Advances in POLYOLEFINS

The World's Most Widely Used Polymers

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Edited by
Raymond B. Seymour
and
Tai Cheng

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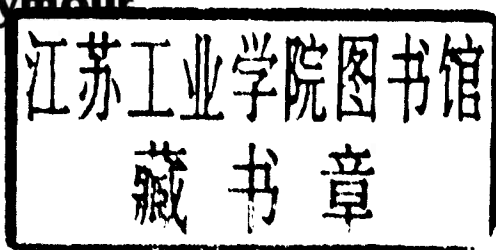## The World's Most Widely Used Polymers

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DEDICATION

Polyolefins, which are the world's most widely used polymers, are the product of Modern Polymer Science Research. Unlike other widely used polymers, such as polystyrene, polyvinyl chloride, the acrylics and condensation polymers of formaldehyde with plenolor utea, these polymers were invented after Staudinger, Mark and Carothers had demonstrated the existence of macromolecules.

It should be an inspiration to researchers to note that significant advances are being made in this mature branch of polymer science. Some of these advances which are described by international experts in the field, in this book, are based on theories championed by Dr. Paul J. Flory who died while preparing his report for the national meeting of the American Chemical Society at Chicago in September 1985 which was the site of the symposium on Advances in Polyeolins.

The delegates to the macromolecular secretariat at this meeting, voted unanimously to dedicate these proceedings on Advances in Polyolefins to the memory of our esteemed colleague, Professor Paul John Flory.

Raymond B. Seymour
Tai Cheng

PREFACE

Because of the many important new developments in other branches of science, some scientists fail to recognize that the volume of polyolefins produced annually is greater than that of all metals. Hence, the American Chemical Society sponsored symposia on the History of Polyolefins at its national meeting at Miami Beach in the Spring of 1985 and a Macromolecular Secretariat on Advances in Polyolefins at its national meeting in Chicago in the fall of that year.

The books on the proceedings of these landmark symposia and another book entitled "The Chain Straighteners" by Dr. F. M. McMillan will provide the scientist with background information which is essential for researchers in this important phase of polymer science.

The presentations at these international symposia and the publications of the reports presented, would not be possible without the dedicated efforts of our assistant editors and publisher. The list of contributors to ADVANCES IN POLYOLEFINS includes most of the leaders in this field, such as Dr. Mark, Mandelkern, Bruzzone, Hsieh, Kaneda, Chien, Tait, Karol, Kaminisky, Scott, Cook, Mirabella, Samuels, Kanamoto and Vigo.

These reports covered many phases of polyolefin science and technology, ranging from elastomers, single crystals, film and fibers to characterizations by modern instrumentation and many new innovations in catalysis which have brought about a revolution in polyolefin production.

We as editors are grateful for the unselfish assistance of those who made this publication possible. We are particularly appreciative of our appointment as cochairs for the Macromolecular Secretariat on ADVANCES IN POLYOLEFINS by the Macromolecular Secretariat Committee. Hopefully, this treatise will set the stage for subsequent publications describing future advances in polyolefins.

Raymond B. Seymour
Tai Cheng

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INTRODUCTION

In spite of the fact that polyolefins were one of the last types of polymers to be commercialized, they have become the most widely used polymers throughout the world. Low density polyethylene (LDPE), which was the pioneer commercial polyolefin, is a highly branched polymer, produced at extremely high pressures, in a capital-intensive process. Nevertheless, over 2 million tons of this product is produced annually in the U.S. and an equal volume of this polymer is produced in other developed nations.

In spite of its higher density, which means higher cost per unit volume, the use of high density polyethylene (HDPE) continues to increase. Over 3 million tons of this linear polymer is produced annually in the U.S. and an equal volume is produced in other developed countries. This versatile product may be produced as a tough ultra high molecular weight polymer, it may be swollen in solvents and chain extended to produce filaments with unusually high strengths and may be used as a mica-filled high temperature resistant sheet, film and blow molded containers.

Sizable quantities (625 thousand tons) of the copolymer of ethylene and vinyl acetate (EVA) are produced annually in the USA but the polymer with the greatest potential is a copolymer of ethylene and alpha-olefins, such as 1-butene. These linear low density polyethylenes (LLDPE) which are characterized by toughness and flexibility, are now produced at an annual rate of 1.5 million tons in the U.S. The Unipol, Dowlex and related processes used to produce these superior products are more efficient, more versatile and less capital intensive than the traditional processes used to produce LDPE and HDPE.

The existence of several types of polyethylene and blends of these polymers provide the designer and molder with unusual versatility in resin specifications. Thus, polyethylene technology has progressed from its dependence on one low density polymer (LDPE) to many linear polymers and copolymers and blends which will extend the use of polyethylene to many heretofore unacceptable applications.

The story of polypropylene is also one of versatility and unusual growth potential. In spite of its greater susceptibility to degradation from outdoor exposure, over 2.5 million tons of polypropylene is produced annually in the USA. The use of about 700 thousand tons of polypropylene fibers and filaments is indicative of the versatility of this polymer. It is also used for blow molding, extruded film and pipe and injection molded packaging and battery cases.

Copolymers of ethylene and propylene (EPDM) are also used as light colored vulcanizable elastomers. These and other applications will increase as the result of the so called revolution in polyolefin catalysts which includes magnesium chloride-supported catalysts. Since this book is a chronicle of

events leading to the polyolefin catalyst revolution, it has been possible to record these events by worldwide authorities in a single volume. However, because of the rapid and continued growth in this field, it will not be possible to describe subsequent events in a single volume.

Accordingly, we, as organizers of this international macromolecular secretariat on "Advances in Polyolefins" recognize that it has been a distinct privilege to edit and publish these important contributions at this time.

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HISTORY OF POLYOLEFINS

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INTRODUCTION

A Brief History of Polyolefins

Polyolefins are, by far, the world's most widely used synthetic polymers. As shown in subsequent chapters, these ubiquitous macromolecules are used as coatings, fibers, elastomers and plastics. Yet, commercial polyolefins were essentially nonexistent prior to World War II. The history of the genesis of these versatile polymers illustrates the inherent genius and good as well as misfortunes of the pioneers in the science and technology of polyolefins.

The term polyolefin is confusing since this is the name given to polymers of olefins, which of course, are neither olefinic (unsaturated hydrocarbons) or alkenes. Actually, polyolefins are polyalkanes with the empirical formula of $H(CH_2)_nH$. This is also the formula for solid alkanes, such as paraffin wax. The latter is an oligomer with 26 to 30 repeat methylene (CH_2) units. Microcrystalline wax has a higher molecular weight and higher melting point (90°C) than paraffin wax. The naturally occurring elaterite is a polyolefin-like polymer.

In a lecture to the Chemical Society in 1863, Berthelot[1] reused the word "polymeric" which had been coined by Berzelius in 1832. Later, he coined the term polyethylene for a hexadecane produced by heating ethylene with alkali. He also obtained a higher molecular weight product i.e. tetramer and pentamer by heating propylene with sulfuric acid.[2] Yet, Goryainov and Butlerov were unsuccessful in their attempts to polymerize olefins by heating the sulfuric acid,[2] but Berthelot and Gaudechon were successful in their attempts to produce oligomers by the photopolymerization of ethylene in 1910.[3]

POLYMETHYLENE FROM DIAZOALKANES

Von Pechman[4] and Bamberger and Tschirner[5] obtained solid polymethylene by the decomposition of diazomethane in 1889 and 1900 respectively. A half century later, Buckley, Cross and Ray produced polymethylene $(CH_2)_n$ polyethylidene $(CH(CH_3))_n$ and polypropylidene $(CH(C_2H_5))$ by the copper-catalyzed decomposition of diazomethane, diazoethane, and diazopropane, respectively.[6] Kantor and Osthoff produced high molecular weight, semicrystalline, polymethylene by the decomposition of diazomethane in the

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presence of diethyl ether-boron trifluoride complex at 0°C.[7] Polymethy-lene was also prepared by Bawn and Rhodes by the copper, copper stearate and boron trifluoride decomposition of diazomethane.[8]

J. Hertzog, R. Schonbach, H. Merwein, W. Burnleit and W. Weile also produced polymethylene by the decomposition of diazomethane in the 1920's and 1930's.[9] Leitch, Gagnon, and Cambron also used this type reaction to produce a deuterated polymethylene.[10] Buckley published infrared specto-grams showing different bands in polymers produced from diazoalkanes[11] and Oakes and Richards determined the average molecular weights of poly-methylene using cryoscopy and intrinsic viscosity.[12] Polymethylene was patented in Germany, but was not produced commercially from diazomethane.[13]

These polymethylenes were characterized by crystalline melting point (137°C) which is in accord with thermodynamic predictions of Mark.[14] The properties of polyolefins, produced by the decomposition of diazoalkane have been summarized[15] and considerable information on these polyolefins has been recorded.[16] According to Nasini and Trossarelli, small amounts of crystalline polymethylene are produced by the decomposition of diazo-methane in the presence of gold, presumably by a heterogeneous reaction but larger amounts of amorphous polymethylene are also produced by a homogeneous reaction.[17]

POLYETHYLENE BY CONDENSATION REACTIONS

Taylor and Jones produced oligoethylene by the thermal decomposition of diethylmercury, in the presence of ethylene.[18] Carothers produced polymethylenes with as many as 100 methylene groups by the condensation of decamethylene bromide.[19] He separated these polymers by fractional crystallization and recorded the melting points of specific polymers, such as $(CH_2)_{50}$, (92°C), and $(CH_2)_{70}$, (105°C).

H. Staudinger produced a crosslinked polythylene by the reduction of polyvinyl bromide[20] and W. Hahn and W. Muller obtained linear polyethylene by the lithium hydride reduction of polyvinyl chloride in the 1950's.[21]

FISCHER-TROPSCH REACTION

Koch and Ibing obtained linear crystalline polymethylene, with an average molecular weight of 200 and a melting point of 117°C, by the Fischer-Tropsch reduction of carbon monoxide with hydrogen.[22] Pichler and Buffleb used a ruthenium catalyst in the Fischer-Tropsch reaction to obtain polymethylenes with average molecular weights as high as 9,000[23] and this technique for the production of polymethylenes, using a metal tungstite catalyst, was patented by duPont in 1955.[24]

POLYISOBUTYLENE

Oligomers of isobutylene were produced in 1873 by the boron triflu-oride-catalyzed polymerization of isobutylene.[25,26,27] This poly-merization was reinvestigated by Hoffman[28] and Otto[29] who obtained and patented this polymer.[30] In 1930, Lebedev, Staudinger, and Bruner obtained oligomers and high molecular weight polymers of isobutylene by polymerization in the presence of Floriden clay at -80°C and Waterman[31] polymerized isobutylene in the presence of aluminum fluoride at -78°C in 1934. After a formal cooperative agreement was signed, Otto was invited to the Standard Oil Co. Laboratories at Bayway, NJ where he remained from 1933-1935.[32]

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Bannon of Standard Oil patented the polymerization of isobutylene in ethylene using a cold, boron trifluoride - slurry technique, which is still in use for the production of polyisobutylene and butyl rubber.[33] Otto patented an endless belt technique for the polymerization of isobutylene.[34] Later, a solution of aluminum chloride in ethyl chloride was substituted for the boron trifluoride catalyst in the production of polyisobutylene.[35] Polyisobutylene was produced in Germany under the trademark of Oppanol and in the U.S. under the trademark of Vistanex.

Thomas and Sparks patented the production of a vulcanizable elastomer (butyl rubber) which was a copolymer of isobutylene, with a small amount of isoprene.[36] Some of the early problems in the commercial production of butyl rubber have been recorded.[37] Earlier studies by Hoffman and Otto[38] and subsequent studies by Polanyi[39,40] and others[41] showed that co-catalysts were essential for these cationic polymerizations. Over 600 thousand tons of isobutylene-based polymers are produced annually world-wide.

PRODUCTION OF LINEAR POLYETHYLENE

Goryainov and Butlerov were unsuccessful in their attempts to poly-merize ethylene in the presence of sulphuric acid,[42] but Ipatiev obtained oligomers of ethylene by polymerization in the presence of zinc chloride and aluminum chloride in 1913.[43] As discussed previously in this report, several investigators have prepared polymethylene by the decomposition of diazomethane. These investigations were repeated by Sailors and Hogan[44] and Hobart and Ziegler[45] in order to characterize these polymers. These polymers had a density of 0.97 grams/cc, a melting point of 135°C, a tensile strength of 3900 psi, a relative viscosity in xylene (0.125%) at 85°C of 1.2 and were 91% crystalline.

LOW DENSITY POLYETHYLENE

The discovery of low density polyethylene (LDPE) was based on a series of fortuitous events which have been described by Swallow,[46] Ballard,[47] and McMillan.[48] This polymer, which was originally called high pressure polyethylene (HPPE), was, in fact, the result of an interest in ultrahigh pressure reactions by Nobel Laureate Robert Robinson, a consul-tant for ICI, who was aware of the pioneering efforts of P. W. Bridgman and A. Michels. Imperial Chemicals Industries (ICI) was formed in 1927 through the amalgamation of British Dyestuffs Company, Brunner Mond, United Alkali and Nobel Explosives Industries in an attempt to compete with I. G. Farben Industrie.

In 1933, E. W. Fawcett and R. O. Gibson attempted to combine ethylene and benzaldehyde at 170°C and 1400 atmospheres. These investigators, who received little recognition, recovered about 1 gram of residue from the reaction kettle. Since they recognized that this residue was polyethylene, they repeated the experiment without benzaldehyde, but the reactor exploded.

Without consent of ICI, Fawcett reported the production of polyethy-lene at the Faraday Discussion on Polymer Chemistry in 1935. H. Staudinger labeled Fawcett's statement as nonsense,[49] but, Fawcett was transferred to other work in ICI. A larger quantity (8g) of LDPE was produced in 1935, by M. W. Perrin, who accidentally used traces of oxygen which was present in ethylene, as a catalyst. It is of interest to note that Fawcett, Gibson and Perrin, who is now Sir Michael Perrin, all left ICI before the end of

World War II and were not involved in further production of LDPE. However, they were recognized as co-patentees in the ICI patent application.[50]

The LDPE produced in the 1930's had the following properties; melting point 115°C, density 0.91 grams/cc, could be drawn into filaments, was partially crystalline[51] and had a Staudinger molecular weight of 2000 to 24,000. Fox and Martin used infrared spectroscopy to show a larger than expected number of methyl groups than should be present in a linear polymer and concluded that LDPE was a branched polymer.[52]

A pilot plant was built, under the direction of J. C. Swallow, and the full scale production facility for LDPE came on stream in September 1939, on the same day that Hitler's troops invaded Poland. LDPE which was used for the insulation of radar cable was also produced by duPont, in the U.S., in 1943. The production of LDPE exceeded that of all other polymers until 1982 when some of this polymer was displaced by linear low density polyethylene (LLDPE) which is produced at moderate pressures.[53] Several reviews on the history of LDPE are available.[54,55,56,57,58] Over 1700 tons of LDPE was produced in the U.S. in 1983.

LINEAR POLYETHYLENE

In 1930, Frederick and Marvel produced polyethylene, by the accidental polymerization of ethylene in the presence of alkyllithium and tetraethyl-arsenium bromide.[59] Marvel then passed ethylene through a solution of butyllithium, in hot mineral oil, and obtained linear polyethylene (HDPE). duPont examined this polymer but declined to consider its commercialization.[60]

Nevertheless, Krase[61] and Larcher and Pease[62] patented HDPE, produced at high pressure with peroxide initiators. These polymers had a density of 0.96 grams/cc, a relative viscosity of 1.2 (0.125% in xylene) at 85°C and a melting point of 127°C.

In 1940, Mayo also produced HDPE, by the free radical polymerization of ethylene, but his employer, U.S. Rubber Co., was not interested in this polymer.[63] M. Fischer patented the production of HDPE by the polymerization of ethylene in the presence of titanium tetrachloride and aluminum chloride.[64]

Karl Ziegler had used alkyllithium to polymerize butadiene in 1928.[65] Gellert used the more soluble lithium aluminum hydride in place of the insoluble lithium hydride.[66] Ziegler and his associates found that lithium aluminum hydride and triethylaluminum added ethylene readily to form 1- butene. After it was discovered that a trace of nickel from the stainless steel reactor was responsible for termination of the addition of ethylene, a search for the effect of other metals was initiated.

Breil obtained negative results with cobalt, copper, iron, gold, platinum, and silver but produced HDPE with zirconium on October 26, 1953.[67] The preferred catalyst system, which was titanium tetrachloride and triethylaluminum was patented by Ziegler.[68] This process was licensed to Petrochemicals Ltd. in England, Montecatini in Italy, Farbwerke Hoechst in Germany, and Hercules in the U.S. It is important to note that Ziegler acted as his own patent attorney and restricted his patent application to HDPE. Ellis also patented the polymerization of ethylene in the presence of alkyllithium supported on silicon dioxide.[69]

Breil noted that HDPE softened at 130-150°C, which was higher than the softening point of LDPE and used an IR spectrograph to show the presence of

only a few methyl groups and, hence, he concluded that HDPE was a linear polymer. The average molecular weight was reported as about 200 thousand.

In 1943, G. Bailey and E. Reid[70] obtained an oligomer of ethylene by use of a nickel oxide catalyst on an alumina/silica support. Later, Hogan and Banks used a chromium salt, supported on alumina/silica and plugged the reactor pipe with solid HDPE. Shell chemists had also used chromium salts as catalysts for the dimerization of ethylene but discontinued the research when "waxy solids" were produced.[71] Hogan and Banks filed patent applications in the U.S., Australia, and Belgium in 1953, 1954, and 1955, respectively.

Considerable production and characterization information is given in a U.S. Hogan and Bank's patent which issued in 1958.[72] The solid HDPE had the following properties; density, 0.95-0.97 grams/cc, intrinsic viscosity 0.2-10 (corresponding to a weight average molecular weight of 5,000 to 250,000) shore D hardness 60-65, tensile strength about 4,000 psi, elongation of 10-40%, softening temperature about 200°F and crystallinity of about 80%. The amorphous portion was soluble in solvents, such as n-heptane but the crystalline portion was insoluble.

The melting point or actually the freezing point of HDPE was determined from a cooling curve of temperature vs. time. Infrared spectrograms showing similarity to Ziegler's HDPE and differences from LDPE were included in this patent application. The history of Phillips' HDPE has been reported in several articles.[73,74,75]

Zletz also patented the production of HDPE using a catalyst consisting of molybdenum oxide or cobalt molybdate, supported on alumina.[76] Plants using the Zletz process were built by Furukawa in Japan, in Sardinia, and by Amoco (formerly Standard Oil) in Texas City, Texas. The latter has been scrapped and Amoco is now producing HDPE, under a license from Solvay-USI. The Phillips' process is now the most widely used process for making HDPE. About 10 million tons of HDPE is produced annually, worldwide.

POLYPROPYLENE

The word "polypropylen" was first used by Buterlov,[77] who obtained tetramers and pentamers by the addition of sulfuric acid to propylene.[78,79] Berthelot also produced oligomers by this technique.[80] Oligomers of propylene were prepared, using copper pyrophosphate, and silica/alumina as initiators. Low molecular weight, amorphous polypropylene, obtained by the use of boron trifluoride with a hydrogen fluoride activator, was used as a viscosity index (VI) improver and as a lubricating oil during World War II.

Much of the early investigations were updated in the post war period, by Fontana at Mobil Oil Co. He obtained polypropylene with a number average molecular weight as high as 830,000 by the cationic polymerization of propylene at -44°C.[81,82,83,84] Fontana recorded a glass transition temperature (T_g) of -30°C for his amorphous polypropylene and stated this polymer had no tendency to crystallize. That this amorphous polymer was soluble in alkanes was evident by its end use as a viscosity improver in lubricating oils.

CRYSTALLINE POLYPROPYLENE

Breil attempted to polymerize propylene in Ziegler's laboratory but since the pressure did not decrease as dramatically as it did when ethylene was used, he concluded that no reaction took place. Hence, he added

ethylene to the reactor and obtained a quantitative yield, which was probably a mixture of polyethylene and polypropylene. He recorded "Propylene cannot be converted into high molecular polypropylene" in his notebook and Ziegler concluded "Es geht nicht" and did not include propylene in his patent application.

Ziegler's next attempt to polymerize propylene was not made until May, 1954, when Martin obtained polypropylene in a new reactor. In the interim, Wright of Petrochemicals, a Ziegler licensee, produced polypropylene in a pilot plant when ethylene was in short supply. Since he mistakenly believed that the Ziegler also covered polypropylene he missed an opportunity to make a patent application.

In contrast, Natta, who had been asked by Ziegler to restrict his investigations to HDPE, directed P. Chini to make polypropylene. After the crystalline polypropylene had been obtained, Natta wrote the following in his laboratory notebook; "Today (March 11, 1954), we made polypropylene." Natta applied for a patent and published his findings in 1955.[85] Ziegler also applied for a patent for polypropylene but was late by 10 days. A patent was issued to Natta, in 1972, after many years of litigation.[86]

Since Natta was a crystallographer, he used x-ray diffraction techniques to obtain a repeat period of 6.50 Å for polypropylene and stated that each portion of the principal chain included in the elementary cell corresponded to 3 monomer units. He also reported that because the asymmetric carbon atoms have the same configuration and because of steric requirements of the chain substituents "a spiralization of the principal chain takes place." He followed his wife's suggestion and used the term isotactic to designate the stereoregularity of these polymers.[87]

That stereoregularity of polymers could be influenced by polymerization condition had been suggested by Huggins[88] and demonstrated by Schildknecht when he polymerized vinyl isobutyl ether cationally at low temperature.[89] Flory suggested an isotactic structure for Schildnecht's polymer[90] and Natta verified this configuration in 1955.[91]

POLYPROPYLENE PATENTS

Since Hogan and Banks and other investigators had produced crystalline polypropylene before Natta, an interference proceeding (No. 89,634) was declared by the U.S. Patent Office in 1958.[92] The contestants were Phillips, duPont, Montecatini (now called Montedison), Standard Oil of Indiana, and Hercules. Hercules was dropped from these proceedings because of late discovery dates and Montedison was awarded the basic composition of matter patent for crystalline polypropylene.[93]

An appeal by the losing parties resulted in a Civil Court trial in the Federal Court of Delaware in 1977-78. The Court awarded a patent to Hogan and Banks in 1980.[94] The losing parties appealed in 1982, but the Federal Appeals Court upheld the decision of the lower court and the U.S. Supreme Court refused to review the decision of the lower courts. Hence, a patent was issued to Hogan and Banks in 1983 with a single claim, "Normally solid propylene, consisting of recurring propylene units, having a substantial crystalline polypropylene content."[95] The losing parties have appealed the latest court's decision.

As stated previously, Vanderburg of Hercules, claimed to have produced polypropylene but was unable to show a sufficiently early date for his research. Baxter, Merkling, Robinson, and Stamatoff of duPont claimed to have produced crystalline polypropylene in 1954, but failed to show utility

requirements of actual reduction to practice. Zletz, Peters, and Carmody of Standard Oil of Indiana, produced a product which was shown to be a copolymer of ethylene and 2-butene, resulting from a rearrangement of propylene to ethylene and 2-butene in the presence of a molybdenum catalyst.[96]

The decision of the court to issue the patent for polypropylene to Hogan and Banks was based on the following: Proof of reduction to practice using a chromic oxide – alumina/silica catalyst system in 1951 and 1952, recognition of the product as polypropylene, recognition of a specific practical use as a molded plastic and constructive reduction to practice by filing a patent application describing how the polymer was produced and stating a practical use for polypropylene.

There were actually 4 patents issued to Hogan and Banks, based on subject matter first disclosed in a patent application dated January 27, 1953. These patents were for polymers, catalysts, poly 4-methyl-1-pentene and polypropylene.[97]

As pointed out by Morawetz, the Zletz patent application claimed a rubbery polymer,[98] the Hogan and Banks application[99] claimed a solid fraction, insoluble in pentane but neither patent mentioned crystallinity.[100] However, Hogan and Banks did indicate the transition of molten polypropylene to solid polymer as a melting point and showed a distinct plateau in their cooling curve which is consistent with crystallinity. A noncrystalline polymer does not exhibit a sharp melting point.[101] Hogan and Banks reported a melting point of 144-150°C and Natta reported a melting point of 160°C. Fontana reported a glass transition temperature of -30°C for amorphous polypropylene which, as expected was much lower than the crystalline melting point.

PROPERTIES OF POLYPROPYLENE

Densities of 0.91-0.92 grams/cc and 0.92 grams/cc were reported by Hogan and Banks and Natta, respectively. The relationship between density and degree of crystallinity had been reported for cellulose in 1937.[102] Boyer has shown that the ratio of difference between the density of the sample less the density of the amorphous polymer and the difference between the density of the crystalline polymer less that of the amorphous polymer to be equal to the degree of crystallinity.[103]

Hogan and Banks had reported intrinsic viscosities in the range of 0.2 to 1.0 which would correspond to Staudinger molecular weights of 5,000 to 25,000. It is now agreed that crystalline polypropylene is a monoclinic crystal with a 3 fold helix having an identity period of 6.50Å and with low energy gauche and high energy transconformations in adjacent chains.[104]

Polypropylene, which is the fastest growing polymer, is produced at an annual rate of 2.2 million tons in the U.S. and at an annual rate of 6.5 million tons worldwide. It is used in the blow-molding of containers, extrusion of filaments, and fiber, and for the injection molding of containers, appliances, housewares, and battery cases.

CROSSLINKED POLYETHYLENE

In 1948, Dole discovered that LDPE may be crosslinked by irradiation. It may also be crosslinked by peroxide initiators.[105]