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FIBROUS ORGANOSILICON POLYMERS DERIVED FROM SILICATES.(U)
MAY 82   J HEFTER, M KENNEY   N00014-75-C-0693

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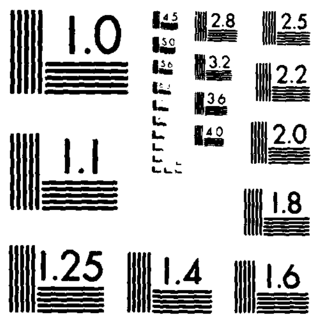

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A new, inherently fibrous organosilicon polymer having pendent trimethylsilyl groups is reported. It has been made from the rare ladder or tube silicate litidionite using a Lentz-type extraction-substitution process. The constituent fibers of this polymer have very small diameters, often 40-60 Å, and are flexible and inert. They are believed to have frameworks closely related to that of the parent silicate ion. A polymer which appears to be the same as this one has been made from the synthetic silicate,

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OFFICE OF NAVAL RESEARCH

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Fibrous Organosilicon Polymers Derived From Silicates

by

Jesse Hefter and Malcolm E. Kenney

Chapter

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James S. Falcone, Editor

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May 28, 1982

Fibrous Organosilicon Polymers Derived From Silicates

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A new, inherently fibrous organosilicon polymer having pendent trimethylsilyl groups is reported. It has been made from the rare ladder or tube silicate litidionite using a Lentz-type extraction-substitution process. The constituent fibers of this polymer have very small diameters, often 40-60 Å, and are flexible and inert. They are believed to have frameworks closely related to that of the parent silicate ion. A polymer which appears to be the same as this one has been made from the synthetic silicate $Na_2CuSi_4O_{10}$, a close structural analog of litidionite. In addition a related polymer carrying dimethylvinyl groups has been made from litidionite by a like Lentz-type procedure. Both silicates have been made by simple thermal procedures.

Recently we have been seeking new types of organosilicon polymers with the hope of finding polymers having unique structures and interesting combinations of properties. Out of this work has come a new siloxane that is, at least in part, inherently fibrous. The fibers characteristic of it have very small diameters and are flexible and inert.

The technique used to make this siloxane is based on a well-known procedure for derivatizing silicates originated by Lentz (1). In this procedure the metal ions are extracted from the silicate and trimethylsilyl or other silyl groups are grafted on the silicate framework thus exposed. (Initially the procedure was used in structural studies of silicates containing monomeric and oligomeric ions (1). Later it was used for the synthesis of silicones from silicates containing polymeric silicate ions (2). Among the silicones yielded by this latter work are sheet and

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scroll silicones carrying pendent trimethylsilyl groups (2, 3, 4). The scroll silicone, like the silicone described in this paper, is inherently fibrous. However, the fibers in it are an order of magnitude larger than those in the new silicone.)

The silicate which has been used most frequently for the synthesis of this new polymer is litidionite, $NaKCuSi_4O_{10}$. This silicate, while occurring naturally, is very rare (so far it has been found only in the crater of Mt. Vesuvius) (5). The silicate ion in it (6), Figure 1, can be described as being a complex ladder ion or as being a tube ion (6, 7). Examination of its structure shows that it is constructed of fused 8- and 16-membered rings. The arrangements of the oxygens about the metal ions in it are those shown in Figure 2.

This silicate has been made by the hydrothermal technique (8, 9). However, relatively elaborate equipment is required for its preparation by this approach and, as a result, it is not well-suited to incorporation in a synthetic sequence requiring litidionite.

Results and Discussion

In the present work two syntheses for litidionite have been developed which are straightforward and require only simple apparatus. In one a sodium-potassium-copper silicate glass is made and then devitrified over a period of weeks at approximately 765 °C. In the other a mixture of sodium carbonate, potassium carbonate, cupric oxide, silicon dioxide, again with a Na:K:Cu:Si ratio of 1:1:1:4, is sintered at approximately 765 °C for a number of days.

The litidionite made by this latter procedure can be purified, after being powdered, by a process involving a combination of washing and decantation. Water buffered at pH 5 is used in this process. In practice the process is repeated a number of times.

As might be expected litidionite is a medium blue. A micrograph of a crystallite of this silicate obtained by crushing a sample of it made by the devitrification process is shown in Figure 3. From this micrograph it is clear that litidionite itself is not fibrous in nature. In accordance with expectations both the litidionite made by the sintering process and that made by the devitrification process are satisfactory for use in the synthesis of the polymer.

The polymer, as already indicated, is made by a Lentz-type procedure. In the version of this procedure used, the litidionite is treated with a mixture of chlorotrimethylsilane, water, and a solvent such as dioxane, tetrahydrofuran, or acetone. The reaction is run over a period of days at room temperature.

Purification of the polymer can be effected by repeatedly subjecting a suspension of it in a solvent such as tetrahydrofuran to sonication and settling, and then isolating the polymer in the upper portion of the suspension. Generally multiple refractionations of the residue are necessary in order to get a sufficient amount of material.

The polymer has a waxy texture and is insoluble in a wide range of organic solvents. It does, however, form gel-like materials with solvents such as tetrahydrofuran, dioxane and chloroform. Not surprisingly in view of this, a mixture of a small amount of it and a large amount of a 1000 cs dimethylsilicone oil forms a stiff, stable grease. When purified the polymer is a very pale blue.

The infrared spectrum of the polymer shows $SiMe_3$, SiOH, and SiOSi bands while its Si $2p_{3/2}$ X-ray photoelectron spectrum shows overlapping SiO_4 and $SiOC_3$ peaks, Figure 4. Micrographs of the polymer show that it is composed at least in part of fibers, Figure 5, and that these fibers are flexible, Figure 6. Fibers that are 40-60 Å in diameter are commonly seen. A few with diameters somewhat above 20 Å are seen.

One sample was found to contain 14.08, 14.27 %C, 3.47 %H, and 38.93 %Si. The Si $2p_{3/2}$ X-ray photoelectron spectrum of this sample indicated that the ratio of SiO_4-type silicon to $SiOC_3$-type silicon was 73:27, while the K $1s_{1/2}$, Na $1s_{1/2}$ and Cu $2p_{3/2}$ spectra of it gave evidence for the presence of a small amount of potassium but no sodium or copper. The same sample gave the differential thermal analysis thermogram shown in Figure 7.

It is concluded on the basis of the available physical and synthetic evidence that some of the fibers in the polymer have frameworks that are like those of its parent silicate ion except for the presence of additional crosslinks, i.e., are at least semitubular in nature. It is further concluded that the rest of the fibers have composite frameworks built up of frameworks which are similar to those just described. These component frameworks, it is believed, are joined by well-spaced oxygen bridges. In the case of the sample of the polymer examined in detail, it seems probable that about 37% of the backbone silicon atoms carried silyl groups.

Further work along these same lines has shown that a polymer of the same general type carrying dimethylvinylsilyl groups can be made using an analogous synthesis. This polymer is of interest because the vinyl groups provide a potential site for the attachment of a wide variety of groups.

Other work has shown that a polymer that is apparently the same as the trimethylsilyl polymer can be made from another silicate. This silicate is the synthetic species $Na_2CuSi_4O_{10}$. It contains the same ladder or tube ion as does litidionite (9). As with litidionite it has been made by the hydrothermal technique (10, 11, 12).

In the present work this silicate has been made by a procedure similar to the sintering procedure used to make litidionite. The polymer has been made from it by a route parallel to that used for making the trimethylsilyl polymer from litidionite.

Acknowledgment

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Figure Captions

Figure 1. Silicate ion in litidionite. Junctions represent silicon atoms; circles represent oxygen atoms (7).

Figure 2. Coordination arrangements of the metal atoms in litidionite. Junctions represent metal ions; circles represent oxygen ions.

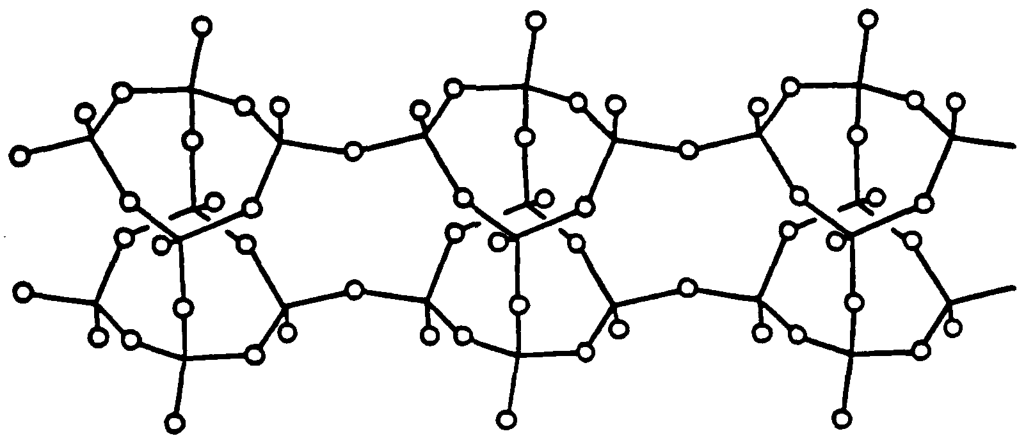
Figure 3. Transmission electron micrograph of a litidionite crystallite.

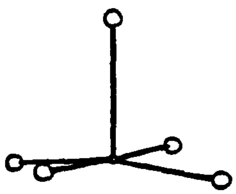
Figure 4. Si $2p_{3/2}$ X-ray photoelectron spectrum of the trimethylsilyl polymer, and the SiO_4 and $SiOC_3$ curves into which it can be resolved.

Figure 5. Composite transmission electron micrograph of the trimethylsilyl polymer showing its fibrous nature.

Figure 6. Transmission electron micrograph of the trimethylsilyl polymer showing the flexibility of its fibers.

Figure 7. Differential thermal analysis thermogram of the trimethylsilyl polymer.





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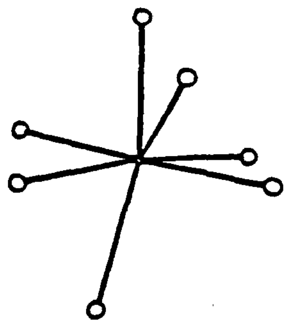
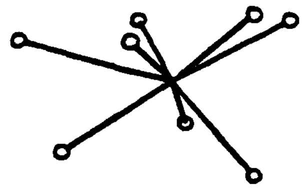


Na



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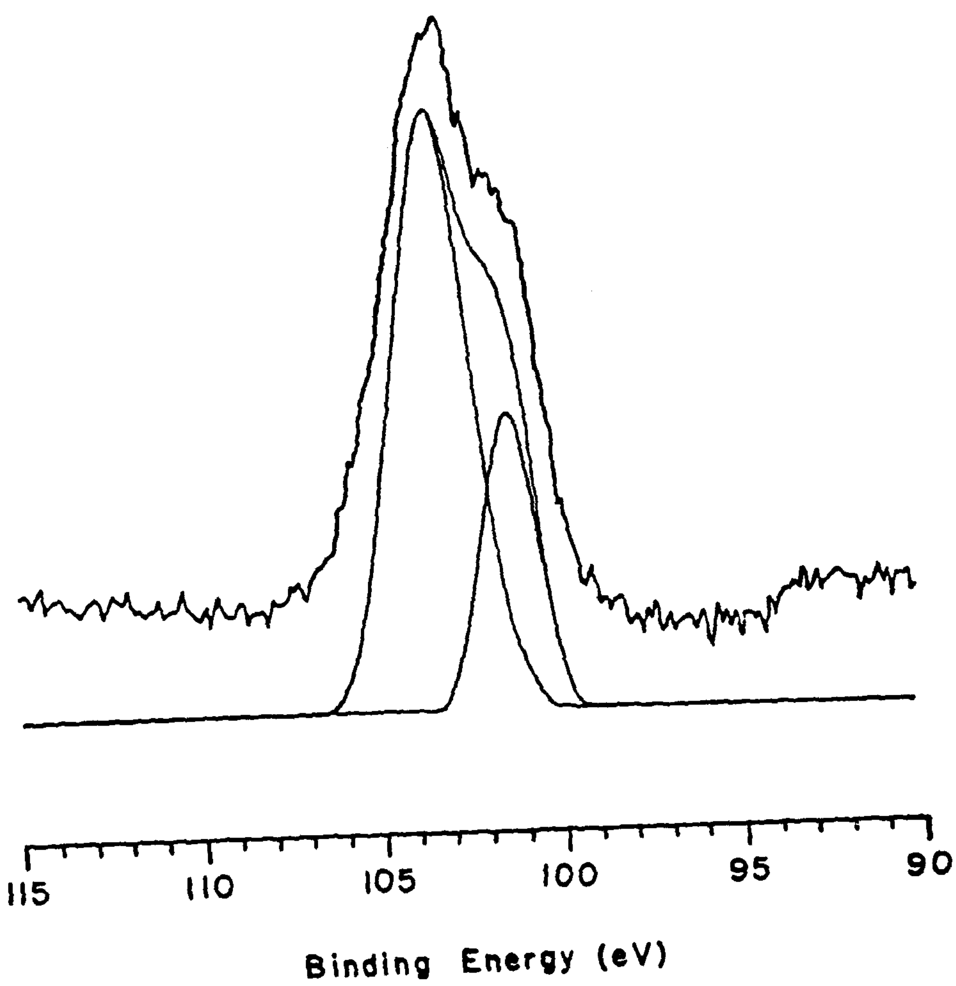
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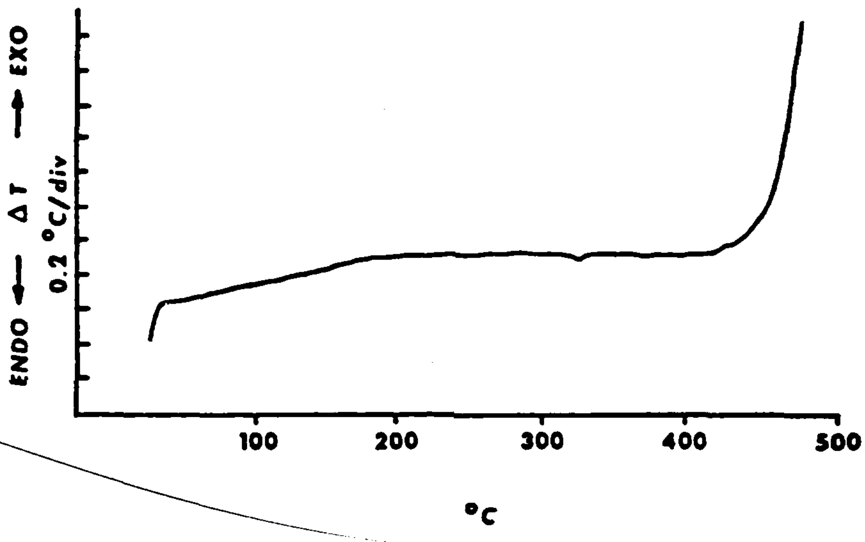
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