

HIGH POLYMERS

Volume XI

POLYETHYLENE

by **R. A. V. RAFF**
and **J. B. ALLISON**

POLYETHYLENE

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PREFACE

Over twenty years ago, one of the authors of this volume was a member of the Austrian State Patent Office. He still recalls his scientific surprise when he received for examination a patent application to Imperial Chemical Industries, Ltd., claiming that solid polymers of ethylene could be obtained by the catalytic polymerization of ethylene at high temperatures and pressures. A sample of a waxlike, colorless, semiopaque solid was subsequently submitted to illustrate and substantiate this invention. Later, it became known that polyethylene had first been obtained unintentionally when two of the inventors, Fawcett and Gibson, attempted to react ethylene with benzaldehyde at 2,000 atmospheres pressure. While repetition of the experiment resulted in an explosion, the importance of the discovery nevertheless had been recognized. Better experimental methods were developed which allowed the preparation of eight grams of the new polymer in a single experiment by the end of the year 1935. Since then, polyethylene has become one of the most important of all plastic materials.

A great discovery and invention it was, since until then, only ethylenes containing an activating atom or group in the molecule, such as styrene or vinyl chloride, had been considered capable of undergoing polymerization to solid products. Attempts to polymerize ethylene itself had, to that time, yielded only gases or low molecular weight liquids which, from their formation and structure, could not, for the most part, be considered simple polymers of ethylene.

This volume attempts to summarize the present state of the knowledge of those polymers of ethylene which, depending upon their molecular weight, range from viscous liquids, through semisolids, to tough, flexible solids suitable for use as plastics.

A book of this kind should explain facts with theories; should integrate structural observations, manufacturing conditions, properties, and suitable fields of application; and convey a deeper insight into proven or assumed relationships. This, as the authors were aware from the start, is possible in isolated instances only, since the theoretical treatment of this intricate subject is but in its beginnings. Moreover, in view of the highly competitive situation, an adequate treatment of more recent developments, that is, the new low-temperature, low-pressure processes which are beginning to operate in this and other countries, can hardly be expected.

For these and similar reasons, the advisability of postponing the writing of this book for one or two years was seriously discussed; but consideration of the broad scope of the subject and the large amount of important information available for critical examination decided the issue. It is a fact that the vast and expanding literature of the polyethylenes has not, to the authors' knowledge, been presented elsewhere in an organized form. This is submitted to the prospective reader as further justification for the existence of this book, with the sincere hope that it may prove an aid to those working in this field. At the same time, the authors' attempts to include the most recent developments in this extremely active field have inevitably resulted in inconsistencies in text and bibliography. It is hoped that these are minor in nature and will be condoned by the reader.

It is particularly pleasant to express to the managements of the Chemical Division and of the Research Department of the Koppers Company, Inc., the authors' very real appreciation for permission to publish this book, and for wholehearted support.

The kind permission to quote from an unpublished paper by Dr. H. Staudinger and Dr. F. Berndt is thankfully acknowledged. For review of the manuscript and valuable advice, the authors wish to express their gratitude to Dr. H. Mark; also to Drs. C. Cousin and H. Sack, Laboratoire de Recherches des Houillères du Bassin du Nord et du Pas de Calais, Bruay-en-Artois, France. The staff members of the Polyethylene Branch of the Research Department of the Koppers Company, Inc., Mr. J. J. Killoran, Mr. R. F. Kratz, Mrs. E. L. Lyle, and Dr. H. E. Tiefenthal, are cordially thanked for valuable discussions and comments, criticisms of the drafts, and proofreading the manuscript and galleys; and Mrs. J. B. Allison for painstaking assistance in typing and proofreading the manuscript.

Thanks are also extended to the publishers for their understanding help, and their patient and competent guidance of the production of the volume.

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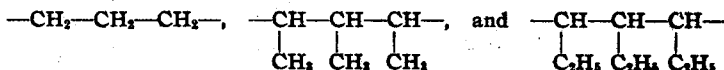
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I. HISTORICAL DEVELOPMENT

1.1. Catalyzed Decomposition of Diazohydrocarbons

As early as 1898, von Pechmann (6) observed that small amounts of a white, flocculent substance which could be crystallized from chloroform separated from an ethereal solution of diazomethane on standing. While the presence of platinum or sodium somewhat catalyzed the formation of this solid, the amount of the product recovered was insufficient to permit further study. Two years later, Bamberger and Tschirner (7) collected a larger quantity of this very voluminous material, dissolved it in isopropylbenzene, and precipitated it by the addition of petroleum ether. The dried powder, somewhat soluble in boiling isopropylbenzene or boiling pyridine, melted at 128°C., corresponded by analysis to the formula $(CH_2)_n$, and was termed "polymethylene." Its formation had apparently taken place by the reaction $n(CH_2N_2) \rightarrow (CH_2)_n + n(N_2)$.

Much later, Buckley, Cross, and Ray (464) studied the copper-catalyzed decomposition of a series of aliphatic diazo compounds in ether solution. Straight-chain, high molecular weight, highly crystalline polymethylene was obtained from diazomethane. Polyethylidene and polypropylidene—hard, amorphous, brittle glasses, similar to polystyrene—were obtained from diazoethane and 1-diazopropane. The three compounds were given the structures:



Products ranging from crystalline waxes to amorphous glasses were prepared by the decomposition of mixtures of diazomethane and increasing amounts of diazoethane.

The infrared absorption spectra of these polymers and copolymers are shown in Figure 1.

The molecular weights of these hydrocarbons were determined, where possible, by the cryoscopic method, benzene being used as the solvent. This was, however, unsatisfactory for molecular weights above 3,000; in such cases, the intrinsic viscosity was measured in diisobutene at 20°C. The relationship given by Oakes and Richards (411), $[\eta] = 1.08 \times \bar{M}_n^{0.7} \times$

10^{-3} , which may be used for polyethylene and polymethylene, was not considered applicable to polyethylidene and polypropylidene. Instead, the equation proposed by Flory (143), $[\eta] = 3.60 \times \bar{M}_n^{0.64} \times 10^{-4}$, which holds for polyisobutene, was used as the best available approximation. The combination of these two methods indicated that the polymers ranged

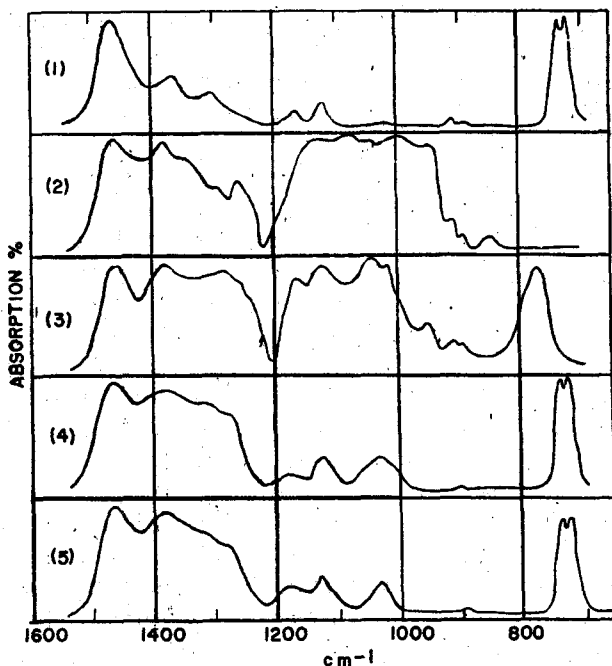


Fig. 1. Infrared absorption spectra of several diazo polymers: (1) polymethylene from diazomethane, (2) polyethylidene from diazoethane, (3) polypropylidene from diazopropane, (4) ether-insoluble interpolymers No. 1 containing 3.0 moles % of diazoethane, and (5) ether-insoluble interpolymers No. 2 containing 6.7 moles % of diazoethane. (*J. Chem. Soc.*, 1950, 2715.)

in molecular weight from 200 to 14,000. Studies by Leitch, Gagnon, and Cambron (478) followed along similar lines by introducing a deuterated polymer $(CD_2)_n$, obtained by the decomposition of diazomethane- d_2 .

These investigations, demonstrating the influence of chain-branching on crystallinity and of crystallinity on physical properties, were carried out for the purpose of clarifying the structure of polyethylenes made by other more involved processes. Actually, products similar to polyethylene

obtained by the conventional catalyzed, high-pressure, high-temperature process, with their moderate degree of crystallinity and lower melting point, could be closely duplicated by the decomposition of mixtures of diazomethane and small quantities of diazoheptane and diazooctane. The significance of these results will be discussed in Sections 4.3 and 5.1.

A polymethylene of molecular weight greater than three million was prepared by Kantor and Osthoff (740) by treating diazomethane in diethyl ether with the diethyl ether-boron trifluoride complex at 0°C. The molecular weight of the resultant polymer was determined from the intrinsic viscosity obtained in xylene solution at 132°C. From the intrinsic viscosity and the Staudinger constants reported by Harris (606), a molecular weight of 3.3×10^6 was calculated. This method of preparation of polymethylene with a molecular weight of at least 500,000 has been recently patented in Germany (1095).

The polymer had a crystal melting point of 132°C., which is close to the convergence temperature of 137°C. for straight-chain paraffins derived by Mark (118) from thermodynamic data. An x-ray examination indicated a very high degree of crystallinity. The polymer had a tensile strength of 4,900 p.s.i. and an elongation at break of 500%. These values, being higher than those common for commercial polyethylenes prepared by high-pressure, high-temperature polymerization methods (compare Chapter VI), are indicative of the greater molecular weight and lower degree of branching of polymers prepared by this method. Dielectric constant, power factor, and breakdown voltage were comparable to those of the commercial high-pressure, high-temperature polyethylenes. Since the catalyst and solvent used in the polymerization are promoters of ionic reactions, Kantor and Osthoff believe that the polymerization takes place through an ionic rather than a radical mechanism.

A further study of the homogeneous decomposition of diazomethane to form high molecular weight polymethylene has been reported by Bawn and Rhodes (824). The reactions were carried out in toluene solution, and copper wire, copper stearate, and boron trifluoride were evaluated as catalysts. The rate of polymer formation, followed by titration and by measurement of the nitrogen evolved, was found to equal $K \cdot [\text{Cat}] \cdot [\text{CH}_2\text{N}_2]$, and an ionic reaction mechanism was proposed.

Molecular weights of the soluble polymers were determined by measurement of the intrinsic viscosity of a xylene solution at 95°C. and by substitution in the equation deduced by Harris (606), where $[\eta] = 1.35 \times 10^{-4} \times \bar{M}_n^{0.68}$. The average molecular weights obtained with copper wire, copper stearate, or boron trifluoride etherate as the catalyst were 17,000,

2,200, and 14,000, respectively. In most cases, linear, not crosslinked polymers resulted. Crosslinking appeared to have taken place when very low concentrations of $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ or $\text{BF}_3 \cdot \text{CH}_3\text{COOH}$ were used.

The melting points of most polymethylenes lie in the range of 127 to 135°C.; the higher melting points lie close to the limiting temperature of the paraffin series. The infrared spectra of the polymers were similar to those reported by Buckley, Cross, and Ray (464).

The kinetics of the decomposition reaction in ether solution of diazomethane, diazoethane, diazobutane, and of their mixtures, catalyzed by cupric stearate or boron trifluoride, were studied by Feltzin, Restaino, and Mesrobian (955), and some physical properties of the resultant polymers were determined. The results of experiments are summarized in Table I.

A polymerization mechanism involving propagation via a carbonium or diazonium ion, and termination by interaction of growing chains with diazohydrocarbons, is presented.

1.2. Action of Sodium on Decamethylene Bromide

An alternate route to essentially straight-chain, high molecular weight paraffins was explored by Carothers (20). By reacting decamethylene bromide with sodium, followed by distillation in the molecular still and by fractional crystallization, the following hydrocarbons (with corresponding melting points) were isolated from the reaction mixtures: $\text{C}_{20}\text{H}_{42}$ (35–35.6°C.); $\text{C}_{30}\text{H}_{62}$ (65–66°C.); $\text{C}_{40}\text{H}_{82}$ (80.5–81°C.); $\text{C}_{50}\text{H}_{102}$ (91.9–92.3°C.); $\text{C}_{60}\text{H}_{122}$ (98.5–99.3°C.); and $\text{C}_{70}\text{H}_{142}$ (105–105.5°C.). Carothers did not, however, succeed in producing appreciable quantities of hydrocarbons with more than 100 carbon atoms.

1.3. Fischer-Tropsch and Related Syntheses

The Fischer-Tropsch reduction of carbon monoxide with hydrogen is generally designed to yield low molecular weight products (567). However, by proper choice of the reaction conditions, essentially linear, highly crystalline solid paraffins can be obtained. Thus, Koch and Ibing (38) identified paraffins having a melting point of 117°C. and a molecular weight of 2,000 among the reaction products of the benzene synthesis. By the use of a ruthenium catalyst, paraffins melting from 117–132°C. and having average molecular weights of 7,000–9,000 were obtained by Pichler and Buffleb (100). The preparation of high molecular weight polyethylene (m.p. 133°C.) by the use of a metal tungstate catalyst is described by Arnold and Herrick in U.S. 2,726,218 [dupont (1105a)].

TABLE I. Decomposition of Diazoethylenes in Ether

Reaction temp., °C.	RCHN ₂ , moles/l.	Catalyst	Catalyst concn., moles/l.	Conversion, %	Appearance of polymer	$[\eta]_{\text{sec. toluene, dcl./g.}}$	\bar{M}_n
Runs with diazobutane							
8	0.5	Cupric stearate	3.17×10^{-4}	92	Glass	0.10	
8	0.5	Cupric stearate	25.4×10^{-4}	91	Glass	0.05	
8	0.5	BF ₃	7.0×10^{-4}	28 ^a	
8	0.5	B(OCH ₃) ₃	5.0×10^{-4}	16 ^b	
Runs with diazoethane							
8.5	0.61	CuSO ₄	Insol. ^c	59	Glass	...	
8.5	0.61	Cupric stearate	6.2×10^{-4}	95	Glass	0.12	
8.5	0.61	B(n-OC ₂ H ₅) ₃	2.0×10^{-4}	23 ^a	
8.5	0.61	BF ₃	5.0×10^{-4}	25 ^b	
Runs with diazomethane							
0	0.55	BF ₃	5.0×10^{-4}	100	Wax	16.2 ^d	
0	0.55	Cupric stearate	12.8×10^{-4}	9 ^a	
0	0.55	B(OCH ₃) ₃	2.0×10^{-4}	15 ^b	
Runs with diazomethane-diazooethane mixtures ^e							
0	0.51(5/1)	B(OCH ₃) ₃	2.0×10^{-4}	80	Rubber	7.3	
0	0.41(8/1)	BF ₃	0.5×10^{-4}	94	Rubber	8.7	
0	0.49(5/1)	BF ₃	0.8×10^{-4}	90	Rubber	7.2	
0	0.22(4/1)	BF ₃	0.5×10^{-4}	91	Rubber	6.19	2.0×10^4
0	0.56(4/1)	BF ₃	5.0×10^{-4}	98	Rubber	6.3	2.07×10^4
0	0.55(1/1)	BF ₃	0.5×10^{-4}	40	Rubber	2.2	
0	0.53(4/1)	Cupric stearate	12.8×10^{-4}	8	

Source: *J. Am. Chem. Soc.*, **47**, 1517 (1955).

^a Conversions are based upon amount of methanol-insoluble polymer obtained after total decomposition of diazoethylenes. Reaction exhibited a pronounced decrease in rate between 10 and 25% decomposition and proceeded at nearly the uncatalyzed rate for the remainder of reaction. Successive additions of catalyst produced only temporary acceleration of decomposition rate.

^b 0.3 g. of CuSO₄ suspended with stirring in 30 ml. of solution.

^c Determined in xylene at 120°C.

^d The numbers in parentheses under column 2 refer to the mole ratio of diazomethane to diazoethane.

1.4. Reduction of Polyvinyl Chloride

Hahn and Müller (963) believed that the structure of polyvinyl chloride could be studied more easily if these polymers were transformed into polyethylenes by reductive removal of the chlorine. Total reduction was achieved by the use of a surplus of lithium aluminum hydride under pressure at 100°C. or above, with a mixture of tetrahydrofuran and decalin as the solvent. The reduction products corresponded to the formula $(CH_2)_n$ and showed the same properties as polyethylene. Polyvinyl bromide was found to be easier to reduce than polyvinyl chloride, but the reduction of chlorinated or brominated polyethylenes gave completely insoluble, cross-linked products, as noted previously by Staudinger (633a).

1.5. High-Pressure, High-Temperature Polymerization Methods

Early studies of the direct polymerization of ethylene resulted mainly in its conversion into various gases, liquids, and mixtures of these by exceedingly complex reactions. In most cases, the polymerization was found to be accompanied by decomposition which became more pronounced as the reaction temperature was increased.

Direct polymerization of ethylene to polythene¹ was achieved in the course of a systematic study on the high-pressure chemistry of organic compounds undertaken by Imperial Chemical Industries, Ltd. This work was made possible by the development, by Dr. A. Michels of the University of Amsterdam, of a pump capable of giving a pressure of 3,000 atmospheres. During the course of this research, carried out in March, 1933, polyethylene was discovered as a trace of white powder in a reaction vessel. The results of these investigations were first reported by Fawcett and Gibson (29) in 1934; the basic patent relating to the production of polyethylene, Brit. 471,590 (60), was issued in the names of the original research team (Fawcett, Gibson, Perrin, Paton, Williams, and I.C.I.) in September, 1937. For its historical and technological interest, a facsimile of this pioneer patent is shown in Figure 2.

From the outset, the development of a commercial process for the production of polyethylene involved numerous technical difficulties. The polymerization reaction was found to be excessively exothermic and required strict control and elaborate safety measures in order to prevent explosive decomposition of the ethylene. As a result, polyethylene was not produced on a scale sufficiently large for technical evaluation until Decem-

¹ A generic name applied only to those polyethylenes which are suitable for use as plastics (225).

PATENT SPECIFICATION

Appointed Date: Feb. 4, 1936. No. 3372/36. **471,590**
 Made Good: Mar. 16, 1936. No. 7899/36.
 Accepted: Apr. 21, 1936. No. 23063/36.

(The Complete Specification Left: Feb. 4, 1937.)
 (Under Section 16 of the Patents and Designs Acts, 1907 to 1932.)

Specification Accepted: Sept. 6, 1937.

PROVISIONAL SPECIFICATION
 No. 3372 A.D. 1936

Improvements in or relating to the Polymerisation of Ethylene.

WE, ERIC WILLIAM FAWCETT, REGINALD OSWALD GIBSON, MICHAEL WILLIAM PIERRE JOHN GREVES PATON and EDMUND GEORGE WILLIAMS, all British Subjects, all of Wilmington Hall, Northwich, in the County of Chester, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the nature of this invention to be as follows:

This invention relates to the polymerisation of ethylene, with the object of producing new and useful products therefrom by effecting the polymerisation under the operating conditions herein after described.

It is already known that ethylene and its homologues can be polymerised to yield a mixture of liquid organic compounds by the use of elevated temperatures, e.g. 200-400° C., and/or of moderate super-atmospheric pressures, say up to 200 atmospheres, with or without the aid of catalysts. The liquid products come in character from relatively light oils up to fairly viscous oils of the lubricating oil type.

We have now found that ethylene may be polymerised to give solid products of a rubber or resin-like character by the use of a very high pressure, or a pressure of at least 1000 atmospheres, and by the use of reaction conditions such that the heat of the reaction is removed as quickly as possible. The products obtained under these conditions appear to be true polymers, i.e. they correspond to the formula $(C_2H_4)_n$, and they are of high molecular weight, e.g. those obtained at 2000 atmospheres have a molecular weight of the order of 3500. The temperature requirements of the reaction, in particular the initial temperature required for polymerisation to occur, have not yet been fully investigated, but it would appear that a moderate elevated temperature, of the order of 100-200° C. should be employed.

It is necessary to provide for the efficient removal of the heat of reaction, otherwise it is impossible to control the reaction, which is then liable to give rise to an explosion of some violence, the end products being carbon and hydrogen. Suitable measures to achieve rapid removal of heat are the use of diluents for the ethylene (e.g. the use of industrial gases containing ethylene such as cracking still gases), and/or the use of a reaction vessel constructed of or lined with a metal or alloy of high thermal conductivity. An internal heating element of small heat capacity, disposed within a cold-walled reaction vessel, is a convenient means of initiating the reaction.

In general, increasing the pressure at which the polymerisation is effected will increase the ultimate yield of the polymer. Alternatively, increasing the pressure will permit of the same yield of polymer being obtained in a shorter time.

EXAMPLE.

Ethylene is compressed under a pressure of 2000 atmospheres in a steel bomb. The vessel is maintained in a constant temperature bath, for 4 hours at a temperature of 170° C. According to whether the pressure is released before or after cooling to room temperature, the product is, respectively, a "coalesced" rubber-like white solid or a white powder. The product softens at about 120° C. At 170° it goes over to the form of a substantially clear resinous or rubber-like material which has plastic properties and can be moulded into various forms at or above the softening temperature. It is fairly soluble in hot benzene and sparingly soluble in cold benzene, hence thin transparent coatings may be deposited on objects from benzene solution, followed by warming until the deposit coalesces. The product has a molecular weight of around 3500 and in composition corre-

Fig. 2. Pioneer British patent 471,590. (Continued on following page.)