

RECENT RESEARCH ON POLYMER STRUCTURE

MAURICE L. HUGGINS†

Stanford Research Institute, Menlo Park, California, U.S.A.

INTRODUCTION

In this paper I shall first discuss the interactions between atoms not directly bonded together — especially those involving only carbon and hydrogen atoms. Then I shall consider the structure of crystalline polymers (linear polyethylene). Finally, I shall consider certain general principles concerned with the packing of *helical* molecules in crystalline polymers.

INTERACTIONS BETWEEN NON-BONDED ATOMS

The interaction between atoms not directly bonded together — often called “van der Waals interactions” — are of prime importance in determining the preferred conformations and distributions of conformations of polymer molecules in any state: crystalline, amorphous, liquid, gaseous, and in solution. Both *intermolecular* and *intramolecular* interactions are important. The latter largely determine the preferred conformations and the magnitudes of the barriers to rotation about single bonds in both small and large molecules.

Many years ago I showed¹⁻³ that atoms of the different elements can be assigned radii which, by addition, give approximately the distances between atomic centres when these atoms are connected by electron-pair bonds. Such atomic radii cannot justifiably be used to deduce the interatomic distances when the atoms are not so bonded together. Nevertheless, it is possible to derive a set of considerably larger radii which give, very roughly, the experimental interatomic distances: for example, the distances between non-bonded atoms in different molecules in crystals. The set of “van der Waals radii” which I proposed⁴ was modified and extended by Pauling⁵ to give the set which has been most quoted in the literature. Bondi⁶, utilizing the much larger amount of experimental data now available, has recently presented a revised set of radii. These are doubtless much better than the early sets.

The problem of deciding on the best van der Waals radius for hydrogen has been an especially difficult one, partly because of the scarcity of precise data on the positions of hydrogen atoms in crystals, and partly because the distances between two non-bonded atoms, when one is hydrogen, vary more than when only other elements are involved. Pauling assigned to hydrogen the value of 1.2 \AA , which we now know to be considerably less than half the usual distance between closest hydrogen atoms in different molecules in crystals.

It is worth emphasizing that the van der Waals radii were deduced to give

† Present address: 135 Northridge Lane, Woodside, California 94062, U.S.A.

MAURICE L. HUGGINS

approximate equilibrium distances between two atoms, *not* when they are isolated from other atoms, but when they are parts of assemblages of atoms, usually molecules, in crystals. Since the other atoms in these assemblages also interact, chiefly by van der Waals *attractions*, the interatomic distance used for computing radii is usually considerably smaller than it would be if the other atoms in the assemblages were not there. This fact has apparently not been realized by some scientists who have attempted to deduce energy-distance functions for interactions between two non-bonded atoms. A valid set of functions — one for hydrogen-to-hydrogen interactions, one for carbon to hydrogen interactions, etc. — would be very useful. As Scheraga pointed out⁷, it would furnish a basis for much better approximations for dealing with intermolecular and intramolecular structure problems than are obtainable with van der Waals radii.

A considerable number of such functions have been proposed and used. In comparing them, I discard as especially unreliable (for the reason I have just given) all which are based on the assumption that the equilibrium distance for *pairwise interaction* is the distance obtained by adding together the van der Waals radii, whether these radii were obtained from Pauling's table or Bondi's table or from some other source.

Figures 1 and 2 show curves representing some of the functions for hydrogen-to-hydrogen interactions which have been proposed in recent years.

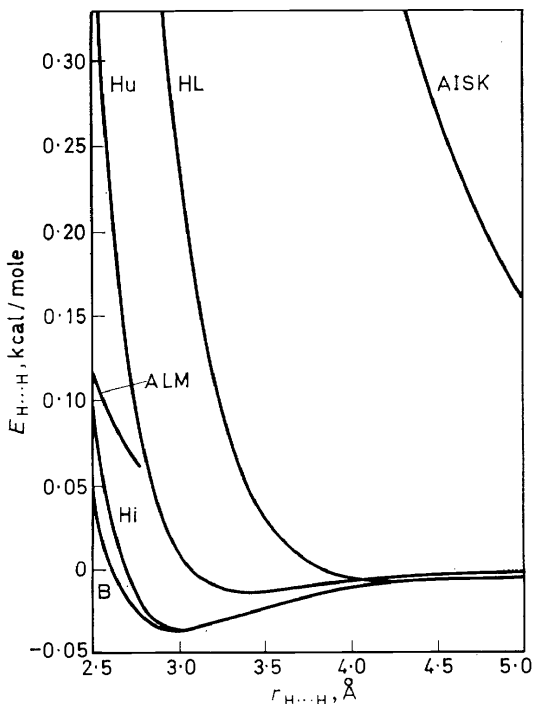


Figure 1. Energy-distance curves for two non-bonded hydrogen atoms (Huggins⁸). Equations for the curves, with references, are given in the text.

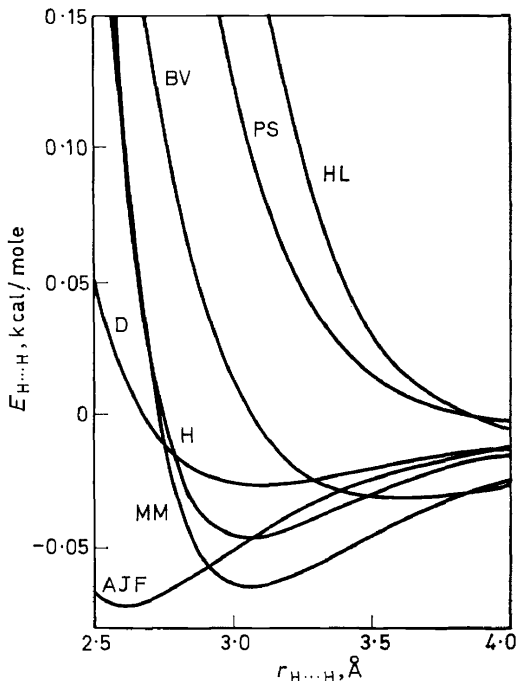


Figure 2. Recently used energy-distance curves for two non-bonded hydrogen atoms (Huggins¹⁷). Equations and references are given in the text.

It is appalling to note the large differences between the different functions. The equations corresponding to these curves, with E_{HH} in kcal/mole and r in Å, are the following:

$$B^9 \quad E_{HH} = 6590 \exp(-4.08r) - 49.26r^{-6} \quad (1)$$

$$Hi^{10} \quad E_{HH} = 24540 \exp(-4.53r) - 48.62r^{-6} \quad (2)$$

$$ALM^{11} \quad E_{HH} = 33.21r^{-6.18} \text{ for } 2.01 \text{ \AA} \leq r \leq 2.77 \text{ \AA} \quad (3)$$

$$Hu^{12} \quad E_{HH} = 57300 \exp(-4.605r) - 31r^{-6} - 40r^{-8} \quad (4)$$

$$HL^{13-15} \quad E_{HH} = 3716 \exp(-3.071r) - 89.52r^{-6} \quad (5)$$

$$AISK^{16} \quad E_{HH} = 499r^{-5} \quad (6)$$

$$AJF^{18} \quad E_{HH} = 9950 \exp(-4.54r) - 45.2r^{-6} \quad (7)$$

$$MM^{19} \quad E_{HH} = 43473r^{-12} - 105.9r^{-6} \quad (8)$$

$$D^{20, 21} \quad E_{HH} = 1727 \exp(-3.54r) - 49.23r^{-6} \quad (9)$$

$$H^{22} \quad E_{HH} = 4.10^5 \exp(-5.4r) - 47r^{-6} - 98r^{-8} - 205r^{-10} \quad (10)$$

$$BV^{23} \quad E_{HH} = 1200 \exp(-2.85r) - 160r^{-6} \quad (11)$$

$$PS^{24-26} \quad E_{HH} = 1858 \exp(-3.071r) - 44.76r^{-6} \quad (12)$$

At best, only one of these equations can give even approximately correct values of the energy in the range of distances of importance in polymer structures. I shall not attempt now to give a critical comparison of the different functions, but shall discuss briefly some of the assumptions underlying all or many of them and then describe an attempt to arrive at a more

valid function for hydrogen-to-hydrogen interactions, together with corresponding functions for carbon-to-hydrogen and carbon-to-carbon interactions.

All of these functions are based on the assumption that the relation between interaction energy and distance is not significantly dependent on the angles between the centre line connecting the two atoms of the pair and the bonds connecting those two atoms with other atoms. Also, any effect of the types and strengths of these bonds on the energy-distance function is neglected.

Some of the functions and curves for hydrogen-to-hydrogen interactions are based on the assumption that this interaction is quantitatively like that computed theoretically, by Hirschfelder and Linnett¹³, for two otherwise isolated atoms in the $^3\Sigma$ non-bonding state. This seems to me very unlikely, at least with regard to the interatomic repulsion. The repulsion is believed to be due to overlapping of the electron clouds of the two atoms, in one terminology. The variation of electron density with distance in the cloud around an isolated proton is certainly very different (in the direction of another hydrogen) from that around a proton which is tightly bonded to a carbon atom, for instance (cf. Bunn²⁷).

Mason and Kreevoy¹⁴ have "assumed that the appropriate force law" for interaction between two hydrogen atoms, each bonded to another atom, "would be similar to that governing the interactions between two isolated non-bonding hydrogen atoms" and so introduce a factor K , multiplying the whole Hirschfelder-Linnett function. The validity of this procedure, which applies the same factor to both attraction and repulsion terms and which alters the factor in front of the exponential but leaves the factor *in* the exponential unchanged, seems doubtful. Mason and Kreevoy and also DeSantis and coworkers¹⁵ give K the value of unity; Pritchard and Sumner²⁴, Pauncz and Ginsburg²⁵, and Opschoor²⁶ use the value of 0.5; Howlett²⁸ uses 0.2.

All of the interaction functions in recent use base the term or terms for the attraction energy on the usual theory of synchronized oscillations of the electron clouds in the two atoms. Using a formula derived by Slater and Kirkwood^{29, 30}, the coefficient of r^{-6} in the attraction energy function can be deduced from atomic polarizabilities. These polarizabilities, in turn, are simply related to the atomic refractions for infinite wavelength, which, for carbon and hydrogen, can be computed from optical dispersion data for normal paraffins. Theoretically, there must also be terms in r^{-8} and r^{-10} , but, except in my own work, these have been neglected as negligible. Calculations I have made show that this neglect is unjustifiable for interatomic distances in the range in which we are most interested.

In my new calculations I recalculate the coefficient of the r^{-6} term from precise National Bureau of Standards data³¹⁻³³ on the optical dispersions of normal paraffins. The effective numbers of electrons needed for the Slater-Kirkwood equation are taken as 1 for hydrogen and 5.6 for carbon, the latter being read from a curve published by Scott and Scheraga³⁴. I add r^{-8} and r^{-10} terms, computing the coefficients from relationships due to Mayer³⁵ and Huggins and Sakamoto³⁶.

In agreement with most of the other functions which have been proposed, I express the repulsion energy in the simple exponential form, Ce^{-ar} . This

seems justifiable, at least as a first approximation, in view of the success which has been achieved, using a similar exponential repulsion term, in dealing with diatomic molecules^{37, 38}, molecular bond energies³⁹, and ionic crystals^{40-42, 36}. In each of these systems, a single value of the factor a (in the exponential) appears satisfactory for many atom pairs, although there is some indication that hydrogen is exceptional — i.e., that a value of a which is satisfactory for interaction between other pairs of elements may not be the best for interaction between two hydrogen atoms or between a hydrogen atom and one of another element. Moreover, the fact that different a factors were required for the different systems mentioned suggests that perhaps a constant a is not satisfactory over a large range of interatomic distances.

Most of those working in this field have either used, for hydrogen, the value of a which fits approximately the computed results for $^3\Sigma$ interactions^{13, 14} or have interpolated, for both hydrogen and carbon, from curves through a values for the inert gas elements³⁴. Both procedures seem to me very questionable, chiefly because they neglect the effect of bonding on the magnitude of a .

Assuming the attraction terms to be known, the magnitudes of the two constants, C and a , remain to be determined for each pair of elements. Obtaining a in one of the ways I have mentioned, some scientists have computed the C values then required to give minima in the curves at distances equal to the sums of van der Waals radii. Other workers in this field have introduced the requirement that computed rotational barriers for simple molecules must conform to the experimental barriers, or¹⁸ that computed energy differences between two conformations for one or more simple molecules must agree with the measured values.

These procedures introduce another complication. Direct atom-to-atom interactions, between pairs of hydrogen atoms in ethane for instance, certainly contribute to the barriers, but there may also be a contribution — possibly the major contribution — from interactions between the bond orbitals, e.g., those for the C—H bonds in ethane⁴³⁻⁴⁵. These interactions, like the direct atom-to-atom interactions, should vary in magnitude with the rotation angle. Some authors, including Abe, Jernigan, and Flory¹⁸, Opschoor²⁶, and Scott and Scheraga³⁴ have added a term, $B(1 - \cos \Phi)$, to allow for this. Others have neglected orbital interactions. At present I am trying to determine if it is possible to account satisfactorily for rotational barrier and other conformational and configurational energy data on the basis of atom-to-atom interactions alone. I shall include a term or terms for angle-dependent orbital interactions if that cannot be done or if there is convincing independent evidence that it is necessary.

It is customary to assume a cosine form of energy dependence on angle of rotation about a single bond, chiefly because this form is simple. The correct functions, however, may depart considerably from this form, as evidenced by the work of Howlett²⁸. This is of minor importance if one is interested only in the magnitude of the rotational barrier or the energy difference between trans and gauche conformations, but it may be of considerable importance in calculations involving relatively small angular departures from the most stable orientations, as in many problems of polymer structure.

In my new calculations, I tentatively assume the same value for the factor

a in the exponential of the repulsion term for H...H, C...H, and C...C interactions. From the differences between the sums of the "constant energy radii," which I have previously deduced³⁹ from data on bond energies and bond lengths in simple molecules, I compute the ratios of the C factors for the corresponding repulsion terms: C_{HH} , C_{CH} , and C_{CC} . This leaves just two constants, a and C_{HH} , to be determined.

A relationship between these two constants can be obtained by computing the sublimation energy of crystalline polymethamer (linear polyethylene) as a function of these constants and equating the result to the experimental sublimation energy. For that, an apparently trustworthy value has been computed from experimental data by Billmeyer⁴⁶. We require precise knowledge of the atomic positions in the crystal. I have provisionally assumed these positions to be the same as those given by Teare⁴⁷ for crystals of the orthorhombic normal paraffin, $C_{36}H_{74}$. The terminal atoms in the paraffin chain are neglected, of course. I shall not take the time or space to present and discuss the details of this calculation here, but I hope to publish them later.

This procedure has the advantage of not involving any assumption with regard to orbital interaction energies. It does, however, involve two approximations which are perhaps questionable. I tentatively assume that gradual twisting of the chain zigzags,^{48, 8} if it exists, has little effect on the sublimation energy. I believe this to be justifiable. Also, the locations given by Teare for the hydrogen atoms were not obtained directly, but with the use of reasonable values for the C—H bond lengths and the H—C—H and H—C—C bond angles. This leads to some intermolecular hydrogen-to-hydrogen distances of about 2.6 Å, at which distances (see *Figures 1* and *2*) the repulsion energies are probably quite large. It seems likely that these large repulsions would force deviations from the usual bond angles, and perhaps also the C—H bond distance. The effect of deviations of this sort on my calculations would be to decrease the magnitude of the exponential factor a in the final result. I have not yet attempted to assess the magnitude of the change to be reasonably expected.

To deduce the values of C and a individually, we need the experimental value of another property which depends on the same interaction curves. Ideally, this, like the sublimation energy of polymethamer crystals, should be independent of any assumption about orbital interactions. The sublimation energy of another hydrocarbon or the difference in energies between two configurations or conformations of some simple hydrocarbon (if these differences do not involve, possibly important differences in orbital interactions) might be suitable for this purpose. Partly because such procedures involve C...C and C...H interactions and partly because of time limitations, I have used the difference in energy between eclipsed and staggered conformations of ethane, tentatively assuming that there is *no* significant rotation-dependent interaction between the C—H bond orbitals. Future work will decide whether or not this procedure is justified.

The tentative equation for H...H interactions, arrived at in the manner I have described, has already been given (Eq. 10). The corresponding curve is that labelled H in *Figure 2*. My new tentative equation for C...C interactions and the corresponding equations deduced by Abe, Jernigan, and Flory and by Bartell are as follows:

RECENT RESEARCH ON POLYMER STRUCTURE

$$H^{22} \quad E_{CC} = 1.58 \times 10^7 \exp(-5.4r) - 418r^{-6} - 574r^{-8} - 787r^{-10} \quad (13)$$

$$AJF^{18} \quad E_{CC} = 9.086 \times 10^5 \exp(-4.59r) - 363r^{-6} \quad (14)$$

$$B^9 \quad E_{CC} = 3.012 \times 10^5 r^{-12} - 327.2r^{-6} \quad (15)$$

The Bartell equation has also been used by DeSantis *et al.*¹⁵

For C...H interactions, my new equation and that of Abe, Jernigan, and Flory are given below:

$$H^{22} \quad E_{CH} = 2.5 \times 10^6 \exp(-5.4r) - 137r^{-6} - 237r^{-8} - 411r^{-10} \quad (16)$$

$$AJF^{18} \quad E_{CH} = 8.61 \times 10^4 \exp(-4.57r) - 127r^{-6} \quad (17)$$

Little reliance should be placed on any of these functions, including my own, until they are further tested.

In spite of the large measure of disagreement between the functions deduced and used by different researchers, I believe that it is significant that *all* of the hydrogen-to-hydrogen functions which I have illustrated have minima — that is, equilibrium distances — at distances which are greater, usually considerably greater, than 2.54 Å, the distance between hydrogen atoms in successive zigs (or successive zags) in a planar zigzag normal paraffin chain (*Figure 3*). This is also true for *all* of the other proposed hydrogen functions of which I am aware, excepting only those which were arrived at by *assuming* the equilibrium distance to have a smaller value.

THE STRUCTURE OF CRYSTALLINE POLYMETHAMER

In a paper⁴⁹ presented 44 years ago, I gave evidence for a zigzag structure for the chain atoms in crystals of normal paraffins and some of their simple derivatives. Much more evidence has accumulated since then showing this idea to be correct. Polymethamer (linear polyethylene) is of course a normal paraffin, and x-ray and other evidence has shown that the molecular chains in its crystals do indeed have a zigzag type of structure (*Figures 3 and 4*).

It is usually assumed that the carbon atoms in polymethamer and other normal paraffin crystals have a *strictly planar* zigzag structure, but I have recently^{48, 8} questioned that assumption.

The x-ray diffraction data show a considerable smearing of the apparent positions of the carbon atoms²⁷. This has usually been explained by the reasonable assumption that there are thermal motions of the chains, especially torsional oscillations around the chains axes, of rather large amplitude, or by assuming distortions of the electron clouds. Alternatively, the experimental data can be accounted for as resulting from departures from strict planarity of the zigzag, either in a random fashion or in a regular way. If regular, each zigzag chain has a slightly twisted ribbon type of structure. In either case, the departures from the mean plane of the zigzag cannot be very large.

If, as seems likely from the energy-distance curves, the closest hydrogen atoms in successive methylene groups on the same side of the chain axis in a planar zigzag polymethamer chain repel each other, a *non-planar* zigzag

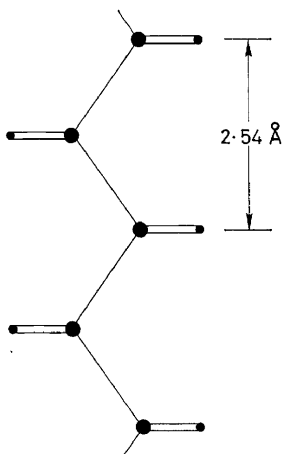


Figure 3. Lateral projection of the planar zigzag structure for a normal paraffin or polymethamer (linear polyethylene) chain (Huggins⁸). Each large dot represents a carbon atom, in the plane of the paper. Each small dot represents 2 hydrogen atoms, one above and one below the plane of the paper.

structure must be more stable than a *planar* one. To decrease the hydrogen-to-hydrogen interaction energy, a given CH_2 can shift to one side or to the other side of the plane defined by the positions of the three preceding carbon atoms. If these shifts are random, the chains are kinked and have irregular shapes which cannot pack together well into crystalline arrangements. Regular alternation, shifting first to one side and then to the other, would also not give good packing. The best packing can be achieved by regular shifting, always in the same direction, to give a twisted ribbon type of structure. Regularly twisted ribbon structures are known in poly(1,1-dimethyl)ethamer (polyisobutylene)^{50, 51} and polydifluoromethamer (polytetrafluoroethylene)⁵², for instance.

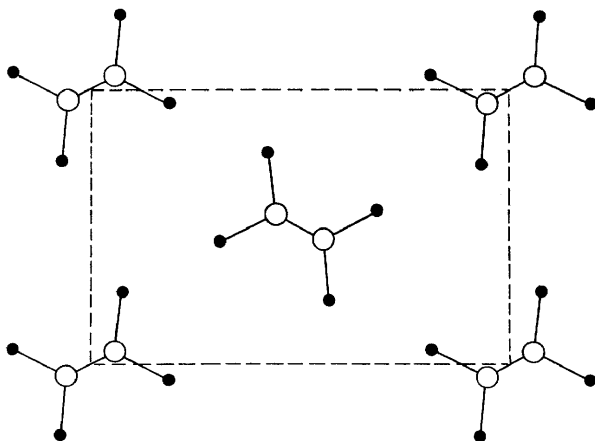


Figure 4. Projection of a portion of the structure of a polymethamer crystallite or crystalline region, assuming a planar zigzag chain structure (Huggins⁸).

RECENT RESEARCH ON POLYMER STRUCTURE

As each polymethamer ribbon twists, so must those around it, to minimize the interchain energy. For relatively small twist angles, the interchain energy must be very little different from what it would be for strictly planar zigzags.

Let us consider a small region of crystal in which each zigzag chain is slightly but regularly twisted. We can represent this, crudely, by a series of parallel, not quite vertical lines (*Figure 5*). Consider the energy required to

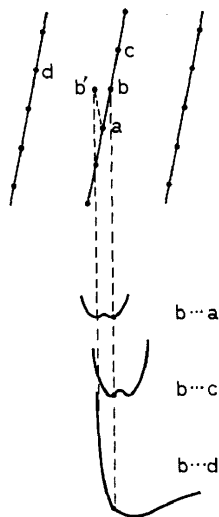


Figure 5. Schematic representation of the energy changes accompanying a shift of orientation of a single methylene group in a slightly twisted polymethamer chain from its equilibrium position to a corresponding position on the other side of the median plane. See text for explanation.

change a methylene group (b) from one of its two equilibrium orientations, relative to the methylene group just below it (a), to the other equilibrium orientation, relative to this lower methylene group. For this, only a small energy barrier must be surmounted. This change, however, requires a large increase in the energy of interaction between the methylene group and the next higher methylene group (c), and also a large increase in the energy of interaction between the moving group and the surrounding chains (d). The total energy increase is so large (using any of the recently proposed functions) that *individual* methylene shifts cannot occur, except at high temperatures. *Simultaneous* shifting of a group of n successive methylene groups from one side to the other would require passage over an internal energy barrier n times the height of a single barrier. Moreover, such a shift could not occur without concurrent shifting of the orientations in neighbouring chains. As in many other crystal structures, I believe that a regular structure, in which the individual units have like conformations, exists, even though the individual units, *if isolated*, might exist in other equally stable conformations and even though the energy barrier between two conformations, for an individual unit, is quite small. The line of reasoning I have outlined for this special case underlies the general principle⁵³⁻⁵⁵ that, in crystal structures, *like atoms (or groups) tend to be surrounded in like manner*.

With the kind of chain packing known to exist in polymethamer crystals, a large *total* angle of twist, measured from the median plane of the zigzag, is impossible, without making hydrogen atoms in neighbouring chains come so close together that their mutual repulsion energies become quite large. This suggests a limit for the total twist angle, beyond which a continuation of the regularly twisted structure would be unstable relative to some other structure. The structural alteration taking place when the limit is reached would be expected to occur at the same, or nearly the same, level for all the chains in the crystal. It must involve no breaking of C—C or C—H bonds, no large departures from most favoured bond angles, and no placing of pairs of atoms not directly bonded together in sites so close as to produce large repulsion energies.

One possible type of structural alteration — probably the only reasonable one if a crystal is being formed from a solution — is a folding of the molecular chain. Folded chain structures have been shown to exist in single crystals of polymethamer and various other polymers. (Keller⁵⁶ and several others have dealt with this subject at this symposium.) If crystalline regions are formed from a previously amorphous solid mass, other types of structural alterations are also conceivable: reversal of the twist direction, a sudden shift to a new orientation of each median zigzag plane, an irregular structure, etc. (*Figure 6*).

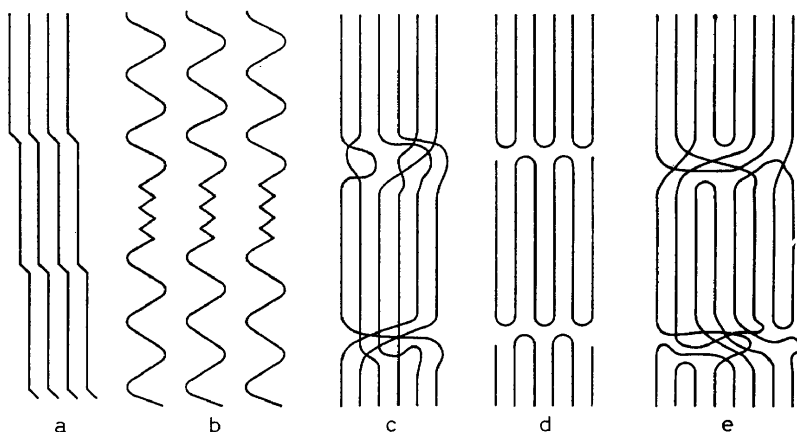


Figure 6. Schematic representations of some hypothetical types of discontinuities (Huggins⁸).

If chain folding occurs at the limit of stability of a twisted chain, the necessity for having stable bond lengths, stable bond angles, and no short (hence unstable) van der Waals contacts in the fold imposes an additional requirement, affecting the limiting twist angle. The carbon-carbon bonds on each side of the fold must be suitably oriented to permit stable folding.

I shall now refer briefly to the dependence of the crystallite thickness — the length of chain between folds or other structural irregularities — on temperature of annealing. The energy curve (for methylene group orientation) near one of the two minima is much steeper on the side away from the central barrier than on the side toward that barrier (see *Figure 7*). This is

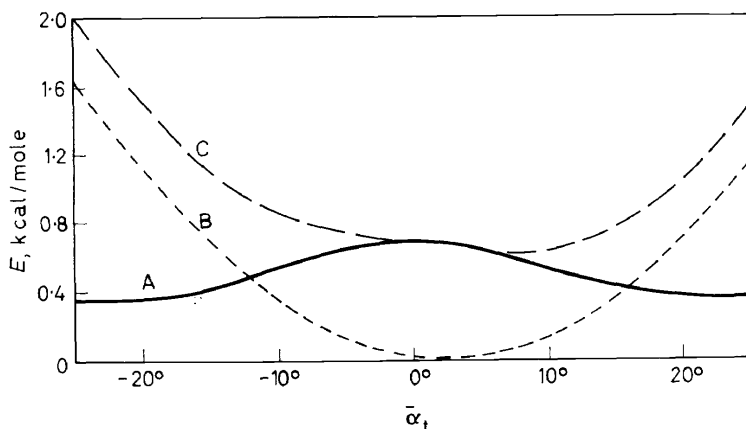


Figure 7. Schematic representation of the energy per mer as a function of the angle of twist per mer, for a uniformly twisted zigzag polymethamer structure (Huggins⁸). (A) Considering only intrachain interactions. (B) Additional energy due to atoms in neighbouring chains. (C) Total energy per mer.

accentuated by the repulsion of neighbouring chains, tending to decrease the twist angle. With this shape of curve, rising temperature shifts the mean position of each vibrating methylene group closer to the symmetrical middle position — that for a planar zigzag. The rate at which the mean position is approached increases as the temperature gets higher. These conclusions are in agreement with experimental observations, such as those of Statton and Geil⁵⁷ (Figure 8), on the temperature dependence of the long x-ray spacing. The straight line in this plot indicates an exponential dependence of the spacing on the annealing temperature. If we assume the x-ray spacing to be the length of twisted chain between structural alterations, such as folds, we can readily calculate the dependence on the annealing temperature of the average twist angle per methylene group, for any assumed total twist angle. Assuming, for illustration, a total twist angle of 90° (which is probably too large), the result is as shown in Figure 9. Assumption of smaller total twist angles would lead to proportionately smaller average twist angles. We thus see that the average twist per methylene group, according to my hypothesis, is very small, of the order of a degree. The twist per methylene group would be expected to be nearly uniform near the middle of the chain (between folds or other structure breaks) but might vary considerably from the average near the chain ends.

In a paper to be published soon, Krimm, Tasumi, and Oposkar⁵⁸ claim that the sharpness of certain infrared absorption bands from polymethamer crystals proves that the methylene groups all have environments which are closely the same and so disproves my hypothesis of twisted chains. If the methylene groups vibrated independently, I would agree with them, but I believe that there is strong coupling between the oscillations of all the CH₂ groups in each segment between discontinuities and probably also between the oscillations in adjacent chains. This, I suggest, should result in narrow infrared bands, in spite of the fact that the environment of a methylene

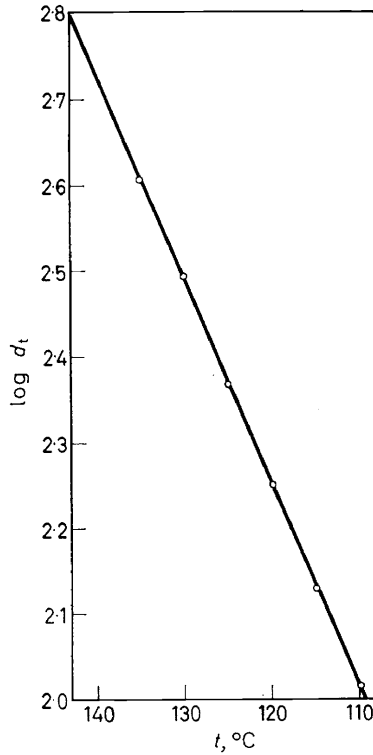


Figure 8. Dependence of long spacing (d_t) on annealing temperature for polymethamer crystals (Huggins⁸). Circles represent points read from curve of experimental data by Statton and Geil⁵⁷.

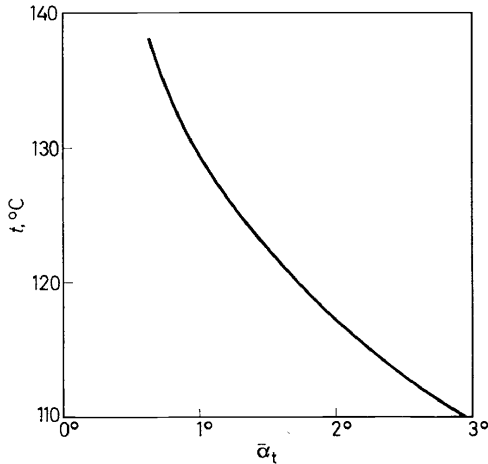


Figure 9. Dependence of average twist angle per mer (\bar{a}_t) on the annealing temperature, for polymethamer crystals, from data by Statton and Geil⁵⁷. The total twist angle is arbitrarily assumed to be 90° at all temperatures (Huggins⁸).

group near a discontinuity would be slightly different from that of a methylene group near the middle of a segment. Perhaps the question can be decided experimentally by the study of widths of corresponding bands in normal paraffins, polyethers, and other compounds having known numbers of methylene groups between discontinuities.

HELICAL STRUCTURES

The polymethamer chain structure can be considered a helix of multiplicity two (meaning two structural units per turn of the helix) if the zigzag is strictly planar, or slightly different from two, if regularly twisted, as I have postulated. The chains in most crystalline linear polymers, if not zigzags, have helical structures of other types. As I have repeatedly pointed out, especially in discussing protein structures^{59, 60} the internal forces, which are usually responsible for the helical arrangement, do not require that the multiplicity be integral or even a simple fraction, such as $4/3$ or $7/2$. On the other hand, external factors, such as the requirements for efficient packing of the chains in the crystal or requirements for disulphide or ester cross-linking or for strong hydrogen bonding between chains, are often much better satisfied by integral or certain other simple multiplicities. For example, if helical polymers, containing *bulky* groups at fixed intervals along the chain axes, are assembled in a close-packed arrangement (*Figure 10*), greatest stability is obtained if the bulky groups fit into the regions between the chains where there is most room (*Figures 11 and 12*). A similar situation exists with other types of structure, such as that illustrated in *Figure 13*.

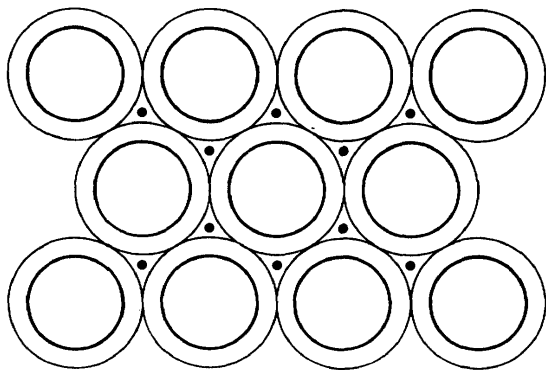


Figure 10. Close-packing of helical chain molecules (Huggins⁸). Heavy circles: Projections of helical chains. Light circles: Projections of van der Waals envelopes. Dots: Centres of channels between chains.

If the multiplicity favoured by the internal forces is close to, but not exactly equal to, a *simple* multiplicity permitting this, three possibilities must be considered.

(i) If the external forces are strong enough, relative to the internal forces, the molecular helix may be forced to assume the simple multiplicity favoured by the external forces.

(ii) If the internal forces are strong relative to the external forces (as, for

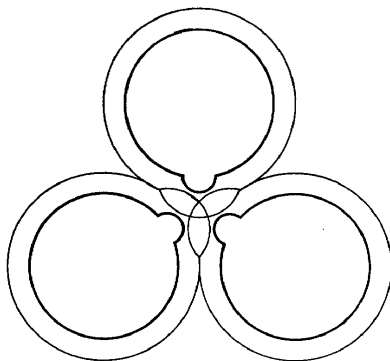


Figure 11. Favourable orientations of protuberant groups in a close-packed structure. The groups are at different levels to avoid mutual interference (Huggins⁸).

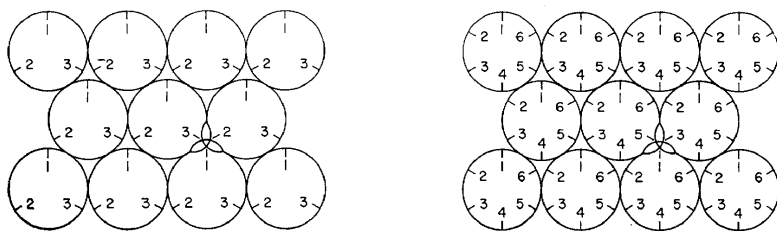


Figure 12. Illustrating how protuberant groups can be accommodated in a close-packed structure without mutual interference. The numbers indicate relative levels (Huggins⁸).
 Left: Three protuberances per turn of helix. Right: Six protuberances per turn of helix.

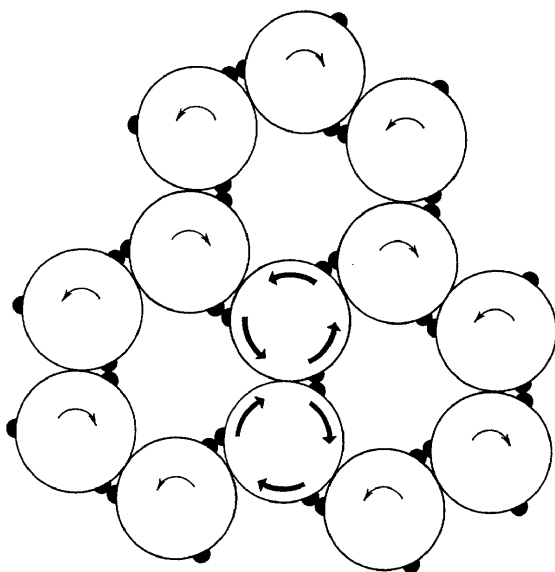


Figure 13. Accommodation of protuberant groups in a non-close-packed hexagonal structure. This also illustrates one of the gear meshing types of structure theoretically favoured for helical polymers without inherent molecular asymmetry.

example, in polypeptides having strong hydrogen bonding between successive folds), the *non-simple* multiplicity may be maintained and the packing of the chains may be sufficiently stable *over a limited range*, as in polymethamer, with folding or some other type of structural alteration when the stability limits are reached (*Figure 14*).

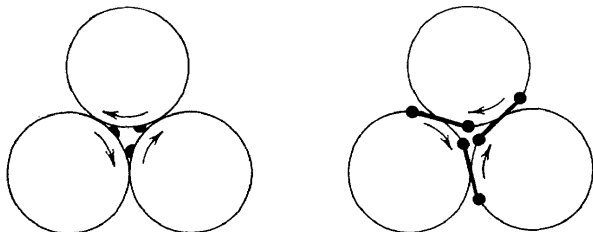


Figure 14. Illustrating limited range stability for helices with non-simple multiplicity. Left: For helices with protuberant groups. Right: For cross-linked helices.

(iii) A different, *non-close-packed*, type of structure, permitting the non-simple periodicity favoured by the internal forces over larger distances, may be formed.

Similar considerations apply, if the external forces are those resulting from interchain hydrogen bonding or crosslinking requirements, rather than those related to bulky groups.

The long x-ray diffraction spacings observed for fibrous proteins such as keratin and collagen may thus be explainable in a manner similar to that which I have proposed for polymethamer. Other reasonable explanations are conceivable, however. Structural studies of synthetic polypeptides of regularly repeated structure — polydipeptides, polytripeptides, etc. — should settle the question.

In the structure (*Figure 15*) proposed by Crick and Rich⁶¹ for one crystalline form of polyglycine, each polypeptide chain is apparently forced to have a simple multiplicity, to permit strong hydrogen bonding to six other polypeptide chains surrounding it. In this case the *intramolecular* forces are much weaker than the *intermolecular* forces.

If the type of model (*Figure 16*) proposed for collagen by Ramachandran⁶²⁻⁶⁴ and Rich and Crick⁶⁵ is correct, its polypeptide chains are helical, with three helices around a common axis. These three chains are strongly hydrogen-bonded together. Internal forces within each chain or bond distance and bond angle requirements in the connecting hydrogen bonds would presumably not be sufficiently well satisfied if the multiplicity within each chain had the simple value required for a triplet structure with the three polypeptide axes parallel to the triplet axis. This reasoning would account for the slow twisting of the polypeptide axes around the triplet axis, which has been inferred from the x-ray data. This explanation is similar to that which I have offered for slow twisting of polymethamer zigzags.

Although the twisted 3-chain structure for collagen is reasonable from several points of view, I should point out that it is not yet proven. The x-ray diffraction data so far published can be explained equally well, in

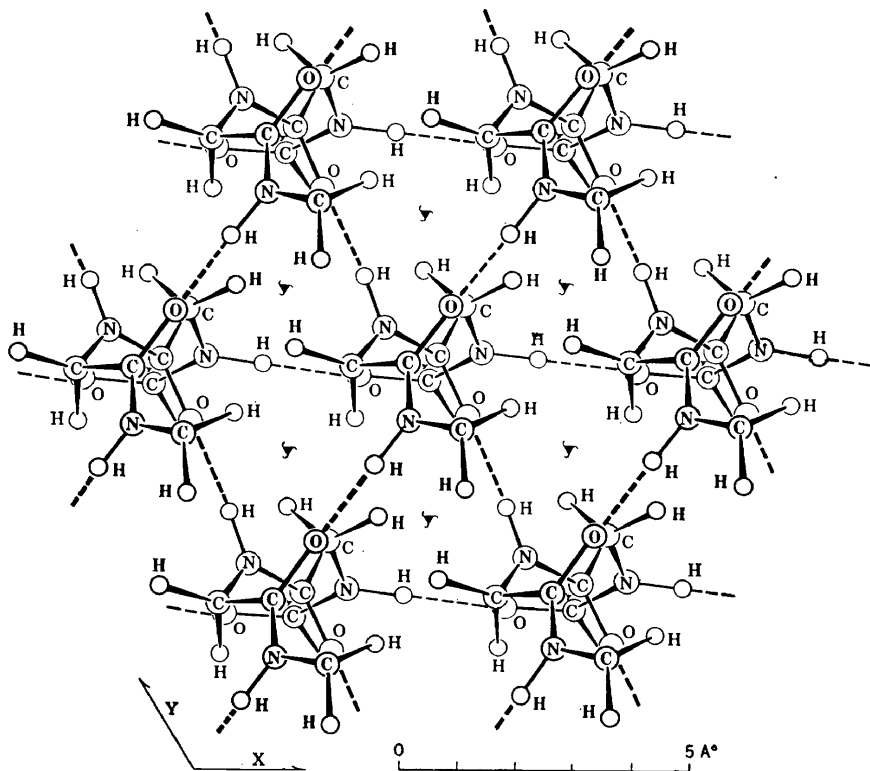


Figure 15. The structure of polyglycine II, according to Crick and Rich⁶¹. Dashed lines indicate hydrogen bonds between neighbouring chains.

my opinion, by the single chain helix model (Figure 17) which I have proposed. It has been claimed by Rich and Crick⁶⁵ that my proposed model cannot be correct, because the Fourier transform for a single chain is not in close agreement with the observed x-ray pattern. That is a very weak argument, however. If the chains are packed together in a regular manner, with corresponding residues in different chains at different heights, according to a regular pattern (as is to be expected), the whole crystal structure must be considered, not merely the arrangement of atoms in a single chain. The Fourier transform of a single chain of any of the Ramachandran-Rich-Crick structures is also in poor agreement with the experimental data. The necessity of considering the mode of packing of the helices is shown by the fact that, although strong x-ray diffractions, which can reasonably be assigned the indices 10·0 for hexagonal close-packing of the single or triple helices, are observed, the corresponding 11·0 reflections are not found.

I shall now discuss the lateral packing of helical chain molecules having regularly spaced side chains that have strong hydrogen bonding or attractions of some other type for side chains, of the same or a different type, in other neighbouring molecules. (This might be the situation in a fibrous protein or synthetic polypeptide, for example.) To be specific, let us assume

RECENT RESEARCH ON POLYMER STRUCTURE

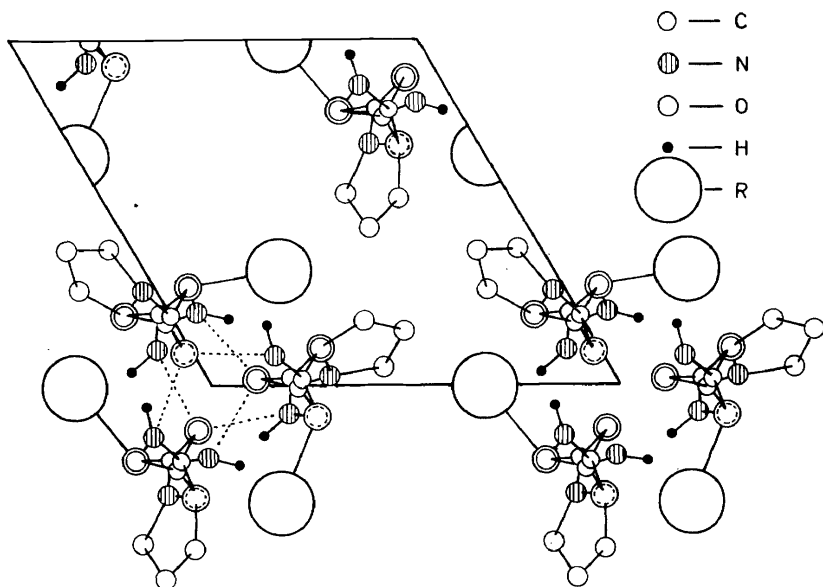


Figure 16. The three-chain structure of collagen, as proposed by Ramachandran and Kartha⁶². Ramachandran's later modifications⁶³ of this structure and the models of Rich and Crick⁶⁵ are similar, as regards the pattern of bonds and hydrogen bonds (Ramanathan and Kartha⁶⁴)

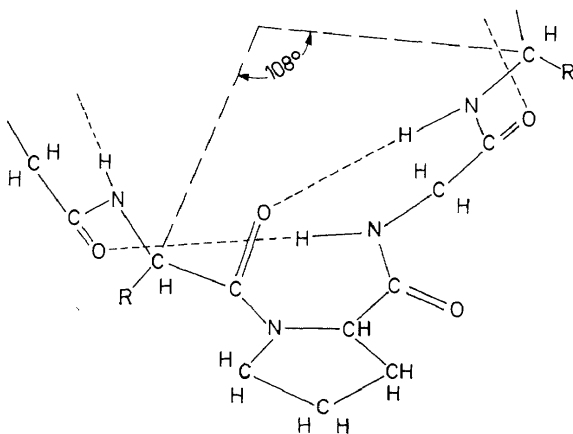


Figure 17. The pattern of bonds and hydrogen bonds proposed by Huggins^{66, 67} for collagen. About one-third of a single turn of the helix is shown (Huggins⁶⁶)

a molecule having strong attractions between side chains of just two types, A and B. The best method of packing of such molecules is one which places A's and B's in adjacent molecules opposite each other, with orientations suitable for their interaction. In general, this requires a regular shift of the structure pattern of each chain (for example, the sequence pattern of amino-acid residues), relative to the structure patterns in the neighbouring chains. If the preferred directions of A—B bonding are all co-planar, a sheetlike structure results. If the preferred directions of bonding of one chain to its two

close neighbours make an angle other than 180° with each other (but equal to a submultiple of 360°), a ring structure may result. A further requirement for a ring structure (to make like groups surrounded in like manner) is that, for n helical rods per ring, n times the vertical shift of A—B bonds per helix must equal either zero or an integral multiple of the vertical distance between successive side chains of the same type in each simple helix. If either of these two requirements is not quite met, with strictly parallel rods and the most stable A—B bonding conformations, a twisting of the ring of parallel rods may suffice to give stability.

The 3-helix structure for collagen may be considered as exemplifying this line of reasoning. α -Keratin may be a more complicated example.

Isotactic linear polymers and others in which opposite asymmetries around chain atoms are unbalanced will be more stable in helical structures with one sense of rotation than in helical structures with the other sense of rotation. In polypeptides in which the orientations are all of the levo type, for example, I have shown⁶⁸ that a right-handed α -helix should be more stable than a left-handed one, because the latter would place the β -carbon atoms so close to carbonyl oxygens as to produce very large repulsions. This has been verified experimentally⁶⁹. In some cases, of course, the difference in energy between right- and left-handed helices may be very small and this difference may be offset by better interchain packing for a mixture of helices of the two types.

For polymers such as polymethamer, $(\text{CH}_2)_n$, poly(1,1-dimethyl ethamer), $[\text{CH}_2\text{C}(\text{CH}_3)_2]_n$, and poly(difluoromethamer), $(\text{CF}_2)_n$, each with no inherent molecular asymmetry, right-handed and left-handed helices are equally stable. Structures of such polymers in which each helix has as close neighbours only helices having the opposite rotation sense would, in the absence of other factors, be more stable than structures in which close neighbours have helices of the same rotational type, because of the "meshing gear effect" (*Figure 18*). Opposite rotations of neighbour helices permit

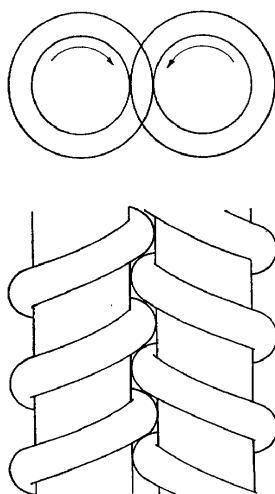


Figure 18. Illustrating the meshing gear effect.

RECENT RESEARCH ON POLYMER STRUCTURE

closer packing and hence stronger van der Waals attractions (and sometimes attractions of other types) than is possible for helices having the same rotation sense.

If the helices are arranged with the axes in hexagonal close-packing, each helix cannot be surrounded by others having opposite rotations. A more open hexagonal structure, however, will permit this (see *Figure 13*), as will a sheetlike structure (*Figure 19*), the tetragonal structure of *Figure 19*, or an orthorhombic structure such as that of polymethamer (*Figure 4*).

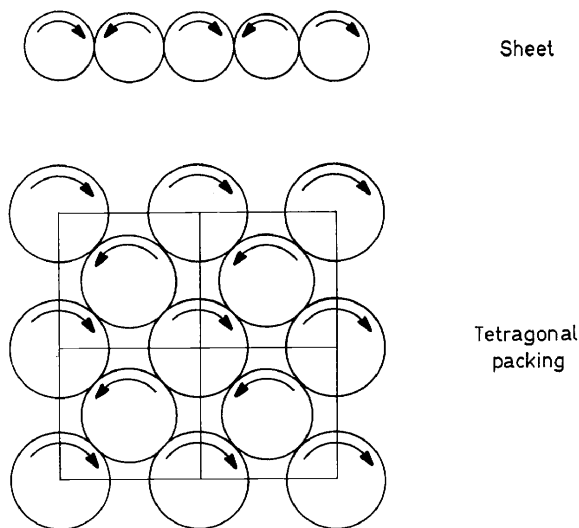


Figure 19. Illustrating the meshing of helices of opposite rotation sense in a sheet-like structure and in a tetragonal arrangement.

It seems likely that the difference in stability of right-handed and left-handed helices for some isotactic polymers is so small that intermolecular packing factors, such as the meshing gear effect I have described, may outweigh these small energy differences and produce crystal structures in which helices with both rotation senses are present. It will be interesting to look for examples of this.

SUMMARY

In summary, I have discussed the important problem of obtaining valid functions for non-bonded H—H, C—H, and C—C interactions and have described my new attack, not yet completed, on this problem. I have pointed out that all the H...H functions which have been seriously proposed and used — except those which incorrectly assume equilibrium at a distance equal to the sum of the van der Waals radii — lead to the conclusion that a planar zigzag structure for polymethamer chains is less stable than a slightly twisted structure. Because the repulsions between different chains increase as the orientations of the zigzags depart more and more from those most favoured, there is a limit to the length of chain which can have the regularly

twisted structure. This line of reasoning leads to the prediction of a structural discontinuity, such as chain folding, when that limit is reached.

I have also extended these ideas to helical structures in which the multiplicity giving greatest internal stability differs from that giving greatest stability of interchain bonding or packing. Finally, I have discussed briefly the "meshing gear effect" for the packing of polymers which can stably exist in helices of both right-handed and left-handed rotation sense.

References

- 1 M. L. Huggins. *Phys. Rev.* **19**, 346 (1922).
- 2 M. L. Huggins. *Phys. Rev.* **21**, 205 (1923).
- 3 M. L. Huggins. *Phys. Rev.* **28**, 1086 (1926).
- 4 M. L. Huggins. *Chem. Rev.* **10**, 427 (1932).
- 5 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, First Edition (1939), p. 174; Third Edition (1960), p. 260.
- 6 A. Bondi. *J. Phys. Chem.* **68**, 441 (1964).
- 7 H. A. Scheraga. *Pure Appl. Chem.* **15**, 503 (1967).
- 8 M. L. Huggins. *Makromol. Chem.* **92**, 260 (1966).
- 9 L. S. Bartell. *J. Chem. Phys.* **32**, 827 (1960).
- 10 T. L. Hill. *J. Chem. Phys.* **16**, 399 (1948).
- 11 I. Amdur, M. S. Longmire and E. A. Mason. *J. Chem. Phys.* **35**, 895 (1961).
- 12 M. L. Huggins, unpublished calculations (1937); see ref. 8.
- 13 J. O. Hirschfelder and J. W. Linnett. *J. Chem. Phys.* **18**, 130 (1950).
- 14 E. A. Mason and M. M. Kreevoy. *J. Am. Chem. Soc.* **77**, 5808 (1955).
- 15 P. DeSantis, E. Giglio, A. M. Liquori, and A. Ripamonti. *J. Polymer Sci.* **A1**, 1383 (1963).
- 16 J. G. Aston, S. Isserow, G. J. Szasz, and R. M. Kennedy. *J. Chem. Phys.* **12**, 336 (1944).
- 17 M. L. Huggins, in *Structural Chemistry and Molecular Biology*, edited by A. Rich and N. Davidson, W. H. Freeman & Co., San Francisco, in the press.
- 18 A. Abe, R. L. Jernigan, and P. J. Flory. *J. Am. Chem. Soc.* **88**, 631 (1966).
- 19 R. L. McCullough and P. E. McMahon. *J. Phys. Chem.* **69**, 1747 (1965).
- 20 D. A. Dows. *J. Chem. Phys.* **35**, 282 (1961).
- 21 A. Odajima and T. Maeda. *Reports on Progress in Polymer Physics in Japan* **8**, 33 (1965).
- 22 M. L. Huggins, this paper.
- 23 N. P. Borisova and M. V. Volkenstein. *Zh. Strukt. Khim.* **2**, 346; *J. Structural Chem.* **2**, 324 (1961).
- 24 H. O. Pritchard and F. H. Summer. *J. Chem. Soc.* 1041 (1955).
- 25 R. Pauncz and D. Ginsburg. *Tetrahedron* **9**, 40 (1960).
- 26 A. Opschoor, Thesis, Technische Hogeschool, Delft (1965).
- 27 C. W. Bunn. *Trans. Faraday Soc.* **35**, 482 (1939).
- 28 K. E. Howlett. *J. Chem. Soc.* 4353 (1957).
- 29 J. C. Slater and J. G. Kirkwood. *Phys. Rev.* **37**, 682 (1931).
- 30 K. S. Pitzer, in *Advances in Chemical Physics*, Vol. 2, edited by I. Prigogine, Interscience Publishers, New York (1959).
- 31 A. F. Forziati. *J. Res. Nat. Bur. Stand.* **44**, 373 (1950).
- 32 D. L. Camin, A. F. Forziati, and F. D. Rossini. *J. Phys. Chem.* **58**, 440 (1954).
- 33 D. L. Camin and F. D. Rossini. *J. Phys. Chem.* **59**, 1173 (1955).
- 34 R. A. Scott and H. A. Scheraga. *J. Chem. Phys.* **42**, 2209 (1965).
- 35 J. E. Mayer. *J. Chem. Phys.* **1**, 270 (1933).
- 36 M. L. Huggins and Y. Sakamoto. *J. Phys. Soc. Japan* **12**, 241 (1957).
- 37 M. L. Huggins. *J. Chem. Phys.* **3**, 473 (1935).
- 38 M. L. Huggins. *J. Chem. Phys.* **4**, 308 (1936).
- 39 M. L. Huggins. *J. Am. Chem. Soc.* **75**, 4126 (1954).
- 40 M. Born and J. E. Mayer. *Z. Physik* **75**, 1 (1932).
- 41 M. L. Huggins and J. E. Mayer. *J. Chem. Phys.* **1**, 643 (1933).
- 42 M. L. Huggins. *J. Chem. Phys.* **5**, 143 (1937).
- 43 G. B. Kistiakowsky, J. R. Lacher, and W. W. Ransom. *J. Chem. Phys.* **6**, 900 (1938).
- 44 K. S. Pitzer. *Quantum Chemistry*, Prentice-Hall, New York (1953), p. 168.
- 45 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, Third Edition (1960), p. 130.
- 46 F. W. Billmeyer, Jr. *J. Applied Phys.* **28**, 1114 (1957).
- 47 P. W. Teare. *Acta Cryst.* **12**, 294 (1959).
- 48 M. L. Huggins. *J. Polymer Sci.* **50**, 65 (1961).
- 49 M. L. Huggins. *Am. Assn. Adv. Sci. Meeting, Boston*, Dec. 1922.

RECENT RESEARCH ON POLYMER STRUCTURE

- ⁵⁰ M. L. Huggins. *J. Chem. Phys.* **13**, 37 (1945).
- ⁵¹ H. U. Lenné. *Kolloid-Z.* **137**, 65 (1954).
- ⁵² C. W. Bunn and E. R. Howells. *Nature, Lond.* **174**, 549 (1954).
- ⁵³ M. L. Huggins. *J. Phys. Chem.* **35**, 1270 (1931).
- ⁵⁴ M. L. Huggins. *J. Chem. Phys.* **13**, 37 (1945).
- ⁵⁵ M. L. Huggins. *J. Polymer Sci.* **30**, 5 (1958).
- ⁵⁶ A. Keller, General Lecture, International Symposium on Macromolecular Chemistry, Tokyo and Kyoto (1966).
- ⁵⁷ W. O. Statten and P. H. Geil. *J. Appl. Polymer Sci.* **3**, 357 (1960).
- ⁵⁸ S. Krimm, M. Tasumi, and C. G. Opaskar. *J. Polymer Sci.* **B5**, 105 (1967).
- ⁵⁹ M. L. Huggins. *Chem. Rev.* **32**, 195 (1943).
- ⁶⁰ M. L. Huggins. *J. Polymer Sci.* **30**, 5 (1958).
- ⁶¹ F. H. C. Crick and A. Rich. *Nature, Lond.* **176**, 780 (1955).
- ⁶² G. N. Ramachandran and G. Kartha. *Nature, Lond.*, **174**, 269 (1954).
- ⁶³ G. N. Ramachandran, V. Sasisekharan, and Y. T. Thathachari, in *Collagen*, edited by N. Ramanathan, Interscience Publishers, New York and London, 1962.
- ⁶⁴ G. N. Ramachandran and G. Kartha. *Proc. Indian Acad. Sci.* **A42**, 215 (1955).
- ⁶⁵ A. Rich and F. H. C. Crick. *J. Molec. Biology* **3**, 483 (1961).
- ⁶⁶ M. L. Huggins. *Proc. Nat. Acad. Sci.* **43**, 209 (1957).
- ⁶⁷ M. L. Huggins, in *Collagen*; see ref. 63.
- ⁶⁸ M. L. Huggins. *J. Am. Chem. Soc.* **74**, 3693 (1952).
- ⁶⁹ E. Katchalski, M. Sela, H. I. Silman, and A. Berger, in *The Proteins*, edited by H. Neurath, Academic Press, New York and London, Second Edition, Vol. 2.