

SHEET POLYMERS AND NETWORK POLYMERS†

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INTRODUCTION

The history of network polymers of definite, known structure started over 50 years ago, when William H. Bragg and his son W. Lawrence Bragg¹ deduced the structure of diamond from X-ray diffraction data. They showed that each carbon atom in diamond has four others tetrahedrally around it and noted the correspondence with the normal valence of 4 for carbon and the tetrahedral arrangement around carbon atoms in many organic compounds.

In the following decade, the Braggs and others determined the arrangements of atoms in a number of other inorganic crystals in which no small molecular units, containing only a few atoms, were evident. The bonding between the atoms in these crystals remained unknown until, in 1922, I showed² that one could apply G. N. Lewis' theory³ of valence and molecular structure to deduce the distributions of electrons and electron-pair bonds. I showed that many of these substances could be considered truly macromolecular, with a three-dimensional network of chemical bonds in some cases, a two-dimensional sheetlike bond system in others and a linear one-dimensional molecular structure in others^{4, 5}.

Among substances which I cited as examples of space-network polymers I may mention silicon carbide², zinc sulphide², iron disulphide^{2, 6}, spinel⁷ and quartz⁸. Those recognized as sheet polymers included antimony², cadmium iodide⁴, and mercuric iodide⁹. Of course, many other examples of these classes are now known.

Space-network macromolecules of *irregular* composition and structure have also been known for many years. Bakelite, other thermoset resins and vulcanized rubber are well-known examples. The formation of sheet macromolecules (presumably of irregular and flexible structure) by condensation reactions between low molecular weight molecules in an absorbed monolayer on a liquid surface has been proposed by Hill¹⁰.

POLYIONS

Multiply charged linear polymer molecules—polyions—are well known. By crosslinking such ions or by removal or addition of hydrogen ions from network polymer molecules, three-dimensional polyions of *irregular* structure can readily be obtained. One-, two-, and three-dimensional polyions of *regular* structure are known in many crystals. For example, asbestos and related minerals contain linear polyions; mica and the clay minerals contain

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sheet polyions; and the zeolites contain network polyions. To balance the charges of these polyions, there are of course counterions of opposite charge, each usually consisting of only one or a few atoms.

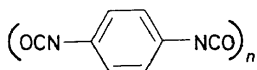
Glasses¹¹⁻¹⁴, including those of the ordinary silicate types with which we are all familiar, usually consist of network polyanions of irregular structure, with interspersed cations such as those of sodium, calcium, and lead. In addition to silicon and oxygen atoms, the polyanionic networks usually contain aluminium or boron atoms or both. Two important parameters which greatly affect the properties of the glass are: the degree of cross-linking of the network, measured by the relative numbers of atoms (silicon, aluminium, or boron) which are junction points of the network; and the charge of the network, relative to the number of atoms in it. These parameters can of course be related to the composition: the relative numbers, coordination numbers and valences of the component atoms. In a glass having relative numbers of atoms of metallic elements, silicon and oxygen as indicated by the formula $M_m\text{SiO}_x$, each silicon atom is surrounded by four oxygen atoms. On the average, the number of oxygen atoms (per silicon) which act as bridges to other silicon atoms is $8 - 2x$. The average charge per network ion is $4 - 2x$ times the average number of silicon atoms per network. Thus, as x increases, the average number of bridges per silicon decreases and the average negative charge on the network (per silicon atom) increases. In quartz and other forms of silica, each silicon is connected by four oxygen bridges to other silicons and the average charge per silicon is zero. In a glass or crystal having the composition of a metasilicate, $M_m\text{SiO}_3$, there are, on the average, two bridges per silicon atom and the average negative charge on the polyion is twice the average number of silicon atoms per polyion. In crystalline metasilicates each silicon atom has two bridging and two non-bridging oxygen neighbours and the polyions are either giant chains or rings. Glasses of the same over-all composition contain rings, linear chains together with branched chains of various sizes, configurations, and conformations. The energies of these coexisting structures are all very nearly the same.

For sheet polyions, a silicate conforming to the general formula $M_m\text{SiO}_x$ must have $x = 5/2$, to give three bridging oxygens per silicon. This gives one unit of negative charge per silicon in each polyion. Although silicate crystals containing sheet polyions conforming to these requirements are known, silicate glasses of this composition contain a wide variety of types of structure, with the *average* number of bridges and the average charge per silicon equal to three and minus one, respectively, as for the crystals.

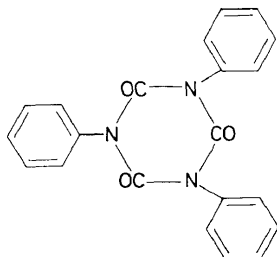
Similar, but more complicated, relationships are readily derived for glasses containing elements of other valences and coordination numbers.

AN ORGANIC SHEET POLYMER

As part of a programme on the synthesis of new types of sheet polymers, we have synthesized poly-*p*-phenylenedi-isocyanate:



and are now engaged in studying its structure and properties. It is well known that phenyl isocyanate readily forms a stable trimer:



It is not surprising, therefore, that *p*-phenylenedi-isocyanate polymerizes easily to give a high polymeric product. Although our characterization, by chemical analysis, infrared spectra, X-ray diffraction, *etc.*, is not complete, it appears to be an assemblage of stacked sheet polymers, each having the structure indicated in *Figure 1*.

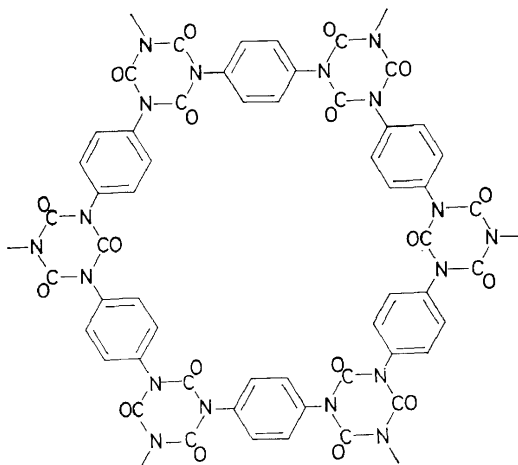


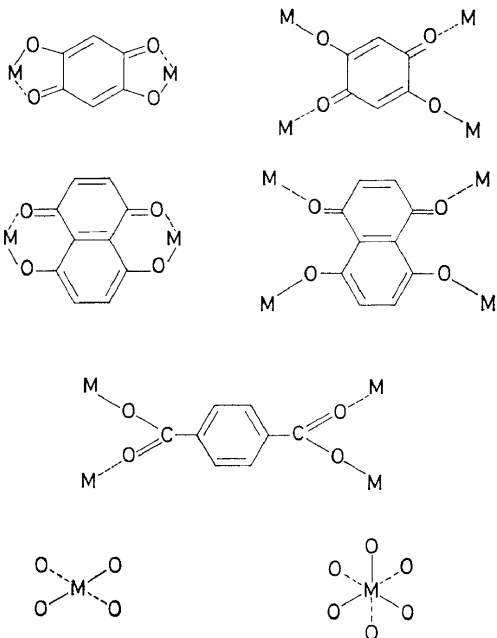
Figure 1. Bond pattern in a poly-*p*-phenylenediisocyanate

The X-ray data from crystalline powders conform to this assumption, provided that the isocyanurate rings in each sheet are in two parallel planes, rather than in a single plane, with the phenyl groups sloping between the two planes. This is a reasonable structure, because of the preferred non-coplanar orientation of the three single bonds around each nitrogen atom. As would be expected, the sheet molecules stack together in such a way that the holes in one are not directly over the holes in the one below it. From the absorption properties, however, it appears that there are still channels in the crystals through which water molecules can pass. Much larger molecules or ions appear to be kept out.

We hope to confirm or disprove these conclusions by means of an X-ray diffraction study of single crystals. We hope also to devise methods for separating the single sheets of the crystals or, perhaps more easily, for synthesizing the polymer in such a way as to produce single sheets or aggregates of a few sheets.

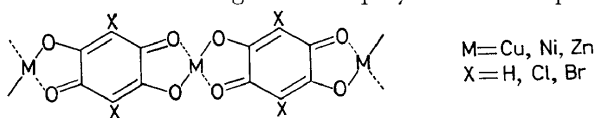
POLYMERIC METAL SALTS OF ORGANIC ACIDS¹⁵

We have recently been synthesizing and studying certain metal salts of organic acids; the metals and acids being chosen to give rigid polymeric structures, with strong bonding throughout. The bond patterns around the organic groups and around the metal atoms in some of the products are, I believe, as indicated in the following diagrams:



In these examples, each anion has two negative charges and four oxygen atoms which (because of resonance) form strong bonds to ions of the transition metals. The oxygen atoms in each anion are in pairs. Except in the terephthalate or other carboxylates, one would expect the two oxygen atoms of each pair to be bonded to a single metal atom or to two different metal atoms, depending on the relative stabilities of the resulting over-all structures or on the concentrations or other factors at the time of the synthesis. For the two oxygens of a carboxylate group to bond a single metal atom, however, would require the formation of a four-membered ring, with bond angles which are not the most stable ones. I suggest, therefore, that in the metal dicarboxylates the two oxygen atoms of each pair are always bonded to different metal atoms. This is in agreement with what information is available on the structures of other metal carboxylates.

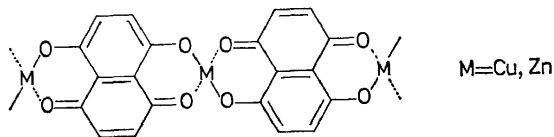
This research was started about 10 years ago, when, at my instigation, Kanda and Saito¹⁶ prepared a number of salts of divalent 4-coordinate metals with 2,5-dihydroxyquinone and some similar acids. Some of these salts have been shown to be rigid rodlike polymers¹⁷⁻¹⁹ as predicted:



M = Cu, Ni, Zn
X = H, Cl, Br

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Similar salts of 5,8-dihydroxynaphthaquinone, which we have recently made, are, I believe, also rigid and rodlike.



If, in some of these products, the two oxygens of each pair are bonded to different metal atoms, the polymer formed must be either a sheet polymer or a three-dimensional network polymer. Mercuric terephthalate, which we have made, is crystalline, giving X-ray diffraction data consistent with a network structure in which the mercury atoms are in planes 9.2 Å apart, and the terephthalate groups are all aligned with their axes normal to these planes.

We have synthesized a number of salts of the acids which I have listed, and some others, in which the metal atoms are trivalent, with octahedral, 6-fold coordination. For these compounds, one can deduce crystalline structures having stable bond angles and bond lengths and no unreasonably

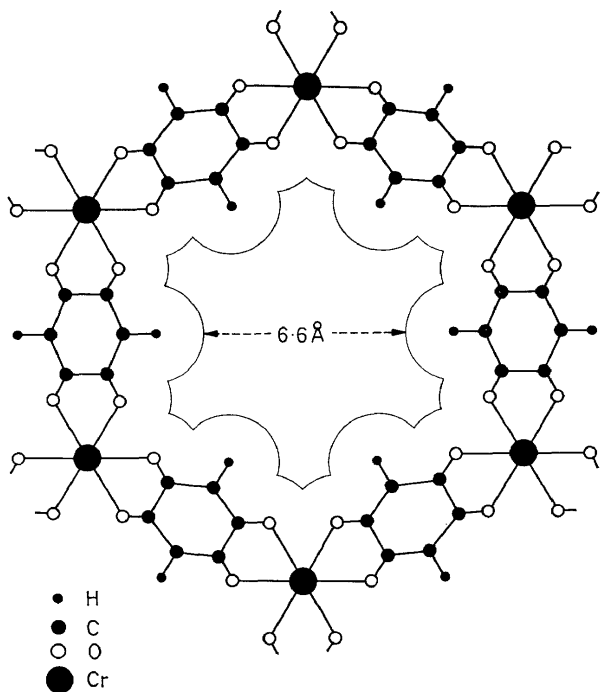


Figure 2. Projection of a portion of the hypothetical structure of a sheet polymer of chromic 2,6-dihydroxyquinonate

close contacts between atoms not directly bonded together. In the hypothetical structures in which the two oxygens of each pair are both bonded to the same metal atom, the polymer molecules are rigid sheets. If the oxygens of each pair are bonded to different metal atoms, the polymers are rigid three-dimensional networks. With the anions which I have mentioned, the regular structures which would be expected to be most stable all contain holes or channels, of dimensions such as to make them useful for separating small molecules or ions from larger ones. For example, I predict a sheetlike hexagonal structure for chromic 2,6-dihydroxyquinonate molecules, with holes within each hexagon and a minimum distance of 6.6 Å between the van der Waals envelopes on opposite sides of these holes (*Figure 2*).

For crystalline chromic terephthalate I predict a hexagonal network structure containing channels having a minimum diameter between van der Waals envelopes of about 10.8 Å (*Figure 3*).

Another possible type of structure (*Figure 4*), in which the terephthalate axes are all parallel, would also give stable bond angles and bond lengths, but some of the distances between non-bonded pairs of atoms are rather short, so I think that this structure would be less stable than the other.

The trivalent metal salts which we have so far obtained in this research are all amorphous. This is readily understandable, because there are alternative orientations, having essentially the same stability, for the three organic anions attached to each metal atom. We are hopeful that by using special techniques (such as synthesizing the polymer at an interface, if the product is to have a sheetlike structure) we shall succeed in producing crystalline products, but we do not yet have them.

Much of our research in this field has been with chromic compounds. To obtain the pure chromic salts it is necessary to use anhydrous materials to avoid H_2O or OH^- ligands attached to the chromium atoms. Heating a product containing these ligands would be expected to give some $\text{Cr}-\text{OH}-\text{Cr}$ or $\text{Cr}-\text{O}-\text{Cr}$ bridges, which would not be replaceable by the organic anion bridges. For many purposes, some oxide or hydroxide bridges would not matter; they might even be advantageous, but they must make it difficult or impossible to obtain crystalline products.

The properties of our amorphous products are interesting and suggestive of a number of possible applications. Because of the rigidity of the organic bridges between the metal atoms and the stereochemical requirements for good coordination bonding at each metal atom, no *compact* stable structures are possible. The amorphous products, like the hypothetical crystalline ones, must be quite porous, on an atomic scale. The range of pore sizes appears to be much less than in ordinary membrane material. Roughly, for the materials we have made, I estimate the average pore diameter as 5–10 Å, with the maximum diameter less than 20 Å.

Another advantage which these products have over customary materials used for molecular separations is the possibility of modifying the chemical composition of the pore walls, within rather wide limits. For example, some or all of the hydrogen atoms of the benzene rings can be replaced by other atoms or groups. Also, the rigidity and strength of these materials should contribute to their usefulness. (Single sheet polymers, of course, would not

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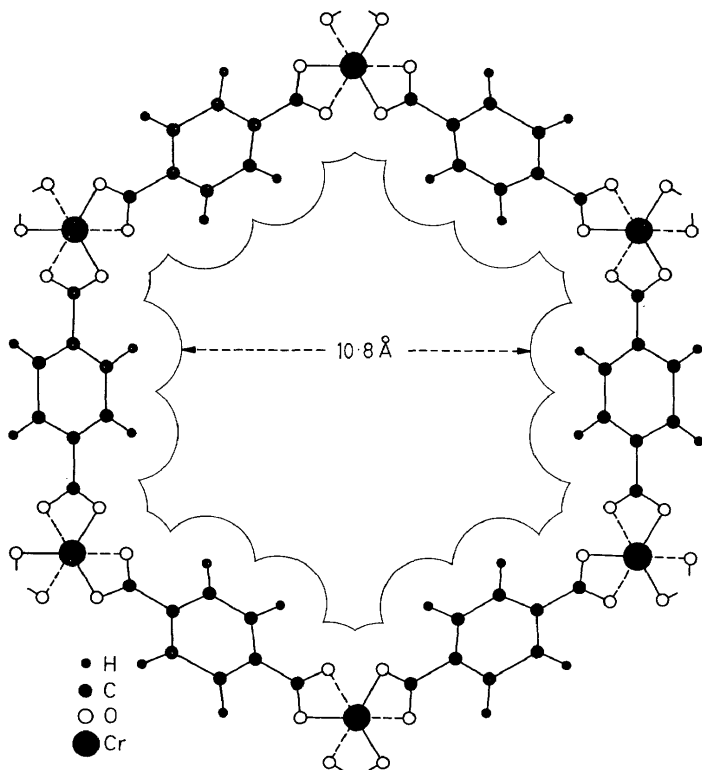


Figure 3. Projection of a portion of hypothetical structure of a crystalline network polymer of chromic terephthalate. The two oxygen atoms of each carboxyl group are bonded to different chromium atoms (both projecting to the same point in the diagram)

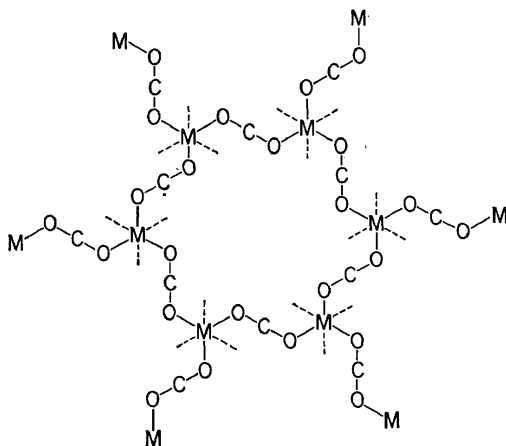


Figure 4. Projection of a portion of another hypothetical structure for chromic (or another trivalent metal) terephthalate. The benzene rings are to be imagined above (or below) the O—C—O groups and at least approximately coplanar with them. The terephthalate axes are normal to the plane of the projection. Only three of the six oxygen atoms octahedrally surrounding each metal atom are shown

be strong enough for membrane use, without being supported on a stronger material with larger pores.)

In separations involving ions in a water solution, the pertinent ionic size is of course that of the hydrated ion, unless, as the ion passes through the pores of the membrane, the hydration shell is rapidly exchanged. Likewise, if there are molecules or ions strongly adsorbed on the walls of the pores of the membrane, the effective pore size is less than it would be without the adsorbents.

Their high porosity suggests the use of these rigid network polymers, especially the amorphous ones, as catalysts or as supports for included catalytic materials. For this the reagents and products must be able to penetrate the pores of the network. The possibility of modifying readily the porosity and the chemical composition (for example, by altering the proportions of the reagents or by including in the composition some water or some metal cations or organic anions differing from the rest) may be very advantageous.

The organic bridges between the metal atoms in the salts I have been discussing are conjugated resonating systems, similar to bridges which Taube²⁰, Kanda and Kawaguchi²¹, and Dewar and Talati²² have shown to be capable of electron conduction. The electronic properties of our products are now under investigation.

By incorporating a monomer of another type of polymer within the pores of a rigid network polymer, and then polymerizing that monomer, one can obtain bipolymeric composites of interesting properties. In general, the rigid network component increases the strength, the elastic modulus, and the resistance to chemical attack of the composite, relative to the properties of the other component by itself.

Our investigations of these and other possible applications of synthetic sheet polymers and space network polymers are just beginning. The interesting things to do in this field are endless and the possible applications of products of these types are very exciting.

Summarizing, I have pointed out that many known substances, mostly inorganic, consist of giant polymer molecules which have either a sheetlike or a space network structure. I have described and discussed some recent experimental results on the synthesis and properties of new organic and organic-inorganic polymers with such structures. Of special interest are rigid crystalline sheetlike polymers and rigid amorphous space network polymers, both types having holes or channels with diameters in the 5–20 Å range. Some of these polymers being studied are entirely organic, others are metal salts of dibasic organic acids.

I have briefly dealt with some applications of these materials as membranes for the separation of molecules and ions of different sizes, as catalysts and catalyst supports, as components of composite materials, and as semiconductors.

In conclusion, I wish to acknowledge the help I have received in this research from various other members of the Stanford Research Institute staff, especially Harold Eding, Paul Brady, Milton Silverstein, Malcolm Barlow, Michael Bertolucci, and Lydia Peters.

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