THE PROBLEM OF ORDER IN POLYMERS

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I. INTRODUCTION

Crystallinity depends on the regularity of the chemical and steric structure of polymers. It is one of the most important factors in the macromolecular field. Some of its most characteristic features, such as the conformation of the chain in the crystalline state, the relative positions of the chains, the degree of freedom of rotation of lateral groups, the rate of crystallization, the size, the distribution and the orientation of the crystals, are related to it. These determine properties such as modulus, tenacity, and ultimate tensile strength (25). For example, at room temperature, natural rubber possesses its characteristic extensibility and recoverability, but on cooling to about −25°, crystallization ensues and the polymer grows hard and relatively inextensible.

The main purpose of the present review is to consider the fundamental principles underlying the various aspects of crystallinity in synthetic polymers and proteins, and also to review critically the important methods used for crystallinity determination. Since the line of demarcation between man-made polymers and those synthesized by nature is not sharp, the general principle should be applicable to both. By this it is hoped to draw attention to those approaches which lead to a confused and misleading concept. The review, therefore, contains neither a compilation of all the experimental results nor an exhaustive bibliography. With the primary aim in view, however, efforts have been made to be as comprehensive as possible. Morphological aspects and the general problem of the thermodynamics and the kinetics of crystallization in terms of molecular and chemical structure have not been included at all in the present discussion. These have been reviewed

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extensively by Bunn (28) and Mandelkern (131), respectively.

II. MEANING OF CRYSTALLINITY

According to the presently accepted "Fringe-Micelle" model, the state of solid polymers may vary from the state of perfect, three-dimensional order to the other extremes of completely random orientation of the chains, possibly convoluted and kinked. However, what is to be included in a crystalline state is more a subject of definition; highly qualified opinions differ on how polymer chains can be packed into a crystal structure with various habits and behaviors (34). While giving a good definition of the crystalline state, one has to bear in mind that the noncrystalline components may comprise a variety of structures. It is, therefore, by no means a foregone conclusion that the noncrystalline portion of various solid polymers constitutes an identical state although this assumption has been implicit hitherto in all references to the "amorphous component." There is no denying that, in the comparison of such divergent objects as native and artificial fibers, this may be an unwarranted and false supposition. Baker, Fuller and Pape (10) for this reason prefer to speak of various degrees of lateral order. The definitions of the terms "crystalline" and "amorphous" are based usually on X-ray investigations. The crystalline portion is that part of the polymer substance which gives rise to selective diffraction of X-rays. Even this, however, is not quite satisfactory since, with diminishing size of the crystallites, the selective diffraction gradually passes over into a more diffuse scattering. The minute regions of perfect order would thus escape this definition. Even the question of whether a certain part of a reflection should be attributed to crystalline or amorphous regions is not easy to answer, as a matter of principle. It should be possible, however, to formulate such a definition, for example, in terms of the sharpness of a molecular distribution function. A possible practical procedure could be developed (108) in terms of the sharpness of the Patterson function:

$$P(\mathrm{u}) = \int \rho(r + u)\rho(r)dr$$

where the integration is taken over a unit cell. Here, $\rho(r)$ is the electron density at r. The behavior of $P(\mathrm{u})$ with large u would be a measure of the persistence of the regularity of the lattice. The procedure is also practical because the Patterson function is the Fourier Transform of the intensities of the X-ray reflections and is, as such, experimentally accessible. Fundamentally the best criterion of what constitutes a polymer crystal should be derived from the polymer itself and the present tendency is to define a crystalline region thermodynamically. Thus a crystalline region can be simply defined as any unit volume containing a group of chains which will behave as a unit on application of some external force. These regions may or may not give sharp X-ray interferences, depending upon their extent and perfection, but they will exhibit lower moisture regain, higher density, and lower chemical reactivity than other less ordered regions. Mathematically speaking (90) the degree of crystallinity χ of a polymeric system is usually defined by

$$\chi = (P_1 - P_x)/(P_1 - P_c)$$

where P is an extensive property of the polymer and the subscripts 1, c, and x refer to the liquid, crystalline and mixed liquid + crystal polymer, respectively. In practice P is most commonly the enthalpy, the volume, or an X-ray line intensity, all expressed on a fractional weight basis. This definition of crystallinity, however, ignores surface energy and internal disorder effects in the crystals.

The "fringe-micelle" model had great merits in explaining a number of experimental facts such as the finite melting range, solubility behavior, and various mechanical, electrical and thermodynamic properties. However, as we shall see later, the model proves to be an over-simplification because it implies that the texture of a polymer is fully characterized, if the amount of crystallinity and the size and shape distribution of the micelles are assessed.

Recently Tobolsky and Gupta (229) have given a Markoff chain model for the structure of crystalline polymers. They postulate that the molecular chains in polymers trace out a path on a cubic crystal lattice. In the amorphous region the link vectors of the chain *successively* point in the three–three directions ($\pm x$), ($\pm y$), ($\pm z$) and in the crystalline regions the chain vectors have preferred directions only along these axes. The model is characterized by two amorphous states r_+, r_- and three crystalline states h_+, h_-, and h_0 with the matrix of transition probabilities for the x vectors.

$$\begin{array}{c|ccccc}
 & r_+ & r_- & h_+ & h_- & h_0 \\
\hline
r_+ & \frac{1-p}{2} & \frac{1-p}{2} & \beta_x p & 0 & (1-\beta_x)p \\
r_- & \frac{1-p}{2} & \frac{1-p}{2} & 0 & \beta_x p & (1-\beta_x)p \\
h_+ & 1-\alpha & 0 & \alpha & 0 & 0 \\
h_- & 0 & 1-\alpha & 0 & \alpha & 0 \\
h_0 & \frac{1-\alpha}{2} & \frac{1-\alpha}{2} & 0 & 0 & \alpha
\end{array}$$

The β_x defines orientation in the x direction. Identical matrices with β_y and β_z can be written for the links in the y and z directions. On this basis the fraction of components that exist in the h_+, h_-, and h_0 states is regarded as the fractional degree of crystallinity and is given by $p/(1 - \alpha + p)$. Similarly the fraction of components in the r_+ and r_- states is regarded as the degree of amorphicity and is equal to $(1 - \alpha)/(1 - \alpha + p)$.

Flory (58) has considered the problems relating to dimensional changes in fibrous proteins. Particular attention is given to the process of disordering of the molecular chains which is treated as a reversible phase change between crystalline and amorphous states.

III. STRUCTURAL ASPECTS OF CRYSTALLINITY

The basic structural requirements for polymer crystallization are now well known and have been authoritatively treated by Flory (55, 59) and Stuart (221). Mandelkern (131) has given a comprehensive account and review of the crystallization of polymer molecules. The factors which affect the extent of crystallinity in polymers are (1) intermolecular forces, (2) chain regularity, (3) segmental mobility and size, (4) rate of cooling during crystallization. Crystallization is rarely determined exclusively by any one factor. Linear polyethylene readily crystallizes even though the intermolecular forces are low, since the molecular chain is extremely flexible and readily fits into a crystal lattice.

Polymers, particularly those prepared by non-stereospecific polymerization, contain a large number of structural irregularities arising from chain ends, with the possibility of large end groups, a broad distribution of molecular weights, and the occurrence of branched chains. These polymers also contain structural irregularities along the chain arising from the random distribution of lateral groups which may be attached to an asymmetric carbon atom. If we consider vinyl polyers with repeat unit (—CH_2—CAB—), substituent A may occupy one of two positions with respect to B, which may be referred to as *d* and *l* type residues. Such residues are enantiomorphous if $A \neq B$. In this case, as is now well known, regular successions of residues can be obtained and are described as syndiotactic, *d l d l d l* . . . , and isotactic *d d d d* . . . , or *l l l l* . . . . The majority of polymers having a random succession of residues (atactic) are found to be amorphous, *e.g.*, polystyrene A = H, B = C_6H_5, although this is by no means exclusively so. When the groups A or B are small, *e.g.*, polyacrylonitrile, A = H, B = CN, polyvinyl alcohol, A = H, B = OH, partial crystallinity is observed. Fordham, McCain and Alexander (64) have prepared syndiotactic polyvinyl alcohol which may be distinguished from atactic polyvinyl alcohol on account of its insolubility in water. Bunn (26, 27, 29) has shown previously that indiscriminate changes in stereo positions of the OH groups did not cause a restriction on crystallization. When groups A and B are identical, *e.g.*, polyvinylidene chloride A = B = Cl, and polyethylene, A = B = H, considerations of stereo regularity no longer apply and some degree of crystallinity usually is found.

The regularity of the chain is the most important requirement for crystallization to occur. This has been realized for a long time (97, 98) and since 1954 has been amply verified by the controlled stereo regular polymerization of vinyl monomers. In all cases stereo regular polymerization has led to either the occurrence of or an increase in crystallinity. Polymethylmethacrylate with large lateral groups, A = CH_3, B = CO_2CH_3 can be obtained in the crystalline form, so that segmented mobility and the bulkiness of side groups are relatively of minor importance.

Comprehensive treatments of these aspects of polymer structure have been given by Gaylord and Mark (74), Natta and Corradini (163), and a limited account by Stille (220).

In many cases where a polymer is reported as non-crystalline, it is quite probable that the proper conditions for crystallization have not been obtained. Crystallization involves two processes, nucleus formation and growth. With increased supercooling the probability of nucleus formation increases. The viscosity of the supercooled polymeric liquid also increases rapidly with fall of temperature, restricting the movement of chain segments so that optimum conditions for crystallization are reached 20–30° above the temperature of transformation to a glass. Since crystallization in polymers is necessarily a coöperative process, growth and nucleation of polymer crystals is a slow process and consequently the rate of cooling and subsequent thermal treatment of the polymer will have a noticeable effect on the extent of crystallinity. Treatment with swelling agents often is necessary when large lateral groups have to be accommodated in the crystal lattice (65).

IV. CONFORMATION OF LINEAR POLYMERS

Regularity of succession of *d* or *l* residues along the chain molecule introduces new elements of symmetry into the conformation and packing of the molecular chains in the crystalline regions. Steric hindrance and van der Waals forces between lateral groups cause the chain to adopt a helicoidal conformation. Syndiotactic polymers adopt either a planar or helicoidal conformation depending on the nature of the lateral groups. For example, syndiotactic polymethylmethacrylate (65) and polypropylene (161) have a helical chain conformation while syndiotactic 1,2-polybutadiene (162) occurs in the planar conformation. Packing density is greater for the syndiotactic polymers than for the corresponding isotactic conformation and leads to a higher melting point.

A. HELICAL CONFORMATIONS

The type of helical conformation of isotactic polymers depends on the bulkiness of the side group and, more particularly, on the steric hindrance of the side group near to the chain axis, as shown in Figure 1.

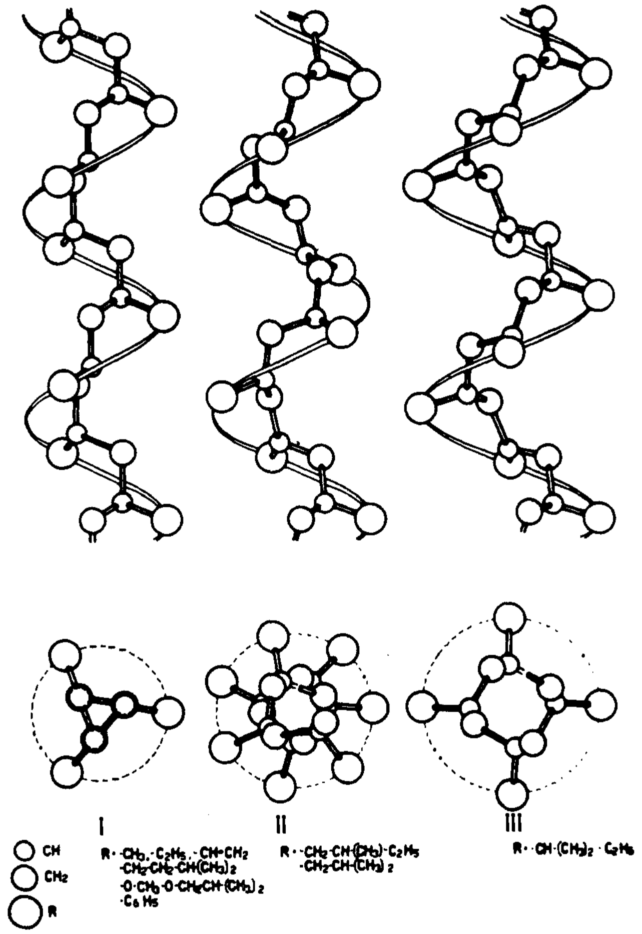

FIG. 1.—Possible types of isotactic chains, according to the nature of the lateral group (by courtesy of *J. Polymer Sci.*, **39**, 20 (1959)).

The majority of polymers conform to a helix with three-fold symmetry. Polybutene-1 has been observed, however, to crystallize in both a three-fold and four-fold helix. The four-fold helix is less stable and the conformation of polybutene-1 changes, on drawing, to that of the three-fold helix. The conformations of a number of stereo-regular polymers have been compiled by Miller and Nielson (147).

The helicoidal conformation is also found in a number of other polymers, notably the α-helix (174) found in several polypeptides. The helical conformation, however, arises from hydrogen bonding and not from steric hindrance, as in the polyolefins. Packing of the fluorine groups in polytetrafluoroethylene is so dense that a helix is the only possible conformation which can be adopted by the carbon chain (32). Helical conformations are also found amongst the inorganic polymers, fibrous sulfur (190) selenium, and tellurium (155).

Shimanouchi and Mizushima (207) have developed mathematical expressions for the helical configuration of a polymer chain in terms of bond lengths, bond angles, and internal rotation angles. From these expressions the stable configurations of several polymer chains have been determined. This work has now been greatly extended by Miyazawa (154, 155), who has given a general method for a normal coördinate treatment of infinitely long helical molecules.

B. PLANAR CONFORMATIONS

Planar conformations of molecules are obtained in the polyamino acids, and arise from hydrogen bond formation. The existence of planar, hydrogen-bonded sheets of parallel molecules has been established for several linear polyamides (11, 31), the carbon backbone being fully extended and nearly planar. Slichter (209, 210) has shown that polyamides prepared from ω-amino acids can exist in two possible planar arrays of hydrogen-bonded linear molecules, with the molecules either parallel or antiparallel. Extended forms of several polypeptides, *e.g.*, polyglycine II and silk fibroin, exist in planar conformation with the molecules arranged antiparallel (139, 196).

C. MODE OF PACKING OF LINEAR CHAINS

Natta and Corradini (163, 164) have given some general considerations on the arrangement and mode of packing of linear chains in the crystal lattice. They define an *equivalence postulate* which assumes that all monomeric units in a crystal occupy geometrically equivalent positions with respect to each chain axis. In order to crystallize, polymers must satisfy the equivalence postulate. Consider a monomeric unit whose conformation may be defined, with respect to a particular axis, by the coördinates of the atoms along its chain in addition to the coördinates of the two atoms defining the direction of the terminal bonds. If reference is made to a cylindrical coördinate system (ρ, ϕ, z) with z along the chain axis, then it is possible to define *intrinsic* coördinates for all monomeric units along the chain by taking one atom of the monomeric unit to be at the origin of the coördinate system, ($z = \phi = 0$). ϕ is taken to be positive when determined in a clockwise direction. Monomeric units which are equivalent with respect to the axis are then those in which the ith atoms have coördinates

$$(\rho_i,\ \phi_i,\ z_i)_{i=0}^{i=n+1},\ (\rho_i,\ \phi_i,\ -z_i)_{i=0}^{i=n+1}$$
$$(\rho_i,\ -\phi_i,\ -z_i)_{i=0}^{i=n+1},(\rho_i,\ -\phi_i,\ z_i)_{i=0}^{i=n+1}$$

Equivalent monomeric units differing only in the sign of one of the intrinsic coördinates (ϕ_i or z_i) can only be made to coincide by reflection and are therefore enantiomorphous. Equivalent monomeric units differing in sign in both ϕ_i and z_i can be made to coincide by rotation about the perpendicular to z and are therefore isomorphous.

Natta and Corradini (163) introduce the idea of isoclined and anticlined monomeric units, opposite being those units which have z coördinates of opposite sign, z_1 and $-z_1$. With reference to a monomeric unit whose intrinsic coördinates are $(\rho_i, \phi_i, z_i)_{i=0}^{i=n}$ these definitions may be given

$(\rho_i, \phi_i, z_i)_{i=0}^{i=n}$	isomorphous isoclined unit
$(\rho_i, -\phi_i, z_i)_{i=0}^{i=n}$	enantiomorphous isoclined unit
$(\rho_i, -\phi_i, -z_i)_{i=0}^{i=n}$	isomorphous anticlined unit
$(\rho_i, \phi_i, -z_i)_{i=0}^{i=n}$	enantiomorphous anticlined unit

From the equivalence postulate it follows that, to allow repetition along the z axis of equivalent isoclined units

$$\begin{aligned} \rho_0 &= \rho_0', \ \rho_1 = \rho_1' \\ z_i - z_0 &= z_1' - z_0' \\ \phi_1 - \phi_0 &= \pm(\phi_1' - \phi_0') \end{aligned}$$

where the superscript denotes a new position, isomorphous and enantiomorphous units being considered. Several important conclusions follow from this:

(1) a regular succession of isomorphous isoclined units must follow an n/p-fold helix containing $2\pi/(\phi_0' - \phi_0)$ monomeric units per pitch, where n is the number of monomeric units and p the number of pitches contained within the identity period (helix-type succession);

(2) a regular succession of alternatively enantiomorphous isoclined units must necessarily take place along a glide plane with translation parallel to the axis (glide-plane succession);

(3) a regular succession of isoclined equivalent units can only assume either helix or glide-plane succession;

(4) repetition of anticlined units may occur along helices associated with two-fold axes perpendicular to z or by a translation along z associated with symmetry planes or centers.

Natta and Corradini (163) have outlined the requirement of the chain to approach a conformation of minimum potential energy and also the effect of lateral packing on the conformation of the molecule.

D. UNIT CELL DATA FOR CRYSTALLINE POLYMERS

A valuable table of unit cell data compiled from the literature has been given by Miller and Nielsen (147). In addition to the polymers listed in this table, data have become available for crystalline polyvinylcyclopropane, -pentane and -hexane (172). Data for polyoxymethylene are given by Tadokoro, Yasumoto, Murahashi and Nitta (224), and for isotactic poly-*m*-methylstyrene by Chatani (33). Stille (220) has given a useful list of data for stereoregular polymers. Crystal structures of the polyamides [—$NH(CH_2)_x$—$NHCO(CH_2)_{y-2}CO$—], [—$NH(CH_2)_{z-1}$ CO—$)_n$ have been given by Miyake [150] for a wide range of values of x, y and z.

Thermal expansion data have been obtained by Cole and Holmes (37) for polymer crystal lattices.

V. STRUCTURAL DISORDER ALONG THE CHAIN

Disordered regions along the chain, which arise from either a random succession of placements l and d, or copolymerization of other residues, limit the formation of a perfect crystalline order. Polymers prepared by stereoregular polymerization mechanisms usually contain stereo-sequence of limited extent. The increasing interest in the properties of isotactic polymers has given rise to a number of papers on the characterization of stereoregular polymers (167, 148), determination of tacticities and the extent of the helical conformation (22, 169, 8, 20, 231, 80), and examination of the properties of polymers with random stereo sequences, by statistical analysis (38, 62, 63, 64, 82, 153, 151, 152).

Flory (56) has given a theory of crystallization in copolymers in which relationships are developed expressing the minimum stable crystallite length ξ^* and the degree of crystallinity w^c as functions of the temperature and sequence length distribution. If the probability that an A residue is followed by another A residue is p, the total number of such residues being N_A and if X_A is the mole fraction of residues A in the molecule, then the concentration of crystalline sequences is

$$\nu^c/N_A = (X_A/p)(1 - p)^2 p\xi^*[(1 - p)^{-1} - (1 - \exp(-\theta))^{-1}]$$

ν^c being the number of crystalline sequences and

$$\theta = (\Delta H_n/R)(1/T - 1/T_m^0)$$

where T is the absolute temperature and $T_m{}^\circ = \Delta H_n/\Delta s_n$, ΔH_n and Δs_n being the heat and entropy of fusion, respectively. The degree of crystallinity is given by

$$\begin{aligned} w^c = (X_A/p)(1 - p)^2 p\xi^*\{p(1 - p)^{-2} - \\ \exp(-\theta)(1 - \exp(-\theta))^{-2} + \xi^*[(1 - p)^{-1} - \\ (1 - \exp(-\theta))^{-1}]\} \end{aligned}$$

This theory has formed the basis for several treatments (38, 167) of the distribution of random stereosequences mentioned above. Newman (167) has given the first direct experimental application of the Flory–Coleman theory using polypropylenes of different degrees of stereoregularity and found very good agreement between theoretical and experimental data.

VI. OPTICALLY ACTIVE POLYMERS

The preparation of optically active vinyl polymers has been explored in a number of recent papers. Interest in these polymers arises in part from the preparation of stereoregular polymers having a helicoidal conformation, and the known optical rotatory properties of polypeptides in the α-helix conformation. It is anticipated that the optical rotatory properties also may be used to determine the degree of tacticity of the polymer.

The occurrence of optical activity in vinyl polymers has been a matter of dispute for several years and it is therefore pertinent to examine briefly the occurrence of optical activity in chain molecules and outline the part played by the asymmetric carbon atom which frequently is considered the *sine qua non* for the existence of optical activity. Although the asymmetric carbon atom plays an important role the sole prerequisite for molecular rotatory power remains Pasteur's principle. A valuable discussion of the application of this principle has been given by Heller and Fitts (85). When optical activity occurs the magnitude of the optical rotation is determined by the groups attached to, and in the neighborhood of, the asymmetric center. Optical activity can arise in the absence of the asymmetric center where, for example, steric hindrance prevents internal rotation of the molecule or in the helical conformation. A helix has no element of reflection symmetry and a molecule with a helical conformation is optically active even in the absence of the asymmetric carbon atoms. Attention may be drawn to the spiral chains of tellurium atoms which have a large optical rotatory power (170). The optical rotatory dispersion of helical molecules with particular reference to proteins and polypeptides has been discussed in the papers of Fitts, Kirkwood and Moffitt (see Djerassi (44) and Doty (46)) and is summarized by the relation of Moffitt and Yang (158)

$$[m] = \left(\frac{3}{n^2 + 2}\right) \times \frac{M}{100} \times [\alpha] = \frac{a_0\lambda_0^2}{\lambda^2 - \lambda_0^2} + \frac{b_0\lambda^4}{(\lambda^2 - \lambda_0^2)^2}$$

where a_0, b_0 and λ_0 are constants, M the residue molecular weight, λ wave length of light, n refractive index of the solvent, $[\alpha]$ and $[m]$ the specific and effective residue rotations. The first term (normal dispersion) contains contributions from the helix and intrinsic residue rotation, *i.e.*, asymmetric centers in the chain, and the second term (anomalous dispersion) contains a further helix contribution. In polypeptides the anomalous helix contribution is large. The magnitude of the helix contribution probably depends on spectroscopic parameters and may well be small for helicoidal conformations of vinyl polymers. Moffitt (157) attempted to calculate $[m]$ for a right-handed α-helix. Natta, Farina, Peraldo and Bressan (165) have now started to make rotatory dispersion measurements for isotactic vinyl polymers.

Frisch, Schuerch and Szwarc (71) and Coleman (38) have discussed the optical activity of vinyl polymers using the Markov chain and Bernouilli trial methods to evaluate the statistics of the placement of residues (either *l* or *d*) along the growing chain. For a vinyl polymer $[\text{—CH}_2\text{—CXY—}]_n$, $X \neq Y$, where X and Y are simple substituents, Frisch, Schuerch and Szwarc (71) obtain an expression for the excess of one configuration

$$N(l) - N(d) = (2y - 1)[F_n(p) - G_n(b)]$$

where $F_n(p)$, $G_n(b)$ are polynomials, p being the probability that placement l occurs in preference to d, and y is the probability that reaction $R + M \rightarrow RM_l$ occurs. Substitution of values for y and p shows that the specific rotation, proportional to $[F_n(p) - G_n(b)]/n$, becomes negligible after the first few residues except when $p = 1$. In the absence of a helicoidal conformation, sequences of similar placements will give no net optical activity which can be utilized to determine the extent of a particular configuration in the chain.

A number of optically active vinyl polymers have been prepared. Asymmetric centers have been introduced into the chain by three methods: (A) use of optically active monomers with asymmetric center in the main chain. Price, Osgan, Hughes and Shambelan (183), and Price and Osgan (182) have prepared poly-(*l*-propylene oxide), $[\text{–O–CH(CH}_3\text{)–CH}_2\text{–}]_n$, obtaining a crystalline, optically active polymer. (B) Optically active monomer with asymmetric center in the side group: Beredjick and Schuerch (14, 15) used *l*-α-methylbenzyl methacrylate; Price, Minoura and Takebayashi (181), *d*- and *l*-propylenimine. Imoto, Sakurai and Kono (99) have prepared poly-(4-methyl-7-isopropyl-2-oxohexamethylenimine). Optically active poly-α-olefins $[\text{–CH}_2\text{–CHR–}]_n$ have been obtained by Pino, Lorenzi and Lardicci (178). There is no direct connection as shown in the table below, between the optical rotation of the monomer and the molar optical activity of the polymer. (C) Formation of the asymmetric center during polymerization, recently carried out by Natta, Farina, Peraldo and Bressan (65) with the polymerization of benzofuran:

R	$[\alpha]^{20}_D$	$[M]^{20}_D$
$\text{–CH(CH}_3\text{)C}_2\text{H}_5$	−11.4	+163
$\text{–CH}_2\text{CH(CH}_2\text{)C}_2\text{H}_5$	+21.3	+278
$\text{–(CH}_2\text{)}_2\text{CH(CH}_3\text{)C}_2\text{H}_5$	+11.7	+67

VII. THE MORPHOLOGY OF POLYMER CRYSTALS

The concept of a random chain for polymer molecules has been successful in explaining and interpreting their thermodynamic and hydrodynamic behavior in solutions as well as some of the bulk physical properties.

In 1945, however, Bunn and Alcock (30) observed birefringent regions in thin films of polyethylene. Each region exhibited a dark Maltese cross whose arms were parallel to the analyzer and polarizer directions. These structures were in many ways typical of the spherulitic structures well known in mineralogy. Electron micrography showed the spherulitic structure to be much more detailed, and has extended greatly the study of spherulitic growth in the polymer. The spherulite has been shown to consist of sheaves of fibrils radiating out from the nucleation center. Along each fibril the polymer crystals grow with a preferred crystallographic direction along the fibril axis. Electron micrograms of carefully annealed polyethylene obtained by Fischer (54), Keller and Bassett (121) and Eppe, Fischer and Stuart (47) have also revealed a laminar structure within and amongst the fibrils for polyethylene. Geil (75) has observed laminar structures in spherulites of acetal resin. These phenomena are difficult to interpret using the fringe-micelle model and consequently have stimulated new thoughts about the arrangement of the polymer molecules in the bulk phase. The undoubted importance of the spherulitic texture and its relationship with the gross physical properties of the polymer has given rise to an active field of research which it is not possible to review here in any detail. To a limited extent the structure of the spherulite could be explained in terms of the fringe micelle (200), but such attempts were extremely unsatisfactory and the spherulitic structure until recently has been discussed without consideration of the polymer matrix in which the structure exists.

The occurrence of single polymer crystals was long thought to be impossible on account of the great chain length of the molecule. In 1953, Schlesinger and Leeper (203) obtained unmistakable evidence of single, hexagonal-sided laminar crystals of α-gutta percha grown from a very dilute solution of the polymer in benzene. Extensive confirmation recently has been given to these observations and a completely new approach has had to be adopted to account for these observations. It is now evident, from the many recent studies of polymer crystallization, that the basic morphological forms are the laminar and fibrillar structures (47, 119). The spherulite frequently is found to contain both these structures and therefore cannot be considered a basic form. Variation in crystallization conditions is sufficient to obtain one form in preference to the other, and both forms can be obtained from solutions of polyethylene given the correct conditions (29). A recent review of these aspects of polymer morphology was given at the Bristol Conference (January, 1961) but has been reported only briefly (13). Earlier accounts have been given in the proceedings of the International Conference on crystal growth in 1958 (45) and by Keller and Bassett (121).

A. SPHERULITES

Following the observation of spherulitic structures in polyethylene (30), spherulites were observed in a large number of semi-crystalline polymers and it was accepted that the spherulitic structure played some part in the crystallization of the polymer (28, 171, 159, 128, 84, 102). Early X-ray investigations (86) of spherulitic structures in polyamides showed the non-birefringent regions surrounding the spherulite to be crystalline. Keller (115), using microbeam X-ray techniques showed this interpretation to be incorrect. It was shown that the spherulite constituted the crystalline part of the polymer. With a suitable solvent spherulites of polyethylene terephthalate could be separated from the polymer matrix (114). In simple substances spherulite formation represents an unusual crystalline habit whereas in polymers it is a general phenomenon and hence is of considerable importance (114).

1. Spherulite Morphology

Spherulites of polyethylene terephthalate, polyethylene and polyhexamethylene sebacamide and adipamide were examined in detail by Keller (114, 115) and Keller and Waring (125) and showed consecutive, periodic extinction patterns when viewed between crossed polarizers. The arms of the Maltese cross were also observed to have a periodic zig-zag pattern. Previous work confirmed by Keller (114) and Point (179, 180) had established that the molecules were arranged in directions normal to the spherulite radius. Keller (114, 115) therefore concluded that only a helical arrangement of molecules along the spherulite radius would account for the observed extinction patterns. A screw-like arrangement of the refractive index ellipsoid had been observed previously in spherulites of low molecular weight. Twisted, helical structures are also a feature of liquid crystals existing in the cholesteric mesophase (145, 70, 197).

In view of the novelty of this proposal alternative explanations were attempted (204, 111). The small scale of the spherulitic structure made normal petrographical methods of investigation impracticable (*i.e.*, use of conoscopic figures). Keith and Padden (112, 113) and Price (185, 186, 187) determined the extinction patterns of various arrangements of uniaxial and biaxial crystals and were able to establish unambiguously the main features of the helicoidal–radical structure proposed by Keller. Keller (120) gave further confirmation to the twisted structure with observations on polytrimethyl glutarate. Spherulites obtained with this polymer were exceptionally well developed and could be observed under lower magnification. This permitted use of a universal stage.

Spherulites in Nylon 66 and Nylon 610 examined with electron microscopy (122, 205) showed a sheaf-like fibrous structure. Electron diffraction of selected fibrils showed the molecules to be at 60–70° to the axis of the fibril and in the plane of the fibril. It was concluded tentatively that the molecules were in folded conformations on the plane of the fibril forming hydrogen-bonded sheets (see section IVB). Conjugate molecular segments would then have an anti-parallel conformation. This would explain the uniform width of the fibrils.

Following the work of Fischer (54) and Keller and Engeman (122), electron microscopy has shown (121, 140) the spherulite to be composed of fibrils radiating out from the primary nucleus, not resolved by the optical microscope, which must be considered the basic structure rather than the spherulite itself. The fibrils are most probably ribbon-like single crystals and the spherulite should be considered as an organized array of single crystals (12).

2. *Spherulite Growth and Nucleation*

Price (184) followed the development of crystallinity in polychlorotrifluoroethylene by observation of the growth of the spherulitic structure. Growth rate was linear with time and dependent on temperature and viscosity of the melt. A large negative temperature coefficient was observed. The kinetics of crystallization of polyethylene oxide, polydecamethylene adipate and poly N,N′-sebacoylpiperazine were determined dilatometrically by Mandelkern, Quinn and Flory (133). The results were satisfactorily accounted for by applying conventional nucleation theory and assuming that nuclei grow at rates proportional to their surface areas (linear rate of radial growth (184)). For isothermal crystallization (132, 133), the volume fraction transformed into the crystalline state, where V_0 and V_∞ are the initial and final volumes, V_t the value at time t, is given by

$$\ln [(V_\infty - V_t)/(V_\infty - V_0)] = -k_s t^4$$

where k_s is the crystallization rate constant given by

$$k_s = [\pi \rho_1/3X_w \rho_c]\dot{N}G^3$$

where ρ_1, ρ_c are the densities of the liquid and crystalline polymer, $1/X_w$ is the proportionality factor relating effective to actual fraction of polymer transformed, G the volume growth rate and $\dot{N}$ is the steady state nucleation rate given by

$$\dot{N} = N_0 \exp [-E_D/RT - (8\pi\gamma_u^2\gamma_e T_m^2)/(RT\Delta H_u^2 \Delta T^2)]$$

where γ_e, γ_u are surface energy parameters, E_D the activation energy required for transport across the nucleus–liquid interface, $\Delta T = T_m - T$ the degree of supercooling, T_m being the equilibrium melting point. At low values of ΔT the second term predominates so that

$$\ln \dot{N} \propto T_m^2/T\Delta T^2$$

Inverse first order dependent on ΔT, obtained by assuming two-dimensional nucleation (106, 107, 48), is not correct.

Flory and McIntyre (61) and McIntyre (146) have determined the nucleation (k_n) and growth (k_g) rate constants for polydecamethylene sebacate and found that

$$k_n k_g^3 \cong k_s$$

Both the radius and number of spherulites showed first order time dependence and a marked negative temperature coefficient. Growth rate was shown (132) to be given by

$$\ln G = \text{const} - C_1 T_m/RT\Delta T$$

Takayanagi and Yamashita (225), assuming a two-dimensional nucleation, obtained

$$\ln G = \ln G_0 - E_0/kT - CT_m/kT\Delta T$$

Flory and McIntyre (61) accounted for the large negative temperature coefficient by introducing the concept of secondary nucleation. Some values of k_n and k_g are given in the table below. Crystallites at the surface of the spherulite are considered to lower the critical free energy ΔF^* for generation of a nucleus by a small fraction of its value for homogeneous nucleation in the bulk polymer. This decrease in ΔF^* will be sufficient to increase, by a large factor, the rate of secondary nucleation compared with the primary rate; hence crystallization will proceed overwhelmingly by the growth of spherulites originating from secondary nuclei.

T, °C.	ΔT, °C.	k_n centers/cc.^{3}/min.	k_g, microns/min.
67.1	12.9	1.50×10^5	5.24
72.0	8.0	1.65×10^1	4.98×10^{-3}

A theory of spherulite growth has been given by Hirai (89) based on absolute reaction rate theory and assumes three-dimensional primary nucleation and two-dimensional secondary nucleation. Sears (206) has discussed the origin of spherulites in terms of the Cahn–Hilliard theory of non-classical nucleation. Barnes, Luetzel and Price (12) have determined spherulite growth rates and bulk crystallization rates for polyethylene oxide in order to obtain the spherulite nucleation rate constant. A theory of spherulite growth as a nucleation controlled process is given.

A systematic study of spherulite growth in linear polymers has been given by Hoffman and Lauritzen (92). This extends and coördinates the theory of polymer crystallization given in their previous paper (127) and lays the foundation for future experimental work.

Keller (117) has pointed to a definite relationship between single crystals and spherulites. He observed lines of thickness along the b axis on the top of the lozenge-shaped polyethylene crystals which presumably are caused by the top layers folding. He suggested that the branching of fibrillar units formed in this way might lead to spherulites. This would also account automatically for the radial b-axis orientation and for the tangential orientation of the molecules within the spherulites. Fischer (54), from a study of the broken surfaces of melt crystallized polyethylenes containing spherulites, observed that the sample consisted of lamellae reminiscent of single crystals. The lamellae were seen to change orientation periodically along the radius of the spherulite, the period being the same as that of the extinction rings.

B. SINGLE CRYSTALS

Schlesinger and Leeper (203) obtained the first evidence of single crystals from a high molecular weight polymer, α-gutta percha, and showed that the formation of the crystals was independent of the distribution of molecular weights and molecular weight of the polymer. Mention should be made, however, of the much earlier work of Sauter (202) who prepared single crystals of β-polyoxymethylene (molecular weight about 3000). Jaccodine (101) prepared single crystals of polyethylene (Marlex 20, $M_W \sim 10{,}000$) from xylene solution, which later were confirmed by Till (228), who showed, furthermore, that the crystals grew in a spiral-terraced structure, each layer having a thickness of approximately 100 Å. Willems and Willems (233), Fischer (54) and Keller (116), who had proposed a mechanism of chain folding, have verified and extended the observations on polyethylene single crystals. Eppe, Fischer and Stuart (47) have proposed a mechanism of chain growth from solution to form the laminar structure.

The spiral-terraced structures of the polymer single crystals suggest a growth mechanism similar to that now observed for many low molecular weight compounds, the center of the spiral being located on a screw dislocation (66) (see *Faraday Society Discussion* No. 5, 1949). Dawson and Vand (43) have shown that single crystals of an n-paraffin also form a spiral-terraced structure, the step height being approximately equal to the c-dimension of the unit cell. Extension of this type of growth to polyethylene does not seem unreasonable.

Single crystals, grown from solution, have now been observed for Nylon 11 and 55 (54), Nylon 6, 66 and 610 (76), polyoxymethylene (77), isotactic polypropylene (194), isotactic poly-4-methylpentene-1 (68), cellulose triacetate (134, 135), cellulose II (13). Eppe, Fischer and Stuart (47) have obtained single crystals from slightly branched polyethylene. Till (228) found that polyethylene in which the number of branches was slightly greater than 2–1 methyls/100 carbon atoms gave very imperfect crystals and laminar structures were not observed.

1. *Polyethylene*

Polyethylene single crystals grow as lozenge-shaped plates with acute angle of approximately 69°. These are shown particularly clearly in the electron micrograms of Keller and O'Connor (123), Keller and Basset (121) and Agar, Frank and Keller (1, 2). Electron diffraction patterns of these crystals are consistent with the orthorhombic unit cell (a = 7.40, b = 4.96, c = 2.53) data obtained by Bunn (24) for polyethylene. Indexing of the diffracted spots shows the c-axis of the unit cell to be normal to the lozenge face, the (001) plane of the crystal. The angle between the (110) and (1$\bar{1}$0) planes calculated from the data of Bunn (24), is 67° 14′ in good agreement with the observed value (228). The crystal therefore grows so that its long and short axes coincide with the a and b directions of the unit cell, as shown by Keller and Bassett (121).

The step height, or thickness in the c-direction, may be roughly judged from shadowed electron micrograms, the reported value being about 100 Å. Keller and O'Connor (123) have used low angle X-ray scattering techniques and obtained values between 115 and 126 Å. It was observed furthermore that the step height was not invariant and increased in a regular manner with increase in the temperature of crystallization. Rånby, Morehead and Walter (194), Price (189) and Keller and O'Connor (123) have obtained results in sensible agreement which are shown collectively in Figure 2. Unpublished data of Keller and Bassett discussed by Frank and Tosi (69) are included for comparison.

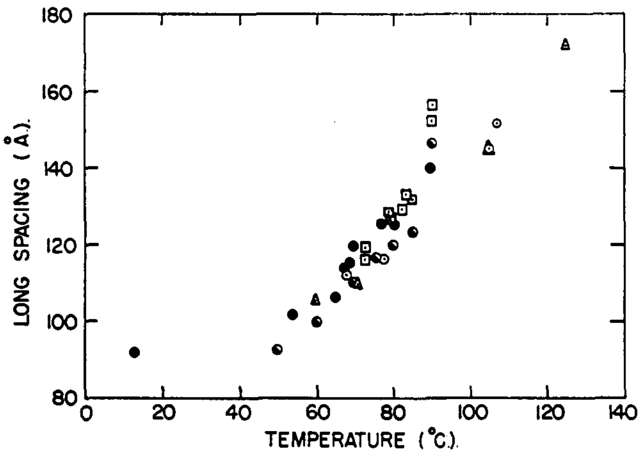

FIG. 2.—The temperature dependence of the long spacing of polyethylene single crystals: ◐ Price (189); ● Keller and Bassett (121); ⊡ Keller and Bassett unpublished, see (69); ⊙ Ziegler, ◬ Marlex 50, Rånby, Morehead and Walter (194).

It is evident from these results that the polymer must take up a folded conformation. In the n-paraffins examined by Anderson and Dawson (4) step height increased with molecular length. For n-hectane [n-$C_{100}H_{202}$] unit cell dimensions a = 7.40, b = 4.90, c = 125 ± 5 Å. Since the length $(-CH_2-CH_3-)_n$ = 2.53 Å. (24) the length of the molecule is 50 × $(-CH_2-CH_2-]$ = 126 Å. (Note a and b dimensions are identical with data for polyethylene (24). Till (228) obtained single crystals from polyethylene for which $\bar{M}_n = 150{,}000$, *i.e.*, n = 5400. The molecule must therefore take up a folded configuration, each fold taking approximately 50 residue units of the chain, with an average value of 100 folds for each molecule (194). Fold length is independent of the molecular weight of the polymer (118, 35). Various theoretical treatments, which will be outlined below, recently have been proposed to explain the formation of the folded structure and its observed temperature dependence.

An important experiment which so far has not been performed is to examine the crystallization of n-paraffins having greater chain length than n-hectane which, as already noted, has a c-dimension of 125 ± 5 Å. What length of paraffin chain is required to start a folded conformation? Keller and O'Connor (124) have attempted to answer this question by examining degraded polyethylene. The number of carbon atoms in the chain was determined from the melting point. Data taken from this paper are given in the accompanying table and compared with data for the n-paraffins. The results give no clear answer to this question of folding and show that carefully designed experiments still need to be performed.

Number of carbon atoms	Chain length,[b] Å.	X-Ray long spacing Å.	Å.[a]	Ref.
36	44	47.5		(43)
39	48	45 ± 10		(4)
39		51.3		(218)
44	53	58		(194)
69	86	89.6		(124)
82	102	108		(194)
87	108	95.5		(124)
100	125	125 ± 5		(42)
111	138	98.0	102	(124)
146	183	104	104	
171	214	107.9	102	
202	253	118.8	104	
443	557	105.9	106	
∞	∞	115	105	

[a] Recrystallized at 54°. [b] Assuming planar conformation, C–C = 1.54 Å., C–C–C 109°28′.

2. Poly-4-methylpentene-1

Frank, Keller and O'Connor (68) have successfully prepared single crystals from isotactic poly-4-methylpentene-1, $[-CH_2-CH(CH_2-CH[CH_3]_2)-]_n$, molecular weight $\bar{M}_v \sim 10^5$, from dilute xylene solution. Crystals formed were square-terraced lozenges of step height approximately 90–150Å. No evidence of the temperature dependence of the step height has, as yet, been obtained. Electron diffraction shows the molecules to be normal to the laminar and pack in a tetragonal unit cell [a = 18.66, b = 13.80 Å.). Two new features arise from this work: (a) the relatively large side group attached to every second carbon atom of the chain obviously does not restrict or prevent the formation of a folded conformation, the formation of single crystals is not restricted, therefore, to the paraffin type chain with its great flexibility; (b) the influence of the configuration of the polymer changes the packing along the lamina.

Isotactic polymers, which have a rod-like character, would be expected to pack hexagonally. The deviation from hexagonal to tetragonal symmetry must arise, in part, from the presence of the large side groups. Frank, Keller and O'Connor (68) suggest that the four-fold coördination is a consequence of the incompatibility of the seven-fold symmetry of the helices (seven-side groups, per helix repeat; class II of Figure 1) with the six-fold coördination of hexagonal packing. There is no alteration in screw sense of the helix in conjugate folds, provided the helix has the same sense along the chain. Packing faults from alternate left and right handed helices do not arise.

3. Polypropylene

Rånby, Morehead and Walter (194) have prepared single crystals of isotactic polypropylene from p-xylene at 60°, obtaining a lozenge, terraced crystal (angle 60°). The X-ray diffraction pattern of the single crystal is reported as being identical with the pattern obtained from melt crystallized polymer. Crystal lattice of isotactic polypropylene, with three residues per helix turn, is of a lower symmetry class (monoclinic or triclinic) than polyethylene.

C. THEORIES OF POLYMER CRYSTALLIZATION FROM SOLUTION

Several theories have been advanced, almost simultaneously, to explain the formation and growth of polymer single crystals. Experimental observations which must be considered in any theory are (1) the existence of a folded structure; (2) constant fold length; (3) ascertaining the factors which determine the magnitude of the fold length; (4) giving the correct temperature dependence. Two types of theory have developed which may be referred to briefly as (1) the equilibrium approach, where the extreme anisotropy of the polymer crystal is considered to result in a decrease in energy of the crystal with increase in thickness in the chain direction. This increase is affected by a decrease in surface energy giving a temperature preferred thickness in the chain direction; (2) a kinetic theory which considers the growth of the crystal to be controlled by the formation of a folded nucleus. Fold length is determined by the interfacial energies and bulk free energy of transformation (supercooling).

1. Kinetic Theories

A preliminary consideration of a theory of kinetic causation has been given by Frank (67), who considered the formation of the folded structure from the tangled molecular chains in solution. As the chain is drawn out of the ball a restoring force arising from the hydrodynamic drag on the ball will be applied gradually and ultimately cause the chain to fold back by itself. The periodic nature of the folding does not readily follow from this picture.

Lauritzen and Hoffman (91, 127) have given a detailed examination of the kinetics of nucleation and growth from solution. The free energy $\Delta\phi_p$, relative to the solution state, of a primary nucleus containing n step elements of length l is taken to be given by

$$\Delta\phi_p = 2na\sigma_e + C\sqrt{(na)}l\sigma_s + 2C\sqrt{(na)}\epsilon_p - nal\Delta f$$

where a is the cross-sectional area of a segment in the crystal, c, a numerical factor depending on the shape of the nucleus, Δf the free energy difference between the polymer in the supercooled solution and in the crystal, σ_s, σ_e are the surface energies for the lateral and end surfaces of the crystal, ϵ_p is the work required to form a unit length of edge from the crystalline phase. The free energy surface as described by this equation is shown in Figure 3, indicating a saddle point. The continuous line shows the most probable path of the chain molecule. Coördinates of the saddle point are obtained by evaluating $(\partial\Delta\phi_p/\partial l)_n$, $(\partial\Delta\phi_p/\partial na)_l$ from which

$$l_p{}^* = \frac{4\sigma_e T_m}{\Delta h_f \Delta T} + \frac{2C\epsilon_p}{\sigma_s}$$

where $\Delta f = \Delta h_f \Delta T/T_m$, Δh_f is the heat of fusion per unit volume at the equilibrium melting temperature T_m, and $\Delta T = T_m - T$ is the degree of supercooling. For polyethylene $T_m \sim 400$°K., $\Delta h_f = 63$ cal./cc., $\sigma_e \sim 30$ ergs cm.$^{-2}$. Lauritzen and Hoffman (127) then consider the growth of the crystal from the primary nucleus and show that the step height of the monomolecular layer will be given by taking $\epsilon_p = 0$

$$l^* = \frac{2\sigma_e T_m}{\Delta h_f \Delta T} + \frac{kT}{h\sigma_s}$$

where k is Boltzmann's constant, and h is the length of a side of the step element. In general

$$l^* > l^*{}_p$$

This equation gives the correct temperature dependence of l^*.

Price (188) has developed a similar analysis obtaining for the mean thickness of the crystal plate

$$\bar{b} = \frac{2\sigma_1 T_m}{\Delta h_v \Delta T} + \left[\frac{kTT_m}{\pi h \Delta h_v \Delta T}\right]^{1/2}$$

where h is the thickness of the nucleus, $\sigma_1 = \sigma_e$, $\Delta h_v = \Delta h_f$. The second term is small compared with the first, so that differences between the expressions of Price and Lauritzen and Hoffmann are marginal. Price (188) has calculated the time of growth assuming the primary nucleus to be a disc of radius 20 Å. to form a crystal radius 20 μ. For supercoolings of 10 and 20°, times are 95 and 4 min., respectively, and roughly comparable with growth times found experimentally. Price (188) has suggested that the part played by screw dislocations in the growth of polymer crystals may be quite different compared with the growth of low molecular weight substances.

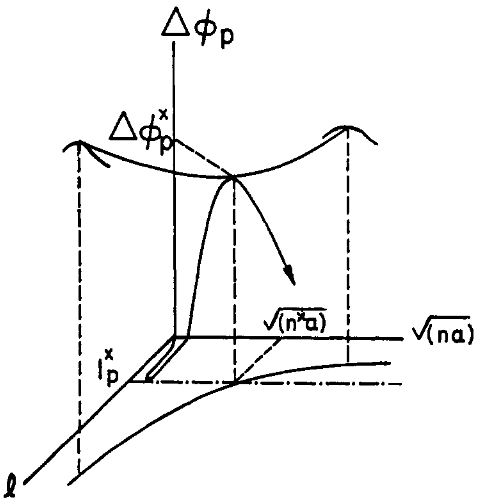

FIG. 3.—Showing the free energy surface with saddle point and the formation of the primary nucleus (127).

Frank and Tosi (69) have considered the free-energy surface, Figure 3, discussed by Lauritzen and Hoffman (127) and Price (188) to be an oversimplification. They replace this surface by a set of discrete free-energy levels, and then re-examine the growth of the crystal from the primary nucleus. This leads to an important difference in the nature of the crystals produced. Lauritzen and Hoffman (127) in order to effect infinite summations, postulated that although the first segment of each new strip had a choice of length (dependent on the degree of supercooling), the length of subsequent folds was invariant. Thus, if the temperature varied during growth no change in lamellar thickness would be obtained. This is not in accord with experiment. In the theory as proposed by Frank and Tosi (69) all crystals grown at the same temperature have the same mean segment length but there is a variation in segment length in each crystal. Frank and Tosi (69) show that the sequence of fold lengths converges to a value l^{**} where l^{**} is similar in magnitude to l^* as given by Lauritzen and Hoffman (127).

In Figure 4 the theoretical results are fitted with the experimentally observed layer thickness and compared with the theoretical relation of Price (198). Fitting was obtained with this set of values:

(1) $T_m = 105°$, $\sigma_s = 4.8$ ergs cm.$^{-2}$, $\sigma_e = 83$ ergs cm.$^{-2}$; (2) $T_m = 115°$, $\sigma_s = 17.2$ ergs cm.$^{-2}$, $\sigma_s = 130$ ergs cm.$^{-2}$. Values of ordinates are given in CH_2 group units, $l^{**} = h'\lambda^{**}$ where $h' = 1.25$ Å., the length of a CH_2 group in the chain.

2. *Equilibrium Theories*

In order to obtain a model in which a folded conformation lowered the free-energy so that a stable equilibrium was reached, Frank (67) considered an ideal picture of the chain molecule in a crystal as a rigid rotator. It then was shown that whilst the partition function $[(z^2/4)(\exp(-u/kT))]$ increased with chain length, the folding energy u does not, thus giving a chain length beyond which folding produces a stable crystal. This model, however, gives the wrong sign to the temperature dependence.

Peterlin and Fischer (176) have considered the effect of a periodic lattice field opposing chain translation in

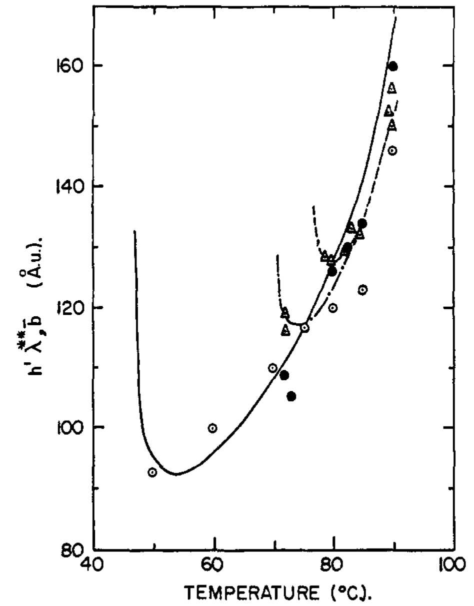

FIG. 4.—Showing the dependence of lamellar thickness ($h'\lambda^{**}$ Frank and Tosi (69), $\bar{b}$ Price (189)) on temperature for polyethylene single crystals; ⊙, Price; ⟁, Keller and Bassett, see reference (121); ●, Keller and Bassett, see reference (121); - - - -, -·-·-·, Frank and Tosi curves I and III; ———, Price.

the c-direction. The surface energy constitutes a positive term which decreases with increase in fold length. These opposing effects give a minimum free energy density at a finite value of fold length and hence a stable crystal. In the expression derived by Peterlin and Fischer (176) the stable fold length is at about $N = 100$ where N = number of chain elements in each fold. Surface energy is about 50 erg. cm.$^{-2}$. The sign of the temperature dependence is uncertain (69) and not easy to evaluate.

Price (189) has given a Markov chain model for growth of polymer single crystals from both solution and the melt. The theory is not an equilibrium theory in the sense of that of Peterlin and Fischer (176) and is more closely related to the kinetic theories of Lauritzen and Hoffman (127) and Frank and Tosi (69). In the theory of Price (189) the equilibrium is restricted in that an equilibrium distribution of segment lengths is allowed within each layer. Markov methods were used to find the most probable chain of N segments where segments could be of various lengths, $b_k + \Delta$. The length Δ is the contour length of a fold and $b_k = x_k B$ where B is the substrate height, and x_k can take values from x_0 to infinity. x_0 is identified with the critical nucleus length as defined by Price (188) and Lauritzen and Hoffman (127). The method of Mullins (160) for the solution of Markov processes by matrix methods is closely followed. Figure 4 also shows the fitted curve given by Price (189) for the parameters $\sigma_1 = 110$ erg. cm.$^{-2}$ (fold surface), $\sigma_2 = 13.3$ erg. cm.$^{-2}$ (lateral surface), $T_m = 133°$. The value of the fold surface energy is closely in agreement with Frank and Tosi (69).

VIII. CRYSTALS OF LOWER DEGREE OF ORDER

Three-dimensional crystals give place to two-dimensional crystals in the mesomorphic state. Paracrystalline structures (synonymous with liquid crystalline, collectively described as the mesomorphic state) are observed frequently in the melting range of many low molecular weight compounds, and such structures have been of interest for many years. A comprehensive review of the mesomorphic state has been given by Brown and Shaw (23). Paracrystalline structures also can exist in solution, and were first examined in detail by Bernal and Fankuchen (18), for aqueous solutions of tobacco mosaic virus. Kacsar (105) has pointed out that there is good evidence that native protein and nucleic acid form paracrystalline structures. Perutz, Liquori and Eirich (175) showed hemoglobin of sickle-cell anemia to be liquid crystalline. Flory (57, 60) has examined the packing of molecules which have rigid-rod properties in solution and has shown that an oriented structure can occur at a concentration dependent on the length (*i.e.*, molecular weight) of the molecules. Tobacco mosaic virus is typical of such molecules (mol. wt. ≈ 2,500,000, $c \approx 1.8$ g./100 cc.). Robinson, Ward and Beevers (199) and Robinson (198) have shown that solutions of the benzyl and methyl esters of poly γ-L-glutamic acid in organic solvents possess liquid crystalline properties (cholesteric mesophase since molecule has intrinsic optical rotatory power). Robinson (198) has further shown that aqueous salt solutions of deoxyribonucleic acid show paracrystalline structures of similar type to poly γ-benzyl-L-glutamate. Luzzati, Cesari, Spach, Masson and Vincent (130) have examined the properties of this ester over a wide concentration range. At high concentration in N,N'-dimethylformamide solution a complex mesophase is obtained in which the conformation of the α-helices is reported as a three-strand helix, an example of the coiled-coil structure proposed by Crick (141). At lower concentrations in other solvents more extended helical conformations are obtained (3_{10} helix). Luzzati, Nicolaieff and Mason (129) find that concentrated aqueous salt solutions of deoxyribonucleic acid exist in the mesomorphic state, the molecules being organized in a two-dimensional hexagonal lattice. Hosemann (96) has contributed to the study of the paracrystalline state by the use of optical transform methods.

So far observation of paracrystalline structures has been confined to solutions of proteins and synthetic polypeptides. Natta, *et al.* (166), however, recently have reported on the presence of crystalline aggregates in the melt and in solutions of some di-isotactic polymers. These structures were revealed by the presence in the infrared spectrum of crystalline sensitive bands found in the solid polymer (see below). Pino, Lorenzi and Lardicci (177, 178) have observed appreciable optical activity in dilute hydrocarbon solutions of the optically active isotactic polymers, (+)(s)-3-methyl-1-pentene, (−)s-4-methyl-1-hexene and (+)(s)-5-methyl-1-heptene. They attribute the observed optical rotatory power ($(\alpha_D)^{18.5}$ 56.5 for (+)(s)-5-methyl-1-heptane in decalin) to the existence and stability of the helical form of the molecule in solution (*cf.* synthetic polypeptides). It is reasonable to expect, given suitable experimental conditions, that paracrystalline structures will be obtained from these polymers. Optically active stereoregular polymers probably will form the cholesteric mesophase.

The paracrystalline properties of natural and synthetic macromolecules undoubtedly will show considerable development in the next few years. Stewart (219) has stressed the importance of mesomorphic state in biological systems and gives particular attention to the occurrence of lipoid in a mesomorphic structure in certain mammalian tissues. Bernal (16) has pointed out that the mesomorphic state is singularly well fitted to provide the complex forms found in biological systems in which organization and lability can be combined to a unique degree.

For such systems Hosemann (94) has developed the theory of X-ray scattering from aperiodic structures obtained by replacing the constant cell edges by statistically determined vectors varying in both length and direction. Discrete X-ray reflections are only observed when the deformations of the unit cells are small, otherwise the discrete reflections will be bridged by intensity ridges. From the ratio of the maximum to minimum intensity along the ridge (*i.e.*, layer line) the mean square deviation of the cell edges both in respect of length and direction, can be calculated. Andreeva and Iversonova (5) have developed a similar analysis by extending the work of Zernicke and Prins (238) on the X-ray scattering of disordered systems, taking the special case of parallel chains with cylindrical symmetry. A review (from 1953) of Russian work on the crystalline state of polymers has been given by Kargin and Slonimskii (109).

IX. DETERMINATION OF THE DEGREE OF CRYSTALLINITY

Many methods such as X-ray diffraction, infrared absorption, nuclear magnetic resonance, dielectric and dynamic and mechanical absorption, heat content, diffusion of penetrants, etc., have been used in the general study of the properties of polymers. Each method has its particular merits and disadvantages. For example, X-ray diffraction cannot establish the position of the hydrogen atoms, one of the main constituents of a polymer. Measurements of dielectric loss depend on the presence of permanent electric dipoles. Many polymers possess no electric dipoles and even when some polymers do have dipoles, *e.g.*, polyamides and polyesters, these are dispersed by nonpolar segments and the characterization of their motion does not necessarily describe the motion of the molecule as a whole. Some of the most frequently used methods for the determination of the degree of crystallinity are reviewed in the following sections.

A. DENSITY MEASUREMENTS

Density measurements have been used for a long time, and still remain one of the most direct methods for estimating the crystallinity of a polymer. Crystallization kinetics are most easily followed by dilatometric methods since such measurements can be made with great sensitivity (192). Recently Ranby and Griffith (193) have determined the crystallization kinetics of poly-4-methyl-1-pentene and Rabesiaka and Kovacs (191) have examined a number of linear polyethylenes. The widely used expression for the specific volume of a polymer is given: V_c, V_a are the specific volumes of the

$$V = \chi V_c + (1 - \chi)V_a$$

crystalline and amorphous domains and χ is the degree of crystallinity. This relation tacitly assumes that the crystalline amorphous phases are well defined domains in the polymer matrix, which is not in accord with observation. A further drawback to the use of this relation is the lack of knowledge concerning the values V_a and V_c to be used in the equation. A value for V_c is frequently obtained from X-ray unit cell data and it has certain reliability. Determination of V_a is normally difficult and quick-quenching is not always a reliable method of obtaining a perfectly amorphous polymer. For semi-crystalline polymers density determinations probably are as reliable and meaningful as any other method. For polymers for which unit cell data are not available or reliable, *i.e.*, polychlorotrifluoroethylene (93) V and χ can be related if χ is determined by some alternative method, *e.g.*, X-ray scattering. For a number of polymers and, in particular, polyethylene terephthalate, it has been reported (49) that no correlation exists between crystallinity and density. A linear relationship between crystallinity, determined by X-ray and nuclear magnetic resonance methods, and specific value has been obtained for several polyolefins (213).

The degree of crystallinity and its dependence on temperature can be more readily estimated for semicrystalline polymers which possess a melting point. Hoffman and Weeks (93) and Swan (223) have made a determination of the degree of crystallinity in polychlorotrifluoroethylene and polyethylene samples from the specific volume-temperature data covering an extended temperature range. Extrapolation of the specific volume-temperature data of the polymer above its melting point are usually not sufficiently reliable.

Density measurements for highly crystalline polymers are probably meaningless. The preparation of single crystals of polyethylene should, in principle, allow estimates of the degree of crystallinity in this polymer to be reliably obtained. Density of the single crystal ($d = 1.036$ g. ml.$^{-1}$) is, however, not identical with the density of the crystalline phase calculated from X-ray data ($d = 1.010$ g. ml.$^{-1}$ (236) and it has been suggested that the statistical variation in fold length in the single crystal lamella creates voids. Matsuoka (142, 143) has shown from density measurements on polyethylene crystallized under high pressures that a discrepancy of approximately 1% in the specific volume of the polymer arises from voids at atmospheric pressure.

Density measurements on oriented fibers are unreliable for the purpose of crystallinity determinations. Geller (78) has investigated density changes in polyacrylonitrile filaments on stretching and has given some theoretical calculations of the specific gravity of a number of polymers.

Griffith and Ranby (193) have shown that poly-4-methyl-1-pentene exhibits unusual density behavior since it is found that at room temperature the crystal density is less than that of the amorphous polymer. At 60° the density of the crystal and amorphous regions are identical.

B. THE X-RAY METHOD

The crystalline parts of a polymer give rise to Bragg reflections while the non-crystalline parts scatter the X-rays in a diffuse manner which may vary from a liquid-like band as in polyethylene to a continuous background as in polymers like polyethylene terephthalate and cellulose. The relative integrated intensities of the discrete reflections and the background depend on the proportion of the two components present. To a certain extent the amorphous material may be associated with side chains on the polymer molecule which disrupt the crystal lattice. However, this does not explain the amorphous scattering completely since even polyethylene with a regular structure and very few or no branches does show a diffuse scattering halo.

The problem of measuring the degree of crystallinity has been the subject of numerous works, *i.e.*, Hermans and Weidinger (87), Matthews, Peiser and Richards (144), Kast and Flaschner (110), Krimm and Tobolsky (126), Nichols (168), Aggarwal and Tilley (3).

The simplest method is the one given by Ingersoll (100). He finds that in cellulose II the $(10\bar{1})$ interference almost disappears for cellulose of low lateral order and shows a large range of intensity depending upon sample history. The height of the (101) interference above the minimum between the (101) and $(10\bar{1})$ interferences (I_1) and the height of the minimum above the background (I_m) expressed as a percentage of the (101) intensity provides a parameter, $[(I_1 - I_m)/I_1] \times 100$, which increases with lateral order. This index is referred to as the radial intensity ratio, and may be in error if the samples are of different orientation, since large differences in orientation change the background corrections and interference intensities. The higher orientation of the (101) plane with respect to the $(10\bar{1})$ or (002) planes will increase the (101) intensity relative to the minimum. This produces an increase in intensity ratio even though there is no change in lateral order. Therefore, a comparison of the lateral order of samples differing widely in orientation can be very misleading unless some correction is made for the difference in orientation. Ant-Wourinen (7) from a similar argument has also defined a crystalline index.

Field (52) has calculated the relative amount of crystallinity in stretched rubber by matching the intensity of the halo with that produced by an unstretched sample of reduced thickness. In order to make this determination, first the intensity of the halo as a function of the thickness of the unstretched rubber must be known. Goppel (79) determined the crystallinity in rubber by an improved method by measuring the background intensity of a partly crystalline rubber sample at a suitable diffraction angle where no diffraction due to crystalline component occurs and then measuring the intensity at the same angle for a non-crystalline (100% amorphous) sample of the same substance. The ratio of the two values would then give the fraction of the amorphous content in the partially crystallized sample.

More accurate procedure for determining crystallinity is based on a comparison of the relative areas under the amorphous peaks. A basic assumption of this method is that the scattering from a unit of polymer is the same whether the polymer is in the crystalline or amorphous state. Matthews, Peiser and Richards (144) have carried out an experimental check on this relative scattering efficiency in the case of polyethylene by comparing two samples differing greatly in amorphous content and examined under rigidly controlled and identical conditions of exposure and development. They find it approximately equals unity. These authors have also described corrections for "plane" orientation and "chain" orientation. All methods are modifications of the procedure developed by Hermans and Weidinger (87) for cellulose. To obtain comparable results they use samples in the form of pellets to exclude any effects of orientation.

The usual method employed for the measurement of total incident radiation by simultaneously recording the primary beam after weakening it by its passage through sheets of known absorption factor and for a known time suffers from serious errors. The spectrum of an ordinary X-ray tube contains the characteristic radiation as well as the radiation of lower wave length and filtering selectively reduces the intensity of higher wave lengths, the hard radiation being little affected. They make use of a Goppel subsidiary camera in which the main X-ray beam after traversing the specimen falls on a standard crystalline powder specimen. A disadvantage of this technique is that low-angle scattering is cut off and an important contribution to the background scattering remains undetermined. One of the reflections from this powder is recorded near the center of the photograph in a region shielded from the radiation scattered by the main specimen. At the end of each exposure the value of $\mu_m \rho_d$ is measured as a control and all exposures are standardized to equal intensity of the primary radiation. The measurements are made within 2θ values varying from 7 to 45° and a check is put on the thickness of the preparation by using a lead sector and employing Astbury's comparison principle. A photograph of the specimen is recorded on one quadrant of the rotating plane film, the other being shielded by the lead sector. Next the cellulose specimen is removed, leaving the comparison sample alone, and simultaneously the lead sector is rotated through 90°. From the intensities of the comparison interference I_c in the cellulose and air quadrants, the value of μd can be computed from

$$\log (I_c)_{\mathrm{air}} = \log (I_c)_{\mathrm{cellulose}} = \mu d$$

This method also facilitates the computation of the correction for radiation scattered by air which usually can be avoided by evacuation of the camera.

While evaluating the radiation scattered by the crystalline and amorphous portions it is assumed that in native cellulose the minimum between the cellulose I and II peaks lies well above the background. In curves of regenerated cellulose it is assumed that the background line touches the minimum. The background radiation is, for the main part, due to the scattering of the disordered fiber portion but is still to be corrected for the radiation due to the thermal agitation of the atoms and due to Compton radiation. For this, exposures are made of single crystal plates of cane sugar. It is again assumed that the Compton plus thermal components of the back-ground for cellulose are equal to those of sugar crystals. Recently Hermans and Weidinger (88) have also applied this method to other polymers. It consists of selecting two (or more) samples of the polymer with unknown and widely different crystalline fractions.

This method is also subject to criticism. Wood (237) has argued that in the photographs of cellulose I, Hermans and Weidinger (87) locate the maximum of the background scattering in a region where there is a very considerable overlap of the Bragg reflections so that any estimate of the height of this maximum must be subject to a good deal of personal error. Further, there is some doubt whether in fibers the condition that the crystallites interact with the radiation in the same way as ordinary crystals whose diffuse scattering is almost entirely accounted for by thermal motion and the Compton effect, is in fact satisfied. It may well be that what we call cellulose crystallites have structural defects which are responsible for an extra component of diffuse scattering.

The most thorough study of the crystalline modifications and degree of crystalline order of cellulose, cellulose I (Ramie), cellulose II (Fortisan) and plant cellulose (Valonia ventricosa), have been made by Mann and Marrinan (136, 137), Jones (103, 104), Mann, Roldan-Gonzalez and Wellard (138) and Fisher and Mann (53).

Krimm and Tobolsky (126) used a Geiger counter spectrometer to replace the photographic film in order to record the pattern scattered by polymers and to estimate the crystalline content of polyethylene. Instead of the height of amorphous peak, they use the integrated intensity.

Wakelin and others (232) have developed two, methods for determining the relative rather than absolute crystallinity of cellulose, using a highly crystalline sample (hydrolyzed cotton cellulose) as the crystalline standard and a ball-milled cotton as the amorphous standard. In the first method, called the "correlation method," the corrected intensity for the amorphous standard at a given scattering angle is subtracted from that for the sample and the crystalline standard at the same angle. These differences at various scattering angles are plotted and the slope of the regression line provides an estimate of crystallinity. In the second method, called the "integral method," the two differences are separately summed without regard for sign and their ratio provides an index for crystallinity.

Urbanczyk (230) has used the method of differential-filtration of the radiation diffracted by the specimen. Kakudo and Ullman (108) recently have developed a procedure which is both theoretically sound and experimentally feasible. They calculate the fraction of amorphous material from the ratio of the areas of the amorphous peak in a polymer to the corresponding scattering area of liquid polymer extrapolated to room temperature. The calculation is made after correcting for incoherent scattering, expansion of the sample, attenuation of the X-ray beam and scattering from the glass plate on which the sample is mounted. The per cent crystallinities are calculated from the symmetric (S) and asymmetric (A) curves as well as the peak heights of the amorphous scattering curves. To obtain the S and A curves they first find the position of the peak of amorphous scattering by extrapolated measurements of scattering from the melt at a series of temperatures.

The low angle side of the amorphous scattering is easily drawn because of the absence of any interfering diffraction peaks. In the S curves the high-angle amorphous curve is symmetric with the low angle. In the A curves a smooth curve is drawn from the peak of amorphous scattering to high angles. These two curves represent the lower and upper bounds of amorphous content.

The basic assumption of the X-ray method that scattering from a unit of polymer is the same whether in the crystalline or amorphous state is invalid as a general proposition, though it may happen to be nearly correct in special cases. The total scattering depends both on the quantity of material and the phase relationship of the scattered waves. The intensity of a crystalline peak may be reduced by thermal vibrations of a crystal lattice, but this is not valid for scattering from amorphous regions. It is, therefore, possible that on changing the temperature, the ratio of the areas of crystalline and amorphous regions would change without any modification of the per cent crystallinity. The intensity of the scattered radiation arising from a reflecting plane in a crystal lattice at temperature T is

$$I_T(hkl) = Ae^{-2M}F(hkl)F^*(hkl)$$

$$F(hkl) = \sum_n f_n \exp\{2\pi i(hx_n + hy_n + hz_n\}$$

Here A is a constant, M the temperature factor which increases with increasing T, hkl are Miller indices, f_n are atomic structure factors, and x_n, y_n, z_n are the relative atomic coördinates of the n^{th} atom of the unit cell. It is seen from the formula that I_T decreases as the temperature increases because of increasing M. $F(hkl)$ may, however, increase or decrease with temperature as the contributions of the atoms move in or out of phase with the changes in the density of the crystalline solid.

Thus the area under the crystalline peak cannot be directly interpreted as representing the amount of crystallinity in the polymer. An appreciable error in X-ray method arises from the inability to draw with certainty that part of the amorphous peak on which crystalline reflections are superimposed, and this is also subject to personal error.

Recently Ruland (201) has developed an X-ray method which takes into account the diffuse scattering due to thermal vibrations and lattice imperfections in the crystalline part of a substance. These effects have also been emphasized by Hosemann (95). The weight fraction of crystalline material χ_{cr} according to Ruland is,

$$\chi_{cr} = \frac{\int_{S_0}^{S_p} S^2 I_{cr}(S)\mathrm{d}S}{\int_{S_0}^{S_p} S^2 I(S)\mathrm{d}S} K(S\ , S_p, D, \bar{f}^2)$$

where I_{cr} = coherent scattering concentrated into the peaks.

$$S = \left(\frac{2}{\lambda}\right) \sin\theta, \; I(S) = \frac{1}{4\pi}\int_0^{4\pi} I(S)\mathrm{d}w, \; \bar{f}^2 = \frac{\sum N_i \bar{f}_i^2}{\sum N_i}$$

f_i is the scattering factor for an atom of type i and there are N_i such atoms.

$$K = \int_{S_0}^{S_p} S^2\bar{f}^2\mathrm{d}S \Big/ \int_{S_0}^{S_p} S^2\bar{f}^2 D\mathrm{d}S$$

and D is a disorder factor.

To a first approximation $D = e^{-KS_2}$ where K includes the effect of thermal motion as well as lattice imperfections in general Integration intervals (limits S_0 and S_p) over large regions of S are chosen such that

$$\int_{S_0}^{S_p} S^2 I(S)\mathrm{d}S = \int_{S_0}^{S_p} S^2\bar{f}^2\mathrm{d}S$$

independent of the crystallinity of the substance.

Ruland (201) has applied the method to a series of polypropylene samples and the results show that the diffuse scattering is predominantly caused by thermal motions.

A certain amount of polymer is neither clearly crystalline nor clearly amorphous, but something intermediate. Since single molecules pass through both crystalline and amorphous regions, the high order in the crystalline state must persist for some distance at the crystallite boundary because of the geometric constraints on the molecule. If the amount of this semi-crystalline polymer is appreciable, the use of the X-ray pattern of the melted polymer as a standard for amorphous scattering becomes questionable. In the liquid polymer there are no crystallites to constrain the configurations of neighboring amorphous regions, while in solid crystalline polymers the constraints do perturb the amorphous pattern. The scattering from amorphous regions in a crystalline polymer would be expected to be intensified at angles corresponding to the most intense reflections from the crystal regions. Consequently the "amorphous peak" might have small humps centered at the crystalline peaks, yet they correspond to scattering from disordered regions.

In view of the differences between results obtained from other methods, the basis of the X-ray methods needs a careful definition. What is the exact degree of three-dimensional order required, *i.e.*, the minimum number of adjacent unit cells necessary to give a discrete X-ray reflection, perfection of crystallites, etc.? Taylor and Robinson (51) are studying this point quantitatively using the optical diffractometer by exploiting the analogy between the diffraction of light by a set of holes and of X-rays by a set of atoms (83). The technique is restricted to two-dimensional arrays so that in comparing the results of optical diffraction with X-ray diffraction photographs only equatorial X-ray reflections can be considered. It must be stressed, however, that the existence of equatorial reflections is not a sufficient condition for the existence of three-dimensional crystallinity. Farrow obtains a good correlation between "two-dimensional" crystallinity from equatorial reflections and three-dimensional crystallinity. Statton (214) has shown that some polymers can be produced with varying amounts of both lateral and longitudinal order so that markedly different crystallinities could be obtained from any one specimen, by measuring different groups of intensities.

In conclusion, brief comments may be made on the X-ray method as compared with the chemical ones. Both are influenced by the size of the crystallites and the degree of perfection. The former represents a volume average of order whereas the latter depends on the number of available sites on the surface of the crystallites. In the X-ray pattern the effects of internal imperfections resulting from mechanical strains, dislocation of side groups, lattice vacancies, *etc.*, cannot be separated from that due to small crystallites. Hence in the case of large crystallites with many internal imperfections the X-ray estimates of crystallinity will be below the chemical estimates. Thus the X-ray and chemical methods often predict quite different values of crystallinity for the same material.

C. INFRARED METHOD

Infrared spectra of polymers when they are subjected to physical treatments which change the crystalline content, undergo changes in intensity of certain absorption bands. If bands can be found which are sensitive to amorphous content and to crystalline content, an absolute measure of crystallinity can be made. If, however, a given polymer shows only sensitivity to changes in crystallinity (21), then it is necessary to compare absorbance, which is the logarithm of the reciprocal of the transmission of the given band with the density or other suitable property of the polymer. Though this is a relative method, yet it has its merits because the data are less subject to fluctuations as compared with the density which is affected by a variable content of voids and other extraneous features in the sample. This is specially true if an internal standard for thickness control is present such as the CH_2 stretching mode 2863 cm.$^{-1}$ for rubber, nylon and polyethylene terephthalate (168). Miller and Willis (149) justify the infrared method as a totally independent way of obtaining an estimate of crystallinity from which the structure of the material may also be assessed by comparison with estimates made by other methods. Where both amorphous and crystalline bands are present, the crystalline-amorphous ratio C/A is equal to

$$K = \frac{\text{observed absorbance for crystalline band}}{\text{observed absorbance for amorphous band}}$$

where K is the ratio of the absorbances for completely amorphous to completely crystalline samples. This constant can be evaluated by the method of successive approximations from data for highly crystalline and highly amorphous samples.

These absorbances refer, of course, to the same thickness of sample. In practice the observed ratio is independent of thickness since the absorbances are determined for two bands in the same sample. Where only a single sensitive band is available, the crystallinity value must be calibrated as indicated earlier by some other method such as density. If orientation affects the intensity of the band, a separation of the effects of crystallinity and orientation frequently can be made by locating a band which has only dichroic properties arising from orientation only. Attention is drawn, however, to the papers of Stein and Norris (217) and Stein (215, 216) who have examined the X-ray diffraction, birefringence and infrared dichroism of stretched polyethylene films. Both uniaxial and biaxial orientation are considered. A resolution of the effects of crystallinity and orientation can be obtained by exploring the effect on the measured parameters of the tilt of the film with respect to a reference direction.

Sutherland (222) observed that the optical densities of the 8.87 and 11.9 micron bands in stretched latex rubber increased on cooling to −140°, whereas the 6.02 micron dichroic band remained unchanged. He has determined the crystallinity figure for highly stretched rubber as approximately 40%, in rough agreement with the results of Goppel and Arlman (79). Thomson (226), Mochel and Hall (156), and Cobbs (36) have obtained by the application of infrared technique very reliable estimates of crystallinity in a number of common polymers. Cobbs and Burton (36) used the crystalline band at 973 cm.$^{-1}$ in the spectrum of polyethylene terephthalate to follow the production of crystalline material as the polymer was heated. They obtained a good correlation of the change in intensity of this band with the density. Since a 100% crystalline specimen cannot be obtained, absolute values of crystalline material are not possible. Further, it is also not safe to extend such measurements to oriented samples since the 973 cm.$^{-1}$ band shows marked dichroic effects. In infrared measurements most of the workers are forced to reply on calibration by methods such as density. Miller and Willis (149) have used pure amorphous bands which arise from the multiplicity of rotational isomers present in the amorphous phase. By this method an absolute calibration of amorphous content is possible. The amorphous spectrum should be obtained at room temperature because the intensity of the band varies with temperature. They have made measurements in polyethylene (1305 cm.$^{-1}$ band), polyethylene terephthalate (898 cm.$^{-1}$ band), and polytetrafluoroethylene (770 cm.$^{-1}$ band). Matsuo (140, 141) finds that in poly-chlorotrifluoroethylene the infrared absorption bands at 1290 cm.$^{-1}$, 490 cm.$^{-1}$, and 440 cm.$^{-1}$ were sensitive to crystalline content and at 754 cm.$^{-1}$

was sensitive to amorphous content. They used the relation $\chi = (R - 2.05)/(R + 6.67)$ where R = ratio of observed absorbance at 440 cm.$^{-1}$ to that at 754 cm.$^{-1}$, and is independent of thickness since the absorbances are determined for two bands in the same sample.

Miller and Willis (149) have pointed out that if the 898 cm.$^{-1}$ bands in polyethylene terephthalate are due to the presence of *gauche* configuration of the $-O-CH_2-CH_2-O-$ group in polyethylene terephthalate, then they only characterize part of the amorphous material, since the transconfiguration can also be present in the amorphous material. When the polymer is heat crystallized, it is possible that the ratio of *trans* and *gauche* isomers in the amorphous material remains constant and thus the decrease in the concentration of *gauche* isomer gives a direct measure of the decrease in amorphous content. This is unlikely to be true when the samples are drawn, since the drawing process will pull out the molecular chains and increase the proportion of *trans* isomers, the latter being the fully extended configuration. This increase in the concentration of *trans* isomers only produces order within a molecular chain and is not necessarily associated with the onset of crystallinity. Thus values of amorphous content derived from this type of infrared measurement would be expected to be lower than the true values. As Grime and Ward (81) point out, this provides an alternative explanation of the apparent decrease of amorphous density in polyethylene terephthalate yarns of high draw ratio found by Thomson and Woods (227). In the measurements of Thomson and Woods (227) the amorphous content was estimated from the intensity of the 900 cm.$^{-1}$ band. The density of a completely amorphous polymer then was calculated using the measured over-all density of the filaments and the calculated X-ray value for the crystalline regions. Thus the very low amorphous densities obtained could be due to an overestimate of the amount of crystalline material present. Grime and Ward (81) also have carried out detailed assignments of the infrared absorptions of polyethylene terephthalate and related compounds in the region of 5.15 μ. They suggested that the major differences between the infrared spectra of amorphous and partially crystalline samples of polyethylene terephthalate are due to rotational isomerism.

The hypothesis that the differences between the infrared spectra of crystalline and amorphous polyethylene terephthalate are due to configurational changes has some bearing on the interpretation of the transitions associated with the loss maxima in dynamic and dielectric measurements (81). If we accept the view that the transitions are due to the onset of some form of molecular freedom and more especially with the freedom of rotation about particular bonds in the molecule, then each transition will be associated with a particular configurational change. The *trans-gauche* configurational change can account for a dynamic loss maximum on this view. This configurational change also gives rise to the change in dipole moment which is required for the dielectric loss process associated with the dynamic loss process.

In conclusion, for the purpose of estimating the quantitative proportions of amorphous and crystalline material, amorphous bands possess many advantages over crystalline bands. They are usually broad and therefore do not require narrow slit widths to resolve them properly; neither is their intensity affected appreciably by orientation effects in the polymer. The chief advantage lies in easy quantitative calibration since it should be possible to obtain the majority of polymers in the completely amorphous condition. Farrow and Ward (51) have made a comparative study of crystallinity in polyethylene terephthalate by X-ray and infrared measurements on spun yarn and thin film. Their results imply that the ratio between *gauche* and *trans* configurations does not remain constant. It has been suggested that this could be because of surface orientation which is difficult to detect.

D. NUCLEAR MAGNETIC RESONANCE

The nuclear magnetic resonance method has been used to determine crystallinity in various polymers and the basic aspects have been reviewed fully by Pake (173), Andrew (6), and Slichter (208). The possibility for distinguishing crystalline and amorphous regions arises through an intrinsic difference between the nuclear resonance absorption line width of the two phases. The rigid crystalline lattice is characterized by a broad absorption line whose width in magnetic field units can be predicted roughly when molecular and crystal structures are known and the amorphous phase is associated with the narrow component. Bloembergen, Purcell and Pound (19) have shown that n.m.r. line widths are sensitive to the amount of motion present in a system—the more violent the motion the narrower the line. This motional effect then leads to an alternate description of the broad and narrow components: namely, that the broad component arises from those regions of the sample which are sufficiently restricted to be considered fixed and the narrow component arises from those regions which are in motion relative to the frequency of measurement. For example, in polyethylene terephthalate the narrow component of the composite signal arises from both methylene and benzene ring protons in the amorphous regions, which are undergoing considerable reorientation and the broad component primarily from rigid benzene ring protons presumably including those in the crystalline regions together with the methylene group protons undergoing hindered rotations.

Studies of the changes in line width, then, are studies of the changes in the extent and type of motion (*i.e.*, of transitions) present in a system and may lead, therefore, to a better understanding of the molecular processes involved in such transitions. Liquids normally are characterized by sufficiently rapid molecular motions to sharpen the line which continues to narrow as the temperature is increased.

The frequencies of molecular motion to narrow the resonance curves are of the order of 10^4 sec.$^{-1}$. The n.m.r technique for determining crystallinity (χ) is based upon the assumption that there exists a temperature at which the average correlation time for molecular motion in the crystalline region is $\bar{\tau}_{cc} > 10^{-4}$ second and the corresponding correlation time for the amorphous region is $\bar{\tau}_{ca} << 10^{-4}$ second. If these conditions are met, the n.m.r. absorption appears as a superposition of a narrow resonance and a broad resonance. With crystalline polystyrene, however, there is no temperature at which both a broad and a narrow resonance can be discovered. The area under the individual components of the absorption curve is proportional to the abundance of the nuclei in the corresponding phase of the polymer. Actually, since one ordinarily observes experimentally the derivative of the absorption curve, the area under the absorption is proportional to the first moment of the derivative curve. The procedure involves a graphical separation of the derivative curve into a broad constituent and a narrow constituent. The manner in which the decomposition is made, whether by a straight line or by some reasonable curve, is entirely arbitrary. Although the straight line is commonly chosen for the sake of convenience, any separation of components inherently causes some uncertainty. Wilson and Pake (234, 235) have applied the technique to polyethylene and polytetrafluoroethylene and find (64 ± 5) per cent. crystallinity for the former and about (72 ± 5) per cent. for the latter. They have also established the coexistence of two phases through relaxation time measurements. There are also some problems encountered in the practical measurement of crystallinity from the nuclear resonance line shape. Among them are weakness of the broad component in highly amorphous samples, variation of crystallinity with temperature in many materials in certain temperature ranges, and overlapping of the line-narrowing transitions for the two phases. These have been partially overcome by spin-lattice and relaxation studies.

Slichter and McCall (211, 212) have studied crystallinity in Marlex 50 and DYNK with temperature. They find that at low temperatures $\bar{\tau}_{ca}$ and $\bar{\tau}_{cc} >> 10^{-4}$ second and thus both phases exhibit broad lines. As the temperature increases the chain segments in the amorphous zones, being subject to smaller constraints than chain segments within crystallites, will begin to move. A narrow component appears and $\bar{\tau}_{ca} \approxeq 10^{-4}$ seconds, but $\bar{\tau}_{cc} >> 10^{-4}$ second. The apparent χ in this range bears no relation to the actual χ because the n.m.r. experiment measures motion and χ depends on order. Marlex 50 exemplifies this behavior near 230°. As the temperature is further increased the condition $\bar{\tau}_{cc} >> 10^{-4}$ second $>> \bar{\tau}_{ca}$ may be reached. At this temperature n.m.r. can be used for a valid determination of χ. However, such a temperature does not necessarily exist for all polymers. It has been reported for a nonpolar polymer, rubber, polystyrene, some polar polymers and the partially fluorinated derivatives of polyethylene, that the resonance curves are devoid of compound structures at all temperatures. With such polymers n.m.r. cannot be used to measure crystallinity. The difficulty in determining whether or not the apparent crystallinity can be associated with the degree of order in the polymer or it merely describes the state of molecular motion also has been well illustrated by Slichter and McCall (212) in the case of Marlex 50 and DYNK. They find a marked difference in the chain motion within crystallites of the branched polymer compared to the linear. The difference is ascribed to the existence of lattice defects in the arrays of the branched material arising possibly from the incorporation of chain branch points into the crystallites. It is also found that the line narrowing occurs at a much lower temperature in the branched polymer than in the linear. This supports the view that the high degree of crystallinity in linear polyethylene imposes constraints upon the "amorphous" regions. With a linear polyethylene χ as found by n.m.r. changes little with temperature over a broad range and is in agreement with the data from other methods. However, with branched polyethylene the n.m.r. result changes rapidly with temperature and agrees with the values from other methods over only a short interval of temperature. In fact the vanishing of the broad component above room temperature precludes an n.m.r. study of χ in branched polyethylene at higher temperatures.

It has not been possible to set forth a foolproof procedure to test the validity of the n.m.r. method. The only reasonable criterion is the constancy of the apparent χ over a broad temperature range. In addition, it is not evident *a priori* that all portions of the disordered (amorphous) regions, must necessarily be in motion; conversely it is not evident that regions of order (crystalline) regions, cannot have a fair degree of motion (*e.g.*, oscillations about the chain axis). The mobility of chains in the noncrystalline region is restricted by the spatial distribution of the crystallites and the presence of chain entanglements. Very large values for the second moments obtained for polyethylene terephthalate by Farrow (50) at low temperatures suggest that there are some very small inter-proton distances in the amorphous regions of the polymer. It is not clear, therefore, that the intensity ratio of the two components, which is a measure of non-motion *vs.*

motion, should necessarily be the same as the X-ray crystallinity ratio, which is a measure of order *vs.* disorder. Fuschillo, Rhian and Sauer (72) observe that in polyethylene the proton resonance method gives reasonable agreement with X-ray χ values in the room temperature region. When studied as a function of temperature the resonance method gives a measure of the relative number of nuclei that are not able to reorient above the critical frequency for line narrowing. The ratio of the narrow to broad components of the n.m.r. absorption signal will only be a measure of the crystalline content provided that all the protons in the noncrystalline region are able to reorient at the critical frequency, whereas those in the crystalline region can not. In general this situation will not prevail and the n.m.r. measure of crystallinity will be temperature dependent.

In linear polymers such as nylon where even at room temperatures the amorphous regions show considerable rigidity because of the presence of strong dipolar and hydrogen bond forces, the n.m.r. gives χ values as 95% whereas the X-ray value is only 57%. This shows that in nylon at room temperature the n.m.r. amorphous phase is "crystalline," not in the crystallographic sense, but that its nuclei have similar correlation times for reorientation compared to the nuclei in the crystalline region. This is further supported by the measurements of Fuschillo and Sauer (73) on irradiated polyethylene. They find that the line shapes for irradiated polyethylenes differ appreciably from that for the non-irradiated sample, the principal change being a substantial reduction in intensity of the narrow line component. They find a crystallinity of 93% for the sample irradiated to 5.5×10^{18} *nvt* and the X-ray determinations indicate "zero" crystallinity for it. It appears very strongly, therefore, that the ratio of the number of protons in the crystalline phase and the number of protons in the sample (N_c/N) bears no relation to crystallinity content for irradiated samples. This is simply because the radiation induced cross linking of the amorphous regions of the polyethylene greatly restricts the chain motions in this part of the polymer, thus decreasing the intensity of the narrow line component. The motion of the chains in crystallites in highly branched polyethylene such as DYNK which are clearly shown by n.m.r. may also have an important effect on crystallinity found by other experiments. It may be, for example, incorrect to take the density of crystalline zones in DYNK as the density of a completely linear paraffin hydrocarbon. Similarly, the X-ray scattering factors of moving molecules are different from those of stationary molecules, and thus X-ray value for χ should be reconsidered. The other methods for the measurement of χ also need to be reviewed in the light of the new evidence of crystalline phase motion. Farrow and Ward (51), for example, find no correlation between the three values of crystallinity from infrared, X-rays and density measurements in the case of polyethylene terephthalate. Values from infrared spectra are high, those from X-ray measurements low and those from density fall roughly between the two. The infrared measurements are only correlated with configurational changes affecting the order within individual molecules. Using the X-ray measurements to define crystallinity, it is found that the density of noncrystalline material increases with orientation so that density measurements based on the concept of constant noncrystalline density (equal to the density of amorphous material) are inevitably in error when applied to oriented samples.

Any agreement with X-ray data is only accidental and is illustrated by the temperature variation of the intensity ratio as measured by n.m.r. and X-ray methods. In case of X-rays and other measurements the χ remains almost constant below a certain temperature, whereas the n.m.r. value gradually increases with decreasing temperature (195). The average crystallite size also has an important effect on the temperature behavior. As the temperature is raised, rotational shear waves entering a crystallite from the portion of the chain in the amorphous region will penetrate further and further into the crystallite. Polymers with large crystallites will have still large interior regions shielded from motion. In polymers with smaller crystallites motion will penetrate into a greater fraction of the crystallite volume and the intensity of the broad component will drop more rapidly with increasing temperature.

Collins (39) has also made a comparison of nuclear magnetic resonance and X-ray diffraction methods in polyethylenes of crystallinities ranging from 59 to 94%. The reproducibility of the X-ray values, he finds, is best at low crystallinities and the reproducibility of the nuclear resonance values is best at high crystallinities. The average difference between the nuclear resonance and X-ray crystallinities is 1.8%, which is within the uncertainty of the relative X-ray scattering efficiencies of crystalline and amorphous polyethylenes. The nuclear magnetic resonance method appears to offer definite advantages of reproducibility, ease of sampling and insensitivity to orientation, but extreme care is needed in interpreting the data.

X. CONCLUSION

The most striking aspects of the problem of order in polymers are the developments of stereo-regular polymerizations, observation of polymer single crystals and the determination of the morphology of the spherulites. The study of synthetic polymers is giving greater insight in understanding the more complicated naturally occurring macromolecular structures. Astbury (9) has pointed out that the folded molecular configuration in fibrils with molecules running perpendicular to the fibril direction may be a general phenomenon. For example, the supercontraction in polypeptides is a manifestation of the tendency of long chain molecules to form folded configurations. Bernal (7) considers this simple folding as one of the possible secondary configurations of long chains and, like the spiralization of polypeptides, it is a step toward the formation of the more complex configurations found in nature.

The last five years have seen a complete reconsideration of the arrangement of the molecules in the bulk polymers and the "fringed-micelle" concept is now of limited interest. The phenomenon of crystallization in polymers is still far from being completely understood. No convincing theory has yet been given to explain how the irregular and random-like chain molecules can disentangle and form regular folded configurations. This is especially so in view of the fact that morphological observations on melt crystallized samples do not show any principal difference from the structures obtained from solutions.

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XI. REFERENCES

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