

## Inorganic Polymers

Research on linear polymers not containing carbon in their backbones promises new kinds of materials.

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The term "inorganic polymer" is used by many for inorganic materials such as silica and silicates, boron nitride, and the many other inorganic compounds that have two- and three-dimensional infinite crystal structures and consequently may be considered macromolecules. Even a crystal of sodium chloride may be considered a three-dimensional polymer. But none of these "polymers" exhibit typical plastic behavior, perhaps because generally their structure is polymeric only in the solid state. We will limit our discussion of inorganic polymers to selected recent studies of linear chain-like giant molecules which are the type generally believed to offer potential for new plastic materials.

Polymers should not contain any carbon in order to be termed inorganic polymers but in accordance with a recently agreed upon definition (1), we will consider inorganic polymers to be those that do not contain carbon in their backbones.

Inorganic polymers are by no means a recent discovery. There are a number of inorganic substances—elements as well as compounds—that are polymeric and have elastomeric, or at least

plastic, properties. For example, a form of sulfur that is elastomeric (rubber-like) can be obtained by rapid cooling of molten sulfur. Most likely this elastomer consists of long chains of interconnected sulfur atoms.

### Inorganic Rubber

In the 19th century a completely inorganic polymeric system was discovered which included a product so strikingly like rubber that it is usually referred to as "inorganic rubber." There are few inorganic chemists who, at one time or another, have not been interested in this fascinating system (2). Inorganic rubber is easily prepared from phosphorus pentachloride and ammonium chloride. Heating these reactants in a suitable solvent (3) leads to cyclic compounds such as trimeric and tetrameric phosphonitrilic chlorides,  $(\text{PNCl}_2)_3$  and  $(\text{PNCl}_2)_4$ . Further heating of these crystalline substances results in the formation of the rubbery polymer,  $(\text{PNCl}_2)_n$ .

Little that is definitive is known of either the chemistry or the structure of this rubber, which presumably consists of linear chains. However, at temperatures above 350°C, the smaller cyclic compounds are regenerated from the rubbery polymer; also the polymer hydrolyzes rather readily. One other generality can be made, rubbery polymers have only been prepared from the smaller cyclic compounds when the

substituents on phosphorus are halogens or pseudohalogens.

Most of the work on phosphonitrilic systems during the last few years has dealt with the synthesis of trimers and tetramers containing substituents other than chlorine on the phosphorus as well as structure work on the cyclic compounds. Two recent findings involve polymers. First is the discovery (2, p. 298; 4) that by incorporating metal chlorides ( $\text{SbCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$  and others) into the reaction of phosphorus pentachloride with ammonium chloride, oils are produced which are stable at temperatures in excess of 500°C. In some cases materials less susceptible to hydrolysis than the simple phosphonitrilic chloride polymers result; in others the products are more readily attacked by water. The structures of these systems have not yet been investigated.

Phosphonitrilic rings have been incorporated (5) into a "ball and chain" polymer by connecting them with siloxane-bonds. The degree of polymerization is reported to be at least 30 units of the structure shown in Fig. 1; not much more information is available.

### Silicones and Analogs

The siloxane polymers ("silicones"), a group of polymeric materials that contain an inorganic backbone of alternating silicon and oxygen atoms, are the only commercially available polymers with no carbon in their backbones. They possess properties that make them useful over a temperature range where organic polymers fail, but it is interesting to note that their heat stability, in the absence of air, is limited because at temperatures above 350°C the linear silicon-oxygen chains are rearranged to cyclic compounds of low molecular weight. The tendency to form small rings is frequently encountered in inorganic polymer systems—for example, the phosphonitrilic halides—and is a well-recognized problem. In air, the organic side groups are seriously attacked at about 200°C, whereas in the

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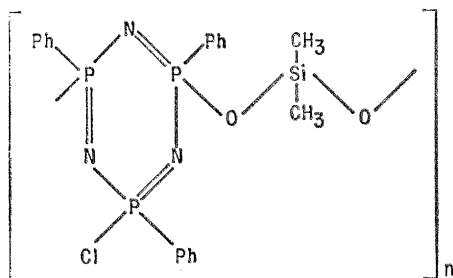


Fig. 1. "Ball and chain" polymer ( $Ph = C_6H_5$ ).

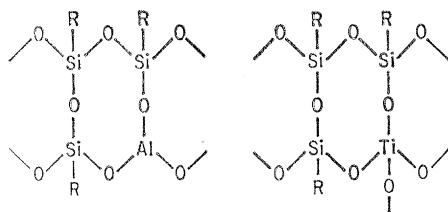


Fig. 2. Polymetallosiloxanes with double-chain structure.

absence of air the silicon-methyl bond, for example, is stable to about  $500^\circ\text{C}$ .

Low molecular weight, and therefore liquid, silicone polymers are used as lubricants and hydraulic fluids. They generally show only slight temperature-dependence of viscosity and are chemically inert and odorless. Their physical properties (boiling points, freezing points, viscosities) vary over a wide range, depending upon the degree of polymerization as well as on the nature of the organic group connected to the silicon atom.

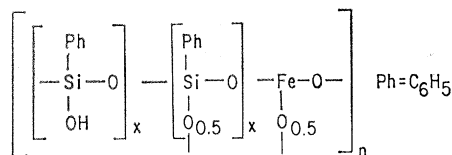
Silicone rubbers have the same basic structure as the liquid products, but in the rubbers many more units are combined into linear chains, which are occasionally cross-linked. The elastomeric properties of the silicone rubbers depend upon the number of such units in the chain and the number of cross-links. The higher the average molecular weight, the higher the elasticity and mechanical strength. On the other hand, only occasional cross-links can be present, or the polymer will lose its elastomeric properties.

Much work has been, and is being, done on preparation, structures, and properties of silicones. No attempt will be made to review this field here, but some recent work on siloxane polymers which might lead to products with still better thermal properties will be discussed.

Andrianov and his group (6) have incorporated other metals such as aluminum and titanium into the silicon-

oxygen backbone. These polymetallosiloxanes represent a new class of polymers that contain double chains. Bradley (7) has pointed out that Andrianov, in assigning structures (see Fig. 2), apparently adopted the view that the metals are present in the coordination numbers corresponding to their valences ( $Al=3$ ,  $Ti=4$ ), in spite of the well-known tendency of these metals to expand their coordination numbers whenever possible. Some of these polymers are reported to be thermally stable, melting above  $600^\circ\text{C}$ . Others are soluble in common organic solvents. Such ladder-type structures are probably desirable for high thermal stability, because rupture of one bond does not result in breakdown of the polymer chain. Practically no information is available on the mechanical properties of these polymers.

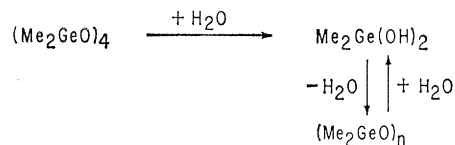
Hornbaker and Conrad (8) attempted to incorporate tin, lead, magnesium, copper, zinc, and mercury into single siloxane chains. Although resinous polymeric materials were obtained, the products decomposed rather easily and were definitely less stable than the silicones. Polyferrosiloxanes and polyaluminosiloxanes on the other hand have been reported (9) to be highly thermostable with melting points above  $500^\circ\text{C}$  and to be soluble in nonpolar and weakly polar solvents:



A phenylsilsesquioxane polymer (Fig. 3) containing double chains but, unlike Andrianov's ladder polymers, not containing other metals, has been reported recently (10). This seems to be the first example of a stereospecific inorganic polymer. Molecular weights up to 4 million have been obtained. The polymer can be heated in a vacuum to red heat without decomposition and seems to hold promise for high-temperature coating applications. The accomplishment here is that uncontrolled cross-linking of the trifunctional monomer—which usually leads to three-dimensional, insoluble networks—has been prevented and soluble polymers have been obtained by giving the phenylsilsesquioxane ( $C_6H_5SiO_{3/2}$ ) units an opportunity to arrange in a well-ordered fashion.

In going from silicon to the next element in the fourth group of the periodic

table, germanium, we find that polymers analogous in structure to the silicones can be prepared. Recently, the tetramer of dimethylgermanium oxide has been reinvestigated (11). Unlike its silicon analog, it is very soluble in water, and hydration occurs to form the diol:



When water is removed from an aqueous solution of dimethylgermanium oxide, this compound remains in a white fibrous form which presumably is polymeric. But this phenomenon is reversible, since the polymer can be dissolved in water. A dilute solution again contains only monomeric units.

Not much is known about the diphenylgermanium oxides other than the information (12) summarized in Fig. 4. Hydrolysis of dibromodiphenylgermane gives the highest melting oxide ( $295^\circ\text{C}$ ), probably a polygermanoxane, but its structure has not yet been determined. Upon distillation it yields the trimer which in turn can be converted back into the oxide melting at  $295^\circ\text{C}$  or into a tetramer, melting at  $218^\circ\text{C}$ . The striking feature here is the ease of interconvertibility of these oxides. Thus it appears that germanium is not a good choice for replacing silicon in silicones if polymers with better thermal properties are desired.

The tin analogs of silicones, the polystannoxanes, do not form rubbers or gums of low softening point and high solubility in organic solvents. Instead they form hard, crystalline, high-melting, and brittle solids. On the other hand, Reichle (13) recently reported that polymeric di-*n*-octylstannoxane was soluble in organic solvents, and showed an average molecular weight of  $8900 \pm 10$  percent (25 units). At about  $280^\circ\text{C}$ , this polymer melts to a clear liquid. The difference in physical properties between stannoxanes and siloxanes has been explained in terms of the highly ionic tin-oxygen bond leading to a  $R_2Sn^{+2}O^{2-}$  ( $R$  represents an organic group such as aryl or alkyl) crystal lattice which would be expected to exhibit the properties found experimentally.

Variations of silicone polymers considered so far have been arrived at by replacing part or all of the silicon in the repeating  $R_2SiO$ -unit by other elements. In other words, we have dis-

cussed siloxane, metasiloxane, and metalloxane polymers, all of which contain oxygen atoms in their backbones. Replacement of oxygen with nitrogen in a siloxane leads to silazanes, which are based on silicon-nitrogen chains. Polysilazanes have been studied in some detail. They are sensitive to water and react to give polysiloxanes with liberation of ammonia.

Late in 1960, Minne and Rochow (14) reported an interesting polymer for which a double-chain structure (Fig. 5, left) was proposed. Their compound is a firm, waxy material which, however, like most compounds containing the silicon-nitrogen bond, is unstable toward water. The double-chain structure is by no means established. It could easily be a single-chain structure in which the ethylenediamine is bonded back to a silicon in the same chain (Fig. 5, right).

In 1962 Breed (15) reported linear silazane polymers made from essentially the same starting materials used by Minne (14) but by a different route. These polymers are tacky, somewhat elastic solids resembling uncured gum rubber. They are soluble in nonpolar solvents and have molecular weights around 8000.

The hydrolytic instability of the Si-N bond in silazane polymers appears to be a serious problem, but there is insufficient evidence—at least according to those working in this field—to establish whether or not a silazane polymer which is really substantially stable to hydrolysis can be made. To quote Aylett (16): "The situation is not hopeless."

### Boron-Containing Polymers

Phosphinoborine polymers and the polyaminoborines can be considered formally analogous to hydrocarbons if we consider that carbon-carbon bonds are replaced by phosphorus-boron or nitrogen-boron bonds. For example,  $(H_2NBH_2)_n$  is formally analogous to polyethylene, although there are important differences in the nature of the bonds. The properties of phosphinoborines are quite interesting. Burg and Wagner (17) pyrolyzed dimethylphosphine borine and obtained cyclic trimers and tetramers. Apparently small amounts of a higher polymer were also formed. The trimer is very stable to heat, decomposing only slowly at 400°C. Chemically it is unreactive and heating

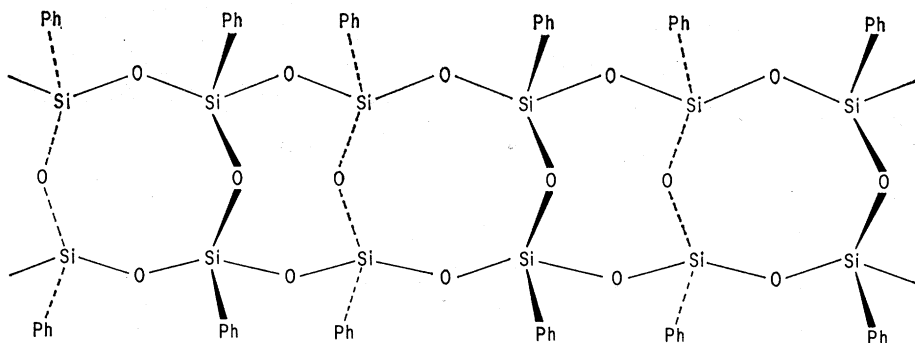


Fig. 3. Polyphenylsilsesquioxane ( $Ph = C_6H_5$ ).

with concentrated hydrochloric acid at 290°C is required to hydrolyze it.

Since 1953 Wagner and his group (18) have reported a number of linear phosphinoborine polymers which they prepared by pyrolyzing dialkylphosphine borines in the presence of blocking groups such as triethylamine. Presumably coordination between this basic group and the boron atom of the monomer suppresses formation of cyclic compounds, thus allowing a linear polymer to grow. Molecular weights up to 13,500 (183 units) have been obtained for the dimethyl polymer, which melts at 170°C and up to 1800 (20 units) for the methylethyl polymer, melting point 125°C. More bulky substituents appear to favor cyclization. Thus pyrolysis of diphenylphosphine borine leads mainly to cyclic products.

Unfortunately the linear polymers are not as stable hydrolytically as the cyclic compounds. Furthermore, they start to decompose at about 170°C, rearranging to the cyclic trimers and tetramers. At about 280°C they spontaneously ignite.

The existence of fused-ring type polymers in the B-N systems has been suspected for some time. Thus Wiberg (19) proposed that the nonvolatile residue of composition  $(BNH)_n$  formed by pyrolysis of borazine ( $B_3N_3H_6$ , also called borazole) was polymeric.

Laubengayer and his students (20) recently reinvestigated the pyrolysis of borazine at 340° to 440°C and isolated a nonvolatile solid of empirical composition  $BNH_{0.8}$ . Heating to 475°C resulted in further loss of hydrogen and a residue of composition  $BNH_{0.3}$ . Evi-

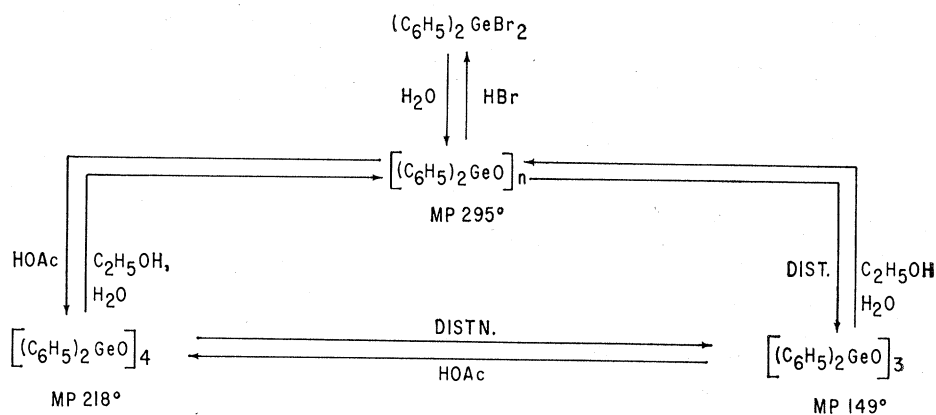


Fig. 4. Formation of diphenylgermanium oxides.

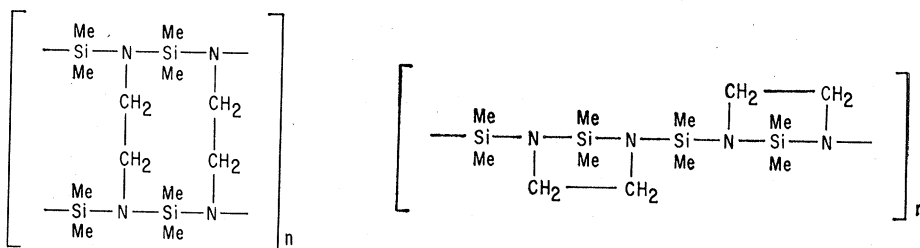
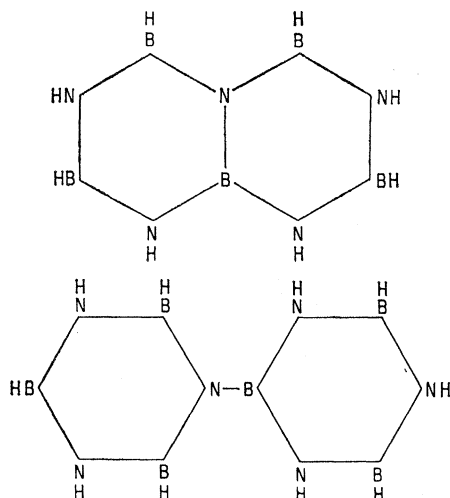


Fig. 5. Silazane polymer ( $Me = CH_3$ ): left, ladder structure; right, single chain.

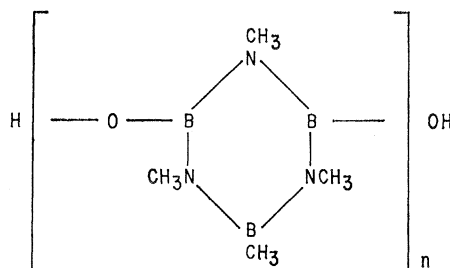
dently both of these residues have a highly condensed polycyclic B-N frameworks similar to the structure of hexagonal boron nitride. In the course of these studies a number of volatile products were isolated, among them  $B_6N_6H_8$ , the analog of naphthalene in the boron-nitrogen system, and  $B_6N_6H_{10}$ , the analog of biphenyl:



Thus, dehydrogenation of borazine occurs rather readily to yield condensed structures.

On the other hand, Wagner and Bradford (21) found that dehydrogenation of pentamethylborazines did not easily result in condensation of two borazine nuclei, the expected product being formed only in trace quantities. The same workers, though, succeeded in making cyclolinear polymers by elimination of LiCl from *N*-dilithiotetramethylborazine and tetramethyl-*B*-dichloroborazine as shown in Fig. 6. The degree of polymerization achieved so far is only 5, and the polymer forms a clear, yellow resin melting between 140° and 160°C.

Degrees of polymerization up to 23 were attained by Wagner and Bradford (21) for polyborazylene oxide in which borazine nuclei are linked by oxygen:

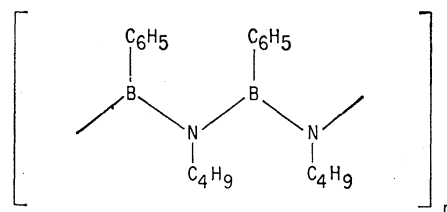


This glassy polymer was formed by hydrolysis of dihalo-substituted borazine

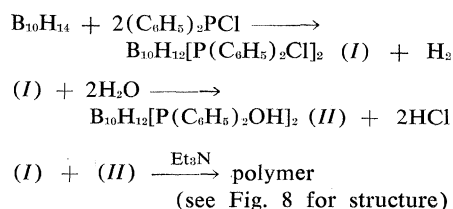
derivatives with the stoichiometric quantity of water. Its melting range is 180° to 200°C.

In view of the high thermal stability of borazine (22) and substituted borazines (hexaphenylborazine melts at 415°C without decomposition) other workers have also investigated borazine-based polymers. A few years ago Lapert (23) found that tris(ethylamino) borane,  $B(NHEt)_3$ , undergoes the pyrolysis reactions summarized in Fig. 7. Not much information is available on the physical properties of the polymers formed other than that some of the intermediates change from very viscous liquids to rubbery solids, the final product being brittle and sensitive to hydrolysis.

Numerous attempts have been made to prepare a linear polymer with a B-N backbone. However, owing to the tendency of boron-nitrogen compounds to form the borazine ring, these attempts have generally not been successful. Gerrard (24), on the other hand, was able to prevent ring formation by using bulky groups. The structure of the linear polymer he prepared, which melts at about 150°C and is readily hydrolyzed by boiling water, follows:



Of much interest are polymers which are based on decaborane chemistry. During the last year, Schroeder, Reiner, and Knowles (25) have succeeded in synthesizing a linear polymer containing decaborane nuclei linked together by P-O-P units as follows:



Molecular weight determination by light-scattering in *N*-methylpyrrolidone gave a value of 27,000. Hydrogen starts to evolve when the polymer is heated to about 270°C, and continued heating at 350°C results in the evolution of approximately four moles of

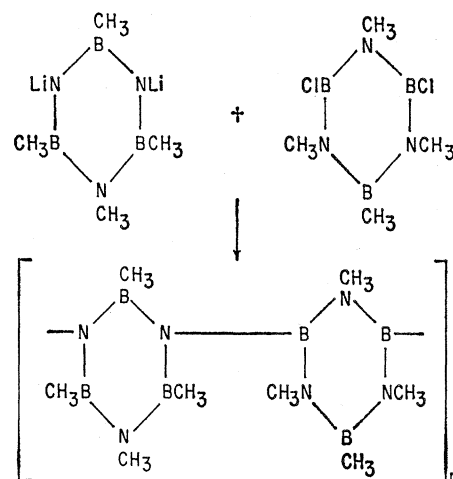


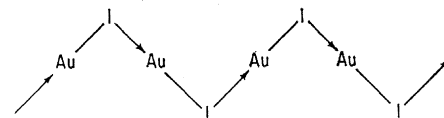
Fig. 6. Formation of cyclolinear B-N polymer.

hydrogen per unit. Preliminary experiments indicate that clear, adhesive films of this polymer can be coated on metals by solvent evaporation, although much more work needs to be done before such coatings are of practical value.

## Inorganic Coordination Polymers

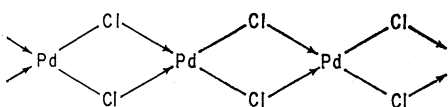
Coordination polymers have been defined in a number of ways. If we combine the definition: "polymers which contain coordinate covalent bonds in the backbone" with the aforementioned definition of an inorganic polymer, the number of known "inorganic coordination polymers" becomes small indeed. Chemists interested in coordination compounds think frequently in terms of organic chelating groups. Consequently many investigations of coordination polymers have involved at least some organic bonding in the backbone. Such systems are not truly inorganic systems and detailed discussions can be found elsewhere (26).

There are a good many inorganic compounds that appear to be coordination polymers on the basis of their structures in the solid state, but that have not been otherwise characterized as polymers. A very simple example of such a compound is gold iodine (27):



Such a structure is typical for elements which exhibit a coordination number of two. In  $PdCl_2$  the central element—

palladium—has a coordination number of four and there are double chloride bridges between palladium atoms (see 28):



These simple structures in which the coordinate covalent bonds are indicated by arrows illustrate one important aspect of coordination polymer chemistry—metal ions have characteristic coordination numbers which they attempt to attain even by sharing groups, if necessary.

The work of Block *et al.* is based upon the concept (29) of creating coordinatively unsaturated entities which can satisfy coordination requirements only by polymerizing. This idea was first applied to the reaction of beryllium acetylacetonate with diphenylphosphinic acid. Fusion (30) of beryllium acetylacetonate with diphenylphosphinic acid indeed led to the composition  $\text{Be}(\text{CH}_3\text{COCHCOCH}_3)_2 [\text{OP}(\text{C}_6\text{H}_5)_2\text{O}]$ . This product turned out to be a dimer. Consequently the diphenylphosphinate ion does act as a catenating, not a chelating group, but only two units combine with each other in order to give beryllium its coordination number of four. So far this dimer has not been converted into a linear polymer.

A similar reaction with chromium (III) acetylacetonate, an octahedral complex, gave the desired composition  $\text{Cr}(\text{CH}_3\text{COCHCOCH}_3)_2 [\text{OP}(\text{C}_6\text{H}_5)_2\text{O}]$ , but again only a dimer was formed (30).

The problem of small-ring formation seems to be particularly acute with these

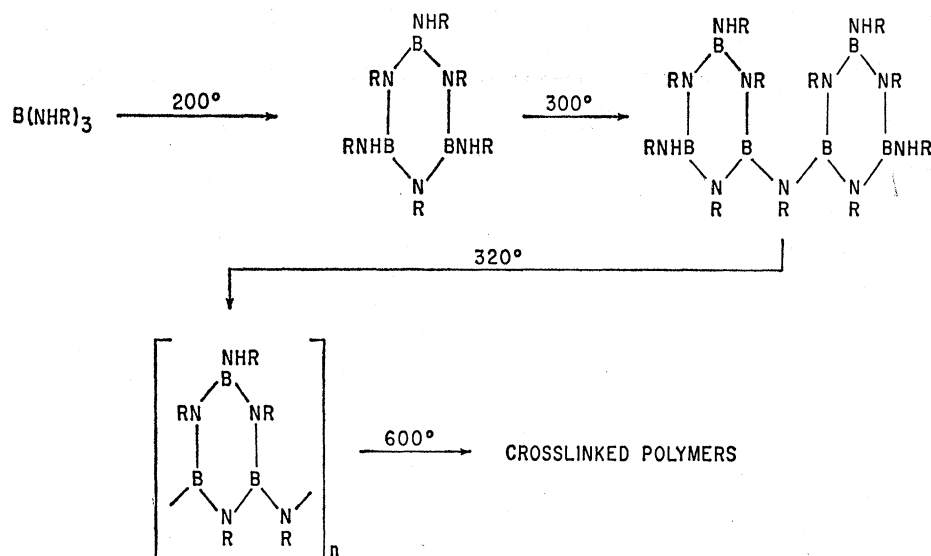


Fig. 7. Polymers from pyrolysis of tris (ethylamino) borane ( $R = \text{C}_2\text{H}_5$ ).

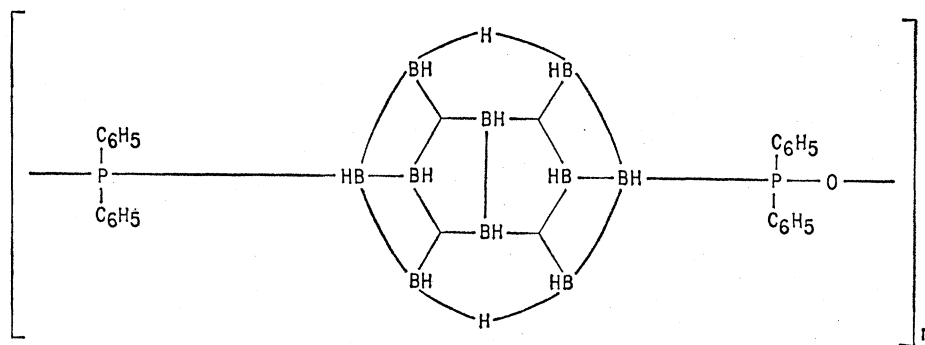


Fig. 8. Structure of decaborane-P-O-P polymer.

systems. In an attempt to surmount it, double bridging was incorporated into the polymers. Zinc acetate reacts with phosphinic acids in benzene to yield zinc phosphinates,  $\text{Zn}(\text{OPR}_2\text{O})_2$ . The methylphenyl derivative, softening at approximately  $100^\circ\text{C}$ , is soluble in

organic solvents and can be formed into fibers and films (31). The molecular weight varies from sample to sample depending on the conditions of preparation. Values up to 10,000 were measured, and there are indications for higher values. The diphenyl compound

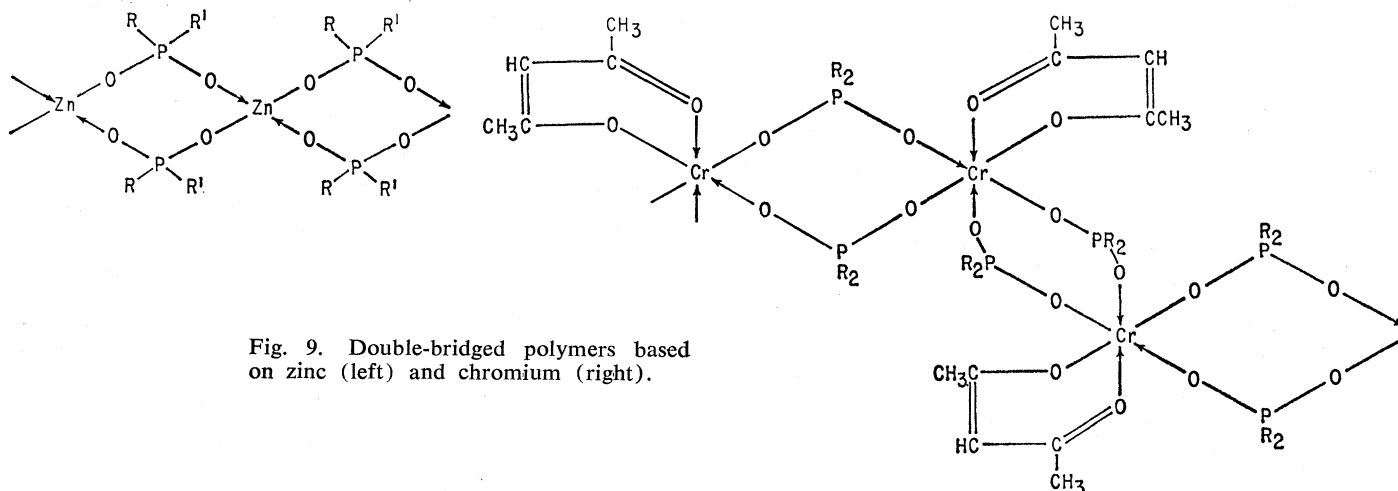


Fig. 9. Double-bridged polymers based on zinc (left) and chromium (right).

is probably also a polymer, but its molecular weight cannot be measured because it is insoluble and infusible. It has marked thermal stability, losing no weight up to about 500°C in a thermobalance.

Closely related is the polymer made by the fusion of chromium(III) acetylacetonate with diphenylphosphinic acid in a 1:2 molar ratio (32). Extraction of the fusion residue with a series of solvents leads to the isolation of fractions with varying molecular weights but with compositions corresponding to  $\text{Cr}(\text{CH}_3\text{COCHCOCH}_3)_3 [\text{OP}(\text{C}_6\text{H}_5)_2\text{O}]_2$ .

As one would expect, the fractions with the higher molecular weights are those which show the higher intrinsic viscosities. Molecular weights of the highest fractions could not be determined because of insufficient solubility but appear to be greater than 10,000. These polymers form green films which start to decompose at somewhat lower temperatures than the polymers formed from tetrahedral elements. The lower stability appears to be primarily due to the acetylacetonate grouping.

An important feature in these polymers is the double-bridged structure which contributes to a stable backbone (Fig. 9.). Two specifically related bonds must be broken in order to rupture the backbone—not a very probable event. Another is the presence of eight-membered rings. These rings are quite flexible; they give rise to a much less rigid backbone than that present in most double-bridged structures. In the octahedral structure there is an additional feature. The presence of the

chelate ring forces the double bridges into a *cis* configuration so that the backbone is not a straight linear structure but zig-zag or spiral.

### Summary

Much of the effort in this exciting field of research is directed toward the eventual production of materials which will maintain, at very high temperatures, the useful properties of organic plastics. With the exception of one class of materials, the silicones, inorganic plastics are now only at about the same stage of development at which organic plastics were in the 1920's. In addition to the practical objectives there are, of course, purely scientific motives for such research. Systematic study should soon open the door to technical application as well as to new chemistry (33).

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33. We thank the Office of Naval Research for supporting much of the work on inorganic polymers in our laboratories.