# A New Structural Parameter of Polymers—The Relative Number of Network Bonds per unit Volume

L. HOLLIDAY and W. A. HOLMES-WALKER, Department of Polymer Science & Technology, Brunel University, Uxbridge, England

### **Synopsis**

In this paper we define a new structural parameter of polymers, and show how this may be employed. This parameter, for which only the structure and the density are needed, is the relative number of network bonds per unit volume; it is written  $N_{er}$ (basis 1 cm<sup>3</sup>), and it is used in conjunction with the average connectivity or connection number CN of the network atoms, where the word connection also refers only to network bonds. The relationship of these two numbers makes it possible to present a unified picture of all polymers, organic and inorganic, including such highly condensed networks as diamond. By plotting  $N_{cr}$  against CN, the region in which inorganic and organic polymers occur can be seen. This is called the polymer zone, and it is evident that carbon polymers occupy only a small part of it. From this graph, an arbitrary measure of bond packing efficiency can be deduced for carbon polymers. In addition, the process of graphitization and carbonization can be followed graphically within the polymer zone.  $N_{er}$  is also related to certain physical properties such as bulk modulus, hardness, and cubical coefficient of expansion, which depend (among other things) on the tightness of bond arrangement. The resultant correlations can be used to predict the value of  $N_{cr}$  required to achieve given values of these properties for the more rigid structures.

### INTRODUCTION

In previous papers,<sup>1-3</sup> one of us has proposed the use of the average connectivity and the relative number of network bonds per unit volume, for deriving additional information about polymers if the structure and density are known. The more detailed discussion of the interrelationship of these two numbers CN and  $N_{er}$  was left over for a later occasion, since  $N_{er}$  was given only brief mention before.<sup>3</sup>

It is clear that little use is being made of the simplest physical property density—in any discussion on polymers, whereas in fact this is a very revealing and basic number. Even a cursory examination of the literature reveals that density is often not quoted for new polymers. This is highlighted by van Krevelen and Hoftyzer<sup>4</sup> in a recent publication. We hope that the importance of density will emerge from what follows.

The average connection number and the relative number of network bonds would be expected to relate to certain physical properties. The average connection number provides a measure for the extent to which a

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network is interconnected in space. Clearly a large number of three-dimensional interconnections should provide a stiffening or bracing effect which would be greatest when the covalent bond lengths are shortest, i.e., when the structure is most compact. This picture is complicated by other factors, of course, since the valence angle, deformability, and other mechanisms of deformation, will also play a part, as discussed in a recent review by Holliday and White.<sup>5</sup> The relative number of network bonds per unit volume should also be related to certain physical properties. Although this number tells us nothing about the configurational aspects of the network, it does reveal how many network bonds there are to perform a given task, e.g., to resist deformation.

Thus the two numbers CN and  $N_{cr}$ , taken separately or together, may correlate to some extent with a property such as bulk modulus. Bearing in mind the slender amount of information upon which these numbers are based (the chemical structure and one physical property—density), it would not be surprising if the relationships are approximate.

# THE CALCULATION OF CN AND $N_{cr}$

Both carbon polymers and inorganic polymers are included in the following discussion.

To form a polymer, each atom in the chain or network must be connected to at least two other atoms by directional covalent bonds (the special case of ionic polymers such as silicates containing ionic as well as covalent bonds is omitted at this stage). In some cases, like graphite, each atom is con-Thus, a chain carbon atom in polyethylene is nected to three other atoms. 2-connected or has a connection number CN of 2; in graphite the carbon atom has a connection number of 3; and in diamond, of 4. Many carbon polymers, for instance, thermosetting resins, contain both 2-connected and 3-connected carbon chain atoms, in which case it is possible to calculate an average connection number that will be between 2 and 3, depending on the relative number of 3-connections. One of us has shown in a previous paper<sup>2</sup> that there is a relationship between the average connection number of carbon polymers and their density. On that occasion, internal chain connections such as occur in a ladder polymer were excluded, on the grounds that a ladder polymer is effectively a one-dimensional structure. It will be shown that this view is unduly restrictive.

The purpose of this paper is to consider a further but related point. The structure of a polymer molecule is such that every chain or network atom has a connection number  $\geq 2$  (apart from terminal atoms, which can be neglected in a long chain), but this implies little or nothing about how tightly the network bonds are arranged in space. It might be anticipated on a priori grounds that the tightness of packing would be related to certain physical properties such as stiffness.

The relative number of covalent network bonds per unit volume (for convenience  $1 \text{ cm}^3$ ) can easily be calculated for any polymer, organic or in-

organic. We call this number  $N_{cr}$ , where subscript c stands for covalent and r for relative. A network bond is defined as a covalent, i.e., directional, bond along the copolymer chain, whether it be in a one-dimensional (linear), two-dimensional (sheet), or three-dimensional (space network) configuration. Bonds connecting side atoms or groups to the main chain are therefore excluded from consideration if they are short in comparison with the main chain. Since many covalent bonds are partially ionic, it is sometimes difficult to say whether they can truly be regarded as directional, but in practice this is not a major difficulty, as the following picture indicates.

We show in Appendix I how the average connection number (CN) and relative number of network bonds per cm<sup>3</sup>  $(N_{er})$  are calculated for three simple polymers: (i) poly(dimethylsiloxane), (ii) poly(ethylene terephthalate), and (iii) diamond. It is unnecessary to give further examples. The calculations are straightforward, although with complicated structures they are more laborious. Expressed algebraically, the two parameters are described as follows:

$$CN = \frac{2a+3b+4c}{a+b+c} \tag{1}$$

where a = number of 2-connected, b = number of 3-connected, and c = number of 4-connected atoms in repeat unit.

$$N_{cr} = \frac{\rho \chi (CN)}{2y} \tag{2}$$

where  $\rho$  = density of polymer,  $\chi$  = number of network atoms in the repeat unit, and y = molecular weight of repeat unit.

Where the structure is not exactly known, as with the PF, UF, and MF resins, we have used a reasonable estimate of the structure, but the figures remain subject to some degree of uncertainty. Appendix II contains data on CN and  $N_{cr}$  for a wide range of inorganic and organic polymers.

What conclusions can be drawn from this information? We first consider some structural features and later the physical properties—bulk modulus, Young's modulus, hardness, and cubical coefficient of expansion.

## THE RELATIONSHIP BETWEEN CN AND $N_{cr}$

In Figure 1 we plot  $N_{cr}$  against CN and show part of this on a larger scale in Figure 2. In this way it is possible to represent all polymers, inorganic and organic, in a single picture. They fall within a relatively narrow area as shown, bounded by the lines AB and CD. We call this the polymer zone.

1. For a given value of CN there is a spread in  $N_{cr}$ . Two-connected polymers vary from about 0.012 (polyvinylcarbazole) to 0.090 (polyformaldehyde); 3-connected polymers vary from 0.106 (red phosphorus) to 0.33 (hexagonal boron nitride and boron, the latter assumed trivalent);

4-connected polymers vary from 0.15 (germanium) to 0.58 (diamond). Polymers of intermediate connectivity fall within these limits, as shown.

Restricting the discussion to synthetic carbon polymers for the moment, the range within which they are to be found is relatively narrow. It is

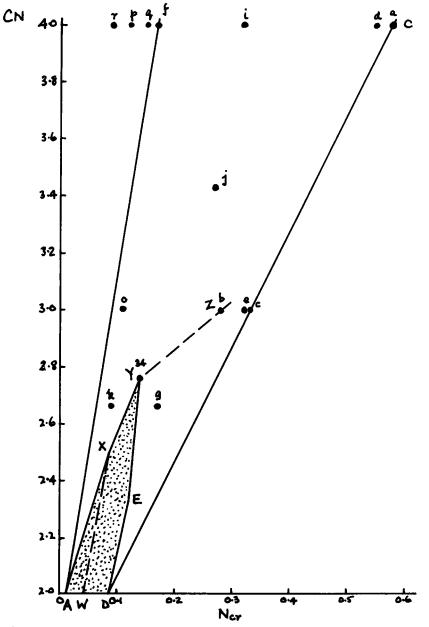
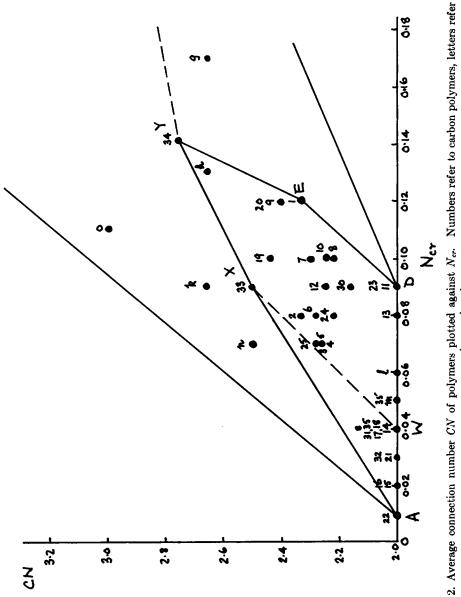


Fig. 1. Average connection number CN of polymers plotted against  $N_{cr}$ . Numbers refer to carbon polymers, letters refer to inorganic polymers listed in Appendix II. Shaded area contains carbon polymers.



# Fig. 2. Average connection number CN of polymers plotted against $N_{cr}$ . Numbers refer to carbon polymers, letters refer to inorganic polymers.

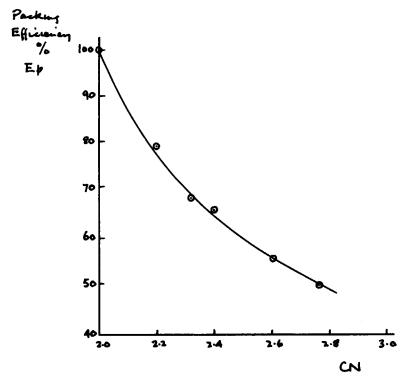


Fig. 3. Efficiency of packing of network bonds plotted against CN, upper bound.

contained in the area AXYED in Figure 1 and forms only a small part of the total area. For this reason, points within this area have been omitted on Figure 1 and are only included in Figure 2, which is drawn to a larger scale. Although the value of CN varies from 2 to 2.76 (the latter point number 30 derives from a structure given by Standage for cyclized and oxidized polyacrylonitrile),<sup>6</sup> the overall range for  $N_{cr}$  is only from 0.012 to 0.14, i.e., one decade. Since carbon polymers fall within the narrow region shown, it can be tentatively concluded that the "efficiency" of bond packing is relatively poor in these materials. In order to be able to assess the picture quantitatively, we arbitrarily assign a value for this efficiency by considering line CD as 100%. Thus, oxidized polyacrylonitrile can now be given a packing efficiency  $E_p$  of

$$\frac{N_{cr} \times 100}{\text{intercept on line CD for } CN \text{ of } 2.76} = \frac{0.14 \times 100}{0.28} = 50\%.$$

In a similar way we assign a packing efficiency for the polymer at point 1 (see Fig. 2) of

$$\frac{0.12 \times 100}{0.175} = 68\%$$

In Figure 3 we plot this measure of packing efficiency of network bonds against CN for the highest value of  $E_p$  for synthetic carbon polymers, which we take to be represented by line DEY. The significance of this line is that it refers to the most condensed structures of normal carbon polymers obtainable by current methods of synthesis. It should not represent an upper limit, since higher figures could doubtlessly be obtained with more regular three-dimensional arrays of network atoms if synthetic routes to such structures were obtainable. However, the curve in Figure 3 takes on additional significance if it can be shown that there is a relationship between  $N_{cr}$  and some important physical property such as stiffness, of such a nature that one wishes to maximize  $N_{cr}$  for a given value of CN. This point is dealt with later.

2. The relatively poor packing of those synthetic linear carbon polymers with a CN of 2 and a low value of  $N_{cr}$  can be ascribed to bulky side groups (although in the case of polymeric sulfur—point  $\ell$ —which also has a CN of 2, it is probably due to the helical conformation of the chains.

For polymers with CN values larger than 2, two explanations for low values of  $N_{cr}$  are possible, depending upon the type of polymer. For resins such as PF, UF, and MF, the explanation lies in the fact that the network has a random structure. Most of the polymers shown, however, are ladder or ring-in-chain polymers, and it appears that the individual molecules, which are stiff, do not pack easily. However, marked differences in values of  $N_{cr}$  between polymers of the same CN can nonetheless be seen.

A related point is the optimum use of functionality of monomers. There is an obvious relationship between CN and functionality. In certain cases, one may wish to maximize  $N_{cr}$  for a given value of CN, or minimize CN for a given value of  $N_{cr}$ . Within limits this freedom exists, and since monomers of higher functionality are generally speaking more expensive, it may be important in certain circumstances to make the best use of the functionality available.

3. A revealing use of this relationship between CN and  $N_{cr}$  illustrates the process of graphitization or carbonization of a polymer. Since the starting polymer and graphite lie within the polymer zone (as also do the disordered carbons), and since intermediate products are polymeric, we might expect this process to be represented by a straight or monotonically curved line joining the starting material to the graphite point at b, that is to say, the intermediate products of this process should fall on such a line.

Support for this suggestion is found in the dotted line joining W, X, Y, and Z, for the case where polyacrylonitrile is the starting material. This line connects the points for polyacrylonitrile (W), cyclized polyacrylonitrile (X), the oxidized version of the (Y; for structure see ref. 6), and graphite (Z).

4. The polymer zone in Figures 1 and 2 bounded by lines AB and CD falls into two regions. Generally speaking, above the line corresponding to a CN of 2.66 (on which lie SiS<sub>2</sub> and the various forms of SiO<sub>2</sub>), the polymers

are prepared by high-temperature reactions involving solids that are themselves polymers. Below this line, the polymers are made by the normal routes to synthetic carbon polymers, i.e., modest conditions and wet chemistry. There are, of course, exceptions to these generalizations.

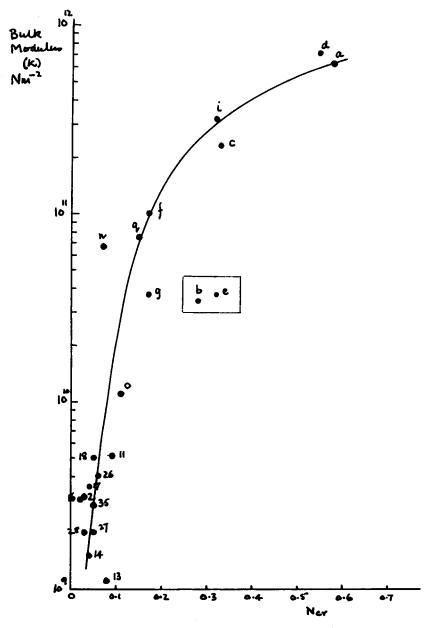


Fig. 4. Bulk modulus K plotted against  $N_{cr}$  for inorganic and organic polymer systems.

## THE RELATIONSHIP BETWEEN N<sub>cr</sub> AND BULK MODULUS

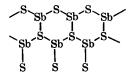
Bulk modulus, which is the inverse of compressibility, is an important mechanical property which might be related to the relative number of network bonds per unit volume. The justification for considering bulk modulus to begin with, rather than Young's modulus, is that, to some extent, the former takes care of any anisotropy in the material. The measurement of Young's modulus depends on the direction of test for anisotropic materials, in contradistinction to bulk modulus. Unfortunately, accurate data on compressibility is scarce for polymers and covalent solids. The results of plotting bulk modulus K against  $N_{cr}$  are shown in Figure 4. It can be seen that a very reasonable relationship emerges for values of  $N_{cr} > 0.1$ , these being the more condensed networks. The line drawn to connect the data points represents a trend rather than a unique relationship between  $N_{cr}$  and K. The carbon polymers for which values of bulk modulus are available have values of  $N_{c\tau} < 0.1$ , and these show a considerable scatter. This is not unexpected, since the bulk modulus is determined in the case of carbon polymers more by the secondary interchain forces than by the primary intrachain or valency forces.<sup>5,7</sup>

The following comments can be made about the points which lie significantly off the full line:

1. Graphite, hexagonal boron nitride, and silica have low bulk modulus values in relation to  $N_{cr}$ . It is interesting to note that this is in agreement with the paper of Barker<sup>8</sup> dealing with the relationship between Young's modulus and linear coefficient of expansion. He finds that quartz and graphite deviate from what he calls the main sequence rule, which is discussed below. In Figure 4, the deviation of hexagonal boron nitride and graphite can be ascribed to their layer structure. Their high compressibility and therefore low bulk modulus stem from the ease with which the layer planes can be squeezed together. The deviation of silica is much less significant.

2. Boron nitride (zinc blende structure). There is some doubt about the measured value of bulk modulus for this diamond-like material. It is reported to have a bulk modulus in excess of  $10^{12}$ Nm<sup>-2</sup>, but we calculate a value of  $7.0 \times 10^{11}$ Nm<sup>-2</sup>, using the method of Plendl et al.<sup>9</sup> based on cohesive energy, which is much closer to that of diamond. This value is also supported by hardness data as shown in Figure 6, where diamond and boron nitride are seen to be very close.

3. The bulk modulus of antimony trisulfide is very high, taking the K value given in the I.C.T.<sup>10</sup> and the structure in Wells.<sup>11</sup> We are led to doubt the high K value as the most likely explanation of this anomaly. The structure of this material quoted by Wells is as follows:



# THE RELATIONSHIP BETWEEN Ner AND YOUNG'S MODULUS

The plot of E against  $N_{cr}$  is shown in Figure 5. Bearing in mind the problem introduced by anisotropy, the relationship is quite good. The

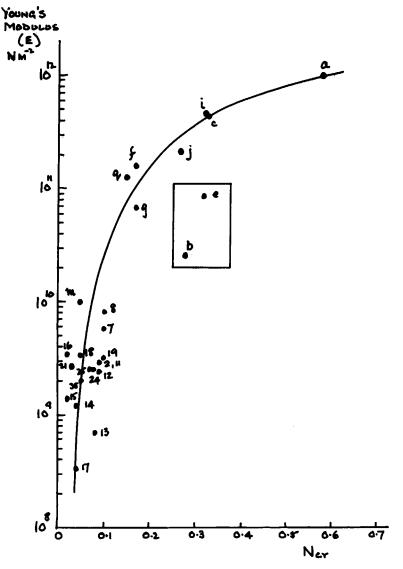


Fig. 5. Young's modulus E plotted against  $N_{cr}$  for inorganic and organic polymers.

points plotted are based on isotropic polycrystalline samples as far as possible, in order to average out the different E values for the different crystallographic directions in the various materials. The points which fall off the line are similar in Figures 4 and 5. For isotropic solids, the relationship between E, K, and  $\nu$  (Poisson's ratio) is as follows:

$$K = \frac{E}{3(1-2\nu)}.$$
(3)

Although there is a broad correlation between  $N_{cr}$  on the one hand and K and E on the other, as shown in Figures 4 and 5, the lines drawn in do not represent unique functions. There is therefore no reason to expect any obvious connection between  $N_{cr}$  and  $\nu$ , and this is borne out in Appendix II.

It should be pointed out that accurate data on Poisson's ratio are very sparse, since little research has been done on this property, and that we know little about the factors which control it. Furthermore, since it is an elastic constant, like E and K, anisotropic materials have more than one value for Poisson's ratio, while for viscoelastic solids Poisson's ratio is time dependent.<sup>12</sup>

Nevertheless, we have thought it of interest to calculate a series of values of  $\nu$  from Figures 4 and 5 for various values of  $N_{er}$  using eq. (3). The results are shown in Table I; they are interesting because the values for bulk and Young's modulus in Figures 4 and 5 were determined quite independently by a variety of workers.

| N <sub>cr</sub> | <i>K</i> , Nm <sup>-2</sup> (from Fig. 2) | <i>E</i> , Nm <sup>-2</sup><br>(from Fig. 3) | Calculated from eq. (1) |
|-----------------|---|--|-------------------------|
| 0.05            | $2.5 \times 10^9$                         | $2.0 	imes 10^{9}$                           | 0.36                    |
| 0.1             | $2.2 	imes 10^{10}$                       | $2.5	imes10^{10}$                            | 0.31                    |
| 0.15            | $6.8 	imes 10^{10}$                       | $8.0	imes10^{10}$                            | 0.30                    |
| 0.2             | $1.4 \times 10^{11}$                      | $1.5 	imes 10^{11}$                          | 0.31                    |
| 0.25            | $2.0 \times 10^{11}$                      | $2.5 \times 10^{11}$                         | 0.29                    |
| 0.3             | $2.7 \times 10^{11}$                      | $4.5 \times 10^{11}$                         | 0.23                    |
| 0.4             | $4.2 \times 10^{11}$                      | $6.0 \times 10^{11}$                         | 0.26                    |
| 0.5             | $5.4 \times 10^{11}$                      | $8.0 \times 10^{11}$                         | 0.26                    |

 TABLE I

 Poisson's Ratio Calculated from Figures 4 and 5

The calculated values of  $\nu$  fall within the range of 0.23–0.36 and are of the same order of magnitude as the experimental values of Poisson's ratio shown in Appendix II, and they suggest that the lines in Figures 4 and 5 are correctly drawn.

# THE RELATIONSHIP BETWEEN $N_{cr}$ AND HARDNESS

Since the factors controlling hardness and elastic behavior are related, we have plotted hardness (expressed in  $Nm^{-2}$ ) against  $N_{cr}$  in Figure 6. In order to cover the range of hardness values from diamond to rubbery polymers, it was necessary to convert hardness data (from a number of sources and measured by different techniques) to a self-consistent scale. In this case we selected BHN values as being the most suitable (since the Brinell

measurement is obtained through indentation and provides an approximate measure of yield strength) and constructed a conversion table. The relationship between scratch and indentation hardness values has already been reported by Tabor in 1954.<sup>13</sup> The range of hardness covered spans about four decades, and the relationship obtained is surprisingly good.

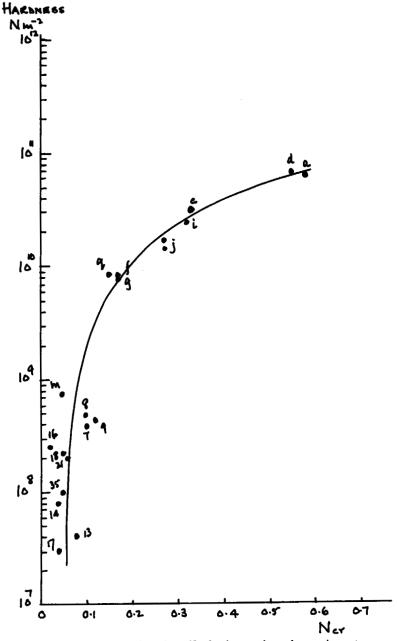


Fig. 6. Hardness plotted against  $N_{cr}$  for inorganic and organic systems.

# THE RELATIONSHIP BETWEEN CUBICAL COEFFICIENT OF EXPANSION $\gamma$ AND $N_{cr}$

In considering the thermal expansion behavior of polymers, it seems intuitively reasonable to suppose that the more tightly packed network will have the lower coefficient of thermal expansion. In order to investigate this, we have selected the cubical coefficient of expansion for study, since

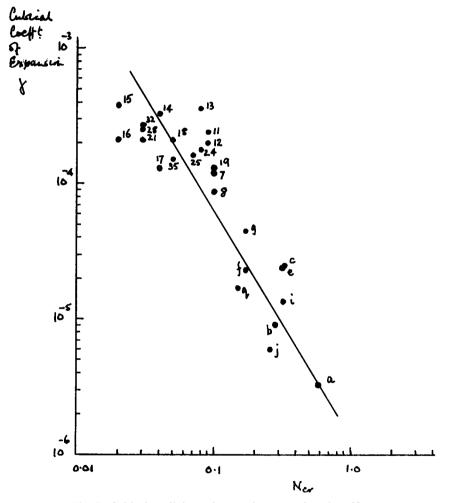


Fig. 7. Cubical coefficient of expansion plotted against  $N_{cr}$ .

this is an overall property of a material which does not depend upon the direction of test, and therefore makes an allowance for anisotropy. The result of plotting coefficient of expansion against  $N_{cr}$  is shown in Figure 7 on a log-log plot, and it can be seen that a reasonable correlation is obtained. The greatest deviation from this is shown by vitreous silica.

|  |                           | A.                             | Appendix II. | Polymer Systems | Systems  |  |                                       |  |                    |
|--|---------------------------|--------------------------------|--------------|-----------------|--|--|---------------------------------------|--|--------------------|
| Polymer  | Ref.<br>no. in<br>figures | Density,<br>g cm <sup>-3</sup> | CN           | Ner             | Bulk<br>modulus $K$ ,<br>Nm <sup>-1</sup><br>$\times 10^{-10}$ | Young's<br>modulus E,<br>Nm <sup>-1</sup><br>×10 <sup>-9</sup> | Hardness,<br>$Nm^{-3} \times 10^{-9}$ | Cubical<br>coefficient<br>of expansion<br>×10 <sup>6</sup> | Poisson's<br>ratio |
| Organic polymers:<br>poly( <i>p</i> , <i>p</i> '-diphenyloxide<br>1,3,4-oxadiazole)    | -                         | 1.37                           | 2.33         | 0.12            | Į  | I  | I                                     | 1  | 1                  |
| poly(p,p'-dipnenyloxide<br>1,2,4-(4-phenyl)triazole)<br>polyarylates from phenanthrone | Ģ                         | 1.29                           | 2.33         | 0.08            | 1  | 2.9  | I                                     | 1  | I                  |
| and:<br>tereohthalic acid  | ~                         | 1.26                           | 2.26         | 0.07            | Ī  | I  | 1                                     | Ī  | !                  |
| isophthalic acid   | <b>.</b> 4                | 1.27                           | 2.26         | 0.07            | T  | 1  | [                                     | 1  | I                  |
| 4,4-diphenyldicarboxylic acid  | 10                        | 1.25                           | 2.27         | 0.07            | 1  | I  | i                                     | I  | i                  |
| cellulose  | 9                         | 1.55                           | 2.28         | 0.08            | I  | 1  | 1                                     | ]  | I                  |
| p.f. resin   | 7                         | 1.39                           | 2.30         | 0.10            | I  | 5.8  | 0.39                                  | 12   | !                  |
| u.f. resin   | <b>20</b>                 | 1.45                           | 2.22         | 0.10            | I  | 8.2  | 0.49                                  | 8.7  | 1                  |
| m.f. resin   | 6                         | 1.48                           | 2.4          | 0.12            | I  | ]  | 0.44                                  | 1  | I                  |
| poly-p-xylene  | 10                        | 1.11                           | 2.25         | 0.10            | 1  | 1  | [                                     | 1  | ļ                  |
| polyformaldehyde   | 11                        | 1.43                           | 7            | 0.09            | 0.51   | 2.8  | ļ                                     | 24.3   | 0.41               |
| polycarbonate  | 12                        | 1.2                            | 2.25         | 0.09            | Ī  | 2.4  | 1                                     | 20   | I                  |
| polyethylene   | 13                        | 0.95                           | 5            | 0.08            | 0.11   | 0.68   | 0.04                                  | 36   | 0.34               |
| polypropylene  | 14                        | 06.0                           | 2            | 0.04            | 0.15   | 1.2  | 0.08                                  | 33   | 0.35               |
| poly(4-methylpentene-1)  | 15                        | 0.83                           | 63           | 0.02            | i  | 1.4  | 1                                     | 38   | ļ                  |
| polystyrene  | 16                        | 1.05                           | 63           | 0.02            | 0.3  | 3.4  | 0.25                                  | 21   | 0.31               |
| poly(tetrafiuoroethylene)  | 17                        | 2.2                            | 2            | 0.04            | 0.35   | 0.34   | 0.03                                  | 13   | I                  |
| poly(vinyl chloride)   | 18                        | 1.4                            | 5            | 0.05            | 0.50   | 3.4  | 0.22                                  | 21   | 0.40               |
| polyimide  | 19                        | 1.42                           | 2.44         | 0.10            | ]  | 3.1  | [                                     | 13   | 1                  |
| macrocyclic polymer <sup>a</sup>   | 20                        | 1.2                            | 2.4          | 0.12            | I  | ľ  | [                                     | Į  | I                  |
| poly(methyl methacrylate)  | 21                        | 1.2                            | 7            | 0.03            | 0.31   | 2.7  | 0.2                                   | 21   | 0.37               |
| poly N-vinylcarbazole  | 22                        | 1.2                            | 6            | 0.01            | 1  | 1  | 1                                     | 1  | I                  |
| polyacetylene  | 23                        | 1.15                           | 7            | 0.09            | I  | Į  | I                                     | 1  | I                  |

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| phenoxy<br>poly(phenylene oxide)   | 24<br>25       | 1.17<br>1.06  | $\begin{array}{c} 2.22\\ 2.28\end{array}$ | 0.08        | 11              | 2.5<br>2.5 | ĪI    | 17.7<br>16 | 1    |
|--|----------------|---------------|---|-------------|-----------------|------------|-------|------------|------|
| polyisoprene (vulcanized)  | 26<br>21       | I             | I   | 0.06        | 0.4             | i          | I     | ļ          | I    |
| polyisoprene (unvulcanized)  | 72             |               | 1   | 0.05        | $\frac{0.2}{2}$ | I          | I     | 1          | I    |
| butyl rubber   | 78             | 0.09          | 1   | 0.03        | 0.2             | i          | I     | 25         | I    |
| styrene-butadiene rubber   | 29             | 1             | [   | 1           | 0.2             | 1          | [     | 60         | I    |
| poly(ethylene terephthalate)   | 30             | 1.38          | 2.16                                      | 0.09        | 1               | 1          | [     | I          |      |
| poly(phosphonitrilic chloride)   | 31             | 2.2           | 7   | 0.04        | I               |            | I     | I          | 1    |
| poly(dimethylsiloxane)   | 32             | 1.14          | 2   | 0.03        | ļ               | ł          | [     | 32         | 1    |
| cyclized polyacrylonitrile   | 33             | 1.17          | 2.5                                       | 0.09        | 1               |            | ļ     | 1          | [    |
| oxidized polyacrylonitrile   | 34             | 1.55          | 2.76                                      | 0.14        | 1               | [          | I     | I          | I    |
| nylon 66   | 35             | 1.14          | 7   | 0.05        | 0.28            | 2.0        | 0.1   | 25         | 0.44 |
| Inorganic polymers:  |                |               |   |             |                 |            |       |            |      |
| carbon diamond C   | đ              | 3.5           | 4   | 0.58        | 62.5            | 066        | 64    | 0.33       | 0.18 |
| carbon (graphite) C  | q              | 2.3           | n   | 0.28        | 3.5             | 25         | I     | 0.90       | 0.27 |
|  | J              | 2.35          | იი  | 0.33        | 33              | 430        | 31    | 2.49       | 0.09 |
| boron nitride (cubic) BN   | q              | 3.45          | 4   | 0.55        | $\sim$ 71       | I          | 69    | 1          | 1    |
| boron nitride (hex.) BN  | e              | 2.3           | n   | 0.32        | 3.7             | 85         | I     | 2.4        | I    |
|  | f              | 2.4           | 4   | 0.17        | 10              | 160        | 8.5   | 2.3        | 0.44 |
| silica (quartz) SiO <sub>2</sub>   | 20             | 2.6           | 2.66                                      | 0.17        | 3.7             | 67         | 7.8   | 4.5        | 0.17 |
| silica (fibrous) SiO <sub>2</sub>  | ч              | 1.97          | 2.66                                      | 0.13        | ł               | Ī          | I     | Ī          | I    |
| silicon carbide SiC  | .1             | 3.12          | 4   | 0.32        | 32              | 450        | 24    | 1.35       | 1    |
| silicon nitride Si <sub>3</sub> N <sub>4</sub>   | •              | 3.1           | 3.43                                      | 0.27        | 1               | 210        | 14/17 | 0.6        | ļ    |
|  | ĸ              | 2.02          | 2.66                                      | 0.09        | ļ               | I          | i     | [          | I    |
|  | -              | 1.9           | 2   | 0.06        | 1               | 1          | I     | !          | ļ    |
| (i)  | н              | 4.26          | 73  | 0.05        | ]               | 10         | 0.75  | 1          | 1    |
| antimony trisulfide Sb <sub>2</sub> S <sub>3</sub>                                       | u              | 4.64          | 2.5                                       | 0.07        | 6.7             | I          | I     | 1          | ļ    |
| phosphorus (red) P   | 0              | 2.2           | ი   | 0.11        | 1.1             | I          | I     |            | 0.34 |
| tin (white) Sn   | d              | 7.3           | 4   | 0.12        | 1               | I          | I     | ]          | l    |
| germanium Ge   | ď              | 5.37          | 4   | 0.15        | 7.5             | 130        | 8.5   | 1.7        |      |
| indium antimonide InSb   | r              | 5.8           | 4   | 0.09        | ]               | 1          | l     | 1          | 1    |
| poly(phosphonitrilic chloride)   | ø              | 2.20          | 4   | 0.04        | ļ               | I          | !     | i          | Ĭ    |
| <sup>a</sup> Polymers made from pyromellitic tetranitrile and 4,4'-diaminodiphenyl ether | ic tetranitril | e and 4,4'-di | aminodiphe                                | enyl ether. |                 |            |       |            |      |

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This result is in line with Barker's findings.<sup>8</sup> In the first of these papers, Barker put forward the following relationship, where E is Young's modulus and  $\alpha$  is linear coefficient of expansion:

$$E\alpha^2 = 150 \, \rm{dyn} \, \rm{cm}^{-2} \, {}^{\circ} \rm{K}^{-2}. \tag{4}$$

This applies within certain stated limits of accuracy for a wide variety of solids. In the second paper, he suggests that a similar relationship may apply to bulk modulus and cubical coefficient of expansion, i.e.,

$$K\gamma^2 = \text{constant.}$$
 (5)

If, as we find, K is related to  $N_{cr}$ , then it is not surprising that  $\gamma$  is also related to  $N_{cr}$  as shown in Figure 6.

### CONCLUSIONS

We have shown that the average connectivity of the network atoms, CN, and the relative number of network bonds per cm<sup>3</sup>,  $N_{cr}$ , are easily accessible numbers which have interesting chemical and physical implications. The plot of CN against  $N_{cr}$  throws light on the following: (a) the zone in which polymers exist and the relationship between carbon polymers and inorganic polymers; (b) the process of graphitization.

The structural parameter  $N_{cr}$  correlates reasonably well with these properties: (a) bulk modulus, (b) Young's modulus, (c) hardness, (d) coefficient of expansion.

The parameters CN and  $N_{cr}$  are single numbers which describe an average structural feature of a polymer, and this inevitably limits their usefulness. Nevertheless, they provide useful additional information about polymers from existing data. Furthermore, within broad limits of accuracy it is possible to use  $N_{cr}$  predictively to estimate the foregoing physical properties.

### Appendix I The Calculation of $N_{cr}$

### (i)Poly(dimethylsiloxane)

CN = 2 (both the Si and O atoms are 2-connected in the chain):

Molecular weight of repeat unit = 74 Network bonds per repeat unit = 2 Density = 1.1  $N_{cr} = \frac{1.1}{74} \times 2 = 0.03$ 

### (ii)Poly(ethylene terephthalate)

 $CN = \frac{(10 \times 2) + (2 \times 3)}{12} = 2.16$  (there are two 3-connected atoms per ten 2-con-

nected atoms):

Molecular weight of repeat unit = 192Network bonds per repeat unit = 13Density = 1.38

$$N_{cr} = \frac{1.38}{192} \times 13 = 0.094$$

(iii)Diamond

CN = 4

Molecular weight of repeat unit = 12

Network bonds per repeat unit =  $\frac{4}{2}$  = 2 (each bond is shared with another carbon

atom)

Density = 3.5  $N_{cr} = \frac{3.5}{12} \times 2 = 0.58$ 

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