

## The Connection Number of Polymers with Particular Reference to Carbon Polymers

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### Synopsis

The use of a connection number is proposed for the simple topological analysis of random networks. This is illustrated with some carbon polymers.

The concept of the connection number is useful in describing highly regular, covalently bonded networks.<sup>1</sup> On this basis graphite is a 3-connected, and diamond a 4-connected, carbon polymer. Similarly, linear polyethylene is a 2-connected carbon polymer (with hydrogen as a heteroatom attached to the one-dimensional chain).

In polymer science the analogue to a network connection is a crosslink; that to a connection number, a crosslink density. I have suggested in another paper<sup>2</sup> that an average connection number is a useful alternative description of polymer networks, and the purpose of this note is to take this idea further.

In calculating the average connection number we consider only those connections which form part of the network. Thus, short side chains (as in polypropylene) or short branches are excluded. A branch is included as part of the network only if it is very long in comparison with the constituent links in the chain. Similarly, internal connections, as in ladder polymers, are excluded, since a ladder polymer is effectively one-dimensional and 2-connected.

A connection (crosslink) that joins one section of the chain or network to another will have a connection number of 3 or 4 in the case of carbon. In most cases it will be 3, since single network junctions are more probable than double junctions. A crosslinked polyethylene having one network junction per 10 chain carbon atoms would therefore have an average connection number of 2.1; that is,

Number of junctions:	10
Number of connections:	$9 \times 2 + 1 \times 3 = 21$
Average connection number:	$\frac{21}{10} = 2.1$

In the field of synthetic polymers a connection number of 2.5 would be a very high value. For example, an idealized structure of urea-formaldehyde resin has an average connection number of 2.5, since 3-connections alternate with 2-connections. In practice, the connection number is  $<2.5$ . In the case of a crosslinked rubber the connection number depends upon the degree of cure, but in general it is  $<2.1$ .

On this basis carbon polymers can be arranged as shown in Table I.

TABLE I

Material	Average connection number	Dimension of network
Polyolefins, polystyrene	2	1
Rubbers (crosslinked)	$<2.1$	3
Resins	$<2.5$	3
Graphite	3	2
Diamond	4	3

It will be seen that the connection number is a useful additional description of a network when considered in conjunction with the dimension. It is a method of describing the "tightness" of the network, which in turn is associated with physical properties such as density and rigidity.

This point emerges more clearly if we plot density against connection number for carbon polymers. Any relationship of this form is complicated by the presence of atoms other than carbon in the network, and therefore I restrict the heteroatoms in the graph to hydrogen, for the sake of simplicity. Typical densities are shown in Table II.

TABLE II  
Densities (g./cm.<sup>3</sup>) at Room Temperature

Some 2-connected carbon polymers	Graphite and "amorphous" carbons	Diamonds
Polyolefins, 0.83-0.97	Graphite, 2.26	Diamond, 3.50-3.53
Polystyrene, 1.04-1.11	Charcoals, 1.46-2.26	Carbonado, 3.15-3.34

Most of the 2-connected polymers shown exist in both amorphous and crystalline forms. The correlation ignores small changes of density arising from change in phase.

The densities shown for the charcoals are measured in kerosine after heating to 3000°C.<sup>3</sup> The samples were evacuated before the density was measured; therefore the values are corrected for open porosity.

The plot obtained (Fig. 1) is a straight line, if it is drawn through points of highest density for graphite and diamond, i.e., when these materials show their most perfectly crystalline form. Since connection number,

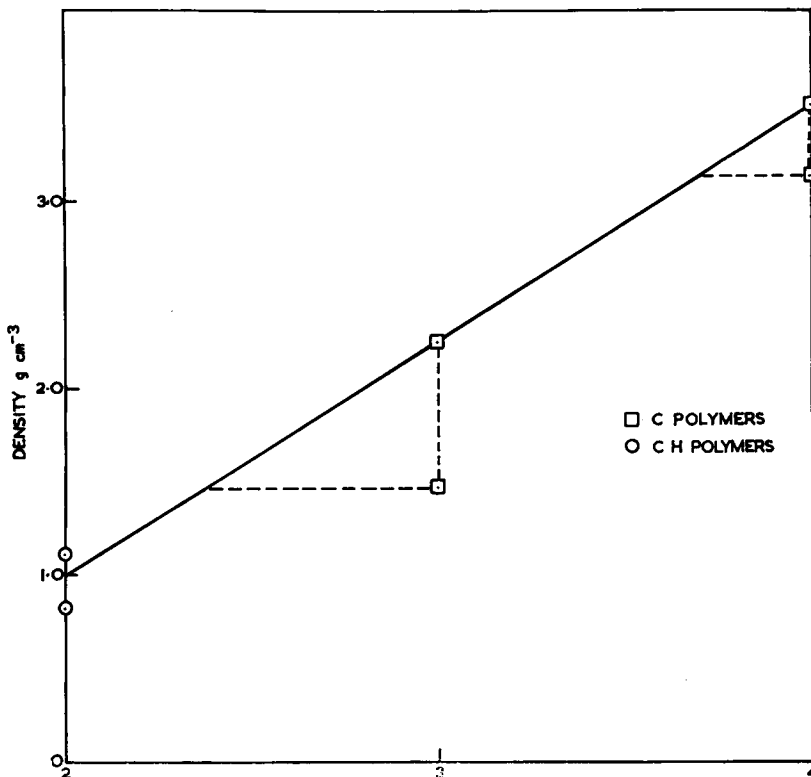


Fig. 1. Density and connection number of carbon polymers.

which is an average quantity, does not uniquely define density, the line in Figure 1 should be regarded as an upper limit rather than a specific relationship. Bearing this proviso in mind, we may first consider the special cases of graphite and diamond. Both of these materials exist in forms with substantially lower densities than the crystallographic density, and it would be interesting to know what form the network takes in these cases.

To some extent the lower densities shown for the charcoals and imperfectly crystalline graphite are the result of closed porosity, but this does not account for the large difference between the densities of charcoal and graphite. A charcoal with a density of 1.46 may correspond, according to the graph, to an average connection number of about 2.4 if closed porosity is ignored. If no 4-connections are present, this would correspond to a maximum ratio of  $3 \times 2$  connections for every  $2 \times 3$  connections.

The density of carbonado, which is a black and impure form of diamond, is complicated by the presence of up to 3% of Fe, Si, and Ca in the material. For approximate calculations this can be neglected, in which case a density of 3.15 could correspond to an average connection number of 3.7. This assumes no porosity. In the absence of 2-connections this would corre-

spond to a maximum ratio of  $3 \times 3$  connections for every  $7 \times 4$  connections.

The foregoing gives a very much simplified picture of these networks and should be regarded as a qualitative rather than a quantitative guide. Nevertheless, the argument can be extended to the carbon-hydrogen polymers. Normally, crosslinking can only be achieved to a limited extent with these materials, and this has a small effect on density. It would therefore be interesting to study the crosslinking of polymers under very high pressures, since this would probably raise the connection number and increase the tightness of the network markedly, with a corresponding effect on density and other physical properties.

### References

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Received June 20, 1967