Crystals and Long-Chain Molecules

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Long-chain molecules of sufficiently regular structure can organize into three-dimensional ordered arrays. Such systems are appropriately termed crystalline since they diffract x rays and display all the changes expected in thermodynamic properties when transformed to the disordered or liquid state.[1] The process of crystallization has an important effect on the physical and mechanical properties of polymers. In the molten state a polymer can, depending on the molecular weight, either exist as a liquid of low fluidity or exhibit rubber-like characteristics. In contrast, a crystalline homopolymer exists as a rigid solid of high tensile strength. During the transition, the elastic modulus changes by a factor of 10^3 to 10^5. For example, nylon fibers exhibit high tensile strength and low deformability because of the presence of oriented crystalline regions.

Crystallization takes place over the complete composition range, from pure polymer to very dilute solution. Statistical thermodynamic theories,[2] supported by a substantial body of experimental observations,[1] have established that the crystallization–melting process involving long-chain molecules is a first-order phase transition, albeit a diffuse one.[1] Thus, the influence on fusion of chain length, diluent concentration, and the distribution and concentration of copolymeric units can be predicted.[1,2] Crystallization from the disordered phase adheres to the general mathematical formulation for the kinetics of phase changes.[1] There is, therefore, another class of molecules whose study can lead to a deeper understanding of all aspects of phase transitions. As with other substances, the crystallization of polymers involves nucleation and growth. The growth process is also nucleation controlled. One of the important and unique characteristics of polymer crystallization is the strong influence that the nucleation requirements have in determining macroscopic properties.

Since the classical formulation is followed, one naturally asks why there are still problems associated with the crystallization and melting of long-chain molecules. Although the correct physical–chemical framework has been established, real crystallization processes always yield nonequilibrium systems. Polymer crystallization must be conducted at temperatures well below the equilibrium melting temperature in order to be observed in a reasonable time scale. For example, a normal hydrocarbon, such as $C_{94}H_{190}$, crystallizes very rapidly at only a fraction of a degree below the melting temperature. In contrast, for linear polyethylene, undercoolings of the order of 25–30°C are required in order to obtain the same crystallization rate. As a consequence a polycrystalline system results with its accompanying complexities of structure. Therefore, the macroscopic properties of crystalline polymers are related to the structure of the crystalline regions, their relative arrangement, and the conformation and organization of the polymer chains. Interfacial structures not encountered in low molecular weight substances can also be anticipated. Therefore, the explanation of morphology in molecular terms is necessary in order to understand the properties. We are, therefore, presented with a rather formidable problem which can be studied in many different ways. In the present context we shall be mainly concerned with a review of the properties of crystalline polymers and the deduction of the molecular structure and gross morphology consistent with both macroscopic properties and the direct microscopic observations. These observations unfortunately do not reveal the details of molecular structure which must be obtained by deductive reasoning from the properties. For convenience we consider first the crystallization from dilute solution.

Dilute Solution Crystallization

When crystallized from dilute solution all homopolymers yield the well-known lamella-like crystallites of the type shown in Figure 1. The lamella are about 100–200 Å thick, the lateral dimensions are the order of several microns, and the chain axes are preferentially oriented perpendicular to the wide faces. The directions of the a and b crystallographic axes are preserved throughout; hence the designation "single crystals" has been given to such structures.

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(2) P. J. Flory, *J. Chem. Phys.*, 17, 223 (1949); *Trans. Faraday Soc.*, 51, 848 (1955).

Figure 1. Typical crystals of polyethylene grown from dilute solution.

Density; size-density relation; intensity wide and low-angle x ray
Selective oxidation; end-group location; gas solubility
Swelling; broad-line NMR; glass formation
Infared and Raman spectroscopy

This crystal habit is found with very high molecular weight chains, so that a given molecule must traverse a crystallite many times in order to satisfy the thickness, orientation, and molecular weight requirements. These facts are quite well established. However, there is still an important problem in describing the molecular structure of the interface associated with the basal plane. The reentrant requirement clearly demands some type of "folded chain", the exact nature of which is not a priori obvious.

Two extreme interfacial structures can be envisaged.[1,3] One is an array of regularly folded chains where crystallization is complete except for the minimum number of chain units required to make the fold or hairpin connection between the crystalline sequences. Sequences from the same molecule are adjacent to one another so that a smooth, regular structured, regularly folded, or pleated 001 interface is formed.[4,5] In contrast to this simple structure, if the adjacent reentry requirement is removed the crystalline sequences can be randomly joined with disordered loops of random length.[3,6] The chain units in the interface are in nonordered conformations and traverse an amorphous overlayer before rejoining the crystal lattice. Lamella-like crystallites are formed in either case, so that each structure is consistent with the major conclusion drawn from the electron micrographs. The present state of this technique does not allow for a distinction to be made between a regularly structured or a disordered interface. Structures between these extremes have also been postulated.[7,8] The regularly structured interface affords the simplest explanation for the external shape of the platelets. However, the supporting evidence comes solely from the interpretation of the electron microscope observations.[9,10a] Transmission microscopy reveals

what are apparently perfectly smooth surfaces. Sectorization, pyramidal habits, epitaxial growth, and interfacial dislocation networks have been interpreted in this manner.[10b]

A large number of different properties of such crystals, particularly those of linear polyethylene, have now been studied. An analysis of these properties allows for some definitive conclusions to be drawn with respect to the interfacial structure. Since these results have been comprehensively reviewed elsewhere,[11,12] we limit ourselves here to a brief summary and to the major conclusions that can be drawn from them. Table I contains a list of properties whose interpretation requires a disordered amorphous overlayer. It is found that about 15–20% of the chain units need to be in nonordered conformations to satisfy the data. It is possible to interpret some individual properties in a different way. However, when the complete body of information is examined, the inescapable conclusion is that the interface is deformable and exhibits a glass temperature, and its density, spectral properties, and chemical behavior are those expected for a disordered amorphous region.

There are, however, two sets of experiments whose conclusions are nondecisive. The relation between the enthalpy of fusion and the crystallite thickness can be formally interpreted by either of the extremes in models.[13,14] Another experiment whose interpretation is ambiguous, and consequently controversial, has been the splitting observed in certain infrared modes of crystals formed from mixtures of hydrogenated and deuterated polyethylene.[15,16] Theoretically, the splitting is caused by a nonuniform mass distribution of the two species within the lattice. Since the melting temperatures of the hydrogenated polymer, as well as the monomeric analogue, are 4–6° greater than the corresponding deuterated samples,[16] the composition of the crystals and the solution from which they are formed cannot be the same. Therefore, a nonuniform mass distribution will automatically be established within the crystals, irrespective of morphological detail. Therefore, the splitting of the infrared bands cannot be unequivocally analyzed in terms of the interfacial structure.

The concept of a disordered interfacial structure is compatible with the gross features observed in the electron microscope.[9,17] This structure is still

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(4) A. Keller, *Philos. Mag.*, **2**, 1171 (1957); *Makromol. Chem.*, **34**, 1 (1959); A. Keller, *Polymer*, **3**, 393 (1962).
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(12) L. Mandelkern, "Morphology of Semi-Crystalline Polymers in Characterization of Materials in Research: Ceramics and Polymers", Proceedings of the 20th Sagamore Army Materials Research Conference, Syracuse University Press, Syracuse, N.Y., 1975, p 369.
(13) R. K. Sharma and L. Mandelkern, *Macromolecules*, **3**, 748 (1970).
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couched in general terms, and the finer details remain yet to be determined. For molecules containing more than about 1000 chain atoms the properties are independent of chain length, even for very high molecular weights. Thus, there can be no meaningful contribution to the interfacial structure from end groups and associated "cilia" or other such structures that have been postulated.

The electron microscope has also revealed some finer details of structure. Interfacial dislocation networks are commonly observed when bilayer crystals are formed.[18,19] In order to observe such dislocations, the interfaces must penetrate one another while crystallographic continuity is maintained. Thus, it was thought that such observations offered strong and very compelling evidence for a regular chain folded interface.[20] However, more recent work, utilizing sharp fractions, has established that for linear polyethylene interfacial dislocation networks are only observed when the molecular weight is less than 3000.[19,21] In addition, very specific crystallization conditions are required.[21] Since these dislocation networks are only found with low molecular weight species, they have no substantive relation to the interfacial structure of crystals formed from high molecular weight chains. The apparent observation with high molecular weight species is due to fractionation.[19,21] We can, therefore, note the extreme care that is required in all electron microscopic studies to establish the molecular properties of the sample being examined. Otherwise, erroneous conclusions can easily be drawn. Fractionation according to chain length and composition (in the case of copolymers) can occur quite readily during dilute solution crystallization.

For monolayer crystals, formed under specific conditions, the lamella are truncated with distinct sectors.[4,21] This morphological element is presumed to result from the crystals growing as hollow pyramids. The flat platelets that eventually are observed would then result from drying. A regularly folded interface offers the simplest explanation for this kind of domain structure. Sectorization probably represents the strongest remaining morphological argument for this type of interfacial structure.[10b] However, it is not necessarily a unique interpretation. There is no reason why such structures are incompatible with a disordered interface. In view of the evidence offered above, this latter possibility is in need of investigation.

It is clear that the discovery of lamella structures, by direct electron microscopic observation, marked a major advance in the understanding of the morphology of crystalline polymers. In retrospect, it appears that the major reason that solution-formed crystals were thought to be regularly folded was that it represented the simplest explanation for the external shape of the platelets. There is, however, a large gap in relating the gross external habit to the molecular details of chain structure. Put another way, the direct

microscopic observations do not reveal important details of molecular structure. These must be obtained by other methods.

Crystallization from the Pure Melt

Virtually all properties of polymers crystallized from the pure melt deviate widely from those expected for a macroscopic crystal. The molecular basis for these widely accepted facts has, however, been a matter of some controversy. Lamella-like crystallites are also the primary morphological entity under these crystallization conditions over the complete molecular weight range. It was initially thought that the thickness of such lamella were restricted to about 100–200 Å.[22] Since this thickness is the same order as crystals formed from dilute solution, an identification was naturally made between the two types of crystallites. When it was further assumed that lamella required a regularly folded interface the properties could apparently be quite readily explained by the finite size of the crystallites and contributions from the smooth, regularly structured interface and from defect structures located within the interior of crystallites. Thus, it was thought possible that a crystalline polymer could be viewed as a crystalline matrix within which disordered material or structural defects were embedded. Ample evidence now strongly indicates that the interface is not regularly folded in solution crystals. Consequently, this assumption cannot be carried over to bulk crystallized samples. One must, therefore, admit the possibility of chain units existing in nonordered conformations, which form amorphous regions connecting crystallites, the lamella-like character of the crystallites still being fully recognized.

The selection of the appropriate model is a very crucial matter since it is the heart of the relation between chain structure, morphology, and properties. A molecular understanding of the macroscopic properties of crystalline polymers depends on the resolution of this problem. Macroscopic properties will depend on the morphological forms and the associated chain conformations. The properties of chains in ordered or disordered conformations are quite different from one another.

Recent studies have shown that this problem can be resolved by an analysis of properties. In contrast to crystals formed in dilute solution, all properties are very dependent on molecular weight. This fact has not been always recognized and has consequently led to a great deal of misunderstanding. A comprehensive study of the molecular weight dependence of the properties of linear polyethylene has led to the formulation of a molecular model for the crystalline state which is in accord with the electron microscopic observations.[12]

Contrary to the original concepts, the thickness of the lamella crystallites can vary from several hundred to several thousand angstroms. The crystallite thickness depends on molecular weight for samples crystallized at high temperatures (low undercooling).[23] This result is very important in the interpreta-

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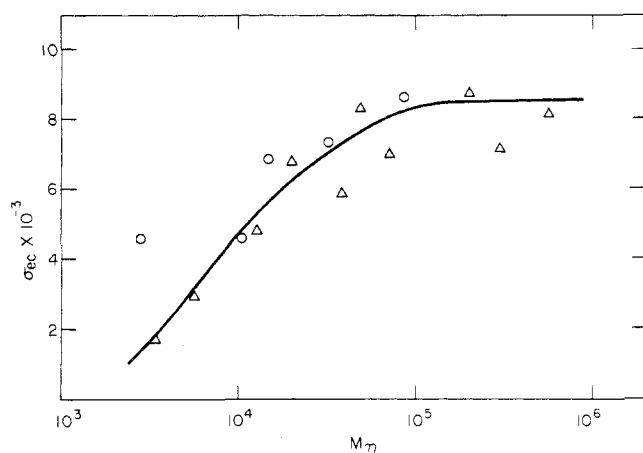(23) L. Mandelkern, J. M. Price, M. Gopalan, and J. G. Fatou, *J. Polym. Sci., Part A*, 4, 385 (1966).

Figure 2. Plot of interfacial free energy σ_{ec} (cal/mol) against molecular weight for bulk-crystallized linear polyethylene.

Figure 3. Plot of density, measured at room temperature, as a function of molecular weight for linear polyethylene fractions.

tion of properties. For chains containing less than about 1000 chain atoms the thickness is comparable to the extended chain length. Hence, "extended-chain" crystals are said to form, in this region.[23,24] As the chain length is increased to about 5000 chain atoms, a slight increase in crystallite size takes place. The ratio of crystallite thickness to extended chain length decreases to about 0.25. With further increases in molecular weight the crystallite size reaches a limiting value of about 1000 to 2000 CH_2 units. Therefore, the ratio of thickness to extended size becomes very small. Despite these large changes in the absolute and relative thickness, the nature of the lamella, as revealed by electron microscopy, is the same. Thus, the observation of lamella crystallites does not by itself allow for the deduction of an interfacial structure.[23,24]

Properties have been found to depend systematically on the molecular weight, or, stated more correctly, on the ratio of crystallite thickness to extended chain length. The interfacial free energy, σ_{ec}, associated with the basal plane of the lamella can be calculated in the conventional manner.[24] The molecular weight dependence of this quantity is shown in Figure 2, where two different methods were used to determine the crystallite size.[23,25] In the "extended crystal" range σ_{ec} has its lowest value the order of 2000–4000 cal/mol of sequences. For molecular weights greater than about 1×10^5, where the relative thickness is very small, σ_{ec} is about 8700 cal/mol, which corresponds to 370 erg/cm^2 for polyethylene. This thermodynamic analysis clearly cannot give any details with respect to the molecular structure of the interface. However, we can deduce that the interfacial structures must be different in the different molecular weight regions. The lowest interfacial free energies are associated with the extended chain crystals. For high molecular weights, the interfacial free energy is unprecedentedly large. It is extremely difficult to reconcile this value with a smooth regularly structured interface.

Other, measured macroscopic properties vary in a quite similar manner. The pattern that is followed is shown in Figure 3 for a very simple property, the
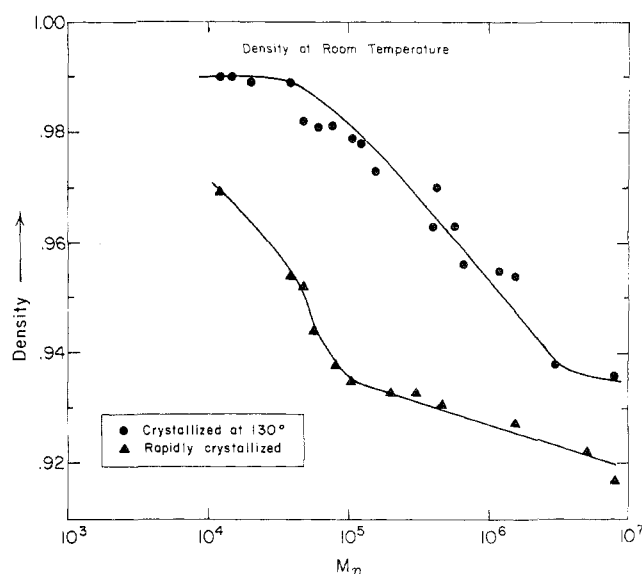
density.[26,27] In this example, the density was determined at room temperature following the two indicated modes of crystallization. The density ranges from 0.99 g/cm^3 to 0.94 for the 130° crystallization and is reduced to 0.92 g/cm^3 for the rapid crystallization. As is indicated in Figure 3, there is a very important and systematic dependence on molecular weight. The density is not restricted to narrow limits, and major deviations from the unit cell value of 1.00 are observed. When the crystallite thickness is comparable to the extended chain length the density approaches that of the unit cell. For higher molecular weights, where the relative crystallite thickness has been severely reduced, the major decreases are observed. These systematic deviations from the unit cell density cannot be attributed to chain ends or associated cilia. The concentration of these species must decrease as the molecular weight increases. Other properties, such as the enthalpy of fusion,[14,28] spectroscopic results,[29,30] wide-angle x-ray diffraction,[31,32] and dynamic mechanical behavior,[33] follow a very similar pattern.

With an understanding of the character of the crystallites and their associated interfacial free energies, as well as the quantitative nature of the deviations of properties from the unit cell, we can return to the central issue of the molecular basis for these deviations. Studies have shown that the lattice parameters do not change over the wide range in macroscopic densities (0.92 to 0.99) that has been developed for linear polyethylene.[34] Thus, there is no experimental basis by which defects within the crystalline lattice can explain the properties in any significant way. Attention therefore must, by necessity, be directed to

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structures external to the crystalline regions.

Contributions from the interfacial region can be anticipated because of the finite crystallite thickness. Such contributions are generally expected from small crystals so their origin is not particularly polymeric in character. However, the magnitude of the interfacial free energy will depend on the molecular structure and thus the chainlike character of the molecules involved. For polymers we must also examine the possibility that there are contributions from chain units connecting crystallites. These would be the amorphous or interzonal regions. The question as to whether such contributions manifest themselves can be answered by examining the quantitative validity of the degree of crystallinity concept.

Classically, the degree of crystallinity calculation involved the additive properties of the crystalline and amorphous phases. The latter represents the properties of the pure melt at the corresponding temperature and pressure. Now one must also be concerned with the possibility of contributions from the interfacial regions. A variety of experimental methods needs to be used to assess this idea rigorously since different properties may be sensitive to different regions. The wide range in properties that is generated by molecular weight fractions presents an ideal set of data with which to test the degree of crystallinity concept. A detailed analysis of the results with molecular weight fractions of polyethylene has been reviewed in detail.[12,27] The major conclusion reached is that the degree of crystallinity is a quantitative concept in accord with the conclusion previously reached with less extensive data.[1] For some properties the simple additivity of the two phases suffices.[12] For others it is found that contributions from the interface must be taken into account.[12] Tentative estimates are that about 5–10% of the units are in the interfacial region. Since amorphous or interzonal regions clearly exist, crystalline polymers must properly be considered to be partially or semicrystalline.

From these considerations one can develop a crystallite model which is the level of order above that of the unit cell. A schematic representation, undoubtedly oversimplified, of such a crystallite is given in Figure 4. There are three major regions, the crystalline, interfacial, and amorphous ones. The lamella-like structures of the crystalline region are represented by the vertical straight lines. These represent a particular ordered chain conformation. The level of imperfection within the crystalline region is no different from comparable monomeric analogues, as evidenced by infrared extinction coefficients[29] and the broad-component contribution to the NMR spectra.[30] Attempts to account for the properties by treating the system as a macroscopic crystal, replete with a large concentration of undefined defects, are unsupported by experiment. In contrast with monomeric systems the interfacial region, or zone, is not sharply defined but rather is quite diffuse. For crystallites of the "extended-chain" type the interface consists of the chain ends and a few of the preceding units. This structure leads to the lower interfacial free energy which, however, is still quite large when compared to that for the smooth interface of a monomeric system. When the crystallite thickness is much smaller than the extend-
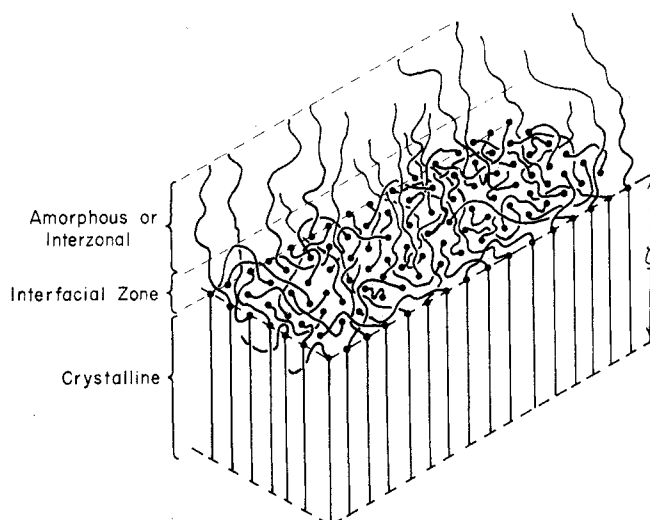

Figure 4. Schematic representation of a crystallite.

ed chain length, some of the chains return to the crystallite of origin, but not necessarily in juxtaposition. Others form the interzonal region and eventually join another crystallite. The interface must again be diffuse and many units thick. The units become distorted and crowded as the chains penetrate this region. The extraordinarily high interfacial free energy is consistent with such a structure.

The interzonal or amorphous regions are composed of chain units which connect crystallites. These units exist in nonordered conformations and their properties are very similar to, if not identical with, the completely molten polymer at the same temperature. These parts of the molecule are not extended or "straightened" out as has been inferred from direct microscopic observation.[35] The strong similarity between the amorphous regions and the pure melt is strongly indicated by the degree of crystallinity calculations, by the direct observation of glass formation in many semicrystalline polymers, and by the fact that for polyethylene the infrared intensity ratio of the gauche bands is the same as in the melt of normal hydrocarbons.[29] Whether there is a precise, quantitative agreement between the two structures remains to be established. They clearly, however, must be very close to one another.

By utilizing this primitive model, the changing interfacial free energy and systematic variation in properties with molecular weight and crystallization temperature can be accounted for in a natural and continuous manner.[12,27] The key quantity in these considerations is the critical nucleus dimension in the chain direction. Utilizing nucleation theory pertinent to finite chains, qualitative agreement is found with experimental results. The same nucleation parameters and concepts are used over the whole molecular weight range and can encompass the large variation in properties.

Properties can be accounted for, in terms of this model, by the relative proportion of the three regions present. For molecular weights greater than about 1 × 10^5 there is a continual decrease in the level of crystallinity, while the crystallite thickness, interfacial free energy, and melting temperature remain un-

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altered. Studies of crystallization kinetics from the pure melt show that the level of crystallinity attained decreases with increasing molecular weight.[36] Thus, the level of crystallinity is dependent on the crystallization mechanism. Although a well-developed phenomenological description of the crystallization process exists, the molecular details still need to be unraveled. An understanding of the molecular basis of crystallization kinetics appears to be the key to the control of the macroscopic properties of semicrystalline polymers.

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Applying Electron Spectroscopy for Chemical Analysis to Industrial Catalysis

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ESCA (electron spectroscopy for chemical analysis), also known as XPS (x-ray photoelectron spectroscopy), is rapidly emerging as an important industrial technique for studying a variety of surface phenomena including catalysis, corrosion, band structure of solids, adhesion, and surface contamination. Because of the broad chemical and economic significance of catalysis, ESCA is being extensively explored as a means of obtaining new insights into both catalytic properties and phenomena.

The information contained in an ESCA spectrum which makes it particularly suited for catalyst investigations is the determination of elemental surface composition, chemical bonding of surface atoms, and chemical and physical changes on the catalyst surface which may occur as a consequence of reaction. In this Account, the manner in which ESCA can be used to investigate catalytically important phenomena will be described. However, before proceeding with applications to specific catalyst systems, a brief review of some of the fundamental information inherent in an ESCA spectrum will be discussed. This will be followed by a general description of sample preparation and handling.

For a more detailed description of the fundamentals of ESCA, the reader is referred to the excellent books of Siegbahn et al.,[1,2] as well as numerous review articles encompassing a wide variety of applications.[3]

Fundamentals of Electron Spectroscopy

In an ESCA experiment, the sample under high vacuum (10^{-8}–10^{-10} Torr) is irradiated by a source of low-energy x rays, generally Al Kα (1486.6 eV) or Mg Kα (1253.6 eV), and the kinetic energy of the ejected electrons is measured under conditions of high resolution and precision. A photoelectron spectrum is a plot of the number of electrons detected vs. their kinetic energy. The kinetic energy of a photoelectron depends on the energy of the exciting radiation and the energy with which the electron is bound to its nucleus. The core electrons are those which are generally monitored in an ESCA measurement. Even though they are not directly involved in chemical bonding, their energies are influenced by the chemistry involved in bond formation. The binding energy of the electrons is calculated from the energy of the exciting x radiation and the kinetic energy of the electrons which escape from the sample without significant energy loss using Einstein's photoelectric equation

$$E_{\text{BE}} = E_{\text{x ray}} - E_{\text{KE}}$$

Although the x-ray photons penetrate deeply into the sample, the electrons which escape without energy loss come from the outermost surface layers since low-energy electrons have very short mean free paths in solids. It is estimated that these electron escape depths range from about 10 Å in metals to about 100 Å in organic polymers. Thus, the electrons detected in an ESCA experiment are representative of a very small amount of material, material which is present on the surface of the sample. Extreme care must

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(3) Only a few of the numerous review articles on applications of ESCA are cited here: (a) D. M. Hercules, *Anal. Chem.*, **42**, 20A (1970); (b) J. M. Hollander and W. L. Jolly, *Acc. Chem. Res.*, **3**, 193 (1970); (c) W. N. Delgass, T. R. Hughes, and C. S. Fadley, *Catal. Rev.*, **4**, 179 (1970); (d) W. E. Swartz, Jr., *Anal. Chem.*, **45**, 788A (1973); (e) W. Bremser, *Fortschr. Chem. Forsch.*, **36**, 1 (1972); (f) W. L. Jolly, *Coord. Chem. Rev.*, **13**, 47 (1974); (g) D. M. Hercules and J. C. Carver, *Anal. Chem.*, **46**, 133R (1974); (h) C. R. Brundle, *J. Electron Spectrosc. Relat. Phenom.*, **5**, 291 (1974); (i) J. S. Brinen, *ibid.*, **5**, 377 (1974).

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