POLYETHYLENE: PREPARATION, STRUCTURE, AND PROPERTIES

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I. INTRODUCTION AND SCOPE

Long considered unpolymerizable, ethylene was first converted to solid polymers in March, 1933, by Fawcett and Gibson, working in the laboratories of Imperial Chemical Industries, Ltd., at Winnington (373). As a part of an extensive study of the effect of high pressures upon chemical reactions, a mixture of ethylene and benzaldehyde had been subjected to pressures up to 1400 atm. and temperatures up to 170°C. but without apparent reaction. When the autoclave was opened, however, a white waxy solid was found coated on the inner walls. The benzaldehyde was recovered unchanged, and the solid product appeared to be a polymer of ethylene. Repetition of the experiment with ethylene gave only trifling amounts of solid product; since violent explosions occurred when the pressure was increased, the experiments were abandoned. After an interval during which other research efforts were pressed, experimentation with ethylene at high pressure was resumed, and in December, 1935, polyethylene was rediscovered (139, 140, 374). The potential industrial value of the material was recognized, and the trade-mark *Alketh* (later *Alkathene*) was registered by Imperial Chemical Industries. Further experiments showed that explosions could be prevented by close control of minute amounts of oxygen in the ethylene. Formidable problems of design of high-pressure equipment were solved, and by the end of 1938 a ton of polymer had been made. The electrical and mechanical properties of polyethylene fitted it for applications in electronics, especially radar, and with the outbreak of World War II the supply was preëmpted for military use. Production was increased as rapidly as possible, yet supply never matched demand. Even to the present day, new applications of polyethylene have kept the polymer in short supply.

Several reviews of the early work on polymerization have appeared (10, 103, 130, 166, 223, 347, 406, 412, 490), as well as a review of early applications (230). The polymerization of ethylene in comparison with other olefins has been discussed (212, 372). Steegmuller (478) has discussed in a review of catalysis and polymerization the optimum conditions for polymerizing ethylene. The German practice during the period 1940–45 has been summarized elsewhere (204, 205, 207, 250, 450) and in the official reports of investigators sent into Germany after the end of the war (214, 264, 411). The electrical properties of the early polyethylenes are described in detail by Myers (341).

In the present review pertinent work on the polymerization of ethylene and the structure and properties of polyethylene published up to August, 1956, has been surveyed. The discussion of two important topics—(*i*) the melting and crystallization of polyethylene and (*ii*) its dynamic mechanical properties—has not been covered in this review. A recent review of the crystallization of polymers (312) covers adequately the important facts on the crystallization and melting of polyethylene. A summary of the dynamic mechanical properties of polyethylene would not be useful without adequate discussion of the dynamic mechanical properties of polymers in general, which is beyond the scope of the present work. No attempt has been made to include every reference in print, especially those in recent trade publications which may contain valuable information but lack detailed documentation.

II. EARLY WORK ON POLYMERIZATION

Historically, the first synthetic hydrocarbon high polymer was probably polymethylene, produced from diazomethane in 1898–1900 (21a, 371a). The first hydrocarbon polymer which resembled present-day high-pressure polyethylenes was very likely the solid obtained by Lind and Glockler (299a) by subjecting ethane to a semicorona discharge, though these investigators did not characterize the product as polyethylene.

Although in this review attention will be devoted mainly to the technically successful production of solid polyethylenes by the application of pressures above 500 atm., a vast amount of preliminary investigation must not be overlooked. Some of this work was directed to the production of gasoline or lubricants from ethylene by high pressures in the presence of various free-radical generators, with or without ultraviolet light or photosensitizing agents. As early as 1927 ethylene and its homologs had been converted to oils by boron fluoride catalysts with cobalt as promoter (366); boron fluoride with hydrogen fluoride was also used (201). Liquid mixtures of open-chain, cyclic, and aromatic hydrocarbons were formed by polymerizing ethylene at high pressures in the presence of phosphoric acid or anhydride at temperatures up to 800°C. (111, 120, 220, 221, 222, 310); other catalysts included air (527a), oxygen (292a), aluminum chloride (524), nickel (256), and titanic acid (382). At room temperature, olefins of low molecular weight were formed and stabilized by hydrogenation (111). The explosive decomposition and polymerization of ethylene to oils at 50 atm. and 380°C. was reported (128). Several papers were published on the polymerization of ethylene by free-radical initiation (30, 105), particularly using biacetyl (413), ethylene oxide (150), methyl radicals (413, 414, 459), and tetraethyllead (98).

McDonald and Norrish (318) found in 1936 that when ethylene was irradiated at pressures below 1 mm. with light from a hydrogen discharge tube a solid polymer was deposited. This discovery led to much photochemical work, in particular with acetone (293, 499), ethyl iodide (232), mercury (294, 295), cadmium (475, 476), and zinc (177) as photosensitizers. Ethylene was early condensed to polymers of low molecular weight by the action of sulfuric acid in the presence of mercuric and cupric sulfates (38). The formation of aluminum alkyls during polymerization was noted (181), but the discoverers failed to realize the significance of this finding. Polymers of low molecular weight have also been produced in the electric discharge (129, 325, 337). Catalytic polymerization at prevailing atmospheric pressures with cobalt and iron catalysts containing promoters was investigated at an early date (254, 257, 258, 259, 260, 261, 399, 458), but the results were very poor and the products were of low molecular weight. Experiments at pressures up to 1800 atm. gave no better results (251, 252, 253, 493, 494, 495, 496, 497, 498).

III. COMMERCIAL POLYMERIZATION OF ETHYLENE

Until recently, all useful polymerization processes for preparing solid polymers of ethylene have been based on the fundamental discovery of chemists at Imperial Chemical Industries that ethylene could be converted to solid polymers in the presence of small concentrations of oxygen, organic peroxides, or other suitable catalysts by the application of high pressures (140).

Within the past five years, new methods of polymerizing ethylene have been developed and are at the present time in the process of translation from laboratory and pilot plant to production units. They depend upon lower pressures (from 1 to approximately 50 atm.) and types of catalysts quite different from those formerly used. Thus there are now in existence two distinct commercial processes for the polymerization of ethylene, designated simply as high-pressure and low-pressure processes. One of the low-pressure processes has been developed by Ziegler and his associates at Mülheim. This so-called Ziegler process has been licensed by at least seven groups in the United States (including Union Carbide and Carbon Corporation, Koppers Company, E. I. du Pont de Nemours and Company, Dow Chemical Company, Goodrich-Gulf, Hercules Powder Company, and Monsanto Chemical Company) and is receiving thorough study at the present time. Another low-pressure process, the Phillips process, is an outgrowth of study of the Fischer–Tropsch synthesis in the United States by the Phillips Petroleum Company. Several firms have evinced sufficient interest in the Phillips process to secure licenses (among them Union Carbide and Carbon Corporation, W. R. Grace & Company, M. W. Kellogg Company, and Celanese Corporation of America). In addition, the Standard Oil Company of Indiana has developed catalysts which are effective at low pressures in polymerizing ethylene and has granted a nonexclusive license to the Eastman Kodak Company and Spencer Chemical Company. These processes are all discussed below.

A. HIGH-PRESSURE POLYMERIZATION

Conventional high-pressure polyethylene has been made in the United States since World War II, principally by the Bakelite Division of Union Carbide and Carbon Chemicals Corporation and by E. I. du Pont de Nemours and Company under license from Imperial Chemical Industries. (Other later licensees include Monsanto Chemical Company, Dow Chemical Company, Spencer Chemical Company, Koppers Company, Eastman Kodak Company, and National Petro-Chemicals Corporation.[1]) Imperial Chemical Industries controlled the basic patent in the United States (139), which has now expired. This patent broadly covered polymers consisting essentially of —CH_2— groups, melting in the range 100–120°C., characterized by a crystalline structure as revealed in x-ray analysis, and having a molecular weight above 6000. Solid polymers are obtained by mixing ethylene with approximately 0.01–5 per cent oxygen, compressing the mixture to at least 500 atm. pressure, and heating in a well-stirred autoclave at 200°C. or above (374). Upon release of the pressure a solid polymer separates, and the unpolymerized ethylene may be recycled or sent to an adjoining process to be made into ethylene oxide and its derivatives. It is of the highest importance that the incoming ethylene stream be free from impurities, particularly acetylene (normally 99.5 per cent ethylene is required). Usually the amount of oxygen is controlled by reducing the oxygen content of the incoming ethylene stream to 0.001 per cent and adding the required amount.

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[1] National Petro-Chemicals Corporation is a joint venture of National Distillers Products Corporation and Panhandle Eastern Pipeline Company to manufacture polyethylene resin. The products are marketed by U. S. Industrial Chemicals Company, a division of National Distillers.

It was found (374) that increasing the pressure increased the molecular weight of the product and accelerated polymerization, and that increasing the temperature accelerated polymerization but gave a product of lower molecular weight. Increasing the oxygen content also reduced the molecular weight, presumably by increasing the number of free-radical centers where polymerization could start. The optimum conditions were difficult to define, but seemed to be 1500 atm. pressure, 0.03–0.10 per cent oxygen, and a temperature of 190–210°C. Percentage conversion varied from 6 per cent at 0.01 per cent oxygen to 25 per cent at 0.13 per cent. With temperature and catalyst constant, the following pressures gave products of the molecular weights indicated: 500 atm., 2000; 1500 atm., 6–12,000; 3000 atm., 12–24,000.[2]

1. Diluents

Since rapid transfer of heat is a critical factor in obtaining a controllable polymerization, diluents have been used: cracking still gases (374), benzene (79, 132, 143, 175, 185, 265, 284, 285, 381, 383, 385, 428, 429, 430, 431, 433, 448, 471), toluene (143), xylene (143, 381), methanol (79, 448), water (47, 50, 117, 183, 184, 206, 213, 282, 283, 284, 285, 320, 433, 451, 452, 471, 536), *tert*-butyl alcohol (79, 184, 186, 213, 446), chlorobenzene (175, 284, 285, 471), bromobenzene (471), liquid ammonia (527), methylcyclohexane (448), isobutane (448), isoöctane (284), propylene (184, 471), isobutylene (184, 471), and styrene (471).

The addition of an emulsifier to aqueous mixtures is said to be beneficial (320, 452), as well as control of pH either at 11–14 with sodium hydroxide or sodium phosphate (383) or at 7–11 with sodium bicarbonate or sodium phosphate (47). Control of pH at 2–4 with hydrogen chloride gave a shorter induction period, high intrinsic viscosity, and improved yield (183).

2. Catalysts

Steegmuller has discussed the effects of catalysts in the polymerization of ethylene (477). In addition to elemental oxygen (124, 280, 374) many other catalysts have been used. These include peroxides such as *tert*-butyl hydroperoxide (428), *tert*-butyl peroxide (434), methyl peroxide (384, 385), ethyl peroxide (384, 385, 446), lauroyl, tetrahydronaphthalene, urea, and acetyl peroxides (122, 123), and benzoyl peroxide (14, 50, 122, 123, 282, 283, 446); per acids and esters such as peracetic acid (122, 123), persuccinic acid (122, 123, 283), diethyl peroxydicarbonate (79, 320, 444, 451, 486, 526), di-*tert*-butyl peroxydicarbonate (167), and *tert*-butyl perbenzoate(432, 448); alkali metal persulfates, e.g., K_2SO_5 (47, 206) and $Na_2S_2O_8$ (121, 123); and hydrogen peroxide (206). Some of these catalysts require high temperatures and pressures; others are active at moderate temperatures and pressures.

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[2] Early values for the molecular weight of the polymer were estimates for comparative purposes only. They were calculated from viscosity measurements by a reasonable assignment of a value to K and α in the Staudinger equation, $[\eta] = KM^{\alpha}$, or some simple modification of this equation, in which $[\eta]$ is the intrinsic viscosity, K and α are constants for a given solvent-polymer system, and M is the molecular weight.

Diborane (0.2 per cent) is an effective catalyst at 55°C., giving polymers which soften at 111–123°C. depending on the pressure (2150–4500 p.s.i.) (189). 3,6-Diphenyl-*s*-tetroxane or polyperoxides from acetone, methyl ethyl ketone, or other ketones have been used (433), as well as 2,2-bis(*tert*-butylperoxy)butane (43). Hypochlorites such as calcium hypochlorite tetrahydrate have been used (186), with a buffer of alkali borates, phosphates, or carbonates.

Nitrogen compounds found effective in catalytic amounts are the amine oxides of trimethylamine, aniline, and dimethylaniline (117); azines such as benzalazine and diphenylketazine (429); azo compounds (262, 284), specifically α,α'-azobis-(α-methyl)-γ-carboxybutyronitrile added in water (425) and α,α'-azodiisobutyronitrile (213); dimethyl azodiisobutyrate (537); azodisulfonates (125); the sodium salt of *N*-chloro-*p*-toluenesulfonamide or Chloramine-T (186, 446); the sodium salt of *N*-chlorobenzenesulfonamide or Chloramine-B (446); oximes from acetone, cyclohexanone, benzoin, D-camphor, benzil, and butyraldehyde (262, 430); hydrazine sulfate and *N*,*N'*-dibenzoylhydrazine (184); and nitrosoacetanilide (125).

Cadmium, zinc, and magnesium have been used in liquid ammonia at pressures up to 10,000 atm. (527); magnesium, zinc, cadmium, and mercury resulted in increased yields and higher molecular weights when used with peroxy catalysts in organic diluents at 30–100 atm. and 150°C. (448). Peroxides with silver or similar ions or metals at 0°C. are said to have produced polymers melting at approximately 120°C., with d_{25} = 0.9745 g./cc. (125). The use of an "Alfin" catalyst (allylsodium, sodium isopropoxide, and sodium chloride) in pentane at 0°C. has been reported (42), but difficulties encountered in attempting to repeat this work make it appear doubtful that the experiments were done with a pure "Alfin" catalyst (335).

Organometallic compounds have been used as catalysts for the polymerization; these include tetraethyllead (262), butyllithium alone at 600–1000 atm. at 70°C. (185) and in combination with nickel on kieselguhr at 48°C. and 1000 p.s.i. pressure (132), ethylmagnesium bromide and ethylzinc at 400–1500 atm. and 100–400°C. (431), an aluminum chloride complex (134), aluminum chloride plus ethyl chloride at atmospheric pressure and 0–20°C. (these conditions produced C_{10}–C_{20} polymers) (535), and beryllium, aluminum, gallium, and indium alkyls at 200–250°C. and 400 atm. pressure (544). (Under other conditions the beryllium, indium, and aluminum alkyls give only dimers of ethylene and homologous olefins (538, 543).)

Solid catalysts have also been used, of the hydroforming or Fischer–Tropsch type. These include silica–alumina containing nickel or cobalt at 200–300°C. and pressures below 500 p.s.i. (90); nickel oxide on silica gel with alumina promoter at temperatures as low as 20°C. and pressures of 200 p.s.i. (16); nickel or cobalt on an active charcoal support at pressures up to 20,000 p.s.i. and temperatures from 15° to 175°C. (the higher pressures and temperatures were required for solid polymers) (378, 380, 381); nickel or cobalt on kieselguhr with copper, silver, or other promotor at 300°C. and 500 atm. pressure (44); chromia–alumina with admixtures of tungsten(VI) oxide, zirconium(IV) oxide, and sodium, lithium, or potassium promoters (143); partially reduced molybdenum(VI) oxide with cobalt molybdate, γ-alumina, titanium(IV) oxide, or zirconium(IV) oxide (198, 377, 427, 550).

The addition of cyclohexane in 0.05–15 per cent concentration is said to act as a chain transfer agent to control branching, thus resulting in a polymer of high density, high stiffness, and good moldability (the process was believed to give a straight-chain polymer, but more recent work indicates that this is unlikely) (165). The use of stainless steel polymerizing equipment is reported to give faster reaction rates, higher yields, and fewer impurities than is possible in vessels made of ordinary low-carbon steel (536).

B. LOW-PRESSURE POLYMERIZATION

Recently the polymerization of ethylene has been accomplished at 1 atm. and somewhat higher pressures. One of these processes utilizes triethylaluminum and titanium(IV) chloride in an elegantly simple laboratory procedure (538, 545, 546). A remarkable discovery was the effect of traces of other metals. Polymerization-active catalysts are not obtained in general if the reaction between the aluminum alkyl and the heavy metal ion present in traces results in the free colloidal metal. Addition of nickel chloride, for example, yields free nickel, and this combination with triethylaluminum leads to dimers of olefins only (543, 546); a similar result is found with iron and silver. Some metals show no activity. The most active catalysts are triethylaluminum with a few hundredths of a per cent of added titanium(IV) chloride. Presumably the titanium is present in an organic complex. The effect of such an amount of titanium is very marked, but zirconium, and almost any of the elements of the fourth, fifth, and sixth groups of the periodic system, including thorium and uranium, are effective. Diethylaluminum chloride does not polymerize ethylene even at 100°C. and 100 atm. pressure, but if a trace of titanium(IV) chloride is added, polymerization proceeds exothermically at normal pressure (544, 546).

In the polymerization as described by Ziegler (544, 546) about 1 per cent of the catalyst by weight, based on ethylene, is suspended in a suitable oil and ethylene is bubbled through rapidly at room temperature. Ethylene is completely absorbed and the yield of polymer is quantitative; no recycle is required. Recent patents describe the use of Ziegler's catalysts and illustrate the variety of combinations of organometallic compounds and salts which can be used: simple alkyl aluminums with titanium(IV) chloride (539); iron with R_nMX where M is a metal of the third periodic group (542); a variety of substituted aluminum hydrides (e.g., $RAlH_2$, R_2AlH, R_2AlX, R_2AlOR) with R_2AlB (where B may be $-N(CH_3)_2$, $-N(CH_3)C_6H_5$, $-NR(COR)$, $-SR$, $-OCOR$, $-OSO_2R$) and a compound (usually a halide) of a metal of Group IV, V, or VI (540); dimethylmagnesium or propylmagnesium chloride, or diethylzinc, or phenylmagnesium bromide with titanium(IV) or zirconium(IV) chloride, or tetrabutyl orthotitanate (541).

In contrast to the high-pressure polymer, the low-pressure polyethylenes have few short-chain branches. This can be shown by the absence of an absorption peak at 7.25 μ in the infrared spectrum (467, 546). The molecular weight can be varied from 10,000 to several million. The handling of polymers having molecular weights of 50,000 to 100,000 on conventional equipment presents difficulties; new techniques will be needed with polymers of molecular weight above 100,000 for commercial exploitation. The properties and applications of these materials have been described (174, 469).

The work of Natta and Ziegler with 1,2-olefins (328, 349, 351, 352) has resulted in crystalline, high-melting polymers with characteristics very different from those shown by the commercial polymers hitherto produced. Heterogeneous solid catalysts are used. There is no agreement as yet regarding the mechanism of their action and the relation between these catalysts and other solid catalysts developed in the United States by the Standard Oil Company of Indiana and the Phillips Petroleum Company.

The Phillips patents disclose (91, 388) a calcined chromium(III) oxide catalyst supported on silica–alumina; it can be used in a liquid- or vapor-phase polymerization. Conversion of ethylene to polymer is quantitative, using a fixed-bed catalyst at 88°C. and a pressure of 600 p.s.i. The catalyst can also be used in suspension. Numerous promoters (nickel, thorium, iron, manganese, uranium, vanadium, molybdenum, tungsten, zirconium, etc.) may be used. The crystalline melting point of the resulting polymers such as Marlex 50 is 113–127°C., the density is about 0.96, and the degree of crystallinity as measured by x-ray analysis is 50 per cent greater than the crystallinity of the conventional high-pressure polyethylenes, or above 90 per cent (231).

Recently a series of patents controlled by the Standard Oil Company of Indiana has been issued, claiming the use of a wide variety of metals and metallic oxides as catalysts for the polymerization of ethylene at moderate temperatures and pressures in a suitable liquid medium. Included are combinations of an alkali metal and an oxide of Periodic Group VIA (336), an alkali metal hydride and an oxide of Group VIA (144), a nickel–cobalt alloy supported on activated carbon in a hydrocarbon medium (473), partially reduced nickel and cobalt oxides (136), lithium (or sodium) aluminum hydride and an oxide of Group VA (145), γ-alumina, titania, and zirconia with partially reduced molybdena (135, 379), lithium or sodium borohydride and an oxide of Group VA (146), borohydrides with an oxide of Group VIA (147, 149), nickel oxide with an alkali metal hydride (141), nickel oxide with an alkali metal borohydride (142), an alkaline earth carbide with an oxide of Group VIA (453), and the hydrides of Group II together with a metallic oxide of Group VIA (148).

Polymerization can also be accomplished by irradiation with γ-rays, x-rays, or neutrons. The efficiency of the process is low, but this method has the advantage of producing polymer free from catalyst, solvent, or other foreign matter. Liquid ethylene is polymerized more rapidly than compressed ethylene, as might be anticipated. In one example, ethylene at 12°C. and 470 atm. pressure underwent a 4 per cent conversion to polymer during exposure for a few hours to 60 millicuries of Co^{60} (59). Work in this field has only started, and it is difficult now to assess progress (20, 94, 298, 313).

In conclusion, a recent report (281a) should be noted, which states that laboratory polymers similar to the Ziegler linear polyethylenes (546) have been made at extremely high pressures (7000–7500 atm.), using as catalysts α,α'-azobisisobutyronitrile, α,α'-azobis(α,γ-dimethylvaleronitrile), 1,1′-azobiscyclohexanecarbonitrile, or benzoyl peroxide in various diluents such as benzene, isoöctane, and methanol. These polymers had crystallinity values 30 per cent greater than those of the conventional high-pressure polyethylenes.

C. KINETICS AND THERMODYNAMICS OF POLYMERIZATION

Studies of the kinetics of the polymerization of ethylene were first reported by Pease (370, 371), who investigated the apparently uncatalyzed process up to 10 atm. at 350–600°C.; in the formation of polymers of low molecular weight, the process was of second order with an abnormally low temperature coefficient. Polymerization in the presence of oxygen was first reported in 1931 (291, 292).

Study of the homogeneous polymerization of ethylene in an isothermal bomb at 315–380°C. indicated a bimolecular process, with an activation energy of 37.7 kcal./mole (267, 268). Later work indicated that the reaction is not a simple bimolecular one, that it is autocatalytic, that oxygen accelerates the rate of polymerization, and that at 377°C. the energy of activation is about 43.5 kcal./mole (487, 488). Support for the chain-reaction mechanism was provided by the discovery that small amounts of nitric oxide inhibit the polymerization of ethylene at 500°C. (70). Bryant has determined (53) that initiation and chain-propagation steps are thermodynamically favorable, that chain transfer reactions vary from favorable to unfavorable, and that chain termination by pairs of radicals is very favorable.

The polymerization of ethylene in liquid naphthalene at pressures sufficiently high to assure the absence of a two-phase system showed that the reaction is initially of second order and is homogeneous, but is later complicated by other processes; an apparent order of 2.6 was reached but not confirmed for the liquid-phase reaction (443). A second-order process characterized the reaction in the gas phase. At identical concentrations and temperatures, reaction rates in the gas and liquid phases were approximately the same, but the authors were unable to come to any conclusion as to whether the reactions were of the same order. The energy of activation was 40.0 kcal./mole for the liquid-phase reaction and 42.1 for the gas-phase reaction. The effect of temperature on the primary reaction was to double the rate for every 14°C. rise in the range 340–415°C.

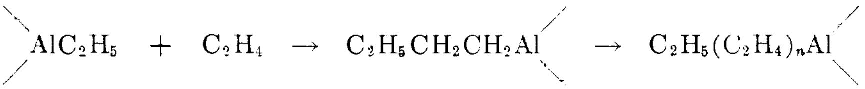
The reaction kinetics of polymerization of ethylene induced by methyl radicals, produced by photolysis of acetaldehyde at 200–350°C., has been studied (401, 402). The amounts of photolysis and polymerization were found nearly linear with time in the early stages of the reaction. From the temperature coefficient of the reaction, the energy for the process, ethylene plus a methyl radical, was estimated to be 6.8 kcal./mole.

The rate of dimerization of ethylene on a nickel catalyst at 260–460°C. was found to be directly proportional to the ethylene pressure (400). The products were 50 per cent 1-butene and *cis*- and *trans*-2-butene in equal amounts.

A summary of the heats of polymerization of forty-two vinyl compounds reveals that ethylene possesses the highest value (421). Equations have been formulated which express heats and free energies of polymerization of ethylene to linear molecules, having from three to an infinite number of methylene units, and at temperatures from 0 to 1500°K., as functions of the number of ethylene units per molecule (228). The rate of the homogeneous thermal polymerization of ethylene has been calculated in satisfactory agreement with experiment by using the Eyring method of activated complexes (225).

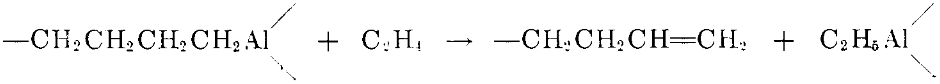
Despite the fact that a great deal of work has been done on the mechanisms and kinetics of vinyl polymerization in general, some of which is applicable to polyethylene (this work has been reviewed elsewhere; see references 15, 104, 157, 218, 314), it is evident from the foregoing summary that more work needs to be done before the polymerization of ethylene is well understood.

The action of the Ziegler catalysts has not been discussed in the literature in detail, but Ziegler describes the process as follows (546). The primary step is the addition of the aluminum or other metal alkyl to an ethylene molecule, followed by addition of ethylene in a step-by-step metal-organic synthesis to build up a high polymer.



$$\text{AlC}_2\text{H}_5 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{Al} \rightarrow \text{C}_2\text{H}_5(\text{C}_2\text{H}_4)_n\text{Al}$$

The intermediate aluminum alkyl does not undergo deactivation or annihilation easily, as occurs with the free radicals of the conventional high-pressure process. The termination has been postulated to be by hydrogen transfer, yielding an olefin and re-forming an aluminum alkyl.



$$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Al} + \text{C}_2\text{H}_4 \rightarrow -\text{CH}_2\text{CH}_2\text{CH}{=}\text{CH}_2 + \text{C}_2\text{H}_5\text{Al}$$

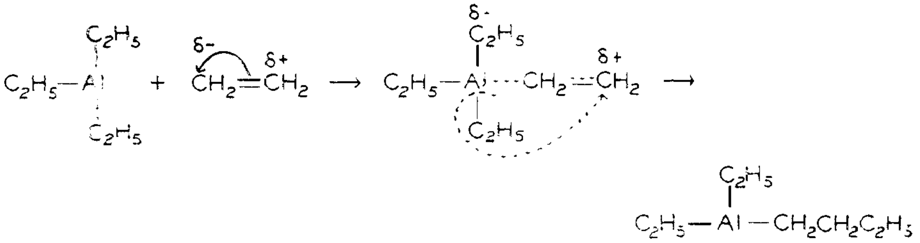
This termination step is presumed to be catalyzed by small amounts of nickel, cobalt, and certain other metals, since with them present only the dimer is produced (butylene in the case of ethylene). Any one of several of the metals of the fourth, fifth, and sixth groups of the periodic table (added as halides or acetonylacetonate complexes, reducible by the metal alkyl not to the free metal but probably to some lower state of oxidation, which remains present in the form of a complex) results in rapid polymerization of ethylene to polymers of high molecular weight; such combinations as triethylaluminum and titanium(IV) chloride owe their effectiveness probably to an ability to activate ethylene molecules at a solid surface.

Recent studies of the kinetics of ethylene polymerization by triethylaluminum alone indicate (352) that reaction proceeds by stepwise addition of ethylene as mentioned above. At a temperature above 100°C., the decomposition rate of the aluminum alkyl becomes appreciable and polymerization proceeds catalytically. The experimental data on reaction rate and molecular = weight distribution of the polymer indicate that the following two termination processes operate simultaneously (neither one alone can explain the results). According to either termination process, each polymer molecule would contain one terminal double bond.

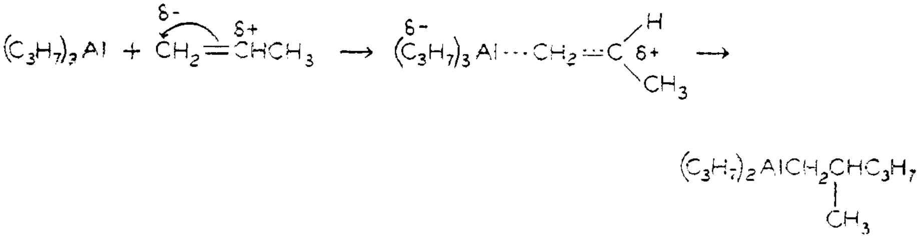
$$\left\{\begin{array}{l} RR'AlC_nH_{2n+1} \rightarrow RR'AlH + C_nH_{2n} \\ RR'AlH + C_2H_4 \rightarrow RR'AlC_2H_5 \end{array}\right.$$

$$RR'AlC_nH_{2n+1} + C_2H_4 \rightarrow RR'AlC_2H_5 + C_nH_{2n}$$

Robinson (426) has pointed out the essential similarity of the action of the Ziegler catalysts to the mechanism of addition of nucleophilic reagents in general, such as the Grignard reagent. By this mechanism, the ethylene molecules are activated and the first step of the process is the formation of an aluminum complex which becomes stabilized by a shift of an ethyl group with its electron pair.



Dimerization and subsequent polymerization of olefins other than ethylene take place in the manner predicted by the Robinson-Ingold theory. Thus with propylene, reaction occurs as indicated.



Olefin molecules become exceptionally well oriented at the solid surface of the Ziegler catalyst, by a mechanism not yet understood, and a rapid organometallic reaction like the first step occurs in order to grow a polymer of very high molecular weight.

IV. CRYSTAL AND MOLECULAR STRUCTURE

The properties of polyethylenes prepared under various conditions of polymerization vary widely. This variation in properties is inherently determined by the differences in the molecular structure that result under different conditions of polymerization. Consideration of the properties of the bulk polymer must include not only the detailed molecular structure but also the arrangement of the polymer chains into ordered or crystalline regions and the arrangement of these crystalline regions.

The following structural features are of importance in considering the properties of polyethylene.

(*1*) *Crystal structure of the unit cell:* The precise geometric arrangement of the methylene groups with respect to each other in the crystalline regions.

(*2*) *Percentage crystallinity:* The weight per cent of the total material that is ordered.

(*3*) *Size and shape of crystallites or aggregates of crystallites:* The crystallites formed on cooling molten polyethylene tend to form aggregates. Under certain conditions the crystallites are massed in spherical clusters of radiating needles, called spherulites (48, 52, 67, 188, 394, 419). The conditions of heating and cooling and the molecular parameters that determine the form of the spherulites in polyethylene are of considerable interest.

(*4*) *Branching:* Because of the various kinetic possibilities of chain transfer by a growing polymer chain the polyethylene molecules may not be linear.

(*5*) *Presence of unsaturation and oxygen-containing groups:* Either because of the kinetics of termination or because of other attendant reactions with initiator or other impurities, the polymer molecules may contain oxygen or unsaturated groups.

Ever since the discovery of polyethylene, considerable effort has been devoted to the study of these structural details of the polymer by infrared absorption, x-ray diffraction, microscopy, solution properties of the polymer, and other means.

A. INFRARED SPECTRUM

Infrared absorption has been found to be a valuable tool in the study of the fine structure of polyethylene. In table 1 are listed the absorption bands in the 2 to 15 μ region that have been observed in polyethylene (1, 39, 56, 100, 158, 248, 249, 274, 436, 439, 440, 441, 467, 482, 501, 502) and their assignment to the various molecular vibrations. Infrared study has recently been supplemented by Raman spectra of crystalline polyethylene and long-chain hydrocarbons (357, 534). The assignments of eight Raman-active unit-cell fundamentals were made.

Of particular interest are the bands in the 1300 to 1500 cm.$^{-1}$ region and the doublet at 721–730 cm.$^{-1}$ The doublet at 721–730 cm.$^{-1}$ is characteristic of solid polyethylene and crystalline paraffin hydrocarbons. When the sample has been cooled to 4°K., the band at 730 cm.$^{-1}$ becomes very sharp, while its companion at 720(721) cm.$^{-1}$ remains unchanged (249). When polyethylene melts, the doublet with maxima at 721 cm.$^{-1}$ and 730 cm.$^{-1}$ is replaced by a broad band centered at 721 cm.$^{-1}$ (441, 482, 501). This characteristic change in the infrared spectrum of polyethylene on melting has been shown to result from the crystalline nature of polyethylene, i.e., segments of polymer chains exhibit order like that of crystalline solids. The absorption band at 721 cm.$^{-1}$, observed in molten polyethylene and in solution, has been assigned to the rocking of the hydrogen atoms in the methylene groups (457). This vibration was found to be perpendicular to the polymer chain axis from studies by polarized infrared radiation (131, 489). On crystallization, splitting of the single absorption band at 721 cm.$^{-1}$ into a doublet absorbing at 721 cm.$^{-1}$ and 730 cm.$^{-1}$ occurs because of the interaction of the methylene groups in the crystalline regions (479, 505). This conclusion is supported by the studies of C_{36} hydrocarbon crystals with polarized infrared radiation (274). The earlier interpretation (249) of this doublet was in error.

With C_{36} hydrocarbon crystals it was shown (274) that the 730 cm.$^{-1}$ band has maximum absorptions when the infrared radiation is polarized parallel to the *a*-axis of the crystals, and the 721 cm.$^{-1}$ band has maximum absorption with radiation polarized parallel to the *b*-axis of the crystals. Theory and experimental evidence from crystalline hydrocarbons suggest that in polyethylene the absorption band at 730 cm.$^{-1}$ arises from the crystalline regions only and the 721 cm.$^{-1}$ band arises from both the crystalline (ordered) and the amorphous (disordered) regions. Further, for an oriented sample of polyethylene in which the polymer chains are aligned in a particular direction, absorption for both the 730 cm.$^{-1}$ and the 721 cm.$^{-1}$ bands would show dichroic properties, i.e., absorption would depend upon the direction of polarization. The absorption would be a maximum for radiation polarized perpendicular to the direction of the polymer

TABLE 1

Infrared absorption bands of polyethylene

Wave-length	Wave Number	Assignment	Dichroic Properties
microns	*cm.*$^{-1}$		
3.38	2958	Unsymmetrical stretching in methyl groups	No dichroism
3.42	2920	Unsymmetrical stretching in methylene groups	Weak perpendicular dichroism
3.48	2880	Symmetrical stretching in methyl groups	Weak perpendicular dichroism
3.51	2858	Symmetrical stretching in methylene groups	Weak perpendicular dichroism
3.66	2735	Methyl groups	
3.74	2678	Methylene groups	
6.79	1470*	Deformation of methylene groups perpendicular to chain axis	Perpendicular dichroism in all three bands
6.82	1465		
6.84	1463*		
6.87	1458	Deformation of methyl groups	No dichroism
7.25	1375	Symmetrical deformation of methyl groups	No dichroism
7.30	1372	Deformation of methylene groups	Parallel dichroism
7.39	1355		
7.45	1340		
7.68	1300		
11.22	890	Rocking of methyl groups	
13.70	730*	Rocking of methylene groups perpendicular to chain direction	Perpendicular dichroism
13.88	721		

* Purely crystalline bands.

chains, i.e., the absorption would show perpendicular dichroism (274, 348, 439). Other absorption bands in the spectrum of polyethylene also show dichroic properties (11, 131, 441, 505, 506). In particular, the 1463–1470 cm.$^{-1}$ bands show behavior similar to that of the 721–730 cm.$^{-1}$ doublet. In table 1 the types of dichroism which the various absorption bands show are indicated. (The words *parallel dichroism* signify that the absorption for radiation polarized parallel to the direction of the polymer chains is a maximum.) The study of the dichroism of various absorption bands, using polarized infrared radiation, is of much importance in the study of orientation of polymer chains in various samples of polyethylene and in the proper assignment of the molecular vibrations responsible for the different absorption bands (11, 246, 348, 360, 489, 506).

In the 1300 cm.$^{-1}$ to 1372 cm.$^{-1}$ region there are four absorption bands centered approximately at 1300 cm.$^{-1}$, 1340 cm.$^{-1}$, 1355 cm.$^{-1}$, and 1372 cm.$^{-1}$ The 1340 cm.$^{-1}$ absorption appears only as a weak shoulder on the 1355 cm.$^{-1}$ band. These bands arise from the deformation frequencies of the methylene groups (505, 506). The band at 1372 cm.$^{-1}$ has been interpreted to arise from a superposition of absorptions from both the crystalline and the amorphous regions. The other bands at 1300 cm.$^{-1}$, 1340 cm.$^{-1}$, and 1355 cm.$^{-1}$ arise from amorphous regions only, are weak in highly crystalline polyethylene, and are absent in crystalline hydrocarbons. All four bands show parallel dichroism (441, 506). These bands therefore should be important in the study of the amorphous content and orientation of the polymer segments in the amorphous regions.

The absorption band at 1375 cm.$^{-1}$ arises from the symmetrical deformation of the methyl groups (441, 500, 502). Presence of this absorption band in the infrared spectrum of polyethylenes is an indication of branched structure, and quantitative measurements at a wavelength corresponding to this absorption band have been used, as discussed later, for the determination of the degree of branching in polyethylene.

Besides the absorption bands discussed above and listed in table 1, several other absorption bands corresponding to unsaturated and oxygen-containing

TABLE 2

Absorption bands in polyethylene corresponding to olefinic unsaturation and oxygen-containing groups

Wavelength	Wave Number	Assignment
microns	*cm.$^{-1}$*	
2.81	3559	Hydroperoxide, R_3COOH
5.692	1757	Anhydride, $(RCO)_2O$
5.738	1715	Ester carbonyl, RCOOR
5.771	1733	Aldehyde carbonyl, RCHO
5.798	1725	Ketonic carbonyl, R_2CO, close to chain end
5.812	1720	Ketonic carbonyl, R_2CO, internal
5.838	1713	Carboxylic carbonyl, RCOOH
6.08	1644	Olefinic unsaturation, total
10.07	990	Vinyl unsaturation, $RCH{=}CH_2$
10.35	964	Trans internal unsaturation, $RCH{=}CHR$
11.00	908	Vinyl unsaturation, $RCH{=}CH_2$
11.25	888	Vinylidene unsaturation, $R_2C{=}CH_2$

groups have been identified in polyethylene, especially in those samples of polyethylene which had been subjected to thermal or photochemical degradation. In table 2 are given the absorptions corresponding to the unsaturated and oxygen-containing groups that have been observed in polyethylenes (56, 100, 156, 348, 440, 460, 501). A typical infrared absorption spectrum of polyethylene is shown in figure 1. For ease of presentation on a linear scale, the wavelengths instead of wave numbers are marked in this figure for the various absorption peaks. Besides these bands, about seventeen other very weak bands appear in the polyethylene spectrum. These are probably carbon–carbon and methylene frequencies, and combination bands (436).

B. CRYSTAL STRUCTURE AND CRYSTALLINITY

In the discussion of the infrared spectrum of polyethylene, the disappearance of certain bands on melting has been mentioned. This was attributed to the presence of regions in polyethylene in which the segments of the polymer chains are able to arrange themselves in the regular three-dimensional order characteristic of crystalline solids. Thus, like many other polymers, notably polyesters and polyamides, polyethylene is a semicrystalline material (18).

The x-ray diffraction pattern of polyethylene consists of sharp diffraction lines from the crystalline regions and a halo from the amorphous regions (63, 67). The crystal structure of polyethylene has been determined from x-ray studies. The unit cell is orthorhombic with $a_0 = 7.40$ A., $b_0 = 4.93$ A., and $c_0 = 2.534$ A. The symmetry elements possessed by the unit cell are found to correspond to the space group Pnam (63). The important elements of symmetry present in the unit cell are three sets of twofold axes parallel to each unit cell axis, a diagonal glide plane perpendicular to the *a*-axis, a glide plane perpendicular to the *b*-axis with glide along the *a*-axis, and a mirror plane perpendicular to the *c*-axis. The crystal structure of polyethylene is shown in figure 2. (For definitions of space group symbols and various symmetry elements, references 65 and 193 should be consulted.) The polymer chains in the crystal are parallel to the *c*-axis of the unit cell. The observed intensities of a number of lines in the diffraction pattern of polyethylene are not in agreement with those calculated from the structure of the unit cell. This failure has been attributed to the nonspherical character of the electron cloud drawn out in the plane of the three nuclei of the methylene groups (63). Essentially the same crystal structure has been found in the newer types of highly crystalline polyethylenes (465a), though some differences exist.

A new crystalline modification of polyethylene, presumably formed by the twinning of the crystallites by a glide parallel to the (110) planes on successive redrawing of polyethylene has been suggested (390). This has not, however, been substantiated by detailed analysis.

The proportion of the crystalline and amorphous material (percentage crystallinity) in polyethylene samples is not fixed and depends upon such factors as the conditions of polymerization and catalysts (174, 419, 435).

Many important properties of polyethylenes are significantly dependent upon the percentage crystallinity of the sample (358, 419, 470), and several methods

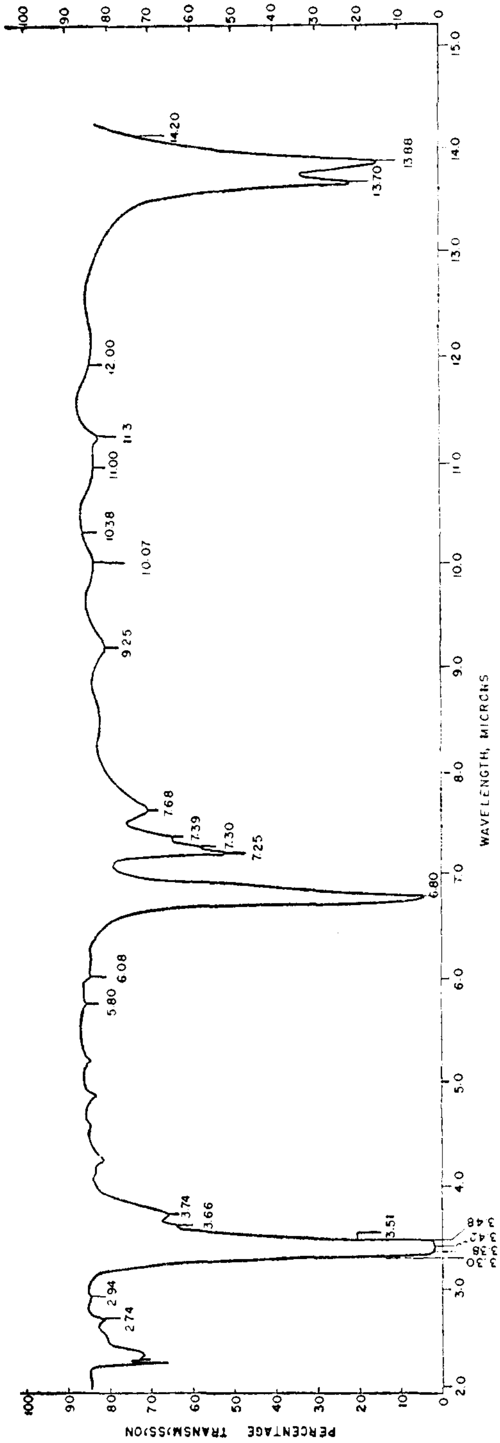


FIG. 1. Infrared spectrum of polyethylene

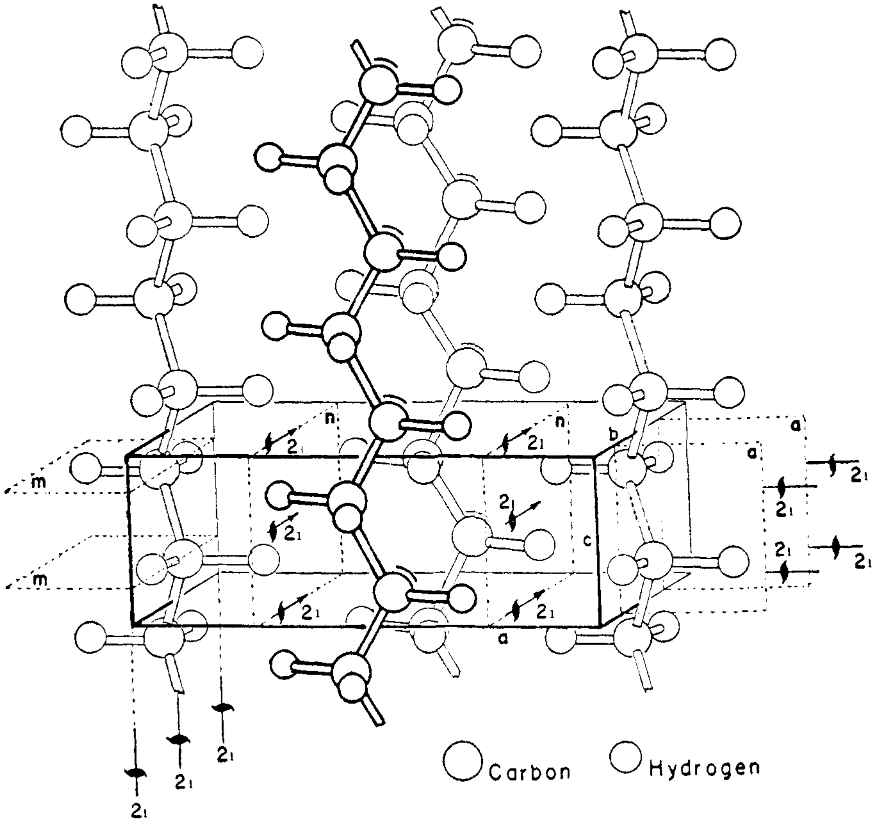


FIG. 2. Crystal structure of polyethylene according to C. W. Bunn, *Chemical Crystallography*, p. 233, Oxford University Press, London (1946).

have been developed to determine this quantity. Unfortunately, there is disagreement among the values determined on similar samples by different methods (355). This disagreement arises not only from the experimental difficulties, but also from the uncertainties inherent in the various methods. Methods that have been used for the determination of polyethylene crystallinity include x-ray diffraction (5, 55, 195, 196, 197, 273, 275, 276, 317, 350, 511, 512), density (216), determinations of heat content (115, 403), infrared absorption (327, 359, 507), and, recently, nuclear magnetic resonance (529).

The x-ray diffraction method is particularly suited to determinations of crystallinity in polyethylene because the peak corresponding to scattering from the amorphous regions is well separated from the peaks corresponding to the reflections from the crystalline regions. The x-ray methods used for the determination of crystallinity in polyethylenes are based either on a comparison of the intensity of radiation scattered from amorphous areas to the intensity scattered by molten polyethylene (196, 197, 273, 275, 276) or upon a comparison of intensities of x-rays scattered by the amorphous areas with the intensity of the crystalline reflections (55, 317, 511, 512). Many of the experimental difficulties in the latter, when the intensities are recorded on a photographic film, have been overcome by the use of the x-ray diffractometer (5). In the x-ray diffraction methods, the main uncertainty is in the background correction to be applied. The scattering from amorphous regions may extend to a lower angular range than has been considered in a number of determinations. The values of percentage crystallinity as determined by x-ray methods tend to be higher than those determined by other independent methods. Also in these methods the sample has to be free from orientation of the crystalline and amorphous regions, or appropriate corrections must be applied.

The determination of crystallinity from density is based on a knowledge of the densities of the crystalline and amorphous regions of polyethylene. The density of crystalline regions may be unequivocally computed from the dimensions of the unit cell (from x-ray data (63)), but the estimation of density of the amorphous polyethylene at a temperature appreciably lower than the melting point is subject to considerable uncertainty. The usual method for calculating the density of amorphous polyethylene has been to construct a plot of the density (or specific volume) versus temperature of molten polyethylene and extrapolate to lower temperatures (216, 276, 403). Other methods for obtaining the density of amorphous polyethylene for use in calculations of crystallinity from density of the sample have been used (355, 422). The values of the density of amorphous polyethylene at 24°C. from extrapolation of densities of polyethylene melts are appreciably higher than those estimated by other methods. Also, in applying the density method for determining crystallinity, the possibility of the inclusion of microvoids in the samples and incomplete wetting of the samples by the flotation liquid should not be ignored.

The crystallinity from measurements of heat content is calculated by dividing the difference between the heat content of the amorphous polyethylene and the measured heat content of the sample by the heat of fusion of entirely crystalline polyethylene (115, 403). The heat content of the amorphous polyethylene is obtained by extrapolation of the results obtained at temperatures above the melting point. The uncertainty in this method is in the exact value of the heat of fusion of entirely crystalline polyethylene, but fairly accurate estimates of this quantity from the study of crystalline long-chain hydrocarbons are now available (367).

In principle, all absorption bands in the infrared spectrum of polyethylene that arise solely from crystalline or amorphous regions may be used for the determination of crystallinity (Section IV,A). The absorption bands at 730 cm.$^{-1}$ (13.7 μ) and 1300 cm.$^{-1}$ (7.68 μ) are most suitable. Recently measurements at 1300 cm.$^{-1}$ have been used for the determination of crystallinity (327, 359, 507). In these methods, absorptions at 1300 cm.$^{-1}$ by a polyethylene sample before and after complete melting are compared. If proper precautions are taken, this method should give accurate crystallinity values, since it seems to be free from the inherent uncertainties which are generally present in other methods.

It has been of interest to establish whether the amorphous regions of polyethylene show some order intermediate between that present in the completely amorphous (disordered) regions and that in the crystalline regions. X-ray evidence is not in favor of any partial order in the amorphous portions of polyethylene (82, 196) at room temperature. On heating, however, as the crystalline regions melt, the fringe areas may have a somewhat higher density than the completely amorphous regions, indicating an order intermediate between that of amorphous and crystalline regions. The change in crystallinity of polyethylene with temperature has been studied by x-ray diffraction, heat content, and density methods (115, 216, 276, 350, 403, 511, 512). A comparison of the data from these methods shows that the density method gives the highest values at temperatures between 80°C. and the melting point. This result has been ascribed to the higher density in the fringe areas on partial melting of the crystalline regions. The variation of crystallinity with temperature of polyethylenes having branching has been compared with that of the linear polymethylenes (350). Linear polymethylenes keep their high crystallinity up to about 110°C., whereas a gradual change in crystallinity with temperature is observed in polyethylenes which have short-chain branching.

The structural feature that primarily determines the crystallinity of polyethylene is the number of short branches present (Section IV,C,1). Molecular weight and molecular-weight distribution have only a minor effect on the crystallinity of polyethylene, if they exert any effect at all (419, 435, 470). Methods of treatment such as stretching, quenching in liquid air, and normal freezing do not affect percentage crystallinity within 5 per cent (514).

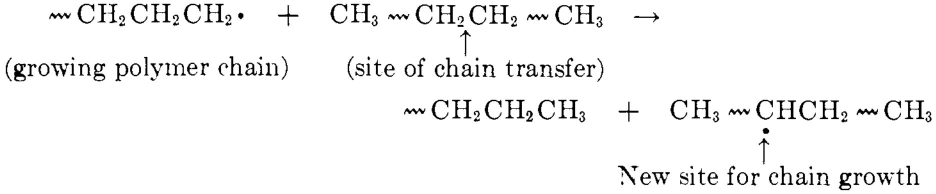
On cooling polyethylene, a transition at −38°C. has been observed from proton magnetic resonance (354). This probably corresponds to the second-order transition temperature of polyethylene, since a transition close to this temperature was also observed from the change in the coefficient of expansion (216). Later studies of the coefficient of expansion of samples with densities from 0.92 to 0.97 g./cc. and melting points from 100 to 138°C. have given a value of approximately −21°C. for the glass transition temperature (105a).

C. BRANCHED STRUCTURE

Soon after the successful polymerization of ethylene, the branched structure of polyethylene was inferred from the estimation of the concentration of methyl groups by infrared absorption (158). Infrared absorption at 3.38 μ (2958 cm.^{-1}) by polyethylene samples indicated that there were more methyl groups per molecule than can be accounted for by the terminal groups. Another absorption band characteristic of the methyl groups in the infrared spectrum of polyethylene is at 7.25 μ (1375 cm.^{-1}).

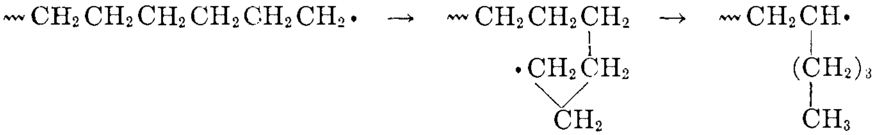
Later studies of infrared absorption at 7.25 μ and 3.38 μ have established that molecules of most commercial polyethylenes have an appreciably branched structure (52, 100, 501). In contrast to this, polyethylene prepared from diazomethane (27, 57, 58, 233, 290, 321) and the polymers prepared in recent years at atmospheric pressure (or somewhat higher pressures) appear to be nearly or completely free from short branches (174, 231, 388, 546).

A mechanism for chain branching in vinyl polymers has been posulated (151). According to this mechanism, the branched structure in polymers may arise because of the kinetic possibility of an active growing chain transferring its activity to another dead polymer chain by withdrawing a hydrogen from it.



$$\underset{\text{(growing polymer chain)}}{\sim CH_2CH_2CH_2\cdot} + \underset{\text{(site of chain transfer)}}{CH_3 \sim \underset{\uparrow}{CH_2}CH_2 \sim CH_3} \rightarrow \sim CH_2CH_2CH_3 + CH_3 \sim \underset{\underset{\text{New site for chain growth}}{\uparrow}}{\underset{\bullet}{C}}HCH_2 \sim CH_3$$

It was, however, realized that this mechanism could not be entirely responsible for all the chain branching present in polyethylene. If it were, it can be shown from kinetic analysis that the average number of branches per molecule, as inferred from infrared measurements on many polyethylenes, would be sufficient to give a polymer system of infinite molecular weight (28). Also under certain conditions the observed extent of branching, occurring according to the above mechanism, would lead to a system crosslinked into an infinite network (163). This is contrary to the observed behavior of polyethylene. Also, it was expected that increase in branching would give polymers of high melt viscosity, low tensile strength for a given molecular weight, and low density of the polymer, i.e., a lower percentage of crystallinity because of the increase in methyl group content. It was observed (435) that under certain conditions of polymerization polymers differing appreciably in density and hence crystallinity could be prepared which showed essentially the same melt viscosity and tensile strength. It was also possible, by carrying polymerization to different extents, to prepare samples having the same density but appreciably different melt viscosity and tensile strengths. It was concluded that to reconcile these facts it is necessary to postulate two mechanisms by which branching in polyethylene may occur (435). It has been suggested that the chain branching in polyethylene may occur not only by intermolecular chain transfer but also by intramolecular chain transfer through formation of transient cycloparaffin structures of four or five carbon atoms (435). The former mechanism leads to *long-chain branching*, while the latter mechanism gives rise to *short-chain branching* only. During the polymerization of ethylene both mechanisms of chain branching may operate simultaneously, giving rise to both long and short branches in a polyethylene sample. The mechanism leading to short-chain branching may be represented as follows:



1. *Determination of short-chain branching*

In principle, any of the infrared absorption bands specific for methyl groups may be used for the determination of short-chain branching. Among these, the absorption bands at 3.38 μ (2958 cm.$^{-1}$), 3.48 μ (2880 cm.$^{-1}$), 7.25 μ (1375 cm.$^{-1}$), and 11.2 μ (890 cm.$^{-1}$) are the important ones for this purpose. The absorption at 11.2 μ has been assigned specifically to ethyl groups either singly or at the end of long alkyl chains (52, 56, 119). The bands at 3.38 μ and 3.48 μ suffer from the defect that there is considerable overlapping by the neighboring strong absorptions from the methylene groups. Accurate measurements, however, of the concentration of methyl groups in some polyethylenes have been made from absorptions at these wavelengths using hot carbon tetrachloride solutions and a grating spectrophotometer of high dispersion (442). The absorption bands more commonly used for determination of short-chain branching in polyethylene are at 7.25 μ and 11.25 μ. In using absorptions at these wavelengths for quantitative determination of methyl group concentration (i.e., short-chain branching), the following are some of the important points that should be taken into consideration (56, 100, 506).

1. The relation between the number of methyl groups per hundred carbon atoms and the specific absorption coefficients K' is linear for only the liquid paraffins. [$K' = \log_{10} I_0/I\ (1/dl)$, where $\log_{10} I_0/I$ is the absorbance, d is the density in grams per cubic centimeter, and l is the path length in centimeters.] There are serious departures from linearity when values from the spectra of the solid paraffins are used. When the solid changes to the molten state, the absorption intensity at the 7.25 μ band decreases almost by half. Therefore, in determining chain branching in polyethylenes from infrared absorption, using the relation between K' and the stoichiometric number of methyl groups present in liquid hydrocarbons, it is necessary to make measurements on molten polyethylene samples.

2. The 7.25 μ band lies close to, and overlaps to some extent, the bands at 7.30 μ (1372 cm.$^{-1}$) and 7.39 μ (1355 cm.$^{-1}$) which are characteristic of methylene groups. The interference from these bands should be taken into account.

3. When polyethylene melts the absorption at 7.30 μ decreases somewhat, while the absorption at 7.39 μ increases. The absorption at 7.39 μ arises from the amorphous regions of polyethylene, while both the amorphous and the crystalline regions contribute to absorption at 7.30 μ.

4. The band at 11.22 μ (890 cm.$^{-1}$) lies away from other absorption bands of polyethylene, and in this respect offers some advantage over measurements at 7.25 μ. The intensity of the 11.22 μ band is about one-tenth that of the 7.25 μ band, however, and the absorption by vinylidene double bonds occurs almost at the same wavelength, namely 11.25 μ (888 cm.$^{-1}$). In many polyethylenes, the vinylidene double bonds may contribute as much as one-third of the total absorption at 11.22 μ. Therefore, in the determination of short-chain branching from absorption at 11.22 μ, an appropriate correction for the vinylidene groups must be applied.

Short-chain branching in terms of the number of methyl groups per hundred carbon atoms has been determined in a number of polyethylene samples from measurements of absorptions at 7.25 μ on molten samples (56, 46[illegible]). Polymethylene, almost free from methyl groups and prepared by the decomposition

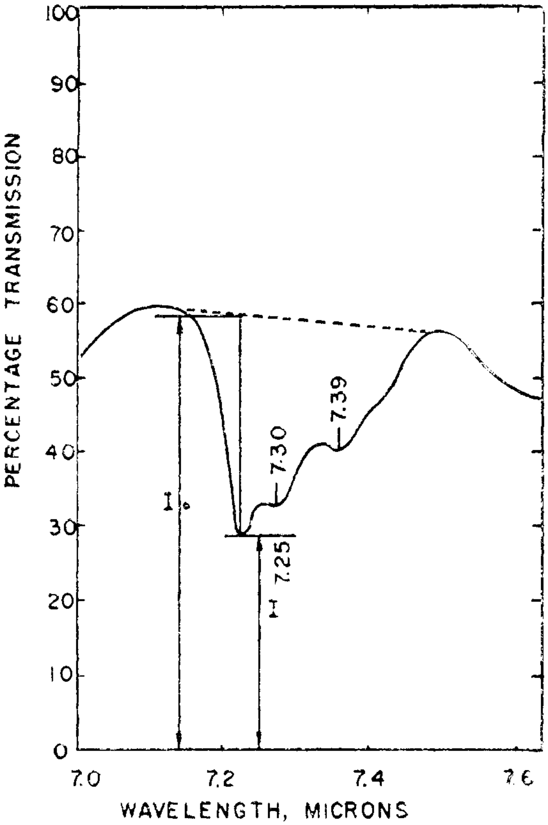


FIG. 3. Infrared spectrum of polyethylene in the 7-micron region

of diazomethane (57, 58, 290), was used to correct for the overlap from the 7.30 μ and 7.39 μ bands. Specific absorption coefficients at 7.25 μ on the same polyethylene samples were measured in both the molten and the solid states. The absorption coefficients at 7.25 μ in the solid polyethylene samples were found to be simply related to the corresponding values for the melt. It is thus possible now to calculate the number of methyl groups per hundred carbon atoms directly from measurements on solid film samples and avoid the inconvenience of melting the samples (56). The correction for the overlap of the neighboring bands was found by plotting specific absorption coefficients for the 7.25 μ band measured on a number of solid polyethylene samples as a function of the number of methyl groups per hundred carbon atoms calculated from the data on the corresponding molten samples, and then extrapolating to zero methyl groups. This correction was found to be independent of the concentration of methyl groups. It should be pointed out that this may be fortuitous. The absorptions at both 7.30 μ and 7.39 μ are dependent on crystallinity and the correction for interference from these bonds would be expected, therefore, to depend on crystallinity (506). Graphical resolution of the bands and application of the appropriate corrections

TABLE 3

Short-chain branching in polyethylenes determined (6) from absorption at 7.25 μ, according to method given in reference 56

Polyethylene Designation	Source*	Methyl Groups per 100 Carbon Atoms
Alathon-10	du Pont	2.04
Alathon-12		2.72
Alathon-120		2.37
Alathon-14		2.97
Alathon-21X		1.94
DFDA	Bakelite, South Charleston plant	2.64
DYNH-3	Bakelite, South Charleston plant	2.56
DYNH-3	Bakelite, Texas City plant	2.65
DYNH-3	Bakelite, Seadrift plant	2.61
Tenite 800E	Eastman	2.70
Tenite 816E		3.23
Tenite 817E		2.60
Alkathene-2F	I.C.I.	2.53
Alkathene-7F		2.73 (2.93)
Orizon 306	Monsanto	2.58
Petrothene 210	U.S.I.	2.50
Polyeth	Spencer, Sample 1010	2.61
Polyeth	Spencer, Sample 2005	2.94
Marlex-50	Phillips	0.00
Hi-Fax	Hercules	0.00
Super Dylan	Koppers	0.00

* du Pont = E. I. du Pont de Nemours and Company; Bakelite = Bakelite Company, a division of Union Carbide and Carbon Corporation; Eastman = Eastman Chemical Products, Inc., a subsidiary of Eastman Kodak Company; I.C.I. = Imperial Chemical Industries Ltd.; Monsanto = Monsanto Chemical Company; U.S.I. = U. S. Industrial Chemicals Company, a division of National Distillers Products Corporation; Spencer = Spencer Chemical Company; Phillips = Phillips Petroleum Company; Hercules = Hercules Powder Company; Koppers = Koppers Company, Inc., Chemical Division.

should be preferred. Figure 3 illustrates the trace of the infrared spectrum of a typical solid polyethylene film from 7.0 μ to 7.6 μ, and shows the various absorption peaks in this region. Table 3 gives the average number of methyl groups per hundred carbon atoms in various commercially available polyethylenes as determined from infrared absorption at 7.25 μ, using data (56) given for calibration. Recent studies have shown that the absorptions at 7.25 μ for terminal methyl groups, methyl branches, and methyl groups in ethyl branches are appreciably different (460). For samples which have few branches it may be necessary to establish a more accurate calibration.

2. *Determination of long-chain branching*

An important consequence of long-chain branching, which arises by the chain transfer to an already formed polymer chain, as discussed above, is the broadening of molecular-weight distribution (22, 23, 24, 28, 163).

The kinetic analysis made by Beasley (28) is particularly pertinent to the elucidation of long-chain branching in polyethylene. The important conclusions of his analysis may be stated as follows: (*1*) With increasing long-chain branching, the molecular-weight distribution function (on a weight basis) shows a longer high-molecular-weight tail. (*2*) Both the number-average and weight-average molecular weight increase with increasing degree of long-chain branching. However, the weight-average molecular weight increases much more rapidly than does the number-average molecular weight. For degrees of long-chain branching at which the ratio of weight-average to number-average molecular weight may assume very large values, the change in the number-average molecular weight is barely detectable. (*3*) For polymers of finite weight-average molecular weight, the branch points from long-chain branching do not exceed one per molecule on a number-average basis. The number of such branch points on a weight-average basis, however, increases sharply as the ratio of the weight-average to number-average molecular weights increases. Thus polyethylenes which may have considerable long-chain branching may not show any appreciable increase in methyl group content, as measured from infrared absorption, for example. The number of methyl groups per molecule, on a number-average basis, will vary only between two and three for samples with no long-chain branching and for those with long-chain branching to such an extent that an infinite weight-average molecular weight is approached.

The weight-average and number-average molecular weights of a number of polyethylene samples have been compared (36, 329). This ratio for polyethylenes has been found to be considerably greater than 2 (the value expected for polymers having no long-chain branching). The large values of the ratios observed in polyethylenes is a qualitative indication of the presence of long-chain branching. The quantitatively precise measure of the weight-average number of long-chain branches in polyethylene is, however, not simple, and is subject to several uncertainties. The principal physical difference between the polymer having long-chain branches and that having an unbranched structure, besides the broad molecular-weight distribution in the former, is the smaller spatial extension of the branched molecules of a given molecular weight. This affects their solution properties, particularly the intrinsic viscosity and mean square radius as measured by light scattering. The scattering function, $P(\theta)$, obtained from measurements of light scattered at different angles from the primary beam, is known to be affected appreciably by the long-chain branched structure of the polymers (41, 504, 547). Quantitative measure of long-chain branching in polyethylene is scarcely possible from the scattering function alone, since the influence of chain branching on this function is counteracted and compounded by the polydispersity (31, 485) which is inherently quite broad in polyethylenes involving long-chain branching.

The method which has been used with some success to obtain a measure of the extent of long-chain branching in polyethylene is based on the comparison of the intrinsic viscosity of the branched and unbranched polymer species of the same weight-average molecular weight (36, 339). The ratio of the intrinsic viscosity of a branched polymer to that of a linear polymer of the same weight-average molecular weight was shown (549) to be equal to $g^{3/2}$, where g is the ratio of the mean square radii of gyration. Later calculations indicated (485) that this relation overestimates the effect of branching on intrinsic viscosity. An improved relation between the ratio of intrinsic viscosity of branched and unbranched polymer of the same weight-average molecular weight has been developed and shown to be equal to the third power of a function, h (485). The two functions h and g are related to each other.

The steps involved in estimating the extent of long-chain branching in polyethylene may be summarized as: (*1*) determination of the intrinsic viscosity of the suspected branched polymer in a suitable solvent, (*2*) determination of the weight-average molecular weight of the branched polymer from light scattering, (*3*) calculation of the intrinsic viscosity of linear polyethylene of the same weight-average molecular weight as the branched polymer under study from a previously established relationship between molecular weight and intrinsic viscosity, (*4*) obtaining a value of g from the ratio of intrinsic viscosity ($= h^3$) of branched and linear polymers (485, 549), and (*5*) estimation of the extent of branching from the value of g. The precise calculations of weight-average number of branch points per molecule by this procedure is still subject to a number of uncertainties, the main one being the form of the function g, which is affected by the molecular-weight distribution and functionality of the branch points. For polyethylenes showing very broad molecular-weight distributions, no satisfactory form of the function g is available for precise calculation of the weight-average number of branch points per molecule. In any case, the above scheme gives a rather good estimate, though empirical, of the extent of long-chain branching in polyethylene. Studies along these lines have shown that polyethylenes possess long-chain branching to an appreciable extent (339).

It is pertinent to point out that the study of molecular-weight distribution in polyethylene and its relation to long-chain branching offers another approach which could be advantageously used in the study of the branched structure of polyethylene. No studies of this kind have been reported.

V. OPTICAL PROPERTIES

A. SPHERULITIC FORM OF CRYSTALLINE AGGREGATES

An estimate of the size of polyethylene crystallites from a broadening of the x-ray reflections has shown that the largest dimensions of the crystallites are not greater than 300 A. and may even be less than 100 A. (67). The presence of crystalline regions of such small dimensions would not be visible in the optical microscope because of the limit on its resolving power, and a sample of the polymer would be transparent, since the crystallites are smaller than the wavelengths of visible light. In contrast to these expectations, most polyethylenes at room temperature are translucent, and the optical microscope reveals in thin crystallized films organized structures considerably bigger than 300 A. The crystallites appear to have become associated into clusters of characteristic form. These aggregates have two principal features: the assemblage of crystallites radiates in all directions from a point and in the polarizing microscope with crossed Nicol prisms exhibits a black Maltese cross (see photomicrographs reproduced in references 52, 67, 188, and 244). By analogy with aggregates of similar characteristic features, observed in many organic materials of low molecular weight and in many minerals (51, 60, 333, 334), these aggregates of crystallites in polyethylene and other crystalline polymers are called *spherulites*. A spherulitic structure seems to be a common feature of many other crystallizing polymers (45, 46, 97, 332, 396). Though a spherulitic structure is easily observed only in thin films, it should not be inferred that in massive specimens and molded shapes spherulites are not formed. In fact, in the case of some polymers, the presence of spherulites in thick specimens has been confirmed from a surface study of blocks or microtomed sections (92, 281).

Ideally, the spherulites would be spherical, but either interference from adjacent growing spherulites or interruption in the growth process may give rise to open sheaflike or other intermediate structures. The sizes of spherulites in a sample of polyethylene, or of any other crystalline polymer, may vary over a considerable range from submicroscopic to a few tenths of a millimeter. Microscopy studies can give an estimate of the approximate average size of the spherulites in a given sample, and it has been possible in this way to establish some general conclusions regarding the factors which affect spherulite size and the effect of spherulite size on the properties of the crystallized polymer.

At least four important factors affect the size of the spherulites: the degree of branching of the polyethylene sample, the thermal history and mechanical working of the melt, the temperature of crystallization of the melt, and the rate of cooling (52, 67). Polyethylenes with the least branching form the largest spherulites. Slow cooling of the melt through the melting range gives large spherulites, whereas sudden quenching to low temperatures gives small spherulites. Mechanical working of the melt, followed by shock cooling, gives materials with very small spherulite size. The most important effect of the size of spherulites is upon the clarity of the samples; the smaller the size of the spherulites, the clearer the sample.

Careful study by the polarizing microscope of spherulites formed during the crystallization of polyethylene at temperatures close to 80°C. shows some interesting details in addition to the cross and radiating fibrous structure usually associated with the spherulites. In samples crystallized at 80°C. and above, a closely spaced ring system can be observed in addition to the usual cross (244). The spacings become increasingly narrower at lower temperature of crystallization, until they can no longer be resolved. Similar studies on other crystalline polymers, particularly polyamides and polyethylene terephthalate, have shown that under certain conditions of crystallization the cross usually observed in spherulites consists of zigzag lines. In some cases, a system of ring-shaped extinction lines perpendicular to the radii of the spherulites is present (239, 240, 244, 247).

X-ray diffraction studies using a special microbeam camera have shown that in the spherulites of polymers, including polyethylene, the polymer chains are perpendicular to the radii of the spherulites (245). In a few special cases, careful observations of the crystallized polymer melts showed closely banded fibrillar structures (247). On the basis of the results from these studies, it has been proposed that the spherulites of crystallizing polymers consist of fibrillar units arranged along a helical path. This helical arrangement of the fibrillar units is believed to arise from a regular branching of the fibrils with a constant branching period and angle in the two-dimensional case, and by a constant branching period, two constant angles, and a constant direction of rotation in the three-dimensional case. The fibrils themselves are believed to consist of a closely coiled ropelike arrangement of the chains. According to this mechanism, in the formation of the spherulites the polymer chains first coil themselves tightly to form the fibrils ("small-scale helices"), which get arranged further along a helical path ("large-scale helices"), with the axes of the large-scale helices parallel to the radii of the spherulites (247).

In contrast to the complex mechanism of spherulite growth just discussed, a comparatively simple mechanism involving statistically outward radial growth from a nucleus has been proposed (54). According to this mechanism, a spherulite originates from a single nucleus. From this nucleus a crystallite grows by lateral accretion of molecular segments of polymer chains. Fine strands of crystalline order proceed outward from the fringes of this crystallite, seeding further crystallizable domains and initiating the growth of additional crystallites. These crystallites in turn send out nucleating streamers, and growth takes place in a statistically radial fashion. Growth stops either because of the high viscosity of the system or because of interference from the neighboring growing spherulites. The optical properties and shapes of the spherulites are determined by the shapes of the crystallites.

An important property pertinent to the structure of the spherulites of polyethylene is the sign of optical birefringence. The spherulites show negative birefringence, i.e., the refractive index along the tangent to the spherulite is higher than that along the radius (52, 67, 245). Since the highest refractive index in both crystalline and amorphous regions of polyethylene is along the chain axis (66, 68), the negative birefringence of the spherulites implies that the polymer chains are arranged perpendicularly to the radii of the spherulites. This is confirmed by x-ray diffraction studies of the spherulites by use of the microbeam camera (245).

B. LIGHT SCATTERED BY POLYETHYLENE FILMS

The light scattered by polyethylene film determines its clarity. Some of this light is scattered because of the roughness of the surface, an aspect which will not be considered here. In addition to the surface scattering, polyethylene, in common with other crystalline polymers, scatters light because of the inherent inhomogeneities in the structure resulting from the different refractive indices of the crystalline and amorphous regions. Thus, the crystalline polymers show more turbidity than the corresponding melts (216, 516). The scattering ability of polyethylene films depends appreciably on the quenching conditions and thermal history of the sample (108, 397). Recent quantitative studies have shown that the light scattered by a thin polyethylene sample quenched to 0°C. from 125°C. is much lower than that scattered by an annealed sample (238).

With rising temperature, the turbidity of polyethylene films decreases steadily until at the melting point the samples are almost clear (188). The temperature–turbidity curve obtained during cooling of the melt shows hysteresis from the corresponding curve obtained during the heating cycle. Also, during the cooling cycle the temperature–turbidity curve shows a maximum. The turbidity first increases sharply at about 106°C., decreases sharply over the temperature range of 106.5°C. to 102°C., and then monotonically increases on cooling from 102°C. to room temperature (188). These results have been interpreted to indicate that the spherulites do not grow from the melt but from a partly ordered phase. The sharp increase in turbidity at about 106°C. was attributed to this organized structure of the melt. Sharp decrease in turbidity over the temperature range of 106.5°C. to 102°C. was attributed to the growth of bigger spherulites, with a consequent reduction in the number of discontinuities in refractive index at the boundaries of the spherulites. Recently, precise measurements of the absolute scattering power of polyethylene as a function of temperature, angle, and thermal treatment have been made (237, 238). These studies substantiate the maximum at about 106°C. in the temperature–turbidity curve during a cooling cycle and the hysteresis between the temperature–turbidity curves obtained during heating and cooling cycles. However, the angular dependencies of scattered light at various temperatures during heating and cooling cycles were found to be identical, indicating that the hysteresis between the temperature–turbidity curves during heating and cooling cycles is not related to changes in the average size of the entities responsible for scattering. It was shown that, at least in part, the observed hysteresis is a rate phenomenon (238).

The turbidity of solid polymers as determined from light-scattering measurements can be related to two parameters, $\langle\eta^2\rangle$ and a. $\langle\eta^2\rangle$ is the average square deviation of the dielectric constant from the mean in the regions in which it is fluctuating, and a is a measure of the dimension of the heterogeneity responsible for the scattering (107). The values of a and $\langle\eta^2\rangle$ have been determined for a number of polyethylenes at different temperatures from light-scattering measurments (238). The value of a remains fairly constant during the melting process, while that of $\langle\eta^2\rangle$ decreases with increase in temperature in much the same manner as the degree of crystallinity changes. This implies that as the melting of the polyethylene proceeds, the average square deviation of the dielectric constant from the mean, $\langle\eta^2\rangle$, decreases, but the size a of the scattering entities remains essentially unchanged. The magnitude of a was found to be of the order of 2000–3000 A., which is intermediate between the size of the polyethylene crystallites and the size of the spherulites. The variation of a with temperature during the cooling cycle was found to be about the same as had been obtained during heating except for the single point, 106°C. The significance of the maximum observed in the temperature–turbidity curve and of the higher values of $\langle\eta^2\rangle$ and a obtained at 106°C. during the cooling cycle are not well understood yet.

The values of $\langle\eta^2\rangle$ and a were found to vary for different polyethylene samples, and are probably related to the molecular properties that determine the size and perfection of the spherulites formed from the melt. The value of $\langle \eta^2 \rangle$ for polymethylene (with no branching) is less than that for polyethylene (with branches) even though the former is more crystalline, probably because the scattering behavior of polymethylene approaches that of a perfect crystal form of polyethylene.

C. STRESS BIREFRINGENCE

In contrast to rubberlike elastomers, polyethylene shows a steep increase in birefringence when stressed to elongate (191). At high elongation a limiting value of birefringence is attained. Except at very small stresses, both the stress–strain and the stress–birefringence plots are not linear and large hysteresis effects are found on reducing the stress (99, 255, 387). The birefringence, however, varies linearly with strain, and the rate of increase in birefringence with strain decreases with rise in temperature. The linear relation between birefringence and strain is valid up to about 25 per cent strain, above which there is departure from linearity, but even in this range of high strains there is no hysteresis effect. These results show that stress birefringence is produced largely by orientation of the crystallites and not by the distortion of the amorphous regions under stress (99, 387).

Of particular importance are the simultaneous measurements of stress relaxation at constant length and of birefringence. From these measurements the configurational changes in polymers during stretching can be followed (481, 483). Simultaneous measurements of stress and birefringence at different temperatures were made on polyethylene (480). These results showed that orientation of the crystallites produces most of the birefringence, while distortion of the noncrystalline material produces most of the stress. Also, stretching at higher temperature produces relatively more orientation of the crystallites and less distortion of the noncrystalline material than stretching at a lower temperature. In other words, the contribution of internal energy to stress is less important at high temperatures, and polyethylene becomes more rubberlike in its stress–birefringence behavior at elevated temperatures.

From studies of stress birefringence the statistical-segment size of the polymer chain, which depends upon the hindrance to internal rotation about the carbon–carbon bonds, can be calculated (484). From measurements on a sample of cross-linked polyethylene it was shown that the size of the statistical segment decreases as the temperature increases (in the range from 120° to 170°C.), and the energy barrier to rotation about the carbon–carbon bond is approximately 6–7 kcal./mole (519).

VI. ORIENTATION IN POLYETHYLENE FILMS

A. a-AXIS ORIENTATION IN POLYETHYLENE FILMS

Polyethylene films prepared by extrusion of the molten polymer through a die, followed by quenching by air or water, show an unexpected preferential orientation of the crystalline regions. One would expect that as the melt issues from a die, the polymer chains would become somewhat oriented in the direction of flow (commonly referred to as the machine direction) and on crystallization, the crystalline regions would be preferentially oriented with the *c*-axes parallel to the machine direction, since the *c*-axis of the crystals is parallel to the polymer chains (see figure 2 for the relation between the crystallographic axes and the direction of the polymer chains). This is not true for extruded polyethylene films or for samples prepared under similar conditions of flow and crystallization.

Two important techniques that have been used in establishing the orientation of the crystalline regions in polyethylene films are x-ray diffraction and dichroism of infrared absorption. To appreciate the interpretation of the results from these methods in terms of the orientation, it is helpful to consider the two limiting cases of orientation in polyethylene films: (*1*) *a*-axis orientation, according to which the *a*-axes of the crystalline regions are preferentially oriented parallel to the machine direction and the *b*- and *c*-axes are in a plane perpendicular to the machine direction, and (*2*) *c*-axis orientation, according to which the *c*-axes of the crystallites are preferentially oriented parallel to the machine direction (or to the stretching direction in the study of stretched films). The expected x-ray diffraction patterns for the *a*-axis and *c*-axis orientations are shown in figures 4 and 5, respectively, for the cases in which the x-ray beam is (A) normal to the plane of the film, (B) parallel to the machine direction, and (C) parallel to the transverse direction (the direction perpendicular to the machine direction in the plane of the film).

For the study of orientation in polyethylene films from the dichroism of polarized infrared radiation, the doublet with absorption peaks at 13.70 μ (730 cm.$^{-1}$) and 13.88 μ (721 cm.$^{-1}$) is particularly suitable. As mentioned in Section IV,A, the absorption at 13.70 μ is from the crystalline regions, while both the crystalline and the amorphous regions contribute to the absorption at 13.88 μ. It has been established (246, 274, 479, 482, 505) that the absorptions at 13.70 μ and 13.88 μ from the crystalline regions of polyethylene correspond to the dipole change vectors which are parallel to the *a*- and *b*-axes of the crystal unit cell, respectively. The absorption of infrared radiation is proportional to the scalar product of the vectors $\bar{E}$ and $\bar{D}$, where $\bar{E}$ is the electric vibration vector of the polarized infrared radiation and $\bar{D}$ is the dipole change vector corresponding to the molecular motion which gives rise to the absorption. Therefore, when the orientation is such that the crystalline regions are preferentially oriented with their *a*-axes parallel to the machine direction, the 13.70 μ band will exhibit maximum absorption for the radiation which has its vibration vector parallel to the machine direction, as compared to the absorption for the radiation which has its vibration vector perpendicular to this direction. Thus for *a*-axis orientation of the crystalline regions in the film, the 13.70 μ band will exhibit parallel dichroism. From similar considerations it can be shown that the 13.88 μ band will show perpendicular dichroism for *a*-axis orientation of the crystalline regions. Since both the crystalline and the amorphous regions contribute to the absorption at 13.88 μ, any orientation of the amorphous regions would also affect the dichroic properties of the 13.88 μ band. But the presence of orientation of the

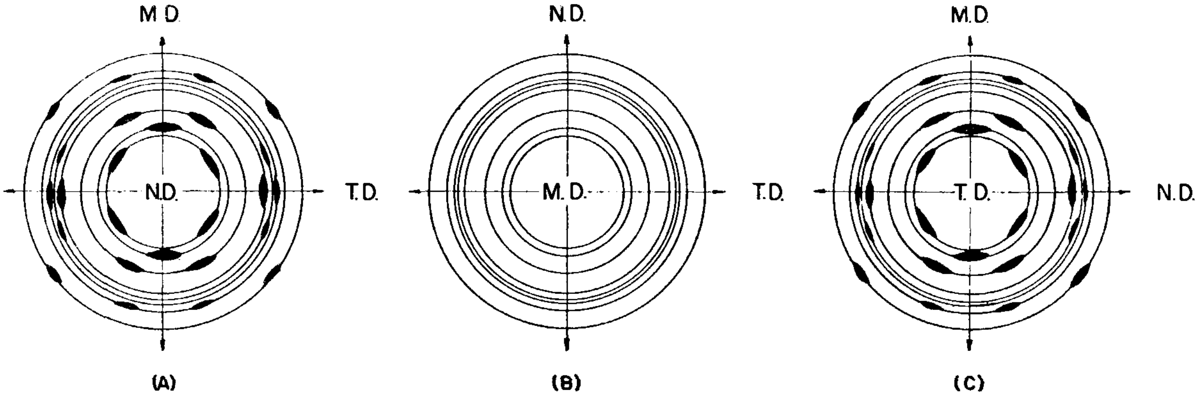


Fig. 4

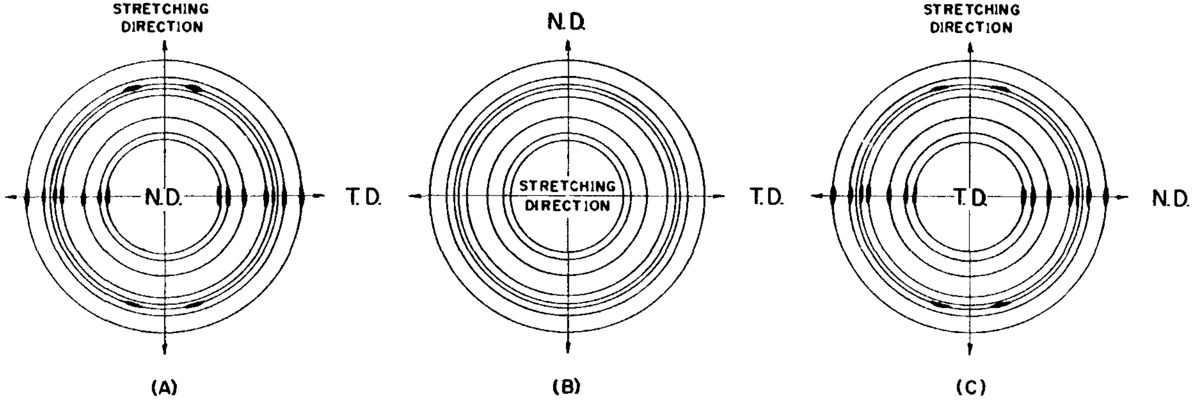


Fig. 5

Fig. 4. X-ray diffraction patterns for *a*-axis orientation of polyethylene crystallites. X ray beam (A) normal to the plane of the film (N.D.), (B) parallel to the machine direction (M.D.), (C) parallel to the transverse direction (T.D.). The reflections from the center are from (110), (200), (210), (020), (120), (011), (310), and (220) planes.

Fig. 5. X-ray diffraction patterns for *c*-axis orientation of polyethylene crystallites. X-ray beam (A) normal to the plane of the film (N.D.), (B) parallel to the stretching direction, (C) parallel to the transverse direction (T.D.). The reflections from the center are from (110), (200), (210), (020), (120), (011), (310), and (220) planes.

TABLE 4

Dichroism of the absorption bands at 13.70 and 13.88 microns for a-axis and c-axis orientations of polyethylene crystalline regions

Orientation in Crystalline Regions	Electric Vibration Vector $\bar{E}$ With Respect to Machine or Stretching Direction	Absorption at 13.70 Microns	Absorption at 13.88 Microns	Type of Dichroism
a-Axis parallel, b- and c-axes perpendicular, to machine direction	$\bar{E}$ parallel to machine direction	Maximum	Minimum	Parallel for 13.70 μ band, and perpendicular for 13.88 μ band
	$\bar{E}$ perpendicular to machine direction	Minimum	Maximum	
c-Axis parallel to machine or stretching direction; a- and b-axes distributed about c-axis	$\bar{E}$ parallel to stretching or machine direction	Minimum	Minimum	Perpendicular dichroism for both 13.70 μ and 13.88 μ bands
	$\bar{E}$ perpendicular to stretching or machine direction	Maximum	Maximum	

amorphous regions can be inferred from the dichroic properties of other bands which are from the amorphous regions alone: namely, at 7.68 μ (1300 cm.$^{-1}$), 7.45 μ (1340 cm.$^{-1}$), and 7.39 μ (1352 cm.$^{-1}$) (11, 505). For the c-axis orientation of the crystalline regions the a- and b-axes will be perpendicular to the machine (or stretching) direction and both the 13.70 μ and 13.88 μ bands will exhibit perpendicular dichroism; i.e., maximum absorption will occur for radiation having the electric vibration vector perpendicular to the machine direction. Table 4 summarizes the dichroic properties of the 13.70 μ and 13.88 μ bands for the a-axis and c-axis orientation of the crystalline regions in polyethylene films.

From x-ray diffraction and dichroism of the 13.70 μ and the 13.88 μ infrared absorption bands, it was deduced almost concurrently in two laboratories (6, 202) that in extruded polyethylene films the crystalline regions are preferentially oriented with their a-axes parallel to the machine direction. After the film has been stretched approximately 200 per cent, the orientation changes to c-axis orientation; i.e., the crystalline regions become preferentially oriented with their c-axes parallel to the stretching direction. Figures 6 and 7 are x-ray diffraction photographs which illustrate this change. They were taken with a flat-plate camera, with the x-ray beam normal to the plane of the film, and clearly show a-axis and c-axis orientation. Figures 8 and 9 represent the infrared spectra obtained with polarized infrared radiation in the 13 to 14.6 μ region for extruded polyethylene film and for the same film after having been stretched approximately 200 per cent in the machine direction. These spectra with polarized radiation show the dichroism expected for a-axis and c-axis orientation, respectively.

The birefringence of extruded polyethylene films does not seem to fit the above inferences concerning a-axis orientation in extruded polyethylene films. Calculations of the principal refractive indexes of the polyethylene crystal and molecule showed (68) that, for the crystal, the highest refractive index (γ_c) is parallel to the chain axis, the lowest refractive index (α_c) lies along the a-axis of the crystal, and the intermediate refractive index (β_c) is along the b-axis. For the polyethylene molecules not in the crystalline regions, the highest refractive index (γ_a) is also along the chain axis, the lowest refractive index (α_a) is perpendicular

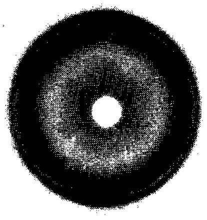


FIG. 6

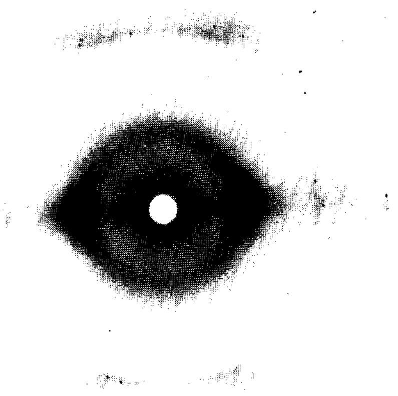


FIG. 7

FIG. 6. X-ray diffraction picture of polyethylene film (x-ray beam perpendicular to the plane of the film sample, and machine direction vertical in the figure).

FIG. 7. X-ray diffraction picture of polyethylene film stretched 200 per cent in the machine direction (x-ray beam perpendicular to the plane of the film sample, and machine direction vertical in the figure).

to both the chain axis and the plane containing the carbon atoms, and the intermediate refractive index (β_n) is parallel to the plane of carbon atoms but perpendicular to the chain axis. In polyethylene films in which the *a*-axes of the crystalline regions are preferentially oriented parallel to the machine direction and the *b*- and *c*-axes are perpendicular to this direction (*a*-axis orientation), it would therefore be expected that a lower refractive index would be exhibited parallel to the machine direction than in the transverse direction when the segments of molecules in the amorphous regions are completely disordered. That is to say, polyethylene films should be expected to show a negative birefringence. Extruded polyethylene films generally show a slight positive birefringence instead.

The small positive birefringence shown by polyethylene films should be interpreted with considerable caution, however, before concluding that this evidence is contrary to that shown by x-ray diffraction and polarized infrared absorption, since a multiplicity of effects may contribute to the birefringence of films. Some of the factors, other than orientation, that may affect birefringence of films are: (*1*) form birefringence (194, 449), which arises purely from the anisotropic shape of regions of one refractive index embedded in a matrix of another refractive index; (*2*) the introduction of stresses, microvoids, or microcracks during crystallization of the films; and (*3*) the branched structure of polyethylene. Branch points are sites where discontinuity in the ordering of chains to form crystallites occurs. When the chains in the crystallites pack preferentially

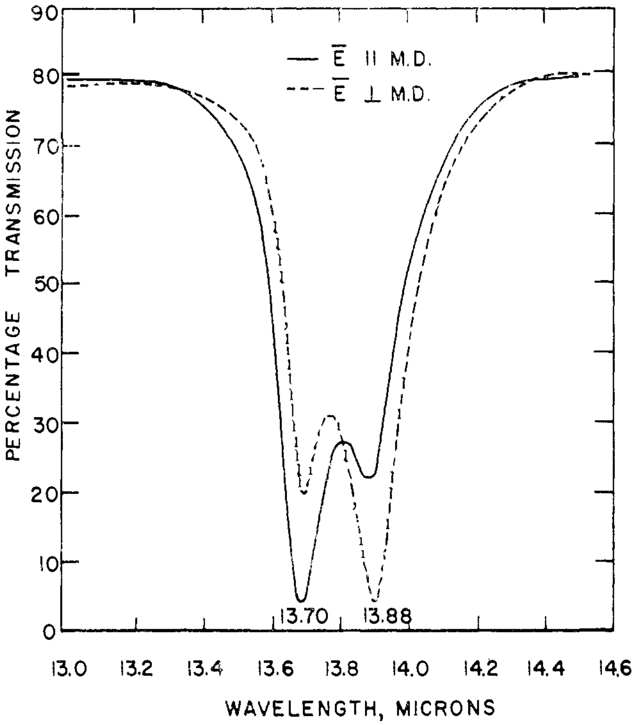


FIG. 8. Polarized infrared spectra of extruded polyethylene film, 13–14.6 microns

perpendicular to the machine direction, the short branches containing the methyl groups may be aligned parallel to the machine direction. The polarizability of the methyl group is large, and even a small degree of alignment of the methyl groups parallel to the machine direction will tend to make the birefringence of polyethylene films positive.

In the early studies on the orientation of polyethylene films it was suggested that the chains in the amorphous regions are oriented parallel to the machine direction, i.e., perpendicular to the orientation of the chains in the crystalline regions of the film (202). The perpendicular dichroism of the 13.88 μ infrared absorption band was considered as evidence for this cross-orientation of the chains in the amorphous and crystalline regions of the film. It now seems that this conclusion was based on erroneous interpretation of the absorption at 13.88 μ as arising solely from the amorphous regions. As discussed in Section IV,A, both the amorphous and the crystalline regions contribute to the 13.88 μ absorption band, and the perpendicular dichroism of this band can arise from the a-axis orientation of crystalline regions alone. No dichroism of the infrared absorption bands which arise solely from the disordered chains has been observed in extruded polyethylene films (61). No appreciable orientation of the chains in the amorphous regions of extruded polyethylene films seems therefore to be present.

It is not yet clearly understood how the a-axis orientation in extruded poly-

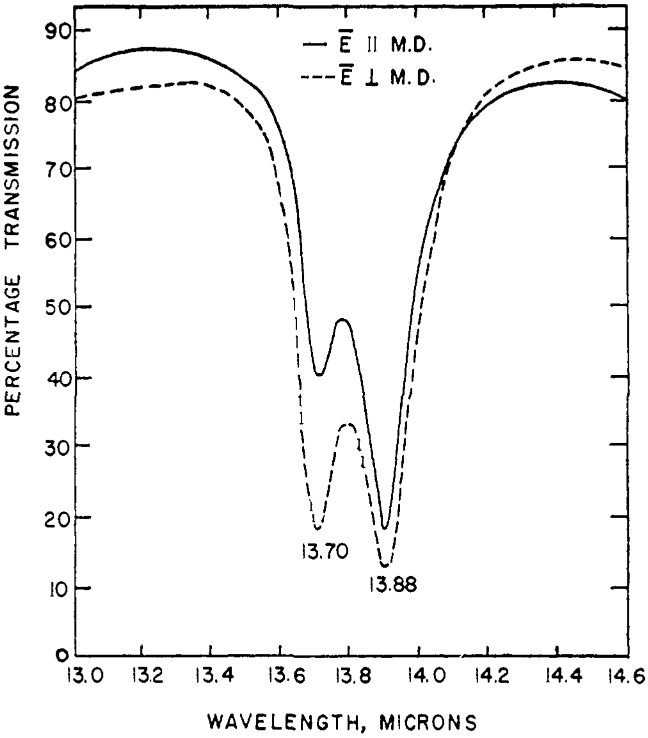


FIG. 9. Polarized infrared spectra of stretched polyethylene film, 13–14.6 microns

ethylene films is brought about. It has been suggested that this orientation may arise from the stretching and relaxation of polyethylene film during extrusion (202). This conclusion was based on the results and interpretation of studies of stretching and relaxation of polyethylene filaments (48, 209). This mechanism for the *a*-axis orientation in films of polyethylene is open to question because of the uncertainties in the interpretation of the published results on stretching and relaxation of polyethylene, as discussed later in this section.

Another mechanism, which seems more likely, has been proposed (137), based on the preferred direction of crystal growth. In the molten polyethylene the polymer molecules are entangled and intertwined. Because of the shearing stresses present during extrusion, some alignment of chain segments occurs. As the molten polymer cools, the crystals probably do not grow in the direction of extrusion, since it is unlikely that the exact spatial arrangement between chains of neighboring molecules, necessary for crystallization, would be present along sufficient lengths of the chains. Crystal growth in the cooling sheet along the direction of extrusion will therefore be inhibited because of the small chance that molecules over extended chain lengths will be in a suitable spatial arrangement. Yet an arrangement conducive to crystallization is likely over short lengths of adjacent chains of carbon atoms. The crystallites in the cooling polymer will have a tendency therefore to grow preferentially in a direction perpendicular to the length of the polymer chains; i.e., the crystallites will have a tendency to grow in the form of needles with the long dimension of these needles perpendicular to the direction of flow. This is schematically shown in figure 10A. Since these needlelike crystallites are formed in a flowing matrix, they tend to become oriented further in a direction governed now by their shape. Thus the crystallites which preferred to grow at right angles to the direction of flow may now slue round in the flowing matrix and line up with their long dimensions parallel to the direction of flow. Schematically, the crystallites shown in figure 10A will attain a position in the final film as shown in figure 10B. This results in a preferential orientation with the polymer chains in the crystalline regions perpendicular to the direction of extrusion, i.e., with the *c*-axis of the crystallites perpendicular to the extrusion (machine) direction.

The diffuse character of the reflections from planes containing an *l* index (0*kl*, *hkl*, etc.) in the x-ray diffraction patterns of polyethylene films suggests and supports the above inference that the lengths of the crystallites along the direction parallel to the chain direction are smaller than in the direction perpendicular to the chains.

It has recently been shown (299) that crosslinked molten polyethylene film allowed to crystallize in a stretched condition results in an orientation of the crystalline regions similar to that discussed above: namely, with the *a*-axis of the crystalline regions preferentially oriented parallel to, and with the *c*-axis perpendicular to, the direction of stretching of the melt. The results have been interpreted to mean that this type of orientation is a thermodynamic effect and represents the equilibrium orientation of crystals in a stretched structure.

B. ROW ORIENTATION IN POLYETHYLENE

Another interesting structure, the so-called row orientation (242, 243, 246), has been proposed to explain the x-ray diffraction patterns, infrared dichroism, and the infrared absorption at 13.70 μ and 13.88 μ shown by samples prepared under conditions similar to those used in extrusion. This proposed orientation is illustrated in figure 11. In this proposed structure the unit which lies parallel to the machine or stretching direction is a cylinder. Within this cylinder a helical arrangement of polyethylene crystallites exists. The axes of the helices, along which crystallites are arranged, lie randomly in planes perpendicular to the axis of the cylinder. The crystallographic *b*-axes of the crystallites are parallel to the helical axes. Further, the helical angle of the helices along which the polyethylene crystallites are arranged is assumed to be quite small, and thus the helices have been postulated to be closely coiled. In figure 11 the radiating rows of equidistant lines represent the helices.

It is pertinent to point out that in this proposed structure it is not the polyethylene chains that are packed in the crystallites in a helical form but rather that the arrangement of the crystallites is along helical paths. The crystalline regions therefore are assumed to have the crystallographic *b*-axis along the helical axis, with the crystallographic *a*- and *c*-axes following a helical path of low helical angle. This complex structure in extruded polyethylene films, or in small sam-

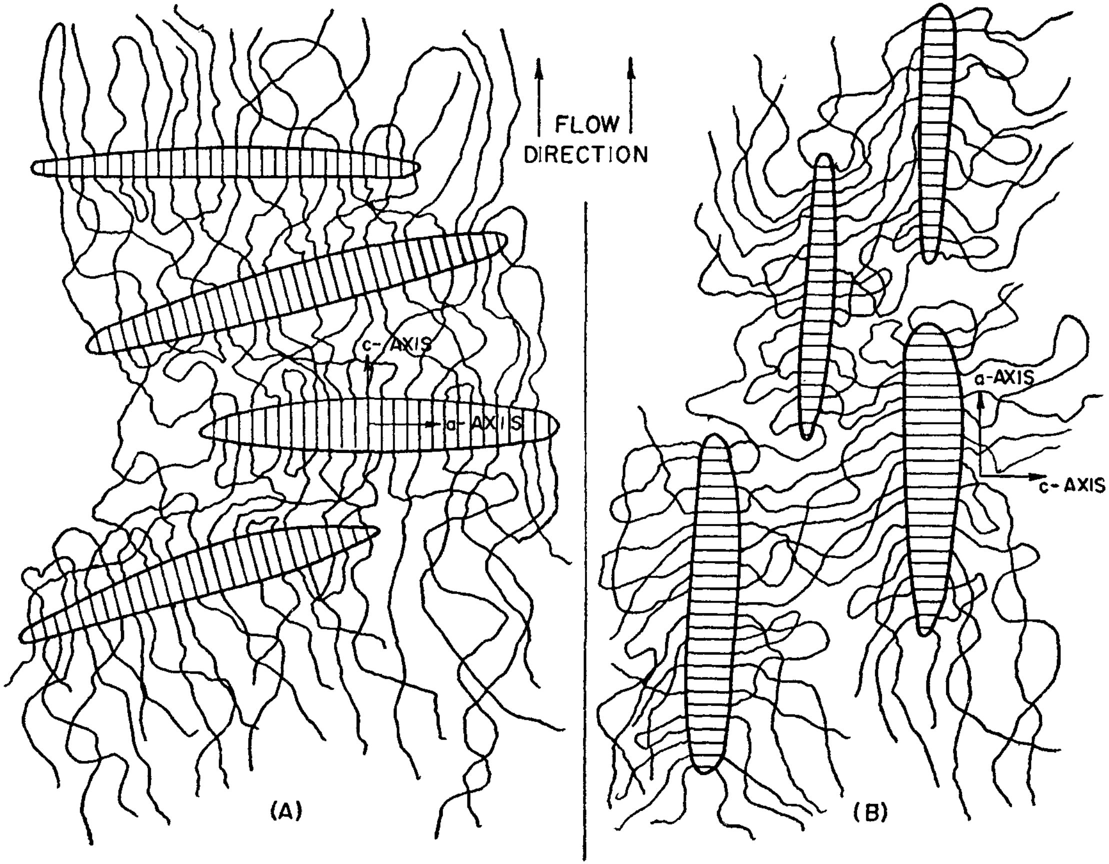


Fig. 10. (A) Schematic representation of growth of crystallites with long dimension perpendicular to flow direction of the melt. (B) Alignment of crystallites with long dimension parallel to direction of flow, resulting in chains in the crystalline regions perpendicular to the machine direction of extruded polyethylene film.

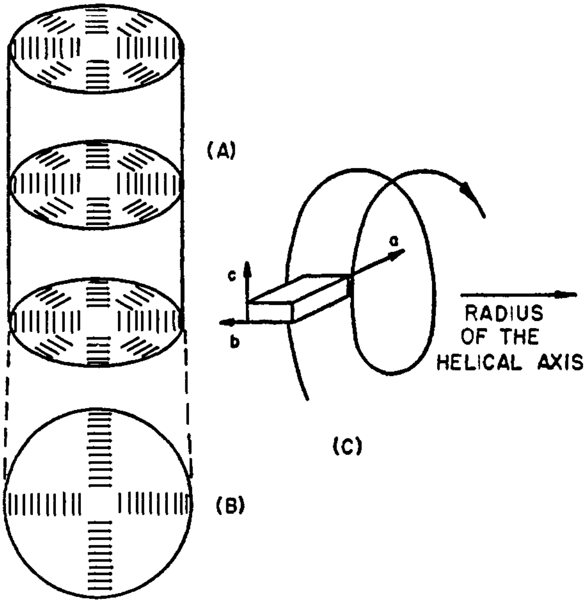


FIG. 11. Row structure in polyethylene as proposed by Keller (246). (A) Perspective view of cylinder containing planes in which helical axes are randomly arranged. (B) Plan, equidistant lines representing helices. Only two rows are shown. (C) Position of unit cell within helix.

ples prepared under controlled conditions, is believed to arise through spontaneous crystallization from the melt when there is a high density of nuclei along the direction of draw. Growth proceeds in directions normal to the line of nuclei, with only small divergence. The arrangement of crystallites about the lines of growth is helical, similar to that postulated for a normal spherulite of polyethylene in which the helical axes were considered to be parallel to the radii of the spherulites, the crystallographic *b*-axes of the crystallites being parallel to the helical axes (see the discussion of spherulitic structure in Section V,A).

It has been shown (243, 246) by an elegant analysis that this proposed model fits the x-ray diffraction patterns and dichroism of infrared absorption shown by samples prepared under specific conditions. Similar interpretation can be made of the results obtained on extruded polyethylene films. Whether row orientation is generally present in polyethylene films is difficult to ascertain, however, from the x-ray diffraction and infrared absorption data. It seems that the analysis based on the row-orientation model would be consistent with the observed data under conditions that the rows be parallel (within a small angle) to the extrusion or draw direction and the helical axes lie in planes perpendicular to the axis of the rows, with only small angular divergence. For such an organized structure to be achieved during the extrusion of film seems rather unlikely.

Careful review of the published results (202, 242, 243, 246) and extensive data on polyethylene films obtained in our laboratories show that it is difficult to the point of uncertainty to distinguish between the row orientation and *a*-axis orientation in polyethylene films on the basis of x-ray diffraction and dichroism of infrared absorption at 13.70 μ and 13.88 μ. The x-ray reflections, on the basis of which one may be able to distinguish between row orientation and *a*-axis orientation, are weak and are close to other reflections which tend to confuse the information. According to the row-orientation model, one expects the values of $E_\perp/E_\parallel$ (ratio of intensities of the bands with light polarized perpendicular to the draw direction to that for light polarized parallel to the draw direction) to be 0.5 for the 13.70 μ band and approximately 1.73 for the 13.88 μ band. In many polyethylene films there are deviations from these values beyond the experimental error. These deviations can be accounted for by introducing deviations of the helices from a perpendicular direction and of the rows from parallelism to the draw direction. But under these conditions it becomes difficult to explain the x-ray diffraction patterns shown by the samples. The authors believe that though the idea of row orientation is an interesting one and the data in most cases are consistent with the model, there are no definite reasons on the basis of x-ray results or infrared dichroism to prefer this row orientation over the *a*-axis orientation. The interpretation of the observed data as *a*-axis orientation does not require so organized a structure in the films as is necessary to assume in order to explain the results with the row orientation.

Though the positive birefringence shown generally by polyethylene films and electron microscopy results obtained on crystallizing polymers are in favor of the row-orientation model, little weight can be attached to these results, because of the multiplicity of effects that contribute to birefringence and because of uncertainty in the interpretation of the electron photomicrographs (e.g., see the discussion in reference 93).

C. STRETCHING AND RELAXATION OF POLYETHYLENE

The changes that occur in the orientation of the crystalline regions of polyethylene films or monofilaments on stretching and relaxation have been the subject of interesting studies. The results have unfortunately not been interpreted with sufficient caution.

In extruded polyethylene films, as already discussed, the preferred orientation of the crystalline regions is unique among high polymers. The results from x-ray diffraction and dichroism of the 13.70 μ and 13.88 μ bands may be interpreted either as *a*-axis orientation or as row orientation. After the polyethylene films have been stretched two- to threefold, the orientation changes to *c*-axis orientation, i.e., with the *c*-axis of the crystallites parallel to the stretching direction.

Two important questions arise from these observations: (*1*) How is this change of orientation on stretching brought about, and how are the crystalline regions oriented at intermediate stages of elongation? (*2*) What is the effect produced on orientation when the stretched samples are allowed to relax?

Answers to these questions were sought by x-ray diffraction studies of stretched and relaxed filaments of polyethylene (48). It was shown that when polyethylene is stretched at room temperature, the (011) reciprocal lattice vector first becomes parallel to the stretching direction, i.e., the (011) planes become normal to the stretching direction. Unfortunately, in the discussion of the results given in this paper (48), the term "crystal direction" has been interchangeably used with reciprocal lattice direction,[3] when in fact the [011] crystal direction, for instance, and the (011) reciprocal lattice direction are not the same (refer to the discussion of the geometry of the reciprocal lattice in references 62 and 64). The authors believe that this confusion has made quite ambiguous the discussion of the orientation effects, in spite of the subsequent correction in the value of the angle between (001) and (011) reciprocal lattice directions from 64° to 26° (49, 272). Unfortunately, later authors, who have carried out a detailed study of the changes in orientation during stretching and relaxing of polyethylene with the x-ray microcamera (209) also did not make the distinction between the direction in the reciprocal lattice and the direction in the crystal lattice, and many of their conclusions must be reëxamined for this reason.

Relaxation of highly stretched samples (in which the *c*-axis of the crystallites is oriented parallel to the direction of stretch) does not merely result in an increased disorientation of the *c*-axis, which would have resulted only in a broadening of the (*hk*0) reflections such as (200), (110), (020), etc. Instead, the positions of the centers of reflections from the (200), (110), etc. planes change on relaxation. Thus, on relaxation, the directions which become parallel are different from the [001] direction. In samples which were stretched fivefold and then fully relaxed, the *a*-axes, i.e., in the [100] direction, become parallel (48). The interpretation of published x-ray data on relaxed samples indicates that the change from the [001] direction in highly stretched samples to [100] in fully relaxed samples proceeds in a continuous manner through intermediate stages, with the restriction that the preferred directions have indices [*h*0*l*]. As relaxation proceeds, the *h* index becomes larger and larger, and the *l* index becomes smaller and smaller.

On the basis of the row orientation postulated (242, 243, 246) for polyethylene films, as discussed in Section VI,B, the changes on stretching and relaxation have been interpreted differently; according to this view the tightly coiled helices, along which the polyethylene crystallites are arranged in the original film, are progressively pulled out on stretching and the *c*-axis is aligned progressively more nearly parallel to the direction of stretch (243). To explain the results of relaxation, two types of helical windings have been postulated (243). In one type of helix (type I) the *a*-axis remains perpendicular to the direction of drawing, and in the other (type II) the *b*-axis remains perpendicular to the fiber or drawing direction. The fully relaxed samples have tightly coiled helices of type II. The relaxation is considered to take place along a helix of type II and the drawing to take place by extension along the type I helix. If, originally, type II helices are present, they are converted partly before and partly during the process of extension into helices of type I. This is an ingenious speculation, and some argu-

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[3] In the present discussion the following notation is used: (*hkl*) refers to a plane in the crystal lattice having Miller indices *h*, *k*, and *l*. In the reciprocal lattice, (*hkl*) refers to the point which represents the crystal planes having *h*, *k*, and *l* as Miller indices, or the direction joining the origin of the reciprocal lattice to this point. [*hkl*] refers to a direction in the crystal lattice or zone axis.

ments in favor of it are given in the original publications (241, 242, 243, 246), but the thesis is not solidly founded.

Further careful x-ray study of the changes during stretching and relaxation of polyethylene will be worthwhile. Analysis of the published x-ray diffraction pictures of stretched and relaxed polyethylene samples (48, 209, 243) indicates that the phenomena involved are interesting but not necessarily so involved as some authors have proposed. Though the published x-ray pictures are not sharp enough to permit definite conclusions, they indicate the following steps in orientation: (*a*) As polyethylene is stretched, the *a*-axis first becomes oriented perpendicular to the direction of stretch. The planes containing the *b*- and *c*-axes are perpendicular to the *a*-axis but otherwise randomly distributed. (*b*) As stretching proceeds, the directions [01*l*] with higher and higher index of *l* become aligned parallel to the direction of stretch. In highly stretched samples the limiting direction [001] is parallel to the stretching direction. (*c*) On relaxation, the *a*-axis, which was the first to become oriented, is also the first to become disoriented. The preferred directions achieved take indices like [*h*0*l*]. As relaxation proceeds, the *h* index increases and *l* decreases. As a limit, highly relaxed samples have the preferred direction [100].

The perfection of orientation on the surface of stretched (cold-drawn) polyethylene film has been studied from the oriented overgrowth of paraffin crystals (420). The distribution of orientation of the paraffin crystals grown on the surface of stretched polyethylene film was found to be sharper than that of the crystalline regions in the film as a whole, indicating that the crystallites on the surface are more perfectly oriented than in the interior.

VII. SOLUBILITY, FRACTIONATION, MOLECULAR WEIGHT, AND MOLECULAR-WEIGHT DISTRIBUTION

A. SOLUBILITY

The solubility of polyethylene in various solvents has been studied (343, 418). Polyethylene generally is not soluble in any solvent below 50–60°C., but at temperatures above 70°C. it is soluble in many solvents. Carbon tetrachloride and highly chlorinated ethylenes are the most effective solvents (343). In toluene and xylenes, polyethylene shows appreciable solubility above 60°C. The solubility decreases rapidly with increasing chain length. Polyethylene samples with branched structure and heterogeneity in molecular weight have a higher solubility than is shown by unbranched polyethylenes of the same average molecular weight and of narrower distribution (338, 343).

The solubility curves of polyethylene in good solvents rise monotonically as a function of temperature, indicating an equilibrium between liquid and crystalline solid. With poor solvents such as amyl acetate and nitrobenzene, however, the solubility curve passes through a maximum at low concentration. This is indicative of liquid–liquid equilibrium between concentrated and dilute solution phases. The phase diagram of polyethylene with either amyl acetate or nitrobenzene exhibits two concentration regions, one over which liquid–liquid phase separation occurs and the other over which equilibrium between liquid and crystalline solid phases exists (155, 418). It is unfortunate that this important difference in phase equilibria between polyethylene and different solvents has not been appreciated in selecting solvents for fractionation studies.

B. FRACTIONATION

In the fractionation of polyethylene several experimental and theoretical difficulties arise. Most fractionations must be carried out at elevated temperatures because of the very limited solubility of polyethylene at room temperature. Furthermore, a main difficulty in obtaining good fractions of polyethylene is that from most solvents polyethylene separates as a semicrystalline phase instead of as the concentrated solution, or gel phase, which usually occurs with most amorphous polymers such as polystyrene. The separation of the crystalline phase is usually a poorly reversible process, attended by large supercooling effects. In a case like this, the crystallization rate plays a role comparable in importance with the equilibrium solubility. Whereas equilibrium factors favor separation of species of the higher molecular weights, the inherent slow tendency to crystallize may prevent them from separating (154). Unless proper care is taken in the selection of a solvent for fractionation, the intermediate fractions may have molecular weights higher than those removed in the early stages of the fractionation, and the fractionation is consequently ineffective. Unfortunately, in most of the reported fractionation studies of polyethylene this has not been taken into consideration, and the solvents used are not those which give liquid–liquid separation.

Fractional extraction by toluene of polyethylene, deposited over a porous support, by varying the temperature of extraction was attempted to obtain fractions of polyethylene (112). A reversing of the intrinsic viscosity values of the isolated fractions was observed, the less soluble fractions having lower values of intrinsic viscosity. The choice of toluene as a solvent probably caused this anomaly, and it is doubtful that efficient fractionation was achieved by the procedure described.

Another procedure based on the addition of a nonsolvent (propanol) to a solution of polyethylene in toluene has also been described (468, 515). In these studies the values of the intrinsic viscosity of the intermediate fractions were not found to be higher than for the fractions which separated first. In a number of fractionations by the procedure described by Ueberreiter, Orthmann, and Sorge (515), it was found, however, that some of the intermediate fractions (see table 5) did have a higher intrinsic viscosity than that of the fractions which had separated earlier (4). Solvents which do not give liquid–liquid separation of phases should be avoided, and neither of these two procedures is suitable for efficient fractionation. Another procedure which has been attempted for the fractionation of polyethylene is coacervation (356). Recently, the successful fractionation of several commercial polyethylenes has been reported (512a). Xylene was used as solvent and triethylene glycol as nonsolvent. The fractionation was done at 130°C. by application of both extraction and precipitation techniques.

A procedure which appears most promising for the fractionation of polyethyl-

TABLE 5

*Comparison of fractionation by fractional precipitation from toluene, and by cooling an amyl acetate solution**

Fractional Precipitation from Toluene Solution by Propanol				Fractionation by Cooling an Amyl Acetate Solution				
Fraction number	Cumulative volume of propanol added to 2% solution in toluene	Weight per cent of total sample	$[\eta]$ in toluene at 80°C.	Fraction number	Temperature of separation	Form of fraction	Weight per cent of total sample	$[\eta]$ in toluene at 80°C.
	ml.		*(g./100 cc.)*$^{-1}$					*(g./100 cc.)*$^{-1}$
1	200	4.3	0.959	1	131	Gel	23.3	1.60
2	275	26.9	1.338	2	120	Gel	13.2	1.15
3	350	7.3	1.194	3	109	Gel	4.7	0.87
4	400	11.0	1.465	4	105	Gel	6.5	0.84
5	550	25.1	0.953	5	95	Granular	7.6	0.57
6	725	10.3	0.509	6	90.5	Granular	10.1	0.54
7	925	6.2	0.386	7	83	Powder	12.7	0.43
8	Complete precipitation	~8.9		8	67	Powder	14.0	0.29
				9	30 (Approx.)	Powder	7.9	0.17

* Experiments were performed with DYNH polyethylene which had an intrinsic viscosity of 0.95 (g./100 cc.)$^{-1}$ in toluene at 80°C.

ene is to cool slowly a solution of polyethylene in amyl acetate. Starting at about 130°C., most of the fractions of high molecular weight separate in gel form down to about 105°C. Below 105°C. the phase that separates is crystalline, but because of the prior removal of most of the material of higher molecular weight, the fractions separating below 105°C. in crystalline form are satisfactory. Results of fractionation by cooling amyl acetate solutions of a polyethylene sample (4) are given in table 5 and are compared with the fractions obtained from the same sample using propanol as nonsolvent and toluene as solvent, according to the method described in reference 515.

C. MOLECULAR WEIGHT AND MOLECULAR-WEIGHT DISTRIBUTION

The determinations of the molecular weights of polyethylene from measurements of such properties as osmotic pressure and light scattering are beset with considerable experimental difficulty because of the necessity of making measurements at temperatures above 70°C. Techniques have been developed, however, to make osmotic pressure measurements at elevated temperatures to determine the number-average molecular weight of unfractionated and fractionated polyethylene samples (4, 187, 391, 472, 515).

Osmometers of the Zimm–Myerson type (548) modified for use at high temperatures (391, 472) have been found quite suitable for osmotic pressure measurements of polyethylene solutions. For polyethylenes of low molecular weight (number-average < 6000), methods based on elevation of the boiling point (187, 330) and depression of the freezing point (13) have been used.

Because of the convenience of measuring intrinsic viscosity, in contrast to measurements of molecular weights by methods such as osmotic pressure and light scattering, attempts have been made to relate intrinsic viscosity to molecular weights determined by other methods. From osmotic pressure and ebulliometric measurements on a number of unfractionated polyethylenes, the following relation between intrinsic viscosity, $[\eta]$, measured in xylene at 75°C., and number-average molecular weight, $\bar{M}_n$, has been proposed (187):

$$[\eta]\ (\text{g./liter})^{-1} = 1.35 \times 10^{-4}\bar{M}_n^{0.63}$$

The viscosity-average molecular weight calculated from intrinsic viscosity is closer to a weight-average than to a number-average molecular weight, however (153). It is doubtful that the relation between number-average molecular weight and intrinsic viscosity can be of general validity for unfractionated polyethylene samples. At best, relations of this type can be valid only for polyethylenes which have similar molecular-weight distribution curves.

A more generally valid relation between molecular weight and intrinsic viscosity has been obtained from the measurements of osmotic pressure of polyethylene fractions obtained by cooling amyl acetate solutions (4). This relation is

$$[\eta]\ (\text{g./100 cc.})^{-1} = 7.25 \times 10^{-5}\bar{M}_n^{0.85}$$

for $[\eta]$ measured in toluene at 80°C. Since this relation was obtained on consistent fractions of polyethylene, it is to be expected that the application of this relation to unfractionated polyethylene will give molecular weights closer to the viscosity average. It would be better still to establish a relationship of this form from molecular weights determined by light scattering (153). It should also be pointed out here that if the polyethylene has long-chain branching its intrinsic viscosity will be lower than that of a linear polymer of the same weight-average molecular weight (485, 504, 549). The molecular weight of polyethylene with long-chain branching calculated from an intrinsic viscosity–molecular weight relation will therefore be lower than the true viscosity-average molecular weight.[4]

Light-scattering measurements have been made on solutions of polyethylene in α-chloronaphthalene at elevated temperatures (ca. 125°C.) to determine weight-average molecular weights (36, 329, 339). The polyethylene solutions are difficult to clarify by filtration, and light-scattering measurements may be in error because of the unavoidable presence of dust or other large scattering particles. In spite of this uncertainty, the noteworthy fact is that the ratios of the weight-average to number-average molecular weights for most of the polyethyl-

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[4] Since the preparation of the manuscript, other relationships of molecular weight and intrinsic velocity have been published. For linear polyethylene in the range of molecular weights from 50,000 to 6,000,000, measured in 1-chloronaphthalene at 125°C.,

$$[\eta]\ (\text{g./100 cc.})^{-1} = 4.3 \times 10^{-4}\ \bar{M}_w^{0.67}$$

(Atkins, J. T., Muus, L. T., Smith, C. W., and Pieski, E. T.: Abstracts of Papers Presented at the 130th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1956, p. 16-S). Another relationship

$$[\eta] = 2.36 \times 10^{-4}\ \bar{M}_w^{0.75}$$

has been reported for linear polyethylenes of molecular weights varying from 50,000 to 1,500,000; viscosities were measured in tetralin at 120°C. (Duch, E., and Küchler, L.: Z. Elektrochem. **60**, 220 (1956)).

enes are notably higher than for most of the common polymers. Ratios of weight-average to number-average molecular weights as high as 40 to 70 have been reported for some samples of polyethylene (13, 36, 329). For polymers which show exponential distribution of molecular weights [$W(m) = ame^{-am}$, where $W(m)$ is the weight fraction of a species of molecular weight m] the ratio between weight- and number-average molecular weights is 2. The high ratios between weight-average and number-average molecular weights is of course indicative of quite broad molecular-weight distribution curves. The molecular-weight distribution curves in the high-molecular-weight range for most polyethylenes are of the form:

$$W(m) = bm^{-n}e^{-am}$$

where a has values between 0 and 1.0. This broad distribution of molecular weights when $W(m)$ is plotted against m is a consequence of chain transfer by a growing radical to a polymer molecule already formed, thus leading to the development of long-chain branching (*cf.* Section IV,C). The presence of a high-molecular-weight tail in the molecular-weight distribution curves gives the observed high values of weight-average molecular weights.

Recently an elegant method for the study of molecular-weight distribution in polymers such as polyethylene which undergo cross-linking on irradiation with high-energy radiation has been proposed (84, 85, 87). Polyethylene on irradiation also undergoes chain scission (26a), and a general mathematical treatment has been developed (26) which takes into account both scission and cross-linking during irradiation. This permits the calculation of the molecular-weight distribution in the original polymer from the measurements of gel fraction as a function of radiation dosage. The general conclusions with respect to molecular-weight distribution from these studies are in agreement with the results indicated from light-scattering studies (36, 329, 339) and predicted from theoretical consideration of chain transfer to a dead polymer molecule (28).

VIII. RHEOLOGICAL PROPERTIES OF MOLTEN POLYETHYLENE

The deformation and flow of molten polyethylene under an applied stress are of interest not only because of the practical importance of these rheological properties in the design of extrusion or molding equipment, but also because of the important relations that may exist between the molecular and flow properties of the polymer. The rheological properties of melted polyethylene are of considerable importance in the design of extruders of high capacity which are suited to polyethylenes of different flow properties. Recently, considerable attention has been devoted to the developing of principles for the design of extruders and extrusion dies which take into account the flow properties of the molten polymer (32, 72, 73, 74, 75, 76, 77, 180, 311, 319, 508). It is therefore surprising to find that the rheological properties of polyethylene have not been given detailed study.

The importance of the melt viscosity of polyethylene has, however, been appreciated in an empirical way ever since the commercial manufacture of this

TABLE 6

Melt viscosities at 202.2°C. by capillary viscometers and melt index at 190°C.

Sample Number	Polyethylene Designation and Source*	Melt Viscosity in Poises × 10^{-4}		Melt Index†	
		Mean	σ	Mean	Average Deviation from Mean
1	DYNH-3, Bakelite	6.28	± 0.81	1.95	± 0.03
2	DYNH-3, Bakelite	8.56	± 0.77	1.48	± 0.02
3	DYNH-3, Bakelite	5.69	± 2.07	1.87	± 0.01
4	DYNH-3, Bakelite	7.15	± 0.70	1.51	± 0.01
5	Alathon-10, du Pont	6.35	± 0.45	1.96	± 0.01
6	Alathon-14, du Pont	9.69	± 0.74	1.73	± 0.04
7	Alathon-10, du Pont	5.46	± 0.17	2.16	± 0.02
8	Alathon-10, du Pont	7.11	± 0.20	2.03	± 0.11
9	Alathon-10, du Pont	7.69	± 0.39	1.90	± 0.04
10	Alkathene-2, I.C.I.	4.91	± 0.39	1.90	± 0.04
11	Experimental sample	3.57	± 0.31	2.37	± 0.02
12	Experimental sample	16.37	± 0.36	0.58	± 0.01
13	Experimental sample	10.75	± 0.55	0.88	± 0.03
14	DYNJ, Bakelite	14.13	± 0.22	0.83	± 0.22
16	Alkathene-7, I.C.I.	1.92	± 0.77	5.45	± 0.24
17	Experimental sample	7.36	± 0.23	1.27	± 0.04
18	Experimental sample	3.78	± 0.14	2.02	± 0.02
19	Experimental sample	5.53	± 0.29	1.68	± 0.04
20	Experimental sample	4.22	± 0.13	2.35	± 0.02
21	Experimental sample	14.63	± 0.41	0.58	± 0.02
22	Experimental sample	12.96	± 0.32	0.92	± 0.02
23	Experimental sample	3.51		2.90	± 0.02
24	Experimental sample	3.32	± 0.13	3.08	± 0.04

* See table 3.

† See footnote 5.

polymer. In the industry the measurements of melt index,[5] which is an empirical measure of the flow properties of the polymer, have long been utilized in the characterization and grading of polyethylenes (12). Melt index, though useful in grading polyethylenes of widely different flow characteristics, is not an adequate measure of the rheological properties or of viscosity of the molten polymer. It is not uncommon to find polyethylenes of the same melt index with markedly different rheological properties.

Since melt index is currently used so commonly in the characterization of polyethylenes, it is pertinent to mention the limitations of this criterion. Melt viscosities of a number of polyethylene resins have been determined (2) by capillary viscometers, using a technique similar to that used for the studies on melt viscosities of polyesters, polystyrene, and polyisobutylene (152, 159). The values of the melt index of the same samples were determined at 190°C. according to the standard procedure (12). Table 6 presents the values of melt viscosities at 202.2°C. as determined in capillary viscometers and the values of the melt index of a number of experimental and commercial polyethylene samples. The plot of melt viscosity as a function of the reciprocal of melt index for these poly-

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[5] The melt index is the weight in grams of polyethylene extruded in 10 min. at constant temperature through an orifice of specified diameter when a given weight is placed on the driving piston.

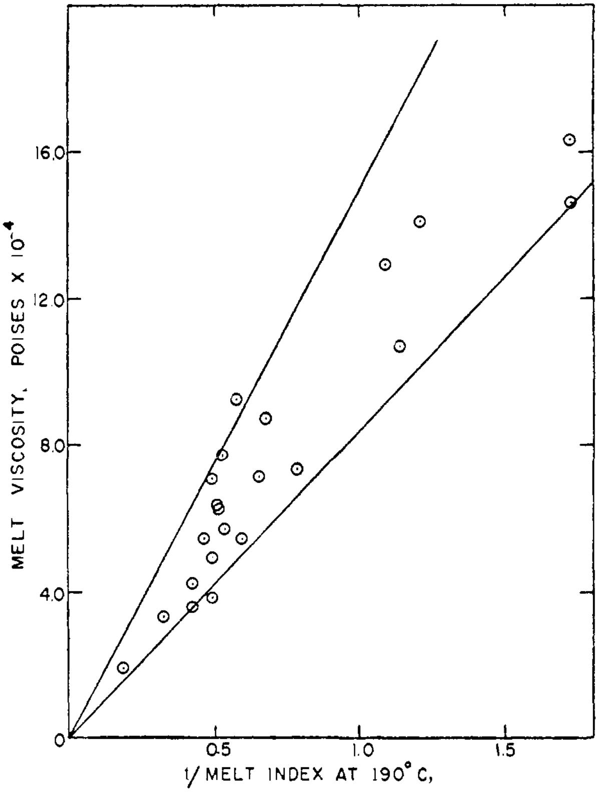


FIG. 12. Melt viscosity of polyethylenes at 202.2°C. as a function of the reciprocal of melt index at 190°C.

ethylenes (figure 12) shows a considerable amount of scattering. The experimental points lie between lines of appreciably different slope. Two important reasons seem to explain this lack of correspondence between the melt-viscosity and melt-index values: (*1*) Molten polyethylene shows a notably non-Newtonian behavior, i.e., at shearing stresses of the magnitude of those under which the melt-index apparatus operates, the rate of shear is not linear with shearing stress. In the measurements by capillary viscosimeters, the shearing stress used is so small that the flow behavior is nearly Newtonian. The relations between shearing stress and rates of shear (a measure of the non-Newtonian character) for the melts from different polyethylenes may vary appreciably. (*2*) The deformation of the polymer melt under a given shearing stress is also dependent on time, and in the measurements of the melt index, account is not taken of the entrance and exit corrections in the flow of the melt through the orifice used in the apparatus. These corrections would be expected to vary for samples of different flow characteristics. Other sources of error also exist in the use of the melt-index apparatus which limit its ability to characterize the flow properties of polyethylene samples adequately, but a discussion of these is beyond the scope of this review.

A simple way to characterize the polyethylene samples on the basis of the flow properties of the melt, which takes into consideration non-Newtonian flow, is to measure the weight of polyethylene extruded through a capillary orifice under different driving forces (i.e., under different average shearing stresses). This can be done conveniently by using different weights on the driving piston of the melt-index apparatus. The weights of polyethylene W extruded in 3 min., as a function of the mass P in kilograms of a weighted piston exerting pressure on the melt, have been measured for several polyethylene samples from different sources and found to obey the linear relation (3):

$$W/P = \Phi + \theta P \tag{1}$$

In this relation Φ and θ are two parameters characteristic of the resins. The relation was obeyed well for values of P up to 4 kg. In table 7 are given the values of Φ and θ found. The results demonstrate the differences in the shear dependence of flow of different polyethylenes, i.e., the non-Newtonian character of flow. The data in table 7 do not characterize the flow behavior of polyethylene as precisely as one might wish, but do show that at least two parameters are essential to characterize the flow of molten polyethylene by the use of the melt-index apparatus. The parameter Φ corresponds to the fluidity of the melt, and θ is a measure of shear dependence of flow, in arbitrary units.

The non-Newtonian behavior of polyethylene melts may also be analyzed by assuming that an equation of the general form

$$\mathrm{d}\gamma/\mathrm{d}t = A(S/S_0)^n \tag{2}$$

holds between the rate of shear ($\mathrm{d}\gamma/\mathrm{d}t$) and the shearing stress S (72). In this equation A (sometimes called the generalized fluidity) and n are two parameters, and S_0 is introduced by the requirements of dimensional analysis. Using an extrusion rheometer, and comparing the rates of flow through a capillary with those expected for a Newtonian liquid (Poiseuille's law), it was shown that, over the range of shear rates studied, the power law relation (equation 2) between the rates of shear and shearing stress holds satisfactorily for polyethylene. For an Alathon polyethylene (du Pont) a value of $n = 2.6$ was found (508).

One aspect of the non-Newtonian behavior of molten polyethylene is that the deformation under a given stress is not purely viscous but has in addition an appreciable contribution from the elastic strain (113, 114, 200). Since the response to stress of elastic and viscous flow components is simultaneous, the deformation produced under a given stress is dependent on time, and the curves showing deformation as a function of time are not linear. Using a concentric cylindrical rotational plastometer coupled with a recording device to obtain plots of shear strain versus time t, it was shown (113) that the data fitted the equation:

$$\gamma = St/\eta + \gamma_e[1 - \exp(-t/\tau_0)] \tag{3}$$

where η = observed viscosity, S = shearing stress, γ_e = total *elastic* shear

TABLE 7

Melt index and parameters Φ and θ in equation 1

Sample Number	Polyethylene Designation and Source*	Melt Index at 190°C.	Φ at 190.4°C.	θ at 190.4°C.
			(g./kg.) × 10²	(g./kg.²) × 10²
1	DYNH, Bakelite	2.76	17.6	9.6
2	DYNH, Bakelite	1.98	10.3	8.0
3	DFDA-Bakelite	3.50	23.2	11.48
4	DYNH-3, Bakelite	2.10	12.10	7.88
5	Alathon-10, du Pont	2.10	13.20	7.72
6	Alathon-12, du Pont	2.53	13.50	9.68
7	Alathon-12D, du Pont	3.32	28.3	8.32
8	Alathon-14, du Pont	1.98	10.4	7.84
9	Alathon 21x, du Pont	2.92	18.0	10.56
10	Polyeth, Spencer	2.50	23.2	5.22
11	Polyeth, Spencer	2.36	18.6	6.72
12	Petrothene, U.S.I.	3.48	35.2	5.96
13	Petrothene, U.S.I.	2.10	19.6	4.72
14	Orizon, Monsanto	2.06	12.4	7.60
15	Orizon, Monsanto	3.36	23.5	10.60
16	Alkathene-2, I.C.I.	2.16	14.0	7.44
17	Alkathene-7, I.C.I.	8.60	56.0	29
18	Lupolen-H, B.A.S.F.	3.26	28.8	7.68
19	Tenite, Eastman		17.6	4.72
20	Tenite, Eastman	9.23	65.6	29.0
21	Tenite, Eastman	2.08	15.5	6.8
22	Marlex-50, Phillips	0.85	4.1	3.7
23	Marlex-50, Phillips	0.89	6.8	2.56

* B.A.S.F. = Badische Anilin und Soda Fabrik; for the others, see table 3.

strain, and τ_0 = retardation time (9). Thus the total shear strain has been divided into a viscous part and the time-dependent elastic strain. Analysis of the data gave the following results: (*1*) The viscosity decreases with increasing shearing stress. The effect of shearing stress on viscosity decreases at low rates of shear, or, in other words, at low rates of shear the melts are Newtonian liquids. (*2*) The elastic shear strain γ_e increases with shearing stress and is independent of temperature. The relation between elastic shear strain and shearing stress is of the form:

$$\gamma_e = c \ln(S/S_0) \tag{4}$$

where S_0 is the shearing stress at which elastic shear strain is zero. (*3*) Temperature dependence of viscosity at constant shearing stress may be expressed by the relation

$$\eta = Ae^{\Delta H_v/RT}$$

where ΔH_v is the heat of activation for viscous flow. ΔH_v is independent of shearing stress and is approximately 12–14 kcal./mole. (*4*) A unique relationship exists between the dependence of the viscosity on shearing stress and the magnitude of the elastic shear strain. This relationship is interpreted to mean that the change in viscosity with shear is associated with an entropy effect similar to that for rubberlike elasticity (510). These conclusions, in particular (*4*), are not based on sufficient data to establish the general validity and quantitative aspects of the relations presented in the original paper (113). Whatever the treatment may lack in rigor, however, is compensated for by the simplicity of the explanation of the phenomena involved in the flow behavior.

Using a resonance method in which shearing oscillations at about 30 cycles per second were induced at small shear amplitudes, further detailed information has been obtained regarding the combination of elastic and viscous components of deformations and particularly the quantitative measure of the elastic shear modulus G (200). These studies showed that the flow behavior of most of the polyethylene melts could be approximated by a mechanical model of a spring of elastic modulus G and a dashpot of viscosity η combined in series (the Maxwell model). On prolonged heating of the melt the flow behavior approximates, however, the Voigt model, in which the elastic and viscous components are combined in parallel. For analysis on the basis of Maxwell's model, a single relaxation time $\tau = \eta/G$ was considered sufficient to describe the results. Reference should be made to Alfrey (9) for a discussion of relaxation times and the Maxwell and Voigt models. Both the elastic shear modulus and the viscosity were found to be strongly dependent on temperature. The activation energies for both functions were found to be dependent on molecular weight. The activation energy of the viscous component, E_η, was found to be lower than that of the elastic component, E_G, at molecular weights below about 40,000, above which they were about equal. The dependence of G and η on molecular weight was found to be different. The relaxation times, η/G, when plotted against molecular weight were therefore found to give S-shaped curves. The elastic shear moduli, G, for polyethylene melts were found to be quite high, of the order of 10^5–10^6 dynes/cm.^{2}, at least at small shear amplitudes.

Considering the viscosity of the melt measured at low rates of shear where the contribution of elastic shear strain is negligible and the flow is Newtonian, it would be expected that a relation between melt viscosity and weight-average molecular weight exists. For polymers in general, it has been proposed that melt viscosity varies as the 3.4 power of the weight-average molecular weight (164), provided that the molecular weight is above a critical value. This is in approximate agreement with the dependence of isothermal melt viscosity on molecular weight expected from theoretical considerations (61). It has been shown recently that the melt viscosity of polyethylene at a given temperature also varies as the 3.4 power of the weight-average molecular weight, provided that appropriate correction for the number of short chains per hundred methylene groups is made (386). Long-chain branching of polyethylene was shown to have no appreciable effect on melt viscosity. The relation between melt viscosity and weight-average molecular weights was found to be (386):

$$\eta_0 = 3.01 \times 10^{-12} \bar{M}_w^{3.4} e^{-2.35 N_c} \qquad (5)$$

where η_0 = isothermal viscosity of the melt under Newtonian conditions of flow, $\bar{M}_w$ = weight-average molecular weight, and N_c = number of methyl groups (equal to the number of short-chain branches) per hundred methylene groups in polyethylene.

Relations between the melt viscosity and the number-average molecular weight of polyethylene have also been suggested (29, 470, 513). Relationships between number-average molecular weight and melt viscosity are not expected from analogy with other polymers (164) and are not predicted by the theory of viscosity of polymers (61, 152, 159, 160, 161, 162, 235, 236). It may be that the theory of segmentwise flow is not applicable to the viscous flow of polyethylene.

In the vicinity of the melting point, the change from flow to immobility has been found to be not smooth (513). This has been interpreted to indicate that between regions of real melting and immobile structures, there is a region over which flow with fixed structure occurs. It has been suggested that the flow of molten polyethylene is best described by the concept of a macromolecule as a vibrating fiber (513). The nodes act as adhesive points. At the melting point the concentration of these nodes is small. Below the melting point the concentration of nodes increases, giving rise to flow with fixed structure. These nodes may serve as nuclei for crystallization at lower temperatures.

In conclusion, though interesting and valuable results have recently been obtained, more precise and detailed data are needed on the rheological properties of polyethylene.

IX. Degradation of Polyethylene

The degradation of polyethylene has been studied over a wide temperature range in the presence and absence of air or oxygen, with and without the influence of light.

A. THERMAL DEGRADATION IN VACUUM

In the absence of oxygen, polyethylene is stable up to about 290°C.; at higher temperatures degradation occurs progressively, but unlike polystyrene and the acrylates which are degraded to monomer, polyethylene yields products which are like the original polymer but of a lower degree of polymerization. Further degradation yields liquids, but only above 370°C. are appreciable amounts of gaseous products formed. About thirty such gaseous products result (summarized in table 8), consisting of straight-chain alkenes, alkanes, and dienes (308, 520). Infrared study has shown (364) the presence of the structures $RCH{=}CH_2$, $RCH{=}CHR'$, and $RR'C{=}CH_2$, the amount of unsaturation increasing as the extent of degradation increases, though the amount of ethylenic and vinylidene unsaturation seems to reach a constant value at a molecular weight of about 700.

It is likely that weak links in the polymer chain are first ruptured and that pyrolysis then proceeds by a chain reaction, particularly at higher temperatures. Such weak links may be at branches or in positions adjacent to carbonyl or other oxygenated structures in the chain (364).

Madorsky has suggested (302) that the polyethylene chains break mostly at random positions, probably related to the nature and frequency of branches. Unbranched polymethylene prepared by the decomposition of diazomethane is

TABLE 8

Pyrolysis products of polyethylene (308) and polymethylene (306)

(Volatiles at room temperature)

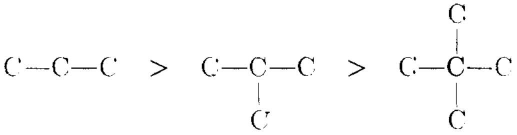
Component*	Polyethylene†	Polymethylene‡	Component*	Polyethylene†	Polymethylene‡
	mole per cent	*mole per cent*		*mole per cent*	*mole per cent*
Ethylene	4.3	12.3	Pentadienes	0.4	2.8
Ethane	12.4	4.3	Pentenes	7.5	9.6
Allene	0.3	1.4	*n*-Pentane	6.2	6.1
Propylene	5.2	20.7	Hexadienes	0.3	2.6
Propane	14.8	3.6	Hexenes	3.2	8.7
Butadiene		2.1	*n*-Hexane	1.2	1.6
Butenes	24.6	13.0	1-Heptene	0.2	
n-Butane	19.1	11.2	*n*-Heptane	0.4	

* Determined by the mass spectrometer.

† Average molecular weight 20,000; pyrolyzed at 360–475°C.

‡ Average values for pyrolysis at 398–435°C. The sample had an intrinsic viscosity of 8.6 ± 1 (100 ml./g.)$^{-1}$ in xylene at 100°C. and was therefore of high molecular weight.

more stable than ordinary commercial polyethylenes, polypropylene, or polyisobutylene (table 9) and shows some differences in degradation products (306) from those previously reported for polyethylene (308), notably in an increase in the amount of unsaturated products (table 8). The results are consistent with the view that polymer chains break at the weakest point when heated, carbon-to-carbon bond strengths being in the order



$$\mathrm{C{-}C{-}C} > \mathrm{C{-}\underset{\underset{\displaystyle C}{|}}{C}{-}C} > \mathrm{C{-}\overset{\overset{\displaystyle C}{|}}{\underset{\underset{\displaystyle C}{|}}{C}}{-}C}$$

Aromatic rings impart thermal stability; a carbon-to-carbon bond beta to a double bond is a point of weakness. Polypropylene in which alternate carbons are of the tertiary type and polyisobutylene in which alternate carbons are quaternary are less stable thermally than polyethylene. The mechanism of the depolymerization of polyethylene has been discussed in detail (461, 463, 522).

The energy of activation for the degradation of polyethylene in the range 375–436°C. was reported to change from 66.1 to 46.0 kcal./mole in passing from a molecular weight of 23,000 to 11,000 (226), but other work in the 9,000 to 23,000 range of molecular weights has shown that the energy of activation is 60–70 kcal./mole and is independent of chain length (364). In plotting rate of loss of weight against per cent volatilized, Madorsky found the rate to start high, decrease linearly, undergo a sharp break at a percentage characteristic of each temperature studied, and then show another linear decline (302). From these results the activation energy was calculated as 68 kcal./mole (227, 302, 304). The low values of the activation energy of degradation result if the calculations are based on the initial rate of volatilization; this may give a misleading result if the high initial rate is the result of loss of polymer of low molecular weight present initially in the sample (302). The decomposition

TABLE 9

Rates of thermal degradation of polymers in a vacuum at 350°C.

Polymer	Volatilization, Per Cent of Original Sample per Minute	Reference	Polymer	Volatilization, Per Cent of Original Sample per Minute	Reference
Polytetrafluoroethylene	0.000002	(305)	Poly-α-deuterostyrene	0.27	(303)
Polymethylene	0.004	(306)	Polyvinylcyclohexane	0.45	(303)
Polybenzyl	0.006	(306)	Poly-*m*-methylstyrene	0.90	(303)
Polyethylene	0.008	(302)	Polyisobutylene	2.4	(306)
Polypropylene	0.069	(306)	Polymethyl methacrylate	5.2	(303)
Poly β-deuterostyrene	0.14	(306)	Poly-α-methylstyrene	230.	(303)
Polystyrene	0.24	(302)			

process approximates a first-order reaction, but this is incompatible with an ordinary random degradation (462). Polymethylene was found to have an activation energy of 76 kcal./mole, polypropylene 61, and polyisobutylene 52 (306).

The thermal degradation of polymers in vacuum as a function of molecular structure and branching has been discussed (307).

B. THERMAL DEGRADATION IN AIR OR OXYGEN

A general review of the early work on the oxidation of hydrocarbons in general and of the effect of oxygen on the chemical properties of polymers has appeared (315).

The pyrolysis of polyethylene in air at atmospheric pressure gives more low-boiling material than does pyrolysis at reduced pressure or in an atmosphere of carbon dioxide (456). All products were unsaturated and could be redistilled with little further decomposition.

The oxidative aging of polyethylene appears to be an autocatalytic free-radical reaction, which can be inhibited by carbon black (known to be effective in deactivating free radicals) and by standard antioxidants (35). The source of free radicals is as yet unproved, but probably involves the decomposition of hydroperoxide groups which are initially formed, according to the commonly accepted view of hydrocarbon oxidation (315). The spectra of some peroxides and hydroperoxides have been examined, and it appears that there is no absorption band characteristic of these groups which is sufficiently strong to permit detection unequivocally of these groups in polyethylene. Investigation of the O—H stretching region during the oxidation of polyethylene at 140°C. has shown, however, a continuous deepening of absorption at 2.81 μ which the authors ascribe to hydroperoxide groups (440); this absorption disappeared when the oxidized sample was cooled to room temperature.

Polyethylene films have been aged in oxygen and in air at temperatures of 170–225°C., in oxygen–ozone mixtures at 25–109°C., and in 90 per cent fuming nitric acid at 25–83°C. (27a). Structural changes were followed by infrared spectroscopy. In oxygen, the O—H band at 2.9 μ developed rapidly at 150–

TABLE 10

Pyrolysis of polyethylene at 400–500°C. (456)

Conditions	Distillation Products			
	Gases	Boiling Point 40–160°C.	Boiling Point 160–250°C.	Boiling Point >250°C.
	per cent	*per cent*	*per cent*	*per cent*
0.5 mm. pressure	14.5	0	0	80
1 Atmosphere	18	12	8	40
CO_2 atmosphere	11.5	8	12	64.5
Vigreux column, atm.	13	16	17	40

210°C. and soon reached a maximum, indicating the formation of hydroperoxide links. The 5.9 μ band ($>$CO absorption) continued to increase throughout aging, but C—O—C bands at 8–8.5 μ were the last to appear, signifying cross-linking by secondary reactions. Among the evolved products water, carbon dioxide, formaldehyde, and aliphatic acids with ketone and aldehyde groups present were identified. Mixtures of ozone and oxygen degraded polyethylene faster than did oxygen, but the chemical processes involved appeared to be the same. Fuming nitric acid at low temperatures produced mainly chain scission, since the C=C band at 6.08 μ became pronounced; at higher temperatures nitration became the principal reaction.

No marked changes in the concentration of carbon–carbon double bonds have been found as a result of heat oxidation of polyethylene (100, 440). A small decrease occurs in methylene side chains and vinyl groups, which is almost exactly offset by an increase in internal double bonds (440).

The oxidation of polyethylene in the range 110–160°C. has a pronounced induction stage; initially the uptake is rapid, with an energy of activation of 25 kcal./mole, followed by a constant rate of absorption of oxygen with an activation of 35 kcal./mole, ending in a sharp drop in oxygen uptake (530).

The rate of oxidation of polyethylene at room temperature in the absence of light is negligible, but photoöxidation is very rapid and cannot be inhibited by the use of antioxidants; only fillers which exclude light, such as lead chromate, iron oxide, and particularly carbon black (35, 523), are effective. The only compounds which equalled carbon black in effectiveness were certain highly colored complexes of copper and nickel (69). The efficiency of carbon black has been ascribed to the ability of the graphitic structure of the material to capture free radicals either by chemical combination with unpaired electrons or by interaction with the condensed aromatic rings present (492a). A polyethylene containing 0.2 per cent of antioxidant and 2 per cent of carbon black is much used for outdoor electric cable.

C. PHOTOÖXIDATION

The mechanism of photoöxidation probably involves absorption of energy in the oxygenated groups of the polyethylene chain (introduced from the catalyst used in manufacture), since saturated hydrocarbons do not absorb radiation at wavelengths greater than 2000 A., and only light within the carbonyl absorption region (2500–3500 A.) causes photoöxidation (69, 398). Prolonged irradiation by a quartz mercury arc gives noticeable deterioration of the power factor and increased tendency to crack after 20 to 40 hr.; oxygen absorption may be followed manometrically; the infrared absorption spectrum shows alteration, with the appearance of carbonyl absorption bands at 5.9 μ, carboxyl at 8.5 μ, hydroxyl at 3 μ, and ethylenic unsaturation at 10.65 μ (398). Similar results have been obtained in other investigations (100, 501).

Infrared absorption studies with a grating spectrophotometer have given further details of the oxidative process (440). Samples oxidized by heat alone show strong absorption only at 5.812 μ, ascribed to ketonic carbonyl groups, but photoöxidized samples show absorptions at 5.84 μ and 5.77 μ also, indicating acid and aldehyde carbonyls in addition to ketonic (no ester or anhydride absorptions were found). In a highly heat-oxidized sample the major part of the oxidation remains ketonic, but in a highly photoöxidized sample the amounts of aldehyde, ketone, and acid are roughly equal. Though the concentration of carbonyl groups is approximately the same for heat-oxidized and photoöxidized samples of polyethylene, changes in carbon–carbon double-bond structures in photoöxidized samples are quite pronounced. The number of internal double bonds is approximately doubled, vinyl unsaturation increases sevenfold, and the concentration of methylene side chains falls to one-fourth of the initial value, with the net result that after photoöxidation twice as many double bonds are present as were initially present in the resin (440).

The high dielectric strength of polyethylene was the principal reason for the rapid commercialization during the war years. The dependence of the electric strength upon temperature from −200 to 100°C. has been studied for polyethylene and for chlorinated and oxidized polyethylenes (362). Considerable amounts of data have been published on electrical loss characteristics after photoöxidative degradation (224, 309, 342, 344, 398). It has been found that the degree of thermal oxidation (as measured by the power factor at 50 Mc.) increases with temperature, time, and milling speed (40).

Accelerated weathering tests of polyethylene indicate that a material containing 1 per cent or more of properly dispersed carbon black of a particle size less than 25 mμ may be expected to have a life of at least 20 years, when exposed to severe conditions in sunlight (523). In extrusion, high melt temperatures and cold quenching increase the resistance to cracking; addition of up to 5 per cent of fillers has no adverse effect on environmental stress-cracking (179).

Environmental cracking of polyethylene is not thoroughly understood. Under biaxial stress the material undergoes conchoidal fracture from forces that would do no permanent damage if the stress were uniaxial (208). This effect is aggravated in the presence of liquid hydrocarbons, alcohols, organic acids, oils, and especially surface-active agents (109). X-ray scattering studies (208) of stressed samples suggest that preferred glide on certain crystallite planes tends to occur as the yield point approaches, thus inhibiting smooth alignment of the long-chain axis in the direction of stressing, which could lead to brittleness. The higher the molecular weight, the more readily the material undergoes orientation and the greater its elongation before rupture. It should be noted also that any other hindrance to alignment such as the changes in the material by the oxidative processes described above would contribute to early failure. The pronounced effect of surface-active agents probably results from interaction with polar groups in the surface of polyethylene, concentrating their effect on microscopic surface flaws, since these materials are absorbed by polyethylene to only a negligible extent, as compared with benzene, toluene, dodecane, etc. which swell polyethylene seriously (0.04–0.08 per cent as compared with 9.29 per cent for *n*-dodecane after 14 days' immersion at 25°C.).

D. EFFECTS OF HIGH-ENERGY RADIATION

Recently the effects of irradiating polymers with x-rays, γ-rays, high-energy electrons (β-rays from radioactive decay or electrons from particle accelerators), and neutrons have been studied. The effects are entirely different from those resulting from thermal degradation and resemble to some extent results from photodegradation, as will appear presently in this discussion. Some of the effects are difficult to interpret, particularly the work done in a nuclear reactor wherein the combined effects of β- and γ-rays and neutrons are difficult to disentangle. Absorption of β- and γ-radiation can result in the formation of an excited molecule which may dissociate into free radicals, or a molecule may become ionized and subsequently yield a radical and an ion (19, 300). These processes may be represented as shown below (M represents a molecule, R a hydrocarbon portion).

$$M + \gamma \rightarrow R\cdot + H\cdot \quad \text{(radical formation)} \tag{I}$$

$$M + \gamma \rightarrow M^* \quad \text{(excitation)} \tag{II}$$

$$M^* \rightarrow R\cdot + R'\cdot \quad \text{(radical formation)} \tag{III}$$

$$M + \gamma \rightarrow M^+ + e^- \quad \text{(ionization)} \tag{IV}$$

$$M^+ \rightarrow R''\cdot + H^+ \quad \text{(radical and ion formation)} \tag{V}$$

It has been deduced that the life of excited molecules and the primary ions formed is extremely short, since most of the experiments can best be interpreted in terms of formation of free radicals and the chemical changes that follow.

Both degradation and cross-linking of polymer chains can occur as a consequence of reactions I to V. Free-radical centers in adjacent chains can become cross-linked, before or after migration of the radical center. Or loss of a proton can occur, with the formation of unsaturated linkages to yield vinyl links if the radical center is at the end of a chain; otherwise, to form ethylenic bonds. Degradation occurs if R″• undergoes dismutation to form a simple unsaturated molecule and a new free radical. The formation of branched molecules results if a link occurs between any terminal free radical and free-radical center within a molecular chain. Diffusion of hydrogen atoms may result in direct combination to give hydrogen molecules or abstraction of a hydrogen atom from a methylene group alpha to a free-radical center to yield an ethylenic link.

All of these effects are considerably modified in the presence of oxygen, and the resulting surface effects of oxygen confuse the essential radiation effects. In some of the early work which was done by irradiating polyethylene (mostly thin films) in the heavy water pile of the Argonne National Laboratory (116), the disappearance of vinylidene groups was observed initially, accompanied by the development of ethylenic unsaturation. Vinyl unsaturation was negligible. From measurements of the amount of hydrogen evolved and the amount of bromine taken up, the fraction of liberated hydrogen which resulted in cross-linking was estimated to be 20 to 40 per cent; it was also estimated that irradiation in the pile produced little or no carbon–carbon bond scission (116).

Basing his conclusions mostly on the irradiation of polyethylene granules in the Harwell B.E.P.O. pile, Charlesby (81) calculated the production of cross-links from the hydrogen evolved (ignoring unsaturation, for which no tests were made) as 1.1 per cent of carbon cross-linked per 10^{17} thermal neutrons per square centimeter, together with the associated fast neutrons and γ-rays; all three radiations seemed to contribute energy in equal amounts. The work of Dole (116) indicates that the calculated efficiency to cross-link is too high. The energy to break a carbon–hydrogen bond was found to be approximately 25 ev. (81). Irradiation with 4 Mev. electrons produced a hydrocarbon fraction of low molecular weight, up to 2.4–2.8 per cent of the polymer, a positive demonstration of chain scission (26a); from the data secured, the ratio of main-chain scissions to atoms cross-linked was calculated to lie between 0.18 and 0.20. This determination has been applied to establish molecular-weight distributions (26) (Section VII,C).

Another study (84) has indicated that about three cross-links are formed for each carbon–carbon bond broken in the main chain, thus showing again the importance of carbon–hydrogen scission, despite the less favorable bond energetics [58.6 kcal./mole (3.4 ev.) for C—C versus 87.3 kcal./mole (4.1 ev.) for C—H], a result usually ascribed to a cage effect resulting from the equalization of excitation energy throughout a long carbon chain rather than localization of the energy in a single carbon–carbon bond.

Possible mechanisms have been suggested to explain why polyethylene so readily cross-links under irradiation (as do polymers of propylene, methyl acrylate, acrylic acid, and styrene), whereas others (methacrylic acid, isobutylene, methyl methacrylate, α-methylstyrene) primarily undergo degradation (8, 34). It has been suggested (on the basis of experiments with high-energy electrons) that cross-linking will occur if the polymer contains at least one α-hydrogen atom (e.g., $—CH_2CH_2—$ or $—CH_2CHR—$) and that degradation will predominate otherwise (i.e., in the structure $—CH_2—CR_1R_2—$) (326). Resonance stabilization with the R group in the radicals of the type $—CH_2\text{-}\overset{\bullet}{C}R—$ is postulated as favorable for cross-linking (326), but this effect cannot occur in polyethylene. Wall has also pointed out (521) that other factors are probably involved. The heats of polymerization of polymers that undergo degradation are all lower than that of those that cross-link, though the difference is generally not large; also, the monomer yields are lower for cross-linking polymers than for polymers which undergo degradation, and this is no doubt related to the presence of α-hydrogens or other labile atoms along the chain. A theoretical treatment of cross-linking by irradiation has been given (365).

Marked changes of properties of polyethylene occur on irradiation. Cross-linking results in decreased solubility in organic solvents, improved dimensional stability at temperatures up to 130°C., a rise in melting point (83, 86, 445), and a decrease in permeability to gases (467a). The effects of pile irradiation on the density and melting point (89) and upon the elastic modulus (88) have been described in detail.

Irradiation with electrons having a peak energy of 800 kv. results in evolution of hydrogen and hydrocarbons up to C_{11} (289), and cross-linking, with resulting decrease of solubility in organic solvents, and an initial increase in tensile strength and elongation, followed by a slow decrease at high dosages (288). This discovery is being applied commercially in the treatment of wire and cable insulation (322). Chain scission appears to occur at or near branch points (289). Investigations of polymethylene, and of three branched polymethylenes containing methyl, butyl, and amyl side chains (prepared from mixtures of the diazoparaffins), permit a preliminary conclusion that treatment with radiation of high energy selectively clips off the short side chains of branched polyethylenes (186a).

The effect of initial molecular weight (7,000 to 35,000) on irradiation effects produced by exposure of 40-mil films to a high-energy electron beam has been studied (287); properties affected include swelling in toluene, stress–strain ratio, tension set, tensile strength, elongation, and elastic modulus.

Exposure of 4-mil film and 1-in. rod to γ-irradiation from Co^{60} resulted in a small reduction in tensile strength, a progressive drastic reduction in elongation and tear strength, a reduction in viscoelastic deformation and heat distortion, and alteration in the infrared spectra in agreement with Dole (116), i.e., increased absorption at 2.9 μ (—OH), 5.85 μ $\left(\rangle CO\right)$, and 10.35 μ (RCH=CHR) (21). It was shown that most of the carbonyl absorption took place at the surface and that the unsaturation absorption was essentially independent of sample thickness, confirming the conclusion that unsaturation develops from ionizing radiation and that oxidation is a surface phenomenon. The effects of ionizing radiation have been exploited to alter the surface of polyethylene to make it printable; in this application, dosages of 0.5 to 20 megaroentgens (γ-radiation from Co^{60}) were required to secure a useful treatment (80).

X. PROPERTIES OF POLYETHYLENE

A. PROPERTIES OF IMPORTANCE IN THE USE OF POLYETHYLENE

Polyethylene is a complex molecular substance, of widely varying molecular weight and molecular-weight distribution, with more or less branched structure, and with more or less incorporated catalyst, depending upon the method of

TABLE 11

Properties of commercial polyethylene resins (17, 126, 127, 174, 219, 231, 263, 393)
(Average values)

Property	Unit	ASTM Test Method	Conventional*	Low-pressure
General:				
Molecular weight, approximate number average			22-25,000	†
Melting point, disappearance of birefringence	°C.		111	133
Melt index		D1238-52T	1.7	0.2-1
Viscosity, 190°C.	Poises		5×10^4	
Compression ratio (bulk factor)		D1182-51T	1.8	
Crystallinity, by x-rays	Per cent		60	80-85
Specific gravity		D-792-50	0.92	0.96-0.97
Refractive index, n_D^{23}		D542-50	1.51	
Thermal coefficient of expansion	n./in./°F.	D696-44	11×10^{-5}	
Thermal conductivity	cal./sq.cm./sec./°C./cm.		8×10^{-4}	
Specific heat				
Solid (70-105°F.)	cal./g./°C.		0.55	
Liquid (250-285°F.)			0.70	
Flammability (1/8-in. thick specimen)	in./min.	D635-44	1.0	1.0
Water absorption, 24 hr., 25°C.	Per cent max.	D570-42	0.01	
Brittleness temperature	°C.	D746-52T	<-70	<-70
Heat of combustion	kcal./g.		11.1	
Mechanical:				
Tensile strength, 73°F.		D412-51T		
At fracture	p.s.i.		1900	
At upper yield	p.s.i.		1500	
Elongation	Per cent	D638-52T	600	100
Tear resistance	p.s.i.	D1004-49T	600	1000
Rockwell hardness (3/4-in. ball and 30-kg. load)		D785-48T	J76	
Shore hardness (durometer)		D676-49T	D53	D63-70
Shear strength	p.s.i.	D732-46	1800	
Vicat softening point‡	°C.		91	
Electrical:				
Dielectric strength (0.030-in. specimen; 60 cycles per second)	v./mil	D149-44		
Short-time			1000	
Volume resistivity	ohm-cm.	D257-52T	10^{19}	10^{15}
Surface resistivity	ohm	D257-52T	$>4 \times 10^{14}$	$>10^{13}$
Dielectric constant, 25°C.		D150-47T	2.3	2.3
Dissipation factor		D150-47T		
At 50 to 100 megacycles per second			<0.0005	<0.0005
At 30 megacycles per second			<0.0005	

* Polymethylene of the same approximate molecular weight has a density of 0.98 g./cc., about 95 per cent crystallinity, a melting point of 130°C., and about 10 per cent extensibility.

† Uncertain, because methods have not been correlated. Estimated in reference 174 to be 60,000 to 200,000 and perhaps higher.

‡ The temperature at which a square needle 1 mm. on a side penetrates the specimen to a depth of 1 mm. under a load of 1 kg.; the rate of heating is 50°C. an hour, starting below 30°C.

manufacture. It is therefore not surprising that a great many ways of characterizing the polymer have been developed. Until now, the most important applications have been in wire coating and similar forms of insulation, and in packaging films, for which the grade number or melt index (12) has been most widely used, but with the extensive use of polyethylene as molded or blown containers, pipes, and household articles, other criteria are being developed.

A bewildering number of polyethylenes, each with its peculiar set of properties, has been developed for commercial uses. A typical set of properties of a conventional polyethylene is presented in table 11; for further information the reader is referred to the current technical bulletins of commercial suppliers (17, 126, 127, 219, 263).

Several authors have reviewed various aspects of the relationship between the mechanical properties of polyethylene resins of the conventional type and their applications and probable future use (103, 166, 215, 217, 223, 230, 323, 324, 341, 347, 363, 406, 412, 416, 424, 447, 490, 491). The newer types of material made by low-pressure methods have also been discussed in terms of possible uses (174, 353).

The physical and chemical properties of polyethylene from a structural standpoint have been discussed (178, 419), and the properties compared with those of other polymers (211).

Since some of the most important applications depend on the resistance to chemical attack, this property has been much studied. Ranalli (404) has reported the resistance to acids and alkalies, and Simonin (464) reviewed the subject several years ago. A thorough recent study (369, 392) of resistance to chemical attack by eighty chemicals, including inorganic acids, alkalies, organic acids, alcohols, esters, ethers, aldehydes, ketones, anhydrides, terpenes, hydrocarbons, and chlorinated hydrocarbons revealed that serious deterioration is wrought only by concentrated nitric acid at room temperature and by 20 per cent nitric acid, diacetone alcohol, acetic anhydride, and *o*-xylene at 130°F. or above. Elastomers can be so compounded as to do no significant damage to polyethylene, since it has been found that of many ingredients used in compounding rubber, only stearic acid and coal-tar distillate cause serious deterioration on prolonged contact at 77°C. (171).

At temperatures up to about 70°C. polyethylene is nearly insoluble in organic solvents (Section VII,A). Some liquids, particularly mineral and vegetable oils (316, 423, 528), toluene, xylene, and other hydrocarbons, and aqueous surfactants (78) permeate and cause swelling of the polymer at room temperature. The remarkably low solubility in nonpolar solvents has been ascribed to the highly crystalline nature of the polymer at any temperature up to about 75°C. (211). Studies have shown that disordering begins to occur at about 50°C. (403), accompanied by increasingly greater swelling and solubility in xylene.

The density of polyethylene has been determined from −178° to +170°C. in relation to average molecular weight (216) and found to be only slightly dependent on average molecular weight; density appears to be more closely related to molecular linearity (174, 338). The compressibility has been found to decrease as pressure increases, up to 2000 atm., in the temperature range 25–160°C. (368, 525). The compressibility at 1 to 100 atm. resembles that of a liquid or elastomer, rather than that of a crystalline solid. (An exception is found in the case of an initially liquid sample to a point where crystallization begins; as solidification progresses, the compressibility increases.) The melting point is raised by about 0.02°C. per atmosphere. In most commercial applications the viscoelastic properties at high temperatures and pressures are very important (114, 199), and a theory of the mechanical properties of hot plastics has been developed (301) combining rubberlike elasticity with strain relaxation, based on extrusion studies at high speed. A basic patent for the compression molding of polyethylene is controlled by Imperial Chemical Industries (409).

The heat of combustion has been determined as 11,095 cal./g., or 311,165 cal. per ethylene unit, by the isothermal bomb method at 25°C. (367), with a precision of about 0.03 per cent. These results indicate a crystallinity of at least 50 per cent at 25°C. (the molecular weight of the sample was about 20,000); and since the heat of combustion of the amorphous polymer was assumed to be the same as for 1-alkenes in the unstrained liquid state, this value could easily be too low by 10–15 per cent.

The stiffness of polyethylene has been evaluated over a temperature range from −60°C. to +25°C. (71); other careful measurements of stress–strain relationships and relaxation times have been made by Lethersich (297). The brittle point (410, 454) appears to rise with melt index, i.e., it varies inversely with molecular weight (95, 96), and the Vicat point and elastic modulus fall with rise in melt index (96).

Polyethylene adheres reasonably well to clean metal surfaces (266, 286, 415), and this property has recently been exploited for the coating of metal articles (169, 174) and the interior coating of steel shipping drums (190). Polyethylene can be flame-sprayed (176).

During the first stage of creep, polyethylene shows high elastic and plastic deformation, as much as three-fourths of the elongation being recoverable; even after 20,000 hr. of continuously applied load, a steady creep rate is not attained (173). In certain environments, particularly in aqueous surfactants, polyethylene undergoes severe stress cracking (109) [the low-pressure polyethylenes are less susceptible (174)] and methods have been developed to measure creep for the determination of cracking sensitivity (133, 296).

Polyethylene has proved to be an exceptionally fine low-loss dielectric material, particularly at the high frequencies employed in television and radar (224, 271, 279, 361, 362, 395, 456).

The possible wide use of polyethylene as a packaging film was recognized early in its development (182, 340, 376), and now it is well established as an approximately 100-million-pound business annually. The low permeability to water vapor is outstanding among plastic films, and its durability and transparency in thin gages make it the preferred wrapping material for many applications. Table 12 presents the average physical properties of a typical packaging film. Polyethylene is sold in 0.5- to 5-mil gages as a packaging film, and as sheeting in heavier gages, up to about 15 mils, for special applications such as tarpaulins, seed-bed covers, and shipping bags. Fiber applications have been proposed (375) but have not come into wide use.

The sorption of water and transmission of water vapor by polyethylene films have been the subjects of many studies (7, 110, 118, 234, 408, 466, 517). Permeability to oxygen, carbon dioxide, helium, nitrogen, and hydrogen has

TABLE 12

Properties of polyethylene film

Property	Unit	ASTM Test Method	Average Values
Tensile strength, lengthwise	lb./in.^{2}	D-882-B-52T	2200
Tensile strength, crosswise			1600
Elongation, lengthwise	Per cent		350
Elongation, crosswise			615
Tear strength, lengthwise	lb./in.	D-1004-52T	405
Tear strength, crosswise			280
Water absorption			
Increase in weight	Per cent, 24 hr.	D-570-42	0.0
Soluble material lost			0.1
Water vapor permeability	g./m.^{2}/24 hr.†	D-697-42T	0.06
Change in linear dimensions, lengthwise	Per cent, 30 min. at 100°C.	D-1204-52T	−6.62
Change in linear dimensions, crosswise			+2.44
Impact strength, pendulum	kg.-cm.		12-15
Coefficient of friction			0.30–0.50

* In those tests wherein gage is important the value cited is for film 1 to 1.5 mils in thickness. The data are from references 17, 126, 219 and other sources.

† Measured on a film 1 mm. thick, with a pressure differential of 1 cm. of mercury.

been determined (25, 106, 405). The permeability to organic vapors varies widely (101, 102, 405, 438, 465) and seems to follow no simple relationship to structure or size of the small molecule, though in general nonpolar, compact, planar molecules (e.g., benzene) diffuse more rapidly than nonplanar, less compact ones of similar molecular weight (e.g., cyclohexane and *n*-hexane), and much more rapidly than those with appreciable dipole moments (e.g., water, acetone, propanol, 1,2-dichloroethane) (101). A series of constants has been calculated which permits simple computation of the approximate permeability of several gas–polymer systems involving nitrogen, oxygen, hydrogen sulfide, and carbon dioxide (474). Polyethylene films exposed to 10^7 roentgens of irradiation (high-energy electrons) showed no decrease in permeability to nitrogen, oxygen, carbon dioxide, and methyl bromide, but dosages of 10^8 roentgens resulted in a decrease in the permeability to half the original values (467a).

In addition to the usual operations of melt extrusion and compression molding, polyethylene resin can be cast from a solvent in the form of films, tubes, filaments, and the like (345), or converted to film by a blowing operation in which the molten material issuing from a circular die is prevented from collapsing by a bubble of entrapped air (16a, 168, 389, 407) or by an internal bell-shaped mandrel (170).

The surface of polyethylene has little affinity for printing inks and decorative or functional coatings. To improve the adherence of these materials, several methods have been described. One of the simplest involves printing with ink to which infrared-absorbing materials have been added, followed by exposure to infrared radiation to soften the polymer and facilitate penetration by ink

(203). Surface treatments with chlorine (192, 346), ozone (531), nitrous oxide (533), or mixtures of ozone and nitrous oxide (532) have been described. Irradiation with Co^{60} may be used (80). Treatment with chlorinated hydrocarbons followed by ultraviolet irradiation is also said to be effective (138).

Other treating methods which have been described are rapid passage of the article through a flame (37, 277, 278), a heat treatment in which the surface is heated (as by a flame) while the bulk of the material is cooled (269), treatment with a saturated solution of sodium dichromate in sulfuric acid (210), treatment with ultraviolet light (33), and treatment with a corona discharge (509, 518).

The reasons why these treatments are effective are not well understood, since a complex combination of chemical, physical, and electrical effects is involved. The adhesion of ink and coatings has been ascribed to a surface oxidation of the polymer (210, 437), but the evidence is not conclusive (270). No experiments have been reported which were done in an oxygen-free atmosphere.

B. RELATION BETWEEN STRUCTURE AND PROPERTIES

Variation in the properties of polyethylene may be related to the following molecular and textural characteristics (358, 419, 435, 470): (*a*) molecular weight and distribution of species of different molecular weight; (*b*) proportion of crystalline material in the polymer; (*c*) texture of solid polymer sample, i.e., size distribution, form, and arrangement of crystalline and amorphous regions in the solid; (*d*) short- and long-chain branching of the polymer molecules; (*e*) presence of oxygen-containing groups and unsaturation.

It is improbable that any functional or mechanical property of polyethylene is determined solely by any of these parameters. The properties are affected simultaneously by all of them to some extent. It is expected, however, that certain physical properties will show a primary dependence on one of the molecular and textural characteristics.

(*a*) The molecular weight and distribution of species of various molecular weights may be expected to affect primarily properties such as melt viscosity of the polymer, tensile strength, low-temperature brittle point, and tear resistance (419, 470), for these properties involve either extensive movements of the polymer segments or rupture of the sample. The percentage of crystalline material in the polymer has a less important effect on these properties. Melt viscosity is determined primarily by the weight-average molecular weight and hence depends upon the distribution of polymer species of different molecular weights (*cf.* Section VIII). The low-temperature brittle point (a measure of flexibility at low temperatures) is also dependent to an important extent on the degree of crystallinity and the texture of the sample (419). Several correlations between melt index (12) and polymer properties have been discussed (470). These correlations are probably true in a general sense, but caution should be used in interpreting the melt index as a true measure either of melt viscosity or of molecular weight.

(*b*) The proportion of crystalline material in the polymer (i.e., percentage crystallinity) affects primarily those properties which are concerned with slight movements of the polymer segments relative to one another (419, 470). Such properties as the crystalline melting point, Young's modulus in tension, bending modulus (related to stiffness), yield point (related to the tension to cause cold drawing), surface hardness, permeability to water vapor, and the sorption of gases and liquids fall in this category. The density of the polymer is determined primarily by the extent of crystallinity, although the thermal history of the sample also has an important effect. The dynamic mechanical properties are significantly affected by the percentage crystallinity of polyethylene (358). The more crystalline materials have the higher dynamic shear moduli and higher melting points.

(*c*) The size and arrangement of the crystalline regions, and the properties of the regions between the crystalline aggregates, have important effects on the properties of the products made from polyethylene resins. These textural properties of polyethylene in the solid state are determined not only by the molecular properties of polyethylene, but also by the conditions under which crystallization of the melt occurs. Polyethylene films which have small crystalline aggregates are more transparent than films with large aggregates. Films with the crystalline aggregates aligned preferentially in a given direction tear easily in that direction. Other important properties which may depend on the size and arrangement of the crystalline regions, and upon the properties of the regions between the crystalline regions, are the cracking of polyethylene samples under stress in a polar organic liquid (208) and the low-temperature flexibility (419).

(*d*) The important molecular property that affects the percentage crystallinity of polyethylene is the degree of short-chain branching (56, 100, 417, 419, 435, 470). The effect of short-chain branching on the properties of polyethylene is, therefore, in principle, similar to the effect of crystallinity as discussed above. Long-chain branching, resulting from the intermolecular chain transfer of a growing chain with a polyethylene chain already formed, on the other hand, has no significant effect on the crystallinity. The prominent effects of the introduction of long-chain branching during polymerization are an increase in the weight-average molecular weight and an increased spread in the breadth of the molecular-weight distribution curve (expressed as weight fraction versus molecular weight) of the resulting polymer (see Section IV,C). These concomitant effects of long-chain branching are most significantly manifest in the properties of the molten polyethylene. An increase in the weight-average molecular weight should increase the melt viscosity of the polymer, and the broader distribution of molecular weights resulting from long-chain branching should affect the shear dependence of melt viscosity. Since both the melt viscosity and the increase in fluidity at high rates of shear are important in extrusion (32, 73, 74, 75, 76, 77, 180, 311, 319, 508), the most important effect of long-chain branching would be upon the extrudability of the material. Long-chain branching also affects other viscoelastic properties of the melt; thus, an increase in long-chain branching results in lowered extensibility of the melt (470).

(*e*) The presence of unsaturation and oxygen-containing groups has only a minor effect upon the mechanical properties of polyethylene, but has an important bearing on the cross-linking and degradation at elevated temperatures, on exposure to ultraviolet light and high-energy radiation. The presence of oxygen-containing groups affects also the electrical properties such as power factor and dielectric loss.

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