POLYMERIZATION OF OLEFINS BY COMPLEX METAL CATALYSTS

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Received January 17, 1958

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I. INTRODUCTION

Recently, the preparation, structure, and properties of polyethylene have been reviewed by Aggarwal and Sweeting (1), who surveyed the work on processes and catalysts for both the high- and the low-pressure polymerization of ethylene. Closely related to this field and somewhat overlapping have been the large number of papers and patents which have appeared during the past six years on the stereospecific polymerization of substituted ethylenes with complex metal catalysts. These catalysts are metal hydrides, metal alkyls, combinations of metal halides with metal alkyls or alkyl or aryl metal halides, and specific reduced metal oxides alone or on supports. This review is primarily concerned with the recent literature on these complex metal catalysts, the polymerization conditions, the stereochemistry of the polymers, the mechanisms of the reactions, and the properties of the stereospecific polymers. Burwell (20) has reviewed stereochemistry and heterogeneous catalysts, but has only briefly discussed the stereochemistry of polymers produced by solid surfaces.

For this paper the literature has been surveyed to November, 1957. Although a complete patent search has not been possible, an effort has been made to include the more important domestic and foreign patents.

II. DISCOVERY OF THE ZIEGLER CATALYST

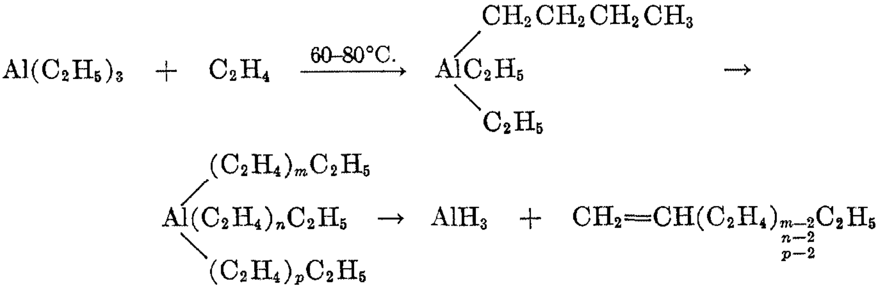
In 1941 Ellis (40) described the polymerization of olefins with lithium alkyls and a hydrogen contact catalyst, nickel or nickel oxide on silica. In a British patent (34) in which the initiation of polymerization in liquid ethylene at low temperatures by peroxide-containing redox systems was described, it was also proposed that organic derivatives of lithium, sodium, potassium, magnesium, and zinc could be combined with compounds of the metals of Group VIII and of Subgroup I for this catalyst system. The two examples given involved nickel and copper. This patent also mentions all the heavy metals such as titanium, chromium, and vanadium, whose salts, in combination with the same alkyl compounds of the alkali metals, magnesium, and zinc, were found later to give good results as catalysts for the polymerization of ethylene. In 1943 Max Fischer (58) had succeeded in converting ethylene to lubricating oils by the use of aluminum chloride. In this process the action of the aluminum chloride was modified by the addition of titanium tetrachloride and a small amount of aluminum powder; this metal was added to take up the hydrogen chloride which was formed during the reaction. When ethylene was polymerized with this catalyst at 130–180°C. under 30–80 atm. pressure, the reaction products consisted of a lubricating oil and a solid white mass. This solid product, polyethylene, was recorded as an unfortunate consequence.

By 1949 it was already known that α-olefins would add to lithium aluminum hydride, aluminum hydride, or aluminum alkyls to form aluminum alkyls with the final result that higher olefins would be formed through polymerization (175–178, 195, 198) (equations 1 to 3).

$$LiAlH_4 + 4C_2H_4 \rightarrow LiAl(C_2H_5)_4 \qquad (1)$$

$$AlH_3 + 3C_2H_4 \rightarrow Al(C_2H_5)_3 \qquad (2)$$

Metal hydrides and alkyls of beryllium, gallium, and indium could be used in place of the aluminum hydrides and alkyls, but it was found that aluminum triisobutyl was the only aluminum alkyl which was not effective for the polymerization of ethylene. Ziegler showed that this polymerization had occurred by the following process:



$$\mathrm{Al(C_2H_5)_3} + \mathrm{C_2H_4} \xrightarrow{60\text{–}80^\circ\mathrm{C.}} \mathrm{Al}\begin{matrix}\diagup\,\mathrm{CH_2CH_2CH_2CH_3}\\ \mathrm{C_2H_5}\\ \diagdown\,\mathrm{C_2H_5}\end{matrix} \rightarrow$$

$$\mathrm{Al}\begin{matrix}\diagup\,\mathrm{(C_2H_4)_{\mathit{m}}C_2H_5}\\ \mathrm{(C_2H_4)_{\mathit{n}}C_2H_5}\\ \diagdown\,\mathrm{(C_2H_4)_{\mathit{p}}C_2H_5}\end{matrix} \rightarrow \mathrm{AlH_3} + \mathrm{CH_2{=}CH(C_2H_4)}_{\substack{m-2\\ n-2\\ p-2}}\mathrm{C_2H_5} \qquad (3)$$

This was a true catalytic process, since the aluminum hydride was regenerated. This stepwise organometallic synthesis should lead to high-molecular-weight polyethylene, but only polyethylenes having molecular weights of 1000 to 5000 were obtained. It remained a mystery for some time that this process could not work at normal pressure. Results indicated that the possibility of deactivation by the reaction of one high-molecular-weight aluminum alkyl with another was improbable and therefore it was believed that the active end of the molecule, the aluminum–carbon bond, should stay alive for any length of time. Ziegler (197) had assumed that the reaction of 1000 moles of ethylene with 1 mole of aluminum triethyl should (after decomposition with water) give a long-chain paraffin with a molecular weight of 28,000. Since this was not the case, he proposed that the growing chain was destroyed through a side reaction with ethylene, shown below. This type of displacement reaction is characteristic for the reaction between aluminum alkyls and ethylene at high temperatures. Ziegler's results indicated that at 100°C., for about one hundred growth steps, there occurs one displacement, and that instead of 1 mole of $C_2H_5(C_2H_4)_{1000}al$, 10 moles of $C_2H_5(C_2H_4)_{98}CH{=}CH_2$ and 1 mole of C_2H_5—al are obtained. The $C_2H_5(C_2H_4)_{98}$-$CH{=}CH_2$ polymer corresponds to a molecular weight of about 2500–3000.

$$—(CH_2)_4—al + C_2H_4 \rightarrow —(CH_2)_2CH{=}CH_2 + C_2H_5—al \qquad (4)$$

Where al is ⅓ Al.

The story of the events which led to the discovery was published (188, 200) after several patents (179, 180, 196) and one preliminary article (199) had appeared announcing the discovery. In an attempt to prepare hexylaluminum and octylaluminum by heating aluminum triethyl with ethylene under 100 atm. pressure at 100°C. in an autoclave there was obtained, instead, a quantitative yield of 1-butene and unreacted aluminum triethyl. Aluminum triethyl had acted here as a catalyst for the dimerization of ethylene. This had been observed in other cases at temperatures of 150–200°C. (198) but was thought to be impossible at 100°C. A search for the catalyst which had caused the dimerization was carried out immediately, and it was found that the autoclave in which the reaction had been run contained a small amount of nickel phosphate which had been subsequently reduced by the triethylaluminum. The possibilities of intentionally adding nickel or cobalt to a polymerization system for α-olefins were immediately exploited (179, 187, 197), and it was hoped that by eliminating all traces of nickel a polymerization of ethylene could be achieved. During the systematic addition of various transition metal compounds, it was observed that cobalt and platinum also acted as cocatalysts, and in one experiment with zirconium acetylacetonate as a cocatalyst, a high yield of polyethylene was obtained. Immediately it was shown that compounds of the transition elements of Groups IV, V, and VI gave similar results. The experiments with aluminum alkyls and the cocatalysts were modified by running the polymerization in solvents, and the polyethylene, which precipitated as a white powder, was easily removed by filtration. Further experiments led to "the Muhlheim Normal Pressure Polyethylene Process" in which the most effective cocatalyst, titanium tetrachloride, was used and the addition of ethylene accomplished at 1 atm.

A detailed description of the catalyst and the laboratory process (186, 202) reveals that when titanium tetrachloride is added to a solution of diethylaluminum chloride in xylene or Fischer–Tropsch diesel oil, a brown precipitate is produced; ethylene is then bubbled into this mixture for perhaps 30 min. By the time Ziegler had published two papers (199, 201) describing the effects of the cocatalysts in the polymerization of α-olefins, in which a molecular weight of 3,000,000 was claimed, Natta had begun his work on the polymerization of α-olefins and had named this catalyst the "Ziegler catalyst" (92, 118).

At the same time that Ziegler was carrying out his work with high-molecular-weight alkyls, several patents were issued (46, 143, 144, 146, 147, 166, 205) which described catalyst systems consisting of partial reduction products of molybdenum trioxide on an alumina support, or nickel oxide on a charcoal support, for the polymerization of ethylene in various solvents from 100° to 260°C. and under 50–15,000 pounds of pressure. This discovery stemmed from observations made while investigating the alkylation of ethylene to light hydrocarbons (148). Patents also appeared (13, 14, 25, 68, 150, 151) which claimed chromium oxide on a silica–alumina support and nickel oxide on a silica carrier with alumina as a catalyst promoter.

III. CATALYST TYPES

A. Complex metal alkyls and hydrides

Since this initial phase of the work, many catalyst systems have been developed for the polymerization of α-olefins. Ziegler's metal hydrides, which were used without a "cocatalyst," were not good catalysts for the polymerization of α-olefins, since only dimer, trimers, and low-molecular-weight polymers were obtained (175, 198). Metal alkyls such as aluminum and beryllium alkyls were not too effective, even when a nickel, cobalt, or platinum "cocatalyst" was added (177, 179, 181–185, 194, 195, 197, 199, 203). Cobalt halides, however, were shown later to be useful for low-pressure polymerization (21). The metal salts which acted most effectively as "cocatalysts" were zirconium salts and especially titanium salts (134b, 200, 201). In general, salts of the metals of Groups IV, V, and VI, including thorium and uranium, were shown to be the best "cocatalysts." The metals of Group VIII, copper, silver, and gold had no effect (185, 200). The cocatalyst salts were used with organometallic compounds of Group II and III metals. The use of aluminum, zinc, and magnesium alkyls, or aryls, alkali metal alkyls (38, 190), and alkali metal hydrides was claimed (191). Extreme examples cited were $Li[Al(CH_3)_2H_2]$ and $Mg[Al(C_2H_5)_2]_2$. Ziegler has also claimed the effectiveness of hydrides of organo compounds of aluminum or the next two higher members of the same group in the periodic system, as well as alkyl metal salts of these metals hydrides, for the polymerization of ethylene (180, 196). Ziegler specifically mentioned diethylaluminum chloride and the "cocatalyst" compounds of chromium, molybdenum, tungsten, vanadium, titanium, and zirconium in his experimental description of this process for the polymerization of ethylene (186, 202).

Imperial Chemical Industries lists one or more of the metals aluminum, beryllium, zinc, magnesium, lithium, and sodium with an aluminum trialkyl or a complex alkali metal with aluminum, gallium, indium, or thallium as the reducing agent portion of the catalyst (72). The most generally used catalyst of this type for the polymerization of α-olefins is aluminum trialkyl and titanium tetrachloride or trichloride (9, 58, 63, 85, 88). At least the metal salt "cocatalyst" must be present along with some reducing agent (60). A du Pont patent (35) claims titanium tetrachloride and a metal alkyl which will reduce titanium at least to a valence below +3. The coördination catalysts include halides of titanium, zirconium, cerium, vanadium, niobium, tantalum, chromium, molybdenum, or tungsten, and oleates or alkoxides of these metals. These salts can be reduced in the reaction mixture with Grignard reagents, metal alkyls, metal hydrides, zinc, and metals above zinc in the electromotive series. Other procedures prefer titanium trichloride and aluminum triethyl (106, 113, 120, 121, 137, 138) or an alkyl metal halide of the type R_nMX, where R is a hydrocarbon, X is a halogen or a hydrocarbon radical, M is a Group II or III metal, and n is a whole number less than the valence of M (86, 87). Ellis (40) originally described a hydrogenation catalyst for the polymerization of α-olefins, consisting of reduced nickel on kieselguhr and an alkali metal hydride or alkali metal hydrocarbon such as butyllithium. A procedure for the polymerization of ethylene using the reducing agents diethyl zinc, phenylsodium, and isoamylsodium has also been described (140). Claims have been made that a mixture of aluminum ethyl sesquidibromide and lead tetraalkyls forms pyrophoric catalysts that give higher degrees of ethylene polymerization than aluminum alkyls (59, 159). Recently vanadium(V) oxytrichloride and vanadium trichloride with aluminum triethyl have been employed for the copolymerization reactions of α-olefins (83, 84, 115). Perhaps the only catalyst precipitate of the Ziegler type which has been isolated in a pure crystalline state is one which has the empirical formula $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$ (133). This blue crystalline compound was prepared by mixing dicyclopentadienyl titanium dichloride and aluminum triethyl in a heptane solvent. It was reported that the formation of this crystalline compound took place with the evolution of a gas and that the complex form was less active for the polymerization of ethylene than the aluminum triethyl–

titanium tetrachloride catalyst. The gas which was formed in this reaction is a mixture of ethylene and ethane (112a). Two other organometallics, $(C_5H_5)_2TiCl_2AlCl(C_2H_5)$ and $(C_5H_5)_2TiCl_2AlCl_2$, have recently been reported as other products of this reaction. Dicyclopentadienyl titanium diphenyl has also been employed for polymerization studies (134). Breslow and Newburg (18) have obtained, however, a crystalline complex from dicyclopentadienyltitanium dichloride and diethylaluminum chloride which, on careful recrystallization, yielded a white crystalline compound whose analysis indicated a complex of dicyclopentadienyl titanium(III) chloride and aluminum sesquichloride:

$$[(C_5H_5)_2TiCl]\cdot 0.5\ [(C_2H_5)_2AlCl]\cdot 0.5\ [C_2H_5AlCl_2]$$

The blue complex obtained before recrystallization is reported to be a poor catalyst, but the freshly recrystallized material is a highly active catalyst, as is the blue complex if the ehtylene contains a trace of oxygen.

Several studies have been made on various catalyst systems in order to determine the most reactive catalyst types. In the course of experimentation on reducing agents for titanium tetrachloride, hexyllithium, lithium aluminum tetraheptyl, aluminum triethyl, and aluminum triisobutyl have been described (78). The titanium halides, and alkoxides on silica–alumina supports have been investigated as possible catalysts with aluminum triethyl; the fluorides and iodides do not give good conversion, and the alkoxides are very poor catalysts (136).

The course of the polymerization reaction of conjugated dienes catalyzed by an aluminum hydride or alkyl and a trihalide or tetrahalide of titanium has been shown to be dependent particularly on the titanium halide employed (152).

A process based possibly on the formation of an aluminum alkyl in the reaction mixture describes the polymerization of ethylene by a catalyst prepared from a mixture of cyclohexene, titanium tetrachloride, aluminum oxide, and a mercuric chloride promoter (165).

B. Catalysts from metal oxides

The metal oxide catalyst systems which have been described for the polymerization of olefins consist of a reduced transition metal oxide on a support. When nickel or cobalt oxides, supported on a charcoal catalyst, are not reduced, dimers, trimers, and tetramers are produced (22, 144, 146, 148, 166). Several patents reveal that nickel oxide which is reduced on a charcoal support is an excellent catalyst for the polymerization of olefins (42–44, 54, 147). Charcoal which has been leached with nitric acid is soaked in a nickel nitrate solution and the nitrate is decomposed to nickel oxide by heating. This mixture is then reduced with hydrogen or a borohydride of an alkali metal. Powdered aluminum oxide or molybdena–alumina can be added before the reduction (45a, 148, 149). A similar catalyst is prepared from nickel or cobalt on an inert carrier such as kieselguhr, and a promoter metal. This is then reduced with hydrogen containing a trace of carbon monoxide (17). Silica–alumina supports have also been employed for nickel or cobalt catalysts. Nickel oxide on silica–alumina supports yields dimers and trimers (25, 69), even with isoölefins (68). The same type of catalyst, however, has been claimed to give high-molecular-weight olefins (13, 14). This catalyst is prepared by impregnating an alumina–silica support with nickel nitrate and thermally decomposing the nickel to the oxide. The olefin which is to be polymerized is, however, diluted with hydrogen (69).

Two types of nickel catalysts supported on silica–alumina have been described (70). Impregnated catalysts are prepared by treating 16–30 mesh silica–alumina cracking catalyst with a 3 per cent solution of nickel nitrate, drying the product, and finally heating the catalyst at 500°C. to decompose the nickel nitrate to nickel oxide. The coprecipitated catalyst is prepared by mixing a solution of sodium silicate with an aluminum nitrate–nickel nitrate solution and adjusting the pH until a gel is formed. The gel is dried and leached with an ammonium chloride solution to exchange the sodium ion. This product is then dried and the nitrates are decomposed to oxides. Silica–alumina-supported hydrogenation catalysts other than nickel have been claimed for the polymerization of gaseous olefins (24).

Group VIA metal catalysts (for the polymerization of ethylene), for example, chromium, molybdenum, tungsten, or uranium, have been described (46–48, 65, 89, 204). These catalysts are prepared by the reduction of these metal oxides on an inert oxide support such as γ-alumina. Hydrogen, sodium hydride, lithium hydride, and lithium aluminum hydride are employed as reducing agents.

The metal or metal hydrides act as promoters and serve three functions: to activate the spent catalyst by reduction, to scavenge poisons (oxygen, moisture, hydrogen sulfide, and carbon dioxide), and, most important, to enter into the catalytic process (57). The promoters sodium, calcium hydride, or lithium aluminum hydride are usually added to the catalyst which has been prereduced by hydrogen.

Silica (51), silica–alumina (56), titanium oxide, and zirconium oxide (52, 53, 161) have also been tested as supports. Alkali metal borohydrides, alkaline earth metal aluminum hydrides of the general formula $M(AlH_4)_2$, where M is magnesium, calcium, or barium, or the metal hydrides of beryllium, magnesium, calcium, strontium, or barium can be used as reducing agents. The carbides of calcium, strontium, or barium also serve as reducing agents (161). Hydrogen can be used, but is not necessary for the regeneration of these catalysts, since activity can be maintained by heating the catalyst in the presence of a decomposable hydrocarbon (67). Oxides of vanadium, niobium, or tantalum supported on prereduced silica gel and reduced with alkali metal borohydrides are active catalysts for the polymerization of ethylene (45, 50). These oxides can also be supported on prereduced γ-alumina and reduced with calcium, barium, strontium, or magnesium hydrides or with lithium aluminum hydride (49, 55). Reduced molybdena–alumina catalysts (145) or molybdenum oxide which is supported on thorium or zirconium oxides and activated by reduction have also been claimed (144, 158, 205).

The Phillips Petroleum Company produces "Marlex" polyethylene with supported chromium oxide catalysts (26, 27). These catalyst systems will also polymerize a variety of α-olefins. The catalyst is composed of 2 to 3 per cent chromium on a silica–alumina support. Chromium oxide or a chromium salt is dried and then activated on a support which is rich in silica and low in alumina (6, 10, 150).

IV. POLYMERIZATION CONDITIONS

A. The Ziegler process

The laboratory polymerization process first described for ethylene takes place at room temperature and pressure (141, 186, 202). Titanium tetrachloride is added under a dry nitrogen atmosphere to dry Fischer–Tropsch diesel oil which contains diethyl aluminum chloride. After the formation of the brown catalyst precipitate, ethylene is bubbled through the solution, forming a high-molecular-weight polyethylene. This method is satisfactory for highly active catalysts or less active catalysts and liquid olefins. Other descriptions reveal that 30 to 80 atm. pressure at 130–180°C. (58) or as much as 400 atm. pressure at 160°C. (180, 196) is necessary for other catalysts. Gaseous olefins are most conveniently polymerized on a practical basis under a pressure greater than 1 atm. (15, 16), although the Badische Anilin- & Soda-Fabrik described a process in which the catalyst is formed in ethyl chloride and ethylene is bubbled through this mixture at 1 atm. pressure (12a, 12b). Temperatures ranging from 35° to 90°C. have been used for the polymerization of various α-olefins in high conversion (96, 114) and for copolymers of α-olefins. The processes for the polymerization of ethylene which involve Ziegler-type catalysis and are being studied at Hercules Powder Company, Koppers Company, Union Carbide & Carbon Corporation, Monsanto Chemical Company, and Dow Chemical Company employ, in general, a heptane solvent, pressures of 100 p.s.i. or greater, and polymerization temperatures from 60° to 70°C. (167).

The polymerization reaction mixture is worked up by destroying the catalyst with water in flash drums where the solvent is removed. The water–polyethylene slurry is centrifuged, and the polyethylene is dried. A Russian industrial operation described the production of crystalline polypropylene with aluminum triethyl and titanium tetrachloride in which only a 21 per cent conversion is obtained from either pure or technical-grade fractions of propylene (170).

B. The Phillips process

The "Marlex" catalyst systems, which utilize chromium on a silica–alumina support, have been reported to require an operating temperature of 135–190°C. and a pressure sufficient to keep the operating solvent in the liquid phase (66, 150). Two types of processes are employed (27). The fixed-bed polymerization system operates at 150–180°C. in a hydrocarbon solvent. Pure ethylene is pumped into the solvent and the solution stream is passed downward over the catalyst bed. The ethylene concentration ranges from 2 to 4 per cent. The slurry-type operation is run in 1500-ml. solvent batches under a pressure of 400–500 p.s.i. Ethylene is pumped into the stirred catalyst solution and the catalyst is removed from the polymer solution at the end of the operation by filtration. Xylene serves as a suitable solvent and the solvent-to-catalyst ratio is high (167). The molecular weight of the polyethylene polymers and the poly-α-olefins is controlled by the temperature and pressure of the reaction as well as the temperature at which the catalyst is activated. In general, polymers of higher molecular weights are obtained at high pressures (500 p.s.i.) and low temperatures (120°C.). These procedures are also favorable for the preparation of copolymers of α-olefins.

The dimerization and trimerization of ethylene over nickel oxide on silica–alumina have the highest reaction rate at 70–93°C. and 600 p.s.i. (69), but lower temperatures and pressures, 40°C. and 300 p.s.i., are described (25).

C. The Standard Oil of Indiana process

The patents issued to Standard Oil of Indiana for the nickel–charcoal catalyst describe the polymerization of ethylene in toluene, xylene, or hydrocarbon solvents (42–44, 146, 147). Polymerization temperatures from 100° to 150°C. and pressures of 1000 p.s.i. are general. Temperatures as low as 50°C. and pressures as high as 15,000 p.s.i. are claimed, but optimum pressures are between 1000 and 8000 p.s.i. (166). The same catalyst on a kieselguhr support requires 100–400°C. and 50–6000 atm. pressure (17). A method for the continuous polymerization of ethylene by regenerating the catalyst through reduction has been described (41). The catalyst systems comprised of Subgroup V metal oxides on silica or alumina supports effect polymerization in benzene, xylene, or decalin at 200–5000 p.s.i. and a temperature range of 130–260°C., although temperatures near 200°C. appear to be most satisfactory (45, 49, 50, 55). The Group VIB oxide catalyst systems contain benzene, toluene, xylenes, cyclohexane, decalin, isoöctane, and other hydrocarbons as solvents (46–48, 52, 56, 89, 145, 161, 204). Temperatures from 130° to 260°C. are the most common, and pressures from 200 to 5000 p.s.i. are reported. Optimum polymerization pressures, however, are about 1000 p.s.i.

The pressure in these catalyst systems is apparently not critical, but must be high enough to maintain the solubility of ethylene in the solvent. The polymer is recovered from the reaction mixture by transfer from the tubular reactor into a series of separator drums (167).

Little catalyst activity is found for either of these catalyst systems unless these catalysts are partially reduced (148). The nickel catalyst (5 per cent) on a charcoal support is reduced at 200–260°C. with hydrogen, and reduction of the molybdenum catalyst (8 per cent) is effected at 430–480°C. Batch reactors containing the solvent and catalyst are pressured to 1000 p.s.i. with ethylene, and the pressure is held for 2 hr. The flow reactors are packed with the molybdenum catalyst, and the catalyst is activated in the tube. The ethylene–solvent feed mix is pumped upward through the tube under pressures of 800–1000 p.s.i. The temperature of these polymerizations has a pronounced effect on the yield. The optimum yield is reached at 200°C., while higher temperatures decrease the yield of polymer. The catalyst particle size affects the polyethylene viscosity, higher viscosities being obtained with large particle sizes.

The catalyst in the feed reactor can be regenerated with hydrogen, and its activity can be completely restored. The solution, which is fed at the rate of 5 l. in 12 hr., drops the catalyst activity from 100 per cent to 25 per cent in 5 to 12 hr.

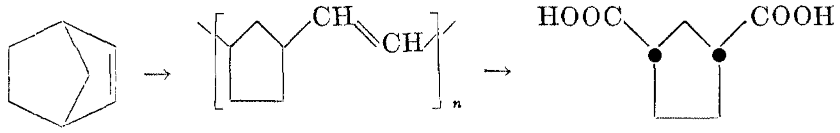
Polyethylene made by the Ziegler process has the advantage that it can be made at 1 atm. pressure, but the process seems to be a slightly more expensive one. The Phillips method gives the most complete conversion to polymer, but the unit operations required for recovery and purification of the polymer, the cost of production, and the electrical properties of the polymer are somewhat poorer than those of the Ziegler polyethylene. The ease of polymer separation and the few variables influencing the process appear to be the main advantages of the Standard Oil process (67). The polymer formed, however, has a larger molecular-weight range (148).

V. OLEFIN TYPES

A. *Monoölefins*

Ethylene was the first olefin studied by Ziegler for polymerization reactions (179, 181, 182, 184). Attention was first drawn to this olefin in Germany and in the United States because the accidental discovery involved this monomer 148, 199) and because of its availability. Since this discovery, the polymerization of many α-olefins has been described. In general, the monoölefin must be an α-olefin with no branching closer than the 3- or 4-position to the double bond (26, 27, 200). For example, 4-methyl-1-pentene gives hard polymers, while 3-methyl-1-butene yields only low-molecular-weight materials, at least with the Phillips catalyst. Propylene has been shown to undergo a polymerization with the Ziegler-type catalyst to yield a highly crystalline polypropylene (86, 98, 105, 106, 122, 123, 127, 185). The polymerization of propylene by supported reduced metal oxides has also been studied (52, 69). The α-olefins propene and butene readily undergo polymerization (92). In addition, 3-methyl-1-butene, an example of an olefin with branching in the 3-position, and pentene have been polymerized by the Ziegler-type catalyst (120, 129). Polymerization of the branched olefins 4-methyl-1-pentene, 4-methyl-1-hexene, and 5-methyl-1-hexene has also been carried out (95, 131). Of the olefins ethylene, propene, and butene, the lower-molecular-weight alkenes are the more reactive (69).

The aromatic substituted olefin styrene, which might be classed as an exception to the branching rule, readily polymerizes to a high-molecular-weight polymer (90, 92, 101, 130). The long chain α-olefins dodecene and octadecene also polymerize in good conversion to high-molecular-weight polymers (80). Bicyclo-[2.2.1]-2-heptene (I) gives either a rigid or a flexible polymer, depending on the molar ratio of lithium aluminum alkyl to titanium tetrachloride employed for the catalyst (171). Two different structures for the two types of polymers have been proposed. The catalyst—a bivalent titanium compound formed by the action of a Grignard reagent, metal alkyls, metal hydrides or alkaline earth metals on titanium tetrachloride—most probably opens the ring before polymerization (2, 36), since no unconjugated olefins other than α-olefins undergo polymerization with the Ziegler catalyst. The structure of the polymer (II) has been shown by its oxidation to *cis*-cyclopentane-1,3-dicarboxylic acid (III).



I II III

(5)

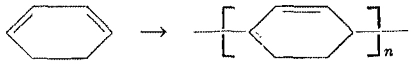
It is interesting to note that the polymerization of substituted acetylenes has been accomplished by use of the Ziegler catalyst (114a). The polymers obtained contain double bonds along the chain backbone.

Olefins which have other attached groups, such as all the carbonyl functional groups, functional groups containing nitrogen, sulfur, phosphorus, etc., easily reducible groups or active halogens and hydrogens, which will destroy the catalyst, cannot be polymerized.

B. Conjugated diolefins

Conjugated diolefins undergo polymerization under the influence of the various catalyst systems described, and the branching rule does not apply to these olefins (26, 27). Goodyear Tire & Rubber Company produces a "synthetic natural rubber" from isoprene with aluminum triethyl and a cocatalyst. The structure of the polymer is nearly identical to that of natural rubber, an all-*cis*-1,4-polymer (9). Organometallic compounds of lithium, sodium, and potassium as catalysts for the polymerization of isoprene have been investigated (66a, 71a). Butyllithium in hydrocarbon solvents produces a 90 per cent yield of the *cis*-1,4-polymer. Phenyllithium in either an ether or a hydrocarbon solvent gives mixtures of the *trans*-1,4-, 1,2-, and 3,4-polymers, as does butyllithium in ether. A Goodrich-Gulf Chemicals patent (63) describes the polymerization of conjugated polyolefinic hydrocarbons, especially isoprene and butadiene, with organometallics. Isoprene is polymerized to the *cis*-1,4-polymer ("Ameripol SN"), and these conjugated dienes can be polymerized either *cis*-1,4 or *trans*-1,4 at will (71). The kinds of polymers obtained seem to depend largely on the metal halide making up part of the catalyst system (152). Aluminum alkyls and titanium tetraiodide are specific for the polymerization of conjugated diolefins to *cis*-1,4-polymers. An alkali metal aluminum hydride, titanium tetrachloride, and a trace of aluminum chloride produce the 1,2-addition product. When the polymerization of isoprene or butadiene is catalyzed by an alkali metal aluminum hydride and titanium tetraiodide, the predominant polymers are the *trans*-1,4 products. Other conjugated diolefins claimed in this patent are 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, chloroprene, 2,3-dimethyl-1,3-pentadiene, 2-methyl-3-ethyl-1,3-pentadiene, 2-methoxybutadiene, and 2-phenylbutadiene. No experimental examples were given for 1-cyanobutadiene, which was listed. The polymerization of conjugated diolefins by reduced metal oxide catalysts has also been reported (65). The conversion of butadiene and isoprene to *cis*- or *trans*-1,4 structures has been further demonstrated and, in addition, two different stereochemical structures (Section VI) for 1,2-polybutadiene have been obtained (93–96, 100, 103, 104, 109, 139).

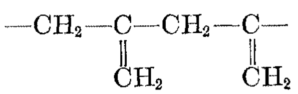
The polymerization of isoprene to 1,2- and 3,4-polyisoprenes and of chloroprene to a 1,4-polymer has been claimed (35, 66a). The structures of the polymers of divinylbenzene, diisopropenylbenzene, and vinylcyclohexene were not discussed, but polymerization through one double bond without any substantial cross linking or polymerization through the other bond was claimed. When the diolefin acts as a conjugated diolefin, even an internal double bond does not hinder polymerization, as in the case of 1,3-pentadiene (109). Alloöcimene is another example of a polyconjugated olefin which can be polymerized to a high-molecular-weight polymer (82). Cyclohexadiene (IV) is polymerized with Ziegler-type catalysts to 92 per cent conversion (79). Here is an example of a conjugated diolefin in which neither double bond is terminal. The failure of open-chain conjugated internal diolefins to polymerize is probably due to their inability to sit down on the active catalyst sites for steric reasons. In cyclohexadiene, however, the substituents on the 1,4-positions are tied back. The postulated structure for the polymer (V), which shows one remaining double bond per monomer unit, requires a 1,4-addition.



VI V (6)

C. *Nonconjugated diolefins*

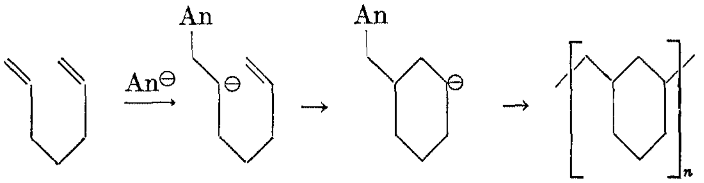
A du Pont patent (35) reveals the polymerization of a series of nonconjugated diolefins—allene, 1,4-pentadiene, 1,5-hexadiene, 1,7-octadiene, and 1,9-decadiene—in which the polymerization reaction takes place with only one of the two double bonds. The polymer obtained from allene consists of a polyethylene chain with methylene groups on every other carbon atom (VI). The white rubbery polymer from 1,5-hexadiene showed 75 per cent vinyl unsaturation and 25 per cent trans unsaturation, indicating that, for the most part, polymerization occurred at only one double bond.



$$\text{—CH}_2\text{—}\underset{\underset{\text{CH}_2}{\|}}{\text{C}}\text{—CH}_2\text{—}\underset{\underset{\text{CH}_2}{\|}}{\text{C}}\text{—}$$

VI

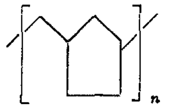
Some of the most interesting polymerization reactions effected by the Ziegler catalyst are those of the nonconjugated dienes 1,6-heptadiene, 1,5-hexadiene, and 2,5-dimethyl-1,5-hexadiene (81). The last alkene, a 2-substituted α-olefin, is a monomer type which does not usually polymerize with metal alkyl coordination catalysts. The polymerization of 1,6-heptadiene gives a white, tough, high-molecular-weight polymer which is soluble in benzene and has an extremely high melting point. On the basis of the facts that this polymer is completely soluble in benzene, that only 5 per cent of the monomer units incorporated in the polymer still retain one double bond, and that the polymer can be dehydrogenated to a polymer whose infrared and ultraviolet absorption spectra show aromatic and meta substitution, the cyclic recurring unit (VII) has been proposed as the main structural feature for the polymer, and the alternating intermolecular-intramolecular mechanism has been given to explain the results.



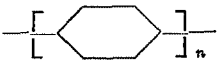
VII

(7)

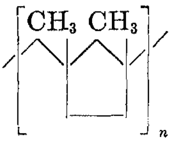
The polymerization of 1,5-hexadiene gave a polymer, 40 per cent of which was soluble in benzene. Since the soluble portion showed a very small amount of unsaturation, the two possible structures VIII or IX have been proposed for the recurring unit formed from the intermolecular-intramolecular process. Similarly, poly-2,5-dimethyl-1,5-hexadiene, a polymer with a molecular weight of only 10,000, has been assigned the structure X or XI.



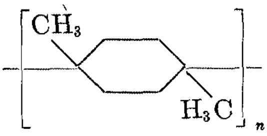
VIII



IX



X



XI

D. Copolymerization

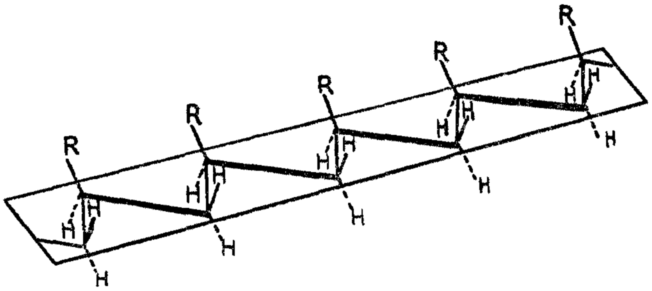
Ziegler indicated that his catalyst systems were useful for the copolymerization of olefins (38, 192, 199, 201). Several patents issued in this country have also shown the possibility of copolymerization of ethylene with other olefins (45, 54, 161) or the copolymerization of olefins in general (205). The copolymer of bicyclo-[2.2.1]-2-heptene with ethylene has been described in patents (3, 36). The preparation of the copolymers butadiene-ethylene, isoprene-ethylene, chloroprene-ethylene, 4-vinylcyclohexene-ethylene, diisopropenylbenzene-ethylene, and divinylbenzene-propylene has been claimed (35). The Phillips Petroleum Company has described the copolymerization of the conjugated dienes isoprene and butadiene with α-olefins containing up to eight carbons plus branched α-olefins such as isobutylene as well as 1,1-dialkyl- and 1,2-dialkylethylenes such as 2-butene, 2-pentene, 2-hexene, 2-heptene, 2-methyl-1-butene, 2-methyl-1-hexene, and 2-ethyl-1-heptene (152). Also claimed in this patent are the olefins 1,5-hexadiene, 1,4,7-octatriene, cyclohexene, and styrene for copolymerization. No experimental description was given for copolymers of the conjugated dienes with acrylonitrile, the acrylates, vinyl acetate, and various vinylpyridines which were claimed. It is unlikely that these would undergo copolymerization reactions without destroying the catalyst. Natta has described the preparation and properties of some ethylene-propylene, ethylene-isoprene, and propylene-isoprene copolymers (96). The incorporation of ethylene in the ethylene-propylene copolymer was varied from 31 to 62 per cent, and determined by use of radioactive ethylene (32, 33), infrared techniques, and analysis for carbon and hydrogen (115). In order to incorporate, for example, 40 mole per cent propylene, a 2:1 ratio of propylene to ethylene was required. It was also found that the polymerization temperature, the concentration of the catalyst in the solvent, or the molar ratio of aluminum trihexyl to vanadium(V) oxychloride did not affect the incorporation. The reactivity ratios of ethylene and propylene in the copolymerization reaction in the presence of this catalyst were found to be 17.95 and 0.065, respectively (83). Even though the high reactivity of ethylene presents some difficulty in copolymerization, polymers of any average composition were obtained by operating the feed charge continuously. By changing the catalyst system to aluminum trihexyl and vanadium(IV) chloride, the reactivity ratios were changed to $r_{C_3H_6} = 0.088$ and $r_{C_2H_4} = 7.08$ (84). By varying the ratio of the monomer charge of propylene to ethylene from 5.1 to 0.98, an incorporation of ethylene of 30.5 per cent to 66 per cent could be obtained.

VI. THE STEREOCHEMISTRY OF POLYOLEFINS

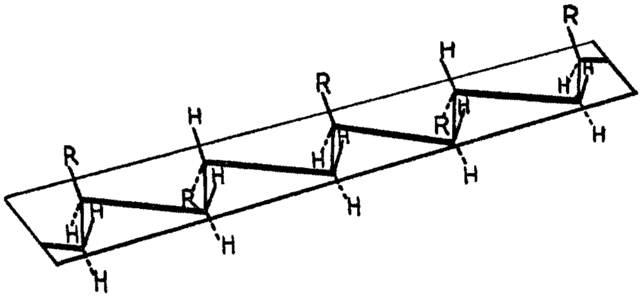
The polymerization of ethylene to polyethylene by these complex metal catalysts produces a polymer which is highly crystalline, since the chain is linear with little chain branching (1). The physical properties of this "low-pressure polyethylene" are quite different from the properties of the amorphous "high-pressure polyethylene," which lacks crystallinity because of the high degree of chain branching along the backbone of the chain (155). The carbon atoms along the chain backbone of linear polyethylene are not asymmetric, by virtue of the fact that each carbon atom carries two hydrogen atoms. When a monomer $CH_2{=}CHR$ is polymerized, there are generated asymmetric centers along the chain. However, if the substituent R of this monomer does not contain an optically active group, the polymer molecule will not show any optical isomerism, since the optical activity which is produced by an asymmetric carbon atom depends on the asymmetry which is caused by the constitutional differences in those parts of the groups joined to the asymmetric carbon atom. Also an asymmetric synthesis would not be expected in most polymerization reactions. In the polymer chain $-CH_2-CHR-$ there is the possibility that the tertiary carbon atoms have the same configuration with respect to the other tertiary carbons (90, 92–95a, 97, 102, 116, 119, 128–130, 169). These stereospecific polymers contain a head-to-tail structure, no chain branching due to a chain-transfer process, and no chain branching through copolymerization of a monomer with a low-molecular-weight polymer; they must be formed by a polymerization process in such a way that the monomer unit takes a steric configuration which corresponds to a determined order of absorption on the catalyst and makes the polymer stereospecific.

This type of isomerism can be visualized by placing the zigzag chain backbone in the same plane. Thus by the relative positions of the R groups on the alternate tertiary carbon atoms there are several different types of configurations of tertiary carbon atoms in relation to each other. When all the R groups are on the same side of the plane, either above or below, the regular sequence of monomer units has every other carbon atom (the tertiary carbon atom) of the same configuration, and the polymer has an isotactic structure (XII). If, however, the R groups are alternately above and below the plane, that is, the regular sequence of monomer units has every fourth carbon atom (every other tertiary carbon atom) in an identical configuration, the polymer has a syndiotactic structure (XIII). A structure in which the R groups are arranged at random and regularity in the tertiary carbon atoms is absent is atactic (XIV).

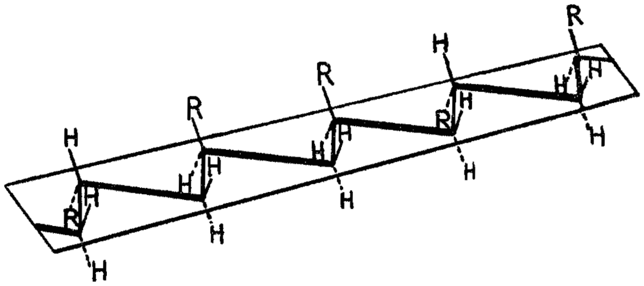
A complete equality of the configurations of all tertiary carbon atoms in isotactic polymers is found actually only in polymers having infinitely long chains, and the isotactic polymers are not optically active because of internal compensation. In molecules with finite chain length and different end-groups, the optical activity of the individual molecules is compensated in solution by the presence of their enantiomorphs and thus no optical activity should be found, as is the case. Natta has excluded the possibility of the presence of sequences of asymmetric carbon atoms having alternating *d* and *l* configurations in the isotactic polymer chain (118). He has attributed to these polymers a structure which has, at least for long portions of polymer chain, asymmetric carbons all with the same configuration. In atactic polymers, intramolecular compensation together with intermolecular compensation renders the molecule optically inactive. These three types of polymers—isotactic, atactic, and syndiotactic—are the simplest polymer types which might be expected from the polymerization of the olefin $CH_2=CHR$.



XII
An isotactic polymer



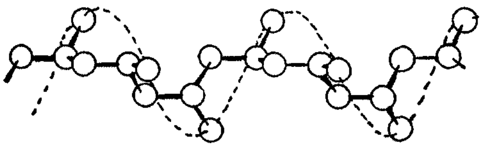
XIII
A syndiotactic polymer



XIV
An atactic polymer

A. Polypropylene

The polymer obtained from the polymerization of propylene by titanium tri- or tetrachloride and an aluminum alkyl is highly crystalline (90–95, 95a, 98, 105, 107, 110, 118, 122–128, 130, 132, 152a). X-ray determinations showed an identity period of 6.50 A. Since the carbon–carbon single-bond distance in a paraffin is approximately 1.54 A., the calculated value for the identity period, if three recurring units all lying in the same plane in a zigzag fashion were considered, would be 7.67 A. The difference is explained by the assumption that the zigzag polymer chain has a helical configuration in which each methyl group on the tertiary carbon atom is displaced 120° from the previous one, so that the first and fourth methyl groups are positioned over one another, when viewed down the axis of the helical chain. This means that, if this arrangement of the polymer chain is correct, the polymer must be isotactic. A planar structure of the polypropylene chain with all the methyl groups positioned on the same side is sterically impossible and therefore the chain must spiral (XV). This regular helical isotactic order in this polymer allows the polymer chains to orient themselves and thus a crystalline polymer is obtained (108).



XV

Isotactic polypropylene

B. Polymers of other α-olefins

Styrene (19, 90–92, 94, 95, 99, 101, 118, 128, 130) and the α-olefins 1-butene, 3-methyl-1-butene, 4-methyl-1-butene, 1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, and 5-methyl-1-hexene (29, 90–92, 94, 95, 95a, 105, 106, 118, 123, 127, 128, 130–132) are polymerized by the titanium halide–aluminum alkyl catalysts to give polymers which are all isotactic, and all have a helical configuration to the chain. The catalysts with which one obtains these isotactic polymers have also been investigated. With propylene, 1-butene, 3-methyl-1-butene, and 1-pentene, titanium trichloride and aluminum triethyl yield 80, 65, 90, and 35 per cent isotactic polymers, respectively, while titanium tetrachloride and aluminum triethyl give 40, 35, 65, and 2 per cent isotactic polymers (120). The remaining percentages are largely atactic polymers. Low stereospecificity is obtained by the chromic oxide type catalyst, usually within the order of 2 per cent. It was found that the highest stereospecificity was observed with the halides of titanium of less than a maximum valency. Titanium dichloride also gives high yields of isotactic polymer (136). Titanium tetrabromide and tetraiodide are as suitable or better than titanium tetrachloride for high isotaxy, but titanium tetrafluoride is a poor stereospecific catalyst. Titanium alkoxides, titanium alkoxychlorides, and titanium alkyls with aluminum triethyl also give poor stereospecificity, and these catalysts supported on silica–alumina oxides give little or no isotactic polymer. The degree of isotaxy obtained depends on the temperature of the polymerization, the composition of the metal alkyl, the olefin, and the valence state of the titanium compound, as well as the titanium salt employed. The molar ratio of aluminum triethyl to titanium tetrachloride, which determines the valence state of titanium and thus is important in obtaining a highly stereospecific polymer, is less than 2 (135, 185). The catalyst must also be solid and crystalline, since soluble catalysts yield atactic polymers. A study of polymerization temperatures and the temperature during the preparation of the catalyst reveals that the highest degree of stereospecificity and viscosity is obtained at low temperatures, usually 0–30°C. (82c).

Some of the factors which determine the steric configuration taken by these olefins are discussed in Section VIII. The principles which determine the crystallinity of high polymers are necessary to understand the correlation of x-ray data with the configuration of the isotactic chains (97). The axes of the principal chains are arranged in the crystal parallel to a singular crystallographic axis. The different monomeric units which are contained in whole numbers in the identity period occupy equivalent positions, i.e., they go into overlapping positions

TABLE 1

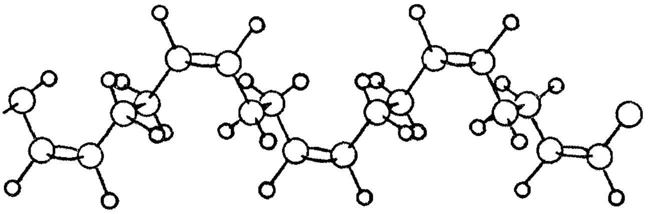
Data on isotactic poly-α-olefins

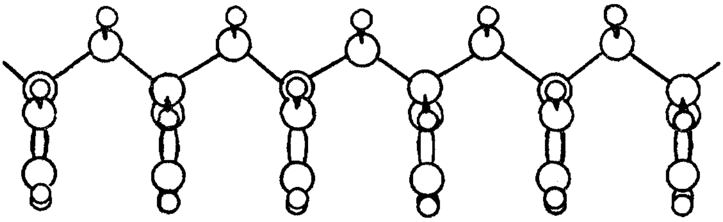
Polymer	Identity Period	Number of Monomers per Identity Period	Number of Monomers in Elementary Cell	Spatial Symmetry	Dimensions of Elementary Cell in Ångström Units						X-ray Density
					A	B	C	α	β	γ	
Propylene	6.50	3	12	C^2h monoclinic	6.65	20.96	6.50	90°	99.2°	90°	0.936
Styrene	6.65	3	18	R_3^-c rhombohedral	21.9	21.9	6.65	90°	90°	180°	1.12
1-Butene	6.50	3	18	R_3^-c rhombohedral	17.7	17.7	6.55	90°	90°	120°	0.96
	6.85	4	—	—	—	—	—	—	—	—	—
3-Methyl-1-butene	6.84	4									
4-Methyl-1-pentene	13.85	7									
1-Pentene	6.60	—									
4-Methyl-1-hexene	14.0	7									
5-Methyl-1-hexene	6.5	3									

through simple displacement operations which depend on the symmetry of the chain. The chains are arranged in such a way as to achieve a minimum distance between atoms of different chains. The most stable configuration of a chain is determined by the constancy of the length of the bonds and the constancy of the bond angles, and the configuration of the chain must be in agreement with the principle of maximum elongation of successive linkages. Further, if steric hindrance does not permit strict adherence of the values of distances between atoms, the chain undergoes elastic deformations which are distributed equally along the chain. Isotactic polymers respect the principle of maximum elongation of linkages and are helical. This does not mean that the identity period in every isotactic polymer corresponds to three monomer units, but that the period may correspond to more than three, with various polymers, depending on these factors. In isotactic polymers the bonds which connect the lateral groups to the tertiary carbon atoms in the chain are inclined with respect to the axis of the chain. In an isotactic chain, all these links are inclined in the same direction (isoclinic) for reasons of symmetry. Since right- and left-handed helices are possible, there is a total of four types of helices, taking into account the inclination. Some of the data concerning the configuration of isotactic poly-α-olefins are given in table 1; it can be seen that there is a tendency for poly-α-olefins with large branches on the tertiary carbons to take a smaller turn per monomer unit in the helix so that branches repeat only at a greater distance from one another.

C. Polymers of conjugated diolefins

It is known that butadiene can polymerize in different ways, yielding either linear or branched chains or, under certain conditions, bridged chains. In the linear chain of diolefins, three types of concatenation, *trans*-1,4, *cis*-1,4, and *cis*-1,2 can be found (91, 95a, 152). Polybutadiene with a 1,4-*trans* arrangement has two crystalline modifications. One, at temperatures below 60°C., has an identity period of 4.9 A., which means that it contains one monomer unit in the identity period and is linear, or nearly so (94, 104). The other modification, which occurs at temperatures above 60°C., is helical. Polybutadiene with a *cis*-1,4 concatenation (XVI) shows four monomer units per identity period, but the cell contains two chains of two monomers each (103). A syndiotactic arrangement was first shown with 1,2-polybutadiene (93–95a, 100, 104, 109). The polymer chain has a rigid linear structure with carbon bond angles of 113° and an identity period of 5.14 A., which corresponds to two monomer units. Thus when the substituents are situated syndiotactically on the polymer chain, there is no need to depart from the zigzag chain (19). Crystalline isotactic 1,2-polybutadiene has also been prepared. This represents the first time that two distinct crystalline forms have been prepared from one polymeric compound (139). The chains contain either left- or right-handed helices, but in each the anticlines are statistically distributed (97).


XVI
cis-1,4-Polybutadiene


XVII
Syndiotactic 1,2-polybutadiene

The probable structures of polyisoprene which correspond to the α, β, and γ structures of gutta-percha have been discussed following the principle of maximum spacing of single bonds (109). The 1,4-*trans* structure prepared has the same crystalline structure as gutta-percha (95). The *cis*-1,4-polyisoprene has a structure which is like that of *cis*-1,4-polybutadiene (103). The stereochemistry of the 1,2-polyisoprenes which have been prepared (152) has not been elucidated.

TABLE 2

Crystalline data on the polybutadienes (95a, 96, 97, 97a)

Polymer	Spatial Group and Symmetry	Identity Period	Number of Monomer Units per Cell	Number of Monomers per Identity Period
		A.		
trans-1,4-	Pseudo hexagonal	4.9	1	1
cis-1,4-	*C* 2/*c* monoclinic	—	4	—
1,2-Syndiotactic	*Pacm* rhombic	5.14	4	2
1,2-Isotactic	$R\bar{3}c$ hexagonal	6.5	18	3

D. Stereoblock polymers

New high linear polymers of α-olefins, characterized by the presence in the same macromolecule of chain segments having an isotactic structure and segments having irregular atactic structure, are defined as stereoblock polymers (114). These differ from the well-known block copolymers because the former are obtained by the polymerization of a single monomer type. Similarly, syndiotactic-atactic segments in the same chain are considered stereoblock polymers (94). The crystallinity in these isotactic-atactic stereoblock polymers ranges from 27 to 64 per cent (97).

VIII. PHYSICAL PROPERTIES OF CRYSTALLINE AND STEREOSPECIFIC POLYMERS

A. Polyethylene

Soon after the announcement of the low-pressure polyethylene speculation was made as to the possibilities of its application (11, 64, 153). Much concerning the structure and physical properties of low-pressure polyethylene has been reviewed (1), so that only a brief discussion of some new developments will be given here. Polyethylene is the first polyolefin which has been obtained in a crystalline state by the growth of single crystals (168). These crystals of linear polyethylene were grown from 0.05 per cent xylene solutions and had molecular weights of 150,000, 29,000, and 850. Low-pressure polyethylene has been found to have a broad molecular-weight distribution (12). The relationship between molecular weight and intrinsic viscosity has been determined for linear unfractionated polyethylene (174). The molecular weights of polyethylene fractions determined by ebulliometric and osmotic pressure methods have been correlated, however, with the intrinsic viscosities of Ziegler, Phillips, and diazomethane polyethylenes. The relationship $[\eta] = 5.10 \times 10^{-4} M^{0.725}$ was found to hold true over a broad range of molecular weights (172).

The degree of crystallinity of polyethylene as determined by nuclear magnetic resonance has been found to agree favorably with x-ray crystallinity (28, 162). Polyethylene with a crystallinity of 55 to 60 per cent as determined by x-rays was found to have good correlation at room temperature with the values determined by nuclear magnetic resonance, but over a temperature range from $-196°$ to 92°C. the correlation was poor (62).

The properties of "Hostalen" of about 80 per cent crystallinity prepared by the Ziegler process have been compared with those of high-pressure polyethylene (15, 16, 156, 160). Molecular weights of polyethylene obtained by this process can be varied from 10,000 to 3,000,000 (167). "Super Dylan," Koppers polyethylene made by the Ziegler process, has a melting point of 120°C. or above (7).

The "Marlex 50" polyethylene of the Phillips Petroleum Company has a tensile strength of more than 4500 lb./sq. in. and a softening point above 120°C. (8). The fixed-bed process produces polyethylene with a molecular weight of 5,000 to 20,000, polyethylene of higher molecular weights (40,000) being obtained by the slurry process (26, 27). A comparison of the physical properties of high-pressure (density = 0.92), Ziegler (density = 0.95), and "Marlex 50" (density = 0.96) polyethylenes show that "Marlex 50" has a higher crystallinity, melting point, stiffness, compressive stress, heat distortion temperature, and hardness (73–76). These properties are in direct correlation with the density. This also corresponds to lower tensile strength, lower elongation, lower impact strength, lower deformation under load, and lower brittleness temperature. Some of these properties can be attributed to the higher molecular weight of the Marlex polymer. A slightly higher dielectric constant for "Marlex 50" was claimed, which would be in agreement with the higher density, but this is contradicted by the fact that there is a higher chemical reactivity to oxygen, which is probably brought about by traces of the metal catalysts. Infrared, nuclear magnetic resonance, and x-ray studies show that the Marlex polymer has no branching and few internal double bonds (163, 164). A comparison of high-pressure polyethylene, "Super Dylan" (Ziegler), and "Marlex 50" shows 0.6, 0.7, and 1.5 double bonds per 1000 carbon atoms, respectively. The double bonds in the high-pressure polyethylene and "Super Dylan" are mostly of the vinyl type, along the chain backbone, while "Marlex 50" has mostly terminal double bonds. A high degree of chain branching is found in the high-pressure polyethylene, which has 21.5 methyl groups per 1000 carbon atoms. "Super Dylan" and "Marlex 50" have 3 and 1.5 methyl groups per 1000 carbon atoms, respectively. The nonbranching and the simple structure account for the high degree of crystallinity of the low-pressure polyethylenes (87 and 93 per cent) as compared to the high-pressure polyethylene (65 per cent). This is undoubtedly due to the combination of the specific catalytic effect and the mild polymerization conditions.

The Standard Oil of Indiana nickel–charcoal catalyst yields an 80 per cent crystalline polyethylene with an intrinsic viscosity of 0.1 to 0.2, while the molybdenum catalysts give an 85 to 90 per cent crystalline polyethylene with an intrinsic viscosity of 0.2 to 0.6 (148, 149). The degree of branching is greater for the polymer produced on nickel–charcoal. This polymer, which has a density of 0.95, is softer and more flexible, contains a ratio of methyl groups to vinyl groups of about 50, and has an even distribution of the internal and terminal double bonds. The molybdenum catalysts give a polymer which has a density from 0.94 to 0.98, a melting point of 130°C., and a ratio of methyl groups to vinyl groups of 500; 70 per cent of the double bonds in the polymer are internal.

B. Polystyrene

It might be expected that isotactic polystyrene, when put in solution, takes a random zigzag chain and assumes solution properties that are the same as those of atactic polystyrene.

It has been found that the osmotic molecular weights correlate well with the molecular weight calculated from viscometry, and the relationship agrees well with that found for atactic polystyrene (4, 5, 111). Isotactic polystyrene with crystallinity in the solid state of 40 per cent and with a light-scattering molecular weight of 8.93×10^6 showed molecular dimensions in solution which agreed with those deduced from a theoretical treatment of the polydispersed random coil (142). Although no difference could be observed between the values of molecular weight calculated by viscometry and osmotic pressure for isotactic and atactic polystyrenes, a noticeable difference exists between the second virial coefficients for the two types for a given molecular weight (30, 31). Calculated values of the "limiting interaction affinity" in toluene and the results of solubility experiments in methyl ethyl ketone and toluene–methanol mixtures show that atactic polystyrene is always more soluble than isotactic polystyrene, regardless of whether isotactic polystyrene is in the crystalline or the amorphous state. This has been suggested as a measure of isotaxy. Isotactic and atactic polystyrenes of the same molecular weight ($[\eta] = 3.8$) show densities of 1.08 and 1.05, respectively (94, 95, 118). The isotactic polystyrene has a transition temperature at 230°C., while the atactic polystyrene has a transition temperature at 85°C.

C. Polypropylene, poly-α-butene, and other poly-α-olefins

The isophasic and volume break temperatures of α-olefins are the same for completely amorphous and highly crystalline samples of high- and low-molecular-weight polymers (112). This is in accord with the result that in the molten or dilute solution state the properties of isotactic and atactic polymers are about the same. Since the transition temperature decreases from polypropene to polypentene, this is the effect of plasticizing by side chains, as in branched polyethylene. The ratios of the values of crystal melting point and glass transition temperatures for poly-1-butene (136°C. and −45°C.), polypropylene (176°C. and −35°C.), and polyethylene (138°C. and −21°C.) are not constant. The specific volumes of various amorphous and crystalline polymers of propylene and 1-butene have been determined as a function of temperature. The dilatometric curves of highly crystalline polymers show a discontinuity near the melting point; the discontinuity vanishes as the polymers are changed from stereoblock to completely amorphous (111a). The increase in melting point from polyethylene to polypropylene is striking. Polypropylene has the highest possible melting point for a poly-*n*-α-olefin. The lengthening of the side chain in the other homologs decreases their melting point with a minimum at polyhexene and then increases it from polyheptene and polyoctene to polydodecene and polyoctadecene (154). Polyoctadecene and polydodecene have essentially the same melting point as polyethylene, indicating that a helical configuration no

TABLE 3

Properties of isotactic and atactic poly-α-olefins

Polymer	Density	Melting Point	Transition Temperature	Solubility in		
				Ether	*n*-Heptane	Toluene
		°*C.*	°*C.*			
Polypropylene						
Isotactic	0.92	165	160–170 (order I)	Insoluble	Insoluble	Soluble
Atactic	0.85	—	–35 (order II)	Soluble	Soluble	Very soluble
Polybutene						
Isotactic	0.91	128	126–128 (order I)	Insoluble	Soluble	Very soluble
Atactic	0.87	—	–42 (order II)	Soluble	Very soluble	Very soluble
Polypentene						
Isotactic	0.87	80	75–80 (order I)			
Atactic	—	—	–50 (order II)			
Poly-3-methyl-1-butene	0.90	245	275 (order I)			
Poly-4-methyl-1-pentene	0.83	205	205 (order I)			
Poly-4-methyl-1-hexene	0.86	188	188 (order II)			
Poly-5-methyl-1-hexene	0.85	130	130 (order I)			

longer occurs. A second transition occurs in polypropylene, polybutene, polypentene, and polydodecene. These are amorphous glass-phase transitions in the case of polypropylene and polybutene. These transitions are shown by the fact that atactic polypropylene and poly-α-butene exhibit breaks in stiffness vs. temperature curves and also a change in the slope of volume vs. temperature curves. The second transitions in polypentene and polydodecene seem to be first-order crystal-phase transitions.

As in the case of polystyrene, measurements of the viscosity, the osmotic pressure, and the density of isotactic and atactic polypropylenes show that the molecular weights may be correlated independently of the particular structural order (23). Atactic poly-α-olefins are more soluble than isotactic polymers in organic solvents, and this is the basis for the separation of isotactic and atactic fractions in a polymer mixture. Atactic polymers are generally soluble in ether, methyl ethyl ketone, and heptane, whereas the isotactic portion is soluble only in benzene, toluene, and xylene (92, 131). The isotactic polymers also show a higher melting point and higher density than the corresponding atactic polymers with viscosities in the same order of magnitude (94, 95, 95a, 118).

The mechanical properties of these polymers depend on the crystallinity, size, and distribution of molecular weights of the percentages of crystallizable isotactic polymer, stereoblock polymer, and atactic polymer present (94, 95a, 97) (table 4). Polypropylene for use as a fiber compares favorably with other known fibers. Polypropylene with a molecular weight from 40,000 to 50,000 corresponds to nylon with a molecular weight of 10,000 to 20,000, as far as properties of the fiber are concerned. The density is low, the fiber can be spun dry, no solvents or plasticizers are needed, and its lower melting point facilitates spinning.

From the point of view of chemical behavior of isotactic polymers, the depolymerization, isomerization, chlorination, and oxidation were studied (128). High-molecular-weight isotactic polymers keep their characteristic regular structure even under prolonged treatment at high temperatures with an iso-

TABLE 4

Mechanical properties of polypropylene and polybutene marketed by Montecatini

	Polypropylene			Polybutene	
Intrinsic viscosity	2.66	5.25	1.84	1.12	2.64
Elongation to rupture point (%)	320	670	100	165	320
Rupture load	385	410	400	150	365
Stiffness (kg./cm.^{2})	8500	8200	10,000	1300	1670
Vicat softening point (°C.):					
1 kg	>150	>150	>150	100	129
5 kg	99	99	150	—	—

merization catalyst like the aluminum halides. A rather quick depolymerization of isotactic polymers has been observed in reactions taking place by radical mechanisms, i.e., oxidation by oxygen in the presence of peroxides, chlorination by chlorine gas, etc. On the contrary, the thermal anionic depolymerization is much slower. The chlorination of isotactic polymers decreases their crystallinity.

D. *Stereoblock polymers*

While isotactic polypropylenes have melting points near 175°C. and are highly crystalline, stereoblock polypropylenes have lower melting points (100–170°C.) and lower crystallinity (114). These polymers of low crystallinity show peculiar mechanical properties such as high elastic elongation in the oriented state and low initial elastic modulus. They represent elastomers which, in the oriented state, behave as thermolabily vulcanized polymers (97a). This is due to the presence of microcrystalline regions in which isotactic segments of different macromolecules are arranged. Their lattice energy hinders the viscous flow of amorphous parts of the same macromolecule inserted between the isotactic segments. The stereoblock portion is separated from the completely isotactic and atactic portions by solubility differences (97).

E. *Polybutadiene and polyisoprene*

The melting points and densities of the four isomers of polybutadiene are shown in table 6 (94–97, 104). Amorphous polymers with the 1,4-linkage have a very small ratio of hysteresis to elastic deformation, lower than that of the 1,2-polymers (97a). Ameripol SN, the all-*cis*-1,4-polyisoprene produced by B. F. Goodrich Company, has a dilute solution viscosity of 3.80, a value which corresponds to a molecular weight of about 230,000 (71). Crystals can be grown at −26°C. and the polymer has a second-order transition temperature at −70°C.

F. *Copolymers*

Copolymers of α-olefins with ethylene are mostly amorphous in large ranges of compositions and show infrared spectra, x-ray spectra, and mechanical properties similar to those of nonvulcanized elastomers (115). The elastic properties of an ethylene-propylene copolymer with low modulus are similar to those of natural rubber (96).

TABLE 5

Properties of polypropylene fractions

Fraction Obtained with Various Solvents	Extraction Temperature	Structure	η	Per Cent Crystallinity	Melting Point
	°C.				°C.
Ether	35	Atactic	0.46	0	
Pentane	36	Stereoblock	0.51	27	114
Hexane	69	Stereoblock	0.61	37	130
Heptane	98	Stereoblock	0.68	54	159
Ethylhexane	120	Stereoblock	1.22	64	170
Residue	126	Isotactic	2.08	68	174

TABLE 6

Densities and melting points of the polybutadienes

Polymer structure	Density	Melting Point
		°C.
1,4-*trans*	0.96-1.02	135-148
1,4-*cis*	1.01	Dependent on degree of crystallinity
1,2-Syndiotactic	0.96	154-155
1,2-Isotactic	0.96	120-125

VIII. MECHANISMS OF POLYMERIZATION

The mechanism that Ziegler postulated for the polymerization of ethylene with aluminum triethyl is discussed in Section II. Ziegler had considered only the effect of aluminum triethyl, and nickel was shown to be a catalyst which was effective in termination or disproportionation. It seems, however, that the catalysts which give high-molecular-weight olefins, aluminum triethyl and a "co-catalyst" metal ion, form a complex metal alkyl catalyst system. This complex metal catalyst has been the subject of much experimentation and controversy as to its exact nature and the mechanism by which it effects polymerization.

The solution to this problem of mechanism has been difficult for two reasons: the exact composition of the catalyst is not known, as investigators disagree even on the valence state of the catalyst; the polymerization reaction takes place in a heterogeneous system so that the rate of the reaction depends upon the surface area or degree of dispersion of the catalyst.

A. Valence state of the catalyst

One reaction between organometallics such as aluminum trialkyls and hydrides with titanium tetrachloride is the reduction of the latter. It has been shown by Frielander and Oita (60, 61) that on interaction of the catalyst components, the properties of the alkyls change to suggest that titanium alkyls are formed. Lithium alkyls and aluminum alkyls produce different products, both in the amount of titanium reduced and in the valence state of titanium. Lithium alkyls at low molar ratios of LiR to titanium tetrachloride effect reduction of titanium to a valence of 3, but at molar ratios of 4:1 the precipitate has titanium present with a valence of 4. In the molar range of 2–4, no alkyl lithium is present in the products, and thus it is argued that a titanium alkyl (in a +4 valence state) must be present in these higher molar ranges. Aluminum alkyls, on the other hand, always reduce titanium to a valence state of 3. With aluminum alkyls, no organometallic was observed below a molar ratio of aluminum alkyl to titanium tetrachloride of 1, so that the aluminum alkyl either reacts with or is held in a complex by the titanium tetrachloride. Above a 2.5:1 molar ratio, the aluminum alkyl is present in the solution.

Whereas the amount of titanium reduced by butyllithium is also a function of the concentration of the butyllithium, the complete reduction of titanium to a +3 valence is independent of the concentration of the aluminum alkyl. The equation for this reaction is given in equation 8.

$$AlR_3 + TiCl_4 \rightarrow AlR_2Cl + TiCl_3 + R\cdot \tag{8}$$

The reduction from +3 to +2 is slow and incomplete because of the heterogeneity of the system. The proposed equation for the reaction of ethyllithium and titanium tetrachloride in low molar ratios is as shown in equation 9.

$$LiC_2H_5 + TiCl_4 \rightarrow LiCl + TiCl_3C_2H_5 \rightarrow TiCl_3 + C_2H_5\cdot \tag{9}$$

In the polymerization of ethylene, the most active catalyst was made from a 1.5 molar ratio of butyllithium to titanium tetrachloride when ethylene was absent during the formation. When ethylene was present during catalyst formation a 4:1 molar ratio proved to be the most effective. This corresponds to a reduction state of 3 in the first case and 4 in the second case. The most active catalyst made by mixing an aluminum alkyl and titanium tetrachloride occurred at a 1:1 molar ratio, which also corresponds to a +3 valence of titanium. The presence or absence of ethylene in this case did not affect the activity of the catalyst towards polymerization.

Good sets of values which would give good curves for valence and activity vs. mole ratio were not usually observed. The data indicated that titanium was reduced to valence states lower than +3. These anomalous points were explained by the heterogeneity of the system and the probability of reduction by the AlR_2Cl in the mixture.

du Pont has claimed divalent titanium as the most effective catalyst for the polymerization of olefins (37). Compounds of the formula $TiCl_2$, $Ti(OR)_2$, or TiR_2 are prepared by the reduction of a titanium compound with a valence state in excess of 2. Titanium trichloride has been established as an ineffective catalyst. A recent investigation has shown that the activity of the catalyst is dependent on the reduction state of the catalyst (78). Studies showed that the polymerization rate was dependent on (*a*) the concentration of titanium tetrachloride, (*b*) the concentration of ethylene, (*c*) the nature of the alkylating agent (metal alkyl), (*d*) the mole ratio of the alkylating agent to titanium tetrachloride, and (*e*) the temperature. With regard to the dependence on temperature, it was found that the maximum rate occurred at 130°C. The mole ratio of the aluminum alkyl to titanium tetrachloride determines the average valence state of the titanium compound produced, and the maximum activity was found at a mole ratio which gave a catalyst with an average valence state of 2. This corresponds to a mole ratio of alkylating agent to titanium tetrachloride of 2 for hexyllithium and lithium tetraheptyl aluminum, 3 for aluminum triisobutyl, and 5 for aluminum triethyl. The dependence on temperature was explained by considering the effect of temperature on the reduction of the titanium compound. Temperatures high enough to completely convert all the titanium into an average valence state of 2 give the most active catalyst, but higher temperatures convert titanium to lower and less active valence states. It was therefore proposed that the reaction in equation 10 took place in the formation of the catalyst. The highly alkylated titanium species can then decompose by a free-radical mechanism so

$$TiCl_4 + n\mathrm{LiR} \rightarrow n\mathrm{LiCl} + TiCl_{(4-n)}R_n \tag{10}$$

that TiClR is more nearly the active catalyst. The molar ratios of various organometallics to titanium tetrachloride for maximum polymerization rate are shown in table 7. The molar ratios have also been shown to affect the intrinsic viscosity and crystallinity of the polymer (82a, 82b).

Natta has also reported that the valence state of titanium in the catalyst is less than 3 but that the maximum activity towards the polymerization of propylene at the two valence states occurred at a mole ratio of aluminum triethyl to titanium tetrachloride of 2 (135). Also, he has shown that the catalytic activity decreases rapidly with time, whether or not propylene is present when the catalyst is first formed or is added any time after the formation of the catalyst. The best intrinsic viscosity of polypropylene is obtained, however, with a 3:1 mole ratio. From these observations he has concluded that the formation of a catalyst of high activity is done either after the reduction of Ti(IV) to Ti(II) or after it is reduced and forms a complex organometallic compound. The activity also depends on the form of the precipitate and the surface area (136). The anion associated with titanium and the original valence state before reduction also appear to affect the activity of the catalyst.

TABLE 7

Polymerization of propylene by organometallics and titanium(IV) chloride (82a, 82b)

Organometallic Compound	Propylene Absorbed in 30 Minutes	Molar Ratio of Organometallic to $TiCl_4$*	Organometallic Compound	Propylene Absorbed in 30 Minutes	Molar Ratio of Organometallic to $TiCl_4$*
	grams			*grams*	
$Al(CH_3)_3$	37	1.7	$Al(n\text{-}C_8H_{17})_3$	24	1.8
$Al(C_2H_5)_3$	17	2.1	$Al(C_2H_5)_2Cl$	30	17
$Al(n\text{-}C_3H_7)_3$	15	2.3	$Be(C_2H_5)_2$	14	1
$Al(n\text{-}C_4H_9)_3$	16	2.4	$Zn(C_2H_5)_2$	20.7†	30
$Al(n\text{-}C_6H_{13})_3$	17	2.3	LiC_4H_9	27†	2

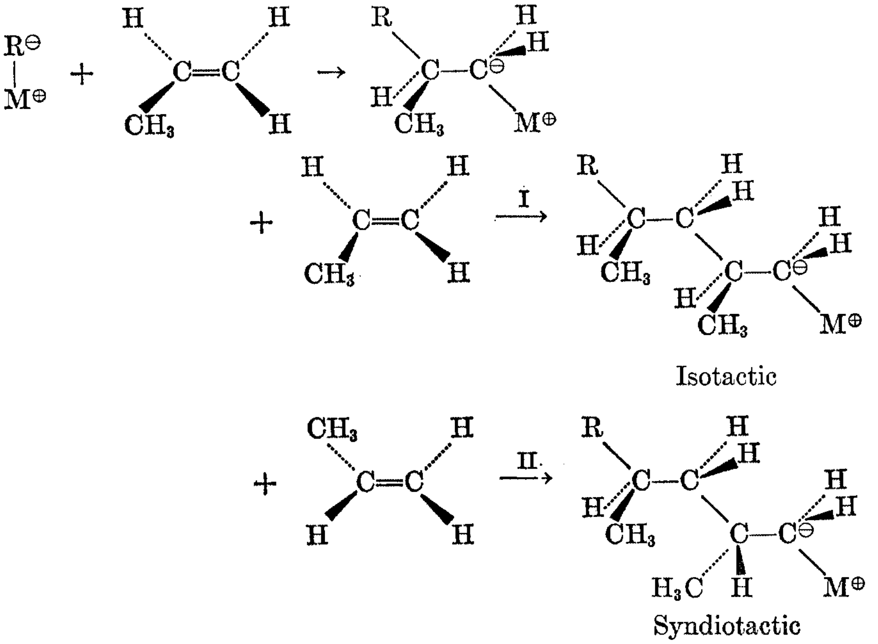
* The mole ratio given is that for the maximum rate.

† 2 hr.

B. Anionic mechanisms

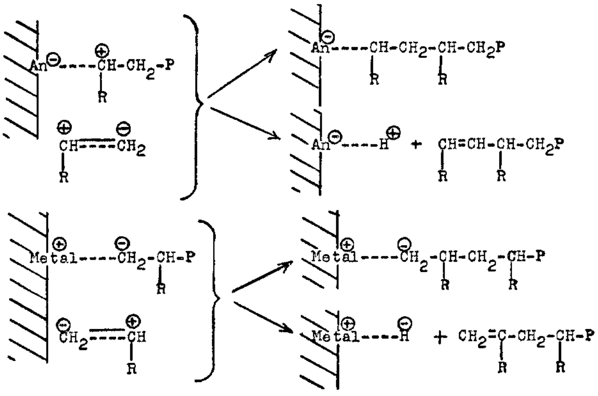
Since it is known that at room temperature titanium is alkylated and then reduced, e.g., with an aluminum alkyl, Natta believes that the true catalyst is a titanium alkyl, but that the reduction state of the catalyst is not completely known. In the polymerization of ethylene with a catalyst formed by mixing the etherate of aluminum triphenyl and titanium tetrachloride or cyclopentadienyl titanium dichloride, phenyl end-groups were detected on the polymer (134, 134a). This did not happen, however, when aluminum triethyl and dicyclopentadienyl titanium diphenyl, or the etherate of triphenyl aluminum alone or dicyclopentadienyl titanium diphenyl were used. Natta concludes from this that the groups bound to aluminum are the groups found on the end of the polymer; this supports the hypothesis that the catalyst is a complex containing titanium and aluminum, and that the polymerization takes place by the introduction of ethylene between aluminum and the growing chain. It was not shown, however, whether phenyl end-groups were obtained when the etherate of aluminum triethyl and cyclopentadienyl titanium diphenyl were employed. Rate studies using titanium trichloride and aluminum triethyl as catalysts showed that the reaction rate, within a wide range, is proportional to the amount of solid catalyst and the olefin pressure, but independent of the concentration of the soluble metal alkyl (117, 117a, 117b, 117c). In order to explain a delay in the adjustment of a constant rate at the beginning of the polymerization, Natta has explained that this can be attributed to the presence of crystals of titanium trichloride which disintegrate under the mechanical effect of polymerization, thereby producing a more reactive surface area. The active center is considered to be a surface complex compound of aluminum alkyl with a titanium compound, so that the polarized organometallic compound which determined the growth process of the polymer chain is concerned with a negative methylene end-group and a positive aluminum atom. Since the polymerization rate is dependent, as his data show, on the concentration of the olefin and titanium trichloride, even when the molar ratio of aluminum alkyl to titanium trichloride was varied from 8.5 to 0.51, and if the true catalyst is a complex, and the polymerization process does indeed depend upon the breaking of an aluminum–carbon bond, it is surprising that at the low molar ratio of aluminum to titanium compound the rate was not dependent on the amount of aluminum alkyl added, especially in the light of what has been discussed concerning the dependence of the activity of the catalyst on the molar ratios.

In an attempt to explain the high grade of crystallinity in polymers of α-olefins, it was suggested that the surface of the catalyst itself acts as a mold on which the polymer molecule takes a special configuration (130). Whichever configuration is taken by the first monomer molecule (*d* or *l*), then this particular isomer could play a further role in the steric configuration of the next monomer unit and thus in the steric configuration of the polymer (91, 129) (equation 11). Natta made the observation that in the synthesis of isotactic polymers, the catalyst could operate at higher temperatures and still obtain a degree of crys-



(11)

tallinity, but that cationic polymerizations, e.g., that of polyvinyl ether, required low temperatures if isomerizations and chain transfer, which do not give a polymer of regular structure, were to be avoided (91, 94, 95a.) Radical polymerizations have been excluded as a possibility, since they are not generally stereoselective. If polarization is attributed to a negative charge on the carbon and a positive charge on the metal of certain organometallic compounds containing metals much more electronegative than hydrogen, and consideration is given to the capacity of certain organometallics to dissociate into hydride and olefin, some correlation can be found between polymerization processes with the Ziegler catalyst and those with ionic catalysts. In the case of a heterogeneous catalyst, the existence of well-defined organometallics is not required, but it is



enough that the metal alkyl bonds be formed in the process of chemisorption. A study of the nature of the process of growth and of breakdown of the polyethylene chains at different temperatures and pressures showed that by comparison of the anionic mechanism with known types of cationic mechanisms, the forces by which the growing chains are bound to the initiator are much weaker in cationic catalysts. Consequently high polymers are formed at low temperatures. The diameter of the ion seems also to be important, since with a cationic catalyst polymers with a regular structure are formed only when ions of small diameter are used. Isotactic polymers require a head-to-tail concatenation and a special mechanism of propagation (91, 95a). When a new monomeric unit is introduced with the breaking of the double bond and the formation of an asymmetric carbon atom, the carbon must assume the same configuration as the asymmetric carbon atoms already present in the growing chain (120). Propagation occurs with insertion of additional monomer units with the terminal vinyl group toward the catalyst metal and is terminated by the transfer of a hydride ion from the chain to a monomer or a catalyst molecule or by chain transfer (94, 95a).

$$RCH_2CHRCH_2^{\ominus} + B^{\oplus} \rightarrow RCH_2CR{=}CH_2 + BH \qquad (12)$$

$$RCH_2CHRCH_2^{\ominus} + RCH{=}CH_2 \rightarrow RCH_2CR{=}CH_2 + RCH_2CH_2^{\ominus} \qquad (13)$$

$$RCH_2CHRCH_2^{\ominus} + R'H \rightarrow RCH_2CHRCH_2R' + H^{\ominus} \qquad (14)$$

Polymerization by this anionic mechanism involving successive additions of ethylene to a polarized titanium alkyl has been proposed by other workers (173). The initiators are believed to be mixtures of alkyl titanium trichloride, alkyl titanium dichloride, and alkyl titanium chloride formed by the alkylation of titanium tetrachloride with aluminum trialkyl.

These intermediate reduction products of titanium alkyls have also been supported as the active catalyst, since diethylzinc, phenylsodium, and isoamylsodium with titanium tetrachloride polymerize ethylene (140, 193). Here the organometallics serve only to alkylate the titanium halide (equation 15).

$$n\mathrm{Ral} + TiCl_4 \rightarrow R_nTiCl_{(4-n)} + n\mathrm{alCl} \quad (n \leq 4) \qquad (15)$$

$\mathrm{al} = \frac{1}{3}\,\mathrm{Al}$.

This initiator can then act either as a free-radical initiator (equation 16) or as an anionic initator (equation 17).

$$RTiX_3 \rightarrow R\cdot + TiX_3 \qquad (16)$$

$$RTiX_3 \rightleftharpoons R^{\ominus} + TiX_3^{\oplus} \qquad (17)$$

C. Free-radical mechanisms

Frielander and Oita (60, 61) have proposed that the catalyst is either a complex between the alkyl and titanium halide or an alkyl titanium compound where an aluminum alkyl is the reducing agent. The reactions between lithium alkyls and titanium tetrachloride are shown in equations 18 to 22. In this case tetravalent titanium is involved, and the alkylation steps are all heterogeneous. The gas evolved during the mixing indicates a breakdown which may involve alkyl radicals, and unless ethylene is present during this breakdown, initiation by the active titanium radical bound to the precipitated complex is lost. A radical mechanism can be postulated for both types of catalysts, since the transition metals have *d* electrons which are available for initiation or since organometallics undergo homolytic fission readily. The biggest difference in the catalyst formed by the alkylation of titanium by an aluminum alkyl is the valence of the titanium alkyl formed. The first step involves the reduction of titanium tetrachloride to titanium trichloride. The initiator is either an absorbed metal alkyl on the surface of the titanium trichloride precipitate (equation 23) or the alkylated titanium species on the surface of the catalyst (equations 24 to 26). The ethylene is chemisorbed on the surface of the catalyst and polymerization takes place on the surface with the proper orientation. If there is a homolytic fission, the olefin is inserted between the metal atom and the bound alkyl radical. The "bound ion radical" mechanism is shown below.

$$TiCl_4 + nLiR \rightarrow TiCl_4(LiR)_n \qquad (18)$$

$$TiCl_4(LiR)_n + LiR \rightarrow TiCl_3R(LiR)_n + LiCl \qquad (19)$$

$$TiCl_3R(LiR)_n + LiR \rightarrow TiCl_2R_2(LiR)_n + LiCl \qquad (20)$$

$$TiCl_2R_2(LiR)_n + LiR \rightarrow TiClR_3(LiR)_n + LiCl \qquad (21)$$

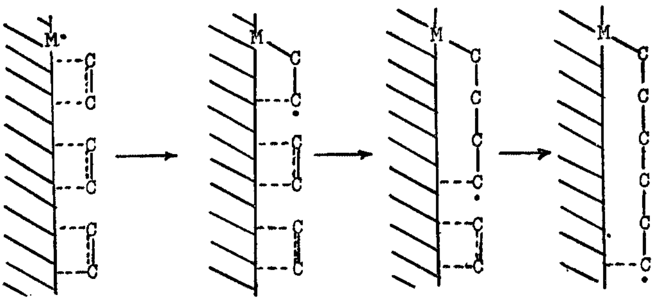
$$TiClR_3(LiR)_n + LiR \rightarrow TiR_4(LiR)_n + LiCl \qquad (22)$$

$$TiCl_3 + nMR \rightarrow TiCl_3(MR)_n \qquad (23)$$

$$TiCl_3 + MR \rightarrow TiCl_2R + MCl \qquad (24)$$

$$TiCl_3 + 2MR \rightarrow TiClR_2 + 2MCl \qquad (25)$$

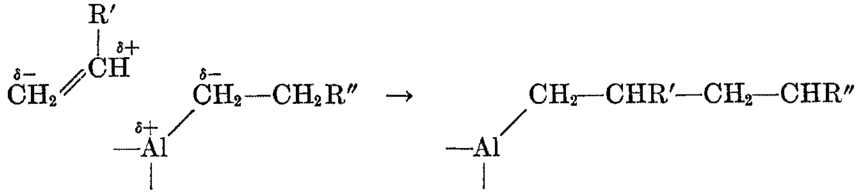
$$TiCl_2 + 2MR \rightarrow TiR_2 + MCl \qquad (26)$$



Termination can occur by heterolytic dissociation, chain transfer, dimerization, or disproportionation.

D. Other mechanisms of polymerization

The insertion of ethylenes between the aluminum–carbon bond in aluminum triethyl as proposed by Ziegler has also been suggested by Robinson (157). The function of the solid salts of titanium is to present a surface on which the ethylene molecules are well activated. The surface of the titanium chloride acts as a base on which the aluminum chloroalkyls dissociate and become absorbed. After some progress of reaction between titanium tetrachloride and aluminum trialkyl, the catalyst consists of titanium chloride crystals with absorbed layers of aluminum chloroalkyls and titanium chloroalkyls. The main property required of the catalyst seems to be that it consist of a dispersed reduced metal compound with basic surface properties and absorbed acid sites. The best absorber would be the aluminum chloroalkyl, since trivalent titanium chloroalkyls should be absorbed as dimers. The olefin becomes polarized and the reaction occurs as shown in equations 27 and 28. The stereoselective process has been explained in that when the reaction occurs, the entering monomer will be steered to a position of lowest energy with respect to rotation around the bond being formed.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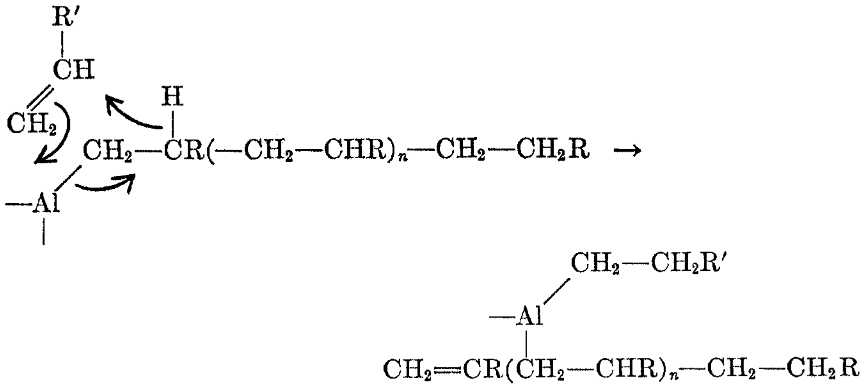
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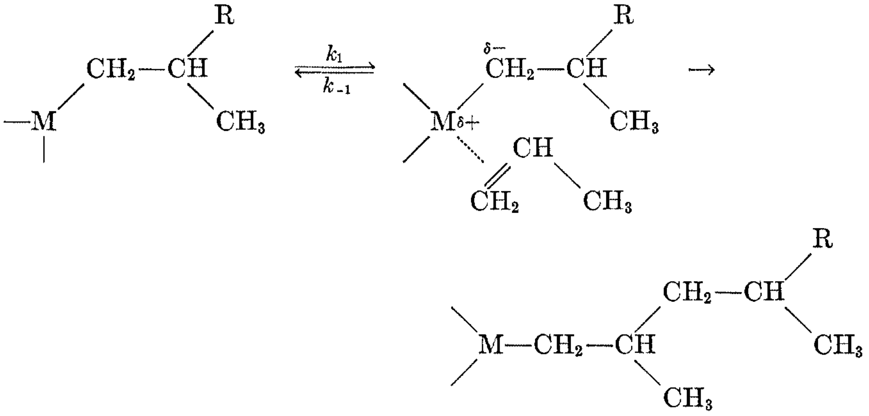
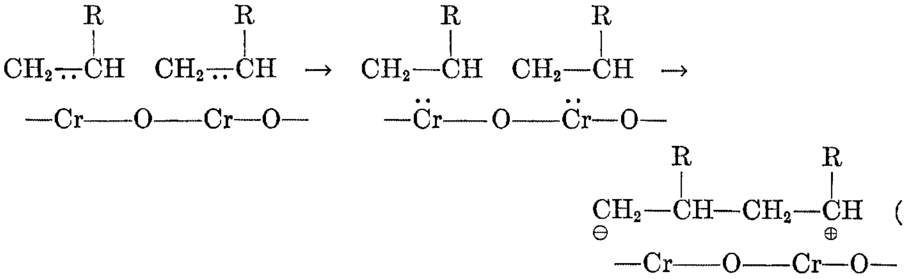
A similar mechanism involving the insertion of an olefin molecule between the polarized metal–carbon bond in the metal alkyl has also been discussed (152b, 152c).



(29)

The Phillips catalyst is believed, however, to be a different one. The chromium ions with their unfilled *d* shells effect polymerization by "loosening bound electrons and drawing them into the absorbed surface." The chromium atoms which are available at the surface of the catalyst act as Lewis acids.



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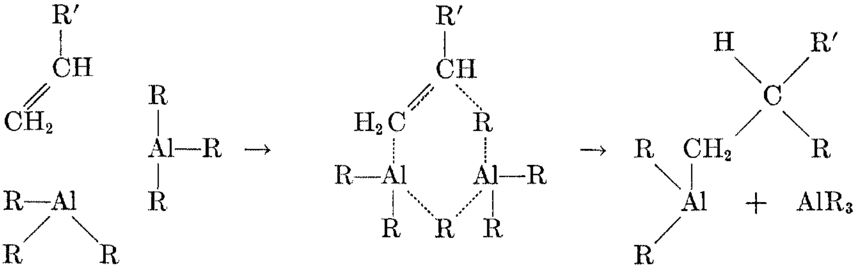
The oxide catalysts of Standard Oil of Indiana must be reduced before they are active as catalysts; thus they act like the reduced metal halide surfaces.

The fast overall rates at low temperature and pressure, the distinct preponderance of linear polymerization, and the regularity of the resulting polymer chains, in particular with respect to stereoisomerism, have been attributed to (*a*) absorption or complex formation, the energy of which permits absorption of well-defined configurations of reactants prior to or in the transition state, (*b*) an effective catalyst which by polarization, adsorption, and electron transfer lowers the activation energies of initiation as well as propagation, and (*c*) a structure and a lifetime of the transition state which lead to a freezing of rotation or permit a suitable rearrangement between the saddle points with relatively small energy conditions (39). The catalyst, lower halides of the transition elements formed through reduction by aluminum alkyls, have close-packed layer lattices, either cubic or hexagonal. Since the unshared valence electrons of reduced titanium are symmetrically distributed around the Ti^{2+} with a certain amount of bonding between these ions, Ti^{3+} may form bonds between two ions which uncouple at room temperature; therefore titanium is not at the crystal surface except at the crystal faults.

A mechanism which is comparable to the Grignard reaction has also been postulated (77). This mechanism demands little energy, and the terminal olefinic end acts as a nucleophile. The influence of the titanium halides in this mechanism is obscure, except that titanium might either serve in place of the second aluminum atom or suppress a radical reaction.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The author wishes to thank Dr. C. S. Marvel for his critical reading of the manuscript and for the copies of patents which he provided.

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