $B_{10}H_{10}S^{2-}$ with a variety of transition metal halides gives a series of icosahedral metalothiaboranes such as $(B_{10}H_{10}S)_2Co^-$. The ion $B_{10}H_{11}S^-$ has also been obtained from the reaction of decaborane(14) with thionitrosodimethylamine along with a new azaborane, $(CH_3)_2NNB_9H_{12}^-$. The N–N bond of the latter compound can be cleaved with sodium metal to give $B_9H_{12}NH^-$, which is isoelectronic and presumably isostructural with $B_9H_{12}S^-$. Acid stability of $B_9H_{12}NH^-$ is considerably lower than that of $B_9H_{12}S^-$.

Introduction

A large number of polyhedral boranes has been synthesized in recent years.[2] These include members of both the simple polyhedral borane series of general formula $B_nH_n^{2-}$ (n = 6–12)[1] and borane anions which are fragments of polyhedra, such as $B_3H_8^-$, $B_9H_{14}^-$, $B_{10}H_{14}^{2-}$, and $B_{11}H_{14}^-$. The binary hydride series is supplemented by a nearly complete series of known carboranes, of general formula $B_nC_2H_{n+2}$ (n = 3–10), in which the carbon atoms occupy polyhedral positions in each respective polyhedron, as well as by a large group of metalocarboranes of icosahedral geometry such as $Co(B_9C_2H_{11})_2^-$,[3] in which some of the metal atom orbitals participate in the icosahedral bonding framework. No compounds in which elements other than carbon fill the polyhedral positions in a framework of boron atoms are known, however.[4] We wish to report

---

[1] Paper XXVIII: F. Klanberg, D. R. Eaton, L. F. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1271 (1967).

[2] See, for example, W. N. Lipscomb, *Science*, **153**, 373 (1966); E. L. Muetterties and W. H. Knoth, *Chem. Eng. News*, **44** (19), 88 (May 9, 1966); E. L. Muetterties, Ed., "Chemistry of Boron," John Wiley and Sons, Inc., New York, N. Y., 1967; M. F. Hawthorne, *Endeavour*, **25**, 146 (1966); E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1967.

[3] (a) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965); (b) M. F. Hawthorne and T. D. Andrews, *Chem. Commun.*, 443 (1965).

[4] Unstable adducts of $B_{10}H_{14}$ with alane and galane, as well as with zinc and cadmium alkyls, have been reported by N. N. Greenwood and F. A. McGinnety, *J. Chem. Soc., Sect. A*, 1090 (1966), and by N. N. Greenwood and N. F. Travers, *Inorg. Nucl. Chem. Letters*, **2**, 169 (1966). Insufficient evidence has been provided to establish whether these compounds are true heteroatom polyhedral boranes of the type $B_{10}MH_{11}$.