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International Classification:—B01j. C08f.

COMPLETE SPECIFICATION

Method of Polymerization of Olefins and the Linear High Molecular Weight Polymers produced thereby

We, MONTECATINI SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA, a Body Corporate organised and existing under the laws of Italy, of 18 Via Filippo Turati, Milan, Italy, and KARL ZIEGLER, a German citizen, of Kaiser-Wilhelm-Platz 1, Muelheim-Ruhr, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The methods hitherto employed for the polymerisation of propylene afford products having a relatively low molecular weight, which range from highly fluid liquids (dimeric, trimeric, and tetrameric propylenes) to more or less viscous lubricating oils, depending on their molecular weight. These products consist of variously branched homologues and isomeric mixtures. By working at very low temperatures of −50 to −100° C, products are obtained which have a higher molecular weight, but which are still for the most part fluid.

It has now been found that the homologues of ethylene can also be converted into polymers having the characteristics of synthetic plastics with catalysts of the herein described type. This applies in particular also to propylene which is usually difficult to polymerise and has not hitherto been polymerised so as to result in linear, regular head-to-tail, high molecular weight polymers. The polymerising action of the catalysts is however not restricted to propylene. Other α-olefins (1,2-olefins), of the general formula

$$R—CH=CH_2$$

(where R is an alkyl, cycloalkyl, cycloalkenyl or aryl group particularly butene-1, pentene-1, hexene-1, and styrene) can also be polymerised in the same way. It is also possible to polymerise mixtures of olefins, for example mixtures of ethylene with propylene, ethylene with butene-1 or propylene with pentene-1.

By the present invention there is provided a method of polymerising an alpha olefin of the general formula R—CH CH_2 (R being an alkyl, cycloalkyl, cycloalkenyl, or aryl group) or a mixture of such alpha olefins, either alone or with ethylene and/or other hydrocarbon having at least one vinyl double bond, wherein there is used a catalyst formed by contacting a halide (other than a fluoride) of a metal of Group IVa, Va or VIa of the Periodic Table as hereinafter defined, with a metal of Group Ia or II of the said table or aluminium, or with an alloy of metals of Group Ia and/or II and/or aluminium, or with a hydride or an organo metallic compound of a said metal of Group Ia or II and/or of aluminium, or with a complex hydride or a complex organometallic compound of boron and a said metal of Group Ia or II, the choice of the constituents of the catalyst and the conditions of polymerisation being such that at least a part of the said metal of Group IVa, Va or VIa is present in the catalyst in a valency state lower than the maximum and that in substantially anhydrous and oxygen free conditions polymerisation of the said olefin results.

For the purposes of this specification and of the claiming clauses hereof, the definition of a metal of the aforesaid groups is as follows:—

Group Ia—Li, Na, K, Rb, Cs.
Group II—Be, Mg, Ca, Sr, Ba, Zn, Cd.
Group IVa—Ti, Zr, Hf, Th.
Group Va—V, Nb, Ta.
Group VIa—Cr, Mo, W, U.

The polymer produced may be an homopolymer, a copolymer or a mixed polymer, depending upon the nature of the starting materials and the conditions of polymerisation. The homo-polymers may include molecules of different structure as hereinafter described.

Of the compounds of metals in Groups IVa,

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Va and VIa, the most active have proved to be compounds of titanium, particularly titanium tetrahalides, for example titanium tetrachloride, and the corresponding zirconium, chromium, vanadium or molybdenum compounds.

The polymerisation catalysts contain these metals in a valency lower than the maximum and are generally obtained by reactions which can at least in part be considered as reductions. It is therefore fundamentally immaterial by what reaction media, and in particular by what reduction means, the metal compounds in question are converted into the actual catalysts, provided that the halide, of a metal of Group IVa, Va or VIa, is contacted with an appropriate metal of Group Ia or II or of aluminium, or with an alloy of such metals, or with an hydride or organometallic compound or complex compound of such a metal or metals as hereinbefore defined. It will be apparent to those skilled in the art that the determination of the best combination of compound of metal of Group IVa, or Va, or VIa with a metal, alloy or compound of a metal of Group Ia or II or of aluminium to give a catalyst with the desired polymerising characteristics for any particular conditions of polymerisation may involve preliminary tests, since we do not suggest that any compound of the first class when combined with any metal or alloy or compound of the second class will give an equally effective result. We believe however that for a compound of the first class there is a compound of the second class which will give a useful result under particular conditions of polymerisation and that by following the directions given in this specification and by having regard to the examples contained herein useful results can without difficulty be obtained.

It will also be apparent to those skilled in this art that it may be possible to combine a compound of the first class with a metal, or alloy, or compound of the second class under such unsuitable conditions that a substance is formed in which the metal of Group IVa, Va or VIa is present in its maximum valency state, or which fails, under the conditions chosen, to act as a polymerisation catalyst, but such cases, if they exist, form no part of our invention.

Favourable results are achieved when a said compound of a metal of Group IVa, Va or VIa is contacted with either compounds of the general formula

$$R^{I}R^{II}AlR^{III}$$

wherein R^{I} and R^{II} are hydrocarbon radicals, particularly alkyl radicals, and R^{III} is a hydrocarbon radical, or hydrogen, or halogen, or an alkoxy group, or compounds of the general formula

$$A[MR^{I}R^{II}XY],$$

(wherein A is an alkali metal, M is aluminium or boron, R^{I} and R^{II} are hydrocarbon radicals, particularly alkyl radicals, and X and Y are hydrocarbon radicals or hydrogen). Organic compounds of magnesium or zinc can also be used.

More particularly the invention provides a method of preparing a polymer of an alpha olefin of the general formula $R—CH=CH_2$ (R being an alkyl group having not more than 4 carbon atoms, or a cyclohexenyl, or a phenyl group) or of a mixture of such alpha olefins, either alone or with ethylene and/or a diolefin having at least one vinyl double bond, wherein there is used a catalyst formed by contacting a halide (other than a fluoride) of titanium, zirconium or vanadium with an aluminium alkyl compound, the choice of the constituents of the catalyst and the conditions of polymerisation being such that at least a part of the titanium, zirconium, or vanadium is present in the catalyst in a valency state lower than the maximum and that in substantially anhydrous and oxygen free conditions polymerisation of the said olefin results.

The best catalysts we have found are reaction products of titanium compounds such as halides, particularly titanium tetrachloride, with aluminium alkyls, particularly aluminium triethyl or diethyl aluminium chloride. Good results can however also be obtained with zirconium compounds, for example zirconium tetrachloride, and with aluminium di*iso*butyl hydride, ethoxydiethyl aluminium, sodium-aluminium tetraethyl, or lithium-aluminium di*iso*butyl hydride. The catalyst is, in the case of zirconium tetrachloride, preferably produced in a ball mill, since zirconium tetrachloride is a solid substance difficultly soluble in hydrocarbons, and which in the reaction with the aluminium compounds becomes superficially coated with an impenetrable crust of the difficultly soluble catalytically active substances, which must be continually removed by grinding in the ball mill.

In general, the polymerisation of ethylene homologues proceeds more slowly and with greater difficulty than that of ethylene. The polymerisation temperature is advantageously between 20 and 150° C., (and preferably between 50 and 100° C.), while the polymerisation pressure may be ordinary pressure or elevated pressure.

The polymerisation in the process of the present invention supplies, even at relatively high temperatures and high polymerisation rates, products having a high molecular weight, and in that respect differs substantially from known polymerisation processes of polymerising alpha olefins using catalysts acting with a free-radical mechanism.

The polymerisation pressure employed may be up to 30 atmospheres although it is also possible to work at normal or reduced pressure.

As a rule it is advisable to polymerise the olefins in the liquid phase, i.e. to use the

liquid olefins either as such or dissolved in inert solvents. The catalyst mixture can also be used in a solvent, preferably in the liquid olefin itself or in a solution of the same in an inert solvent. The quantity relationship chosen between, on the one hand, the said compound of a metal of Group IVa, Va or VIa and, on the other hand, the metal, alloy or said compound, or complex compound of a metal of Group Ia or II or of aluminium affects the rate of the polymerisation and the molecular weight of the polymer produced. When aluminium trialkyls are used, the most active catalysts are obtained if the mole relationship between the titanium compound or analogous metallic compound and the aluminium compound is between 1:1 and 1:12, preferably between 1:1 and 1:3. If, in the production of the catalysts, an organic aluminium compound other than aluminium trialkyl is used, then the quantity relationships are rather different. For instance, when using dialkyl aluminium halides, for example diethyl aluminium chloride, it is not advisable to go below the ratio of 2 parts of diethyl aluminium chloride to 1 part of titanium tetrachloride or zirconium tetrachloride or the like compound. Finally if magnesium or zinc alkyl compounds are used, then the special relationships, as determined by the changing valency of the metals concerned, must be taken into consideration.

It was further found that, by the process of the present invention polymers of propylene or of certain of the other alpha-olefins can be produced, the properties of which are quite different from those of the polymers known hitherto and which, as a result of their regular steric structure have a tendency to crystallise.

No mention is made in literature of crystalline propylene polymers. It has always been assumed that propylene is not suitable for the production of crystalline polymers. Further, other alpha olefins which after polymerisation contain regular rows of asymmetric carbon atoms, are generally not solid even when they are of high molecular weight, and if they are solid (e.g. polystyrene), they are, so far as is known, never crystalline. In many scientific publications there is mention, too, of the fact that these polymers cannot be crystalline, on account of the theoretically possible steric configurations of the carbon atom of the main chain. In the book "Fibres from Synthetic Polymers" by Rowland Hill, published by the Elsevier Publishing Company in 1953, on page 319, the following is stated:

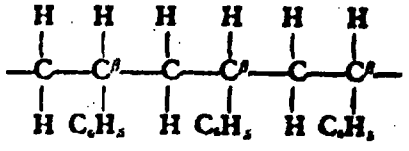
"Polymers in which one of the hydrogen atoms of a CH_2 group is replaced by a CH_3 group, are usually non-crystalline, owing to stereochemical irregularity; left and right hand groupings occur indiscriminately."

Until now, no one has succeeded in producing a polymer from an alpha olefin, in which the asymmetric carbon atoms of the main chain have the same steric configurations at least for long stretches of the molecule, so that the polymer shows a distinct tendency to crystallise.

According to the present invention a product can be obtained by the polymerisation reaction which is a linear, essentially unbranched, head-to-tail polymer of an alpha olefin of the general formula $R—CH=CH_2$ (R being an alkyl, cycloalkyl, or cycloalkenyl group) or of a mixture of such alpha olefins, either alone or with ethylene and/or other unsaturated hydrocarbon having at least one vinyl double bond, the average molecular weight exceeding 10,000 as determined by the herein described viscosimetric method of measurement. By the term "linear, essentially unbranched" as employed in this specification and in the claiming clauses hereof we mean that the main polymer chain has substantially no branches longer than R.

A particularly useful class of polymer yielded by the present invention is a linear, essentially unbranched, head-to-tail polymer of an alpha olefin of the general formula $R—CH=CH_2$ (R being an alkyl group having not more than 4 carbon atoms, or a cyclohexenyl, or phenyl group) or a mixture of such alpha olefins either alone or with ethylene and/or with a diolefin having a least one vinyl double bond, the average molecular weight exceeding 10,000 as determined by the aforesaid method of measurement.

Another product which can be obtained is a linear, essentially unbranched, head-to-tail, crystalline or crystallisable polymer of an alpha-olefin of the general formula $R—CH=CH_2$ (R being an aryl group) either alone or with ethylene and or other unsaturated hydrocarbon having at least one vinyl double bond, the average molecular weight exceeding 10,000 as determined by the herein described viscosimetric method of measurement. An example of such a product is a solid crystalline or crystallisable linear essentially unbranched, head-to-tail polymer of styrene, the polymer having an average molecular weight of more than 20000 and being made up substantially of macromolecules having a regular sequence of $>CH_2$ groups and $>CH.C_6H_5$ groups in long linear chains which correspond to the general structural formula

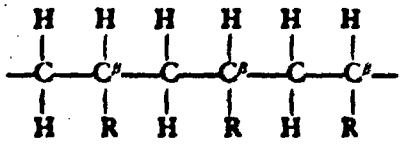


in which the asymmetric carbon atoms of the main chain (C^p) have the same steric configuration, at least for long parts of the molecule.

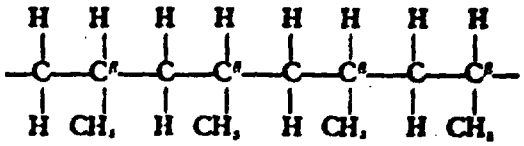
We are aware that polymers of styrene and of certain other polymers of alpha-olefins of the general formula $R—CH=CH_2$ (R being an aryl group) are old but crystalline or cryst-

allisable polymers made from the aforesaid alpha-olefins have, so far as we are aware, never been produced previously.

There can also be obtained, according to the present invention, a polymer which is a mixture consisting, on the one hand, mainly of a crystalline or crystallisable homo polymer with an average molecular weight of more than 20,000 and made up substantially of macromolecules with a regular head-to-tail sequence of $>CH_2$ and $>CHR$ groups in long, linear chains, which conform to the general structural formula



and in which the asymmetric carbon atoms of the main chain (C′) have the same steric configuration, at least for long stretches of the molecule, and on the other hand mainly of an amorphous polymer which has an average molecular weight of more than 2,000 and is made up of linear, essentially unbranched, head-to-tail macromolecules in which the main chain asymmetric carbon atoms of the two possible steric configurations, are randomly distributed along the main chain. If the main chain of these polymers is supposed as fully extended in a plane then in the case of crystallisable polymers substantially all the substituent R-groups are to be found on one side of a plane and the H-atoms attached to the asymmetric carbon atoms on the other side. Polymers of alpha-olefins which have the regular structure referred to in this paragraph are herein and in the claiming clauses hereof referred to as "isotactic polymers." In the case of the amorphous polymers according to this invention the R-groups and H-atoms attached to the asymmetric carbon atoms are on the other hand randomly distributed on the two sides of the plane. In the case of the propylene polymers, the mixtures contain, in addition to the amorphous, linear, essentially unbranched polymers with an average molecular weight of more than 2,000, solid polypropylenes with an average molecular weight of more than 20,000, consisting of macromolecules with a regular sequence as hereindefined of $>CH_2$ groups and $>CH—CH_3$ groups in long, linear chains, which correspond to the general structural formula



in which the asymmetric carbon atoms of the main chain (C′) have, at least for long stretches of the molecule, the same steric configuration.

The molecular weights indicated were estimated on the basis of specific viscosity measurement at 135° C. of solutions which contained 0.1 g. polymer in 100 g. tetrahydronaphthalene, or on the basis of intrinsic viscosity measurements. By specific viscosity is understood the difference between the viscosity of the solution and the viscosity of the solvent, divided by the viscosity of the solvent; by intrinsic viscosity, the limit of the ratio between specific viscosity and concentration for concentrations tending to 0. The concentrations are expressed in grams of polymer per 100 cc of solution; molecular weights are evaluated by applying the formula.

$$[\eta] = 1.18 \times 10^{-4} . M^{0.9}$$

where $[\eta]$ is the intrinsic viscosity and M the molecular weight.

The attainment of linear polypropylenes and higher polyolefins with regular, head-to-tail linkage is believed to be due to the activity of the catalyst. Particularly active catalysts within the range of the catalysts described can be produced by various means, for example, by bringing together a dispersion or solution of an aforesaid compound of a metal of Group IVa, Va or VIa, in an inert solvent, with a dispersion or solution of an aforesaid compound of a metal of Group Ia or II or aluminium in an inert solvent.

A particularly active catalyst can be obtained by producing the catalyst in the presence of an olefin, preferably the olefin or mixture which is to be polymerised, particularly in a high concentration, in one fluid phase.

When fluid olefins are used, an aluminium alkyl compound or organo-metallic compound of a metal of Group Ia or II can be dissolved at the polymerisation temperature in the fluid olefin and the aforesaid compound of the metal of Group IVa, Va, or VIa, e.g. the titanium compound, can be added, preferably at higher temperatures. This addition can take place during the polymerisation, the dispersion or solution of the titanium compound in an inert solvent or with part of the olefin which is to be polymerised being gradually introduced into the polymerisation apparatus. This introduction should preferably be continuous, e.g. at temperatures of 60—100° C. This mode of operation is particularly suitable if the reaction is exceedingly lively and is accompanied by an appreciable rise in temperature. By the continuous addition of the solution of the titanium compound in small quantities, the polymerisation temperature can be easily con-

trolled. However, alternatively, the dispersion or solution of the titanium compound as well as the solution of the organo-metallic compound can both be added gradually, preferably continuously during the polymerisation.

The catalyst produced contains in a different bond from the starting substances, at least a part of the radicals which were bonded to the metal of Group IVa, Va or VIa, or at least a part of the alkyl group which was bonded to the metal of Group Ia or II or aluminium. Frequently the catalyst contains an alkyl group of a different composition than that in the organo-metallic compound which was used as one of the starting substances.

This is corroborated by the following tests. If the catalyst is produced in the absence of olefin by reaction between titanium tetrachloride and an aluminium trialkyl, then the formation of a black precipitate can be observed, which contains titanium, aluminium, and halogen atoms and alkyl groups in quantitative proportions dependent upon the conditions of reaction. The precipitate contains alkyl groups with a number of carbon atoms which is greater than that of the alkyls which were contained in the aluminium alkyl at the outset. For example, if 1 mol triethyl aluminium is allowed to react with 0.75 mol. titanium tetrachloride in a saturated solution of a non-volatile hydrocarbon, a gas is given off which consists largely of ethane and contains also a small percentage of ethylene, butane and hydrogen. At the same time, a black product is precipitated, which spontaneously ignites on contact with the air and which upon decomposition with water or alcohols, gives off a gas, which consists largely of saturated hydrocarbons with unbranched chains (mainly ethane and n-butane), which contain an average of 3 carbon atoms and a certain quantity of hydrogen.

On the other hand, if the catalyst is produced from the same starting substances, in the presence of free alpha olefins, preferably with heating, then a black product is also produced, which, however, contains longer alkyl chains. This catalyst is much more active than that which is produced in the absence of the free olefins.

The polymerisation mechanism may be explained by assuming that the olefin pushes its way into the bond between a metal and a carbon atom of the growing chain, finding its way not only because of the polarisation of the double bond, but also for steric reasons which may be ascribed to the particular construction of the complex catalyst and the growing chain.

It can be assumed that the CH_2 group of the alpha olefin is absorbed by the catalyst which then promotes the reaction between the carbon atom of the CHR group of the olefin and the CH_2 end group of a growing alkyl chain, which is bound to a metal of the catalyst.

When carrying out the process of the invention, the alpha-olefins are surprisingly selectively polymerised. Starting from a mixture of alpha-olefins with olefins which possess no vinyl group, macromolecules are obtained, which have a regular sequence as herein defined of CH_2 groups and CHR groups in long, linear chains, in which the asymmetric carbon atoms of the main chain, at least for long stretches of the molecule, have the same steric configuration and can therefore only originate from the alpha-olefins. If, for example, a mixture of butene-1 and butene-2 is used as the starting substance, then the crystalline part of the polymer obtained, differs in no way from that which is obtained by polymerising pure butene-1 according to the same process, whilst the remaining part of the monomeric mixture is essentially richer in butene-2 than was the starting substance.

The polymerisation products obtained may be treated with water or alcohol, in order to decompose the catalyst and then, if necessary, washed with acids, in order to dissolve the metal compounds produced by the decomposition. The polymerisation products obtained after decomposition of the catalyst, and which are mixtures of polymers of varied steric structure and different molecular weight, can be separated by solvents into fractions, which contain polymers of differing structure. The separation is carried out at a temperature which is below the melting point of the polymer; the solvents should not cause the highly crystalline polymers to swell and if boiling solvents are used, their boiling point should be below the said melting point, Suitable solvents are aliphatic ethers, paraffinic hydrocarbons, for instance n-heptain, *iso*-octane and light petroleum fractions of a non-aromatic character, or chloro-hydrocarbons, e.g. carbon tetrachloride. The separation is preferably done by first removing the amorphous polymers, then the partially crystalline polymers leaving the highly crystalline polymer undissolved. In the case of polypropylene this can be done, for instance, by extracting first with boiling diethyl ether to remove the amorphous polymer, then with boiling n-heptane to remove the partially crystalline polymer, the residue being highly crystalline polymer.

The following example is given of a mode of working a crude polypropylene of specific viscosity of approximately 0.2, prepared by the process of the present invention.

The polymerisation products are first treated with boiling diethyl ether. From the ether extract, polypropylenes are obtained which have molecular weights between 2,000 and 45,000 and a specific viscosity of less than 0.12 (for solutions of 0.1 g. polypropylene in 100 cc. tetrahydronaphthalene at room temperature). These polypropylenes are not or only slightly crystalline and have viscous-elastic properties like those of a non-vulcanised

elastomer. A part of the product with a specific viscosity of 0.106 appears under X-ray analysis to be completely amorphous. It only becomes mobile at 135° C. and has a density of less than 0.90.

The subsequent extraction is done with boiling n-heptane and gives products which have a molecular weight of between 45,000 and 100,000, and a specific viscosity of between 0.12 to 0.20 and which are partly crystalline. A part of the product with a specific viscosity of from 0.121 to 0.128 has an average molecular weight of between 45,000 and 55,000, melts at 150° and is shown under X-Ray analysis to be prevailingly crystalline. The crystallinity remains until above 100°, and only disappears completely at above 150°. At temperatures at which a part of the crystallinity has disappeared, these products behave as elastomers. Only at still higher temperatures do they liquify into very viscous solutions. Generally, as the crystallinity increases, the viscous-elastic properties only make themselves manifest at a higher temperature. On the other hand, as the crystallinity decreases, the product tends to take on the properties of a fluid of very high viscosity.

After the n-heptane extraction, products are left which have a molecular weight of more than 100,000 a specific viscosity of more than 0.20, a melting point above 160° C. and high crystallinity. The crystallinity is retained up to about 160° C. When this temperature is reached, the polymers do not change from the solid direct to the fluid state, but retain, over a comparatively wide temperature range, the properties of an amorphous, plastic mass. They can be worked at lower temperatures than those at which the crystalline structure completely disappears, but only really easily at temperatures above 160° C., according to the known methods for artificial or synthetic resins, e.g. by pressing, extrusion, injection moulding or spinning.

These high molecular weight, highly crystalline propylene polymers have specific gravities between 0.90 and 0.94. The products which have the greatest density of about 0.94 have the greatest molecular weight and are highly crystalline. The presence of amorphous parts with low molecular weight lowers the melting point and reduces the density of the product.

The most intensive and most important X-Ray diffractions of the crystalline polypropylenes correspond to lattice distances of 6.2, 5.2 and 4.7 Angstrom units (1 ten-millionth part of one millimetre) between lattice planes parallel to the chain axis, and of 4.1 Angstrom units between planes not parallel to the axis.

If these high molecular weight, highly crystalline products are spun, fibres are obtained, which can be cold drawn, have outstanding mechanical properties for example a breaking load exceeding 30 kg./sq. mm. (e.g. from 30 to 70 kg/sq. mm.) and an elongation at break of at least 30% and can also be used in the field of textiles. From diffraction photographs of drawn test-pieces, which show the orientation of the crystals, it is possible to infer that these crystalline products show an identity period along the chain of 6.4 Angstrom units or a multiple of this value, as well as a non-planar, probably spiral-type structure of the paraffinic main chain. This structure lends the products characteristic properties which were not hitherto known for any hydrocarbon.

The crystalline polypropylenes are not brittle, as are the crystalline polyethylenes, and have a greater elasticity than the latter, which is probably due to their spiral type structure. On the other hand, the crystalline polypropylenes differ from the poly-*iso*butylenes obtainable by known methods which similarly have a linear, spiral type chain. The poly-*iso*-butylenes are elastomers and have a different identity period.

The high molecular weight polypropylenes are pressable in the range 130° to 150°, whereby transparent sheet material is obtained when the polymer is well purified. This sheet material can be cold drawn up to 700% and hot drawn even further. The breaking load, referred to the section of the drawn test piece, can exceed 30 kg. per sq. mm., and even more, if the product is drawn out to fine fibres. The drawn out fibres are silk-like in appearance and possess high-grade mechanical properties, particularly a high breaking load and a high elongation at break. They are especially suitable for the manufacture of textile fibres. The polypropylene sheet material is of great interest for all applications for which higher mechanical properties are required than those of the ordinary polyethylene, and above all for the manufacture of elastic, flexible materials.

If was found that the properties described of the crystalline polypropylenes are retained even if slight changes are brought about in the structure by adding to the propylene small quantities of other vinyl hydrocarbons, or ethylene.

The product obtained according to Example 14 can, for instance, be extruded at 170° to 200° through a nozzle. The extrusion can be carried out using nitrogen at a pressure of a few atmospheres. The continuous filament obtained, possesses mechanical properties which are dependent upon the diameter of the filament and the degree of stretching. From the non-fractionated product obtained according to Example 14, filaments can be obtained by extrusion at a pressure of 1 to 2 nitrogen atmospheres under heat, which have the following properties:

	Diameter of Filament mm	Breaking load referred to starting cross-sectional area kg/mm²	Elongation at break %
not drawn	0.5	2.3	520
cold-drawn to 400%	0.2	30	50

If, from the same product, the fractions with lower molecular weight are removed, a material is obtained which has better mechanical properties but which is more difficult to draw unless the process is carried out at higher temperatures and under greater pressure. The products with lower molecular weight thus act as softeners, lessen the viscosity of the mass and favour the orientation of the molecules during the drawing-out.

These fractions of lower molecular weight can be removed after the filaments have formed, and by, for instance, passing the fibres before or after stretching through a solvent, e.g. ether, which dissolves the low molecular polymers without causing the rest to undergo any essential swelling. In this way, the working properties of the starting product are retained and, at the same time, filaments are produced which, after the solvent has been removed, have the following mechanical properties:

Cold-stretching %	Diameter of Filament mm	Breaking load referred to the starting cross-sectional area kg/mm²	Elongation at break %
0	0.6	3.5	470
150	0.25	20.5	130
0	0.1	12.7	500
300	0.05	52	50

In this way, breaking loads of more than 70 kg/mm² can easily be attained, this value being referred to the cross-sectional area at break. The highly stretched filaments possess extraordinarily high reversible elasticity properties as well as other analogies to wool. However, the polypropylenes obtained according the invention possess better mechanical properties than wool. The stretched polypropylene filament may not show a yield point corresponding to a maximum in the load/elongation graph during subsequent stretching.

Polymers of alpha-olefins of the

$$CH_2 = CHR$$

type, with more carbon atoms than propylene, which are obtained in accordance with the invention, can also give crystalline products. As the length of the radical R increases, the temperature at which transition from the crystalline to the amorphous state occurs drops. Polypropylene is an exception in that it remains crystalline at higher temperatures than polyethylene. In the case of polybutene-1, the temperature at which the crystalline structure disappears is lower than the corresponding temperature in the case of polypropylene.

Polybutene-1, too, has the property of being easy to spin, and gives cold-drawn fibres with good mechanical properties, especially high-flexibility, very high tensile strength and elastic elongation, and high elasticity, together with good insulating properties. As polybutene loses its crystallinity at lower temperatures than does polypropylene, it is also less dimensionally stable at higher temperatures.

When compared with polyethylenes, polypropylene possesses much greater reversible elasticity in the stretched state. Polyhexene, has the properties of a non-vulcanized elastomer and has high elasticity. If it is shaped by drawing it will show very great elongation capacity. If it is stretched rapidly it will show a greater tensile strength.

The particular mechanical, elastic, chemical and electrical properties of the polyolefins produced in accordance with the invention make it possible for them to be used advantageously, for example, as plastic masses, in the insulation of electric cables and other electrical parts and for the manufacture of cable or

ropes which float on water. Polypropylene and polybutylene, in the oriented state, have exceptionally high impact strength. The polymers and copolymers of the aliphatic alpha-olefins higher than butene-1 are particularly suitable for use as elastomers. The polymers of the alpha-olefins with a strong tendency towards crystallisation, above all in the case of the products orientated by mechnical treatment, are of special interest for the production of fibres, foils and filaments. Copolymers of the alpha-olefins, with small quantities of another olefin, still have a certain crystallinity and properties similar to those of the alpha-olefin polymer. For example, a propylene polymer or homo-polymer may contain such an amount of polymerised ethylene or other polymerised alpha-olefins as does not substantially change its properties. Elastomeric products or compositions may also be obtained which consist of, contain or are derived from the amorphous polypropylene.

The following Examples are given to illustrate the invention.

EXAMPLE 1.

Into a solution of 5.7 g. aluminium triethyl in 250 cc. Fischer-Tropsch Diesel oil, which has been suitably freed from unsaturated constituents by hydrogenation and then distilled from sodium, is run 4.75 g. titanium tetrachloride, in a nitrogenous atmosphere and whilst stirring. This is stirred for one hour at room temperature. A suspension of solid, brown-black coloured substance forms in the Diesel oil. This suspension of the thus produced catalyst is transferred to a 5-litre agitator autoclave filled with nitrogen, in which there is already 1 litre of the same Diesel oil, and 600 g. of well dried and air free propylene is then injected. Stirring all the time, the temperature is increased to 70°, whereby an initial pressure of max. 21 atmospheres is built up. In the course of 72 hours, the pressure drops to 11 atmospheres. The not yet transformed propylene is vented from the still warm autoclave and 225 g. propylene is thus recovered. After opening, one finds in the autoclave a semifluid suspension of a solid propylene polymer in the Diesel oil, said suspension being still dark in colour on account of parts of the catalyst. The polypropylene is filtered off from the solvent by suction, the Diesel oil is washed out with acetone and, whilst stirring, the polymer is warmed with methanolic hydrochloric acid. It is thereby rendered colourless. After filtration, the hydrochloric acid is washed out with water, and the moisture removed with acetone and dried. From the Diesel oil mother liquor of the autoclave contents, it is possible to precipitate other certain parts of the polypropylene by adding acetone. These parts are worked up in like manner. Altogether, 338 g. polypropylene can be obtained. The grainy, solid polypropylene obtained can be pressed at 140° into flexible sheets, which are transparent if thin and opaque if thick.

The new synthetic plastic is distinguished by a very characteristic infra-red spectrum, shown in Figure 1 of the accompanying drawings.

EXAMPLE 2

1.8 g. of $TiCl_4$ dissolved in 50 ml of anhydrous petroleum (b.p. 98° C.) are added dropwise, at a temperature slightly lower than room temperature (5°—10° C.), to a solution of 11.4 g. triethyl-aluminium in 150 ml. of petroleum. The solution is further diluted to 500 ml. and introduced into an oscillating stainless steel autoclave of about 2 litres capacity, which was previously thoroughly dried and evacuated. 190 g. of liquid, carefully dried propylene are then pumped into the autoclave and this is heated, while in motion, up to about 55°—60° C. After the pressure has fallen from about 10 to about 2 atm. a further 160 g. propylene are added. The pressure falls now at a lower rate, and after about 20 hours, no further pressure decrease being observed, the residual gases are vented. These latter consist chiefly of propylene (72.5 N. litres) and contain a small amount of ethylene (0.2 N. litres) probably originating from the decomposition of the catalyst. 95 g. of methanol are then pumped into the autoclave in order to decompose the catalyst: 5.7 N litres of gas are evolved, more than 50% of which is propylene. The reaction product, consisting of a solid mass drenched with petroleum and methanol is then extracted.

In order to remove the inorganic compounds originating from the decomposition of the catalyst, the polymer is suspended in di-*iso*propylether and the suspension is heated while strongly stirring and bubbling through gaseous HCl. After 4 hours a little methanol is added to the suspension, in order to precipitate the polymer which might have been dissolved, and the suspension is then filtered under suction. Said polymer, after being dried at 100° C. under reduced pressure, weighs 180 g. and has an ash content of 0.22%. This product, containing a very wide range of propylene polymers, appears as a white, spongy solid, which at 140° C. has a transparent rubber-like appearance, melts only above 155° C. It can be moulded at 130° C. to flexible sheets, which by X-Ray diffraction patterns are shown to contain amorphous and crystalline portions.

From the filtered liquid after distillation of the solvent a few grams of a very viscous oil are recovered.

The solid polymer obtained is fractionated by hot extraction with solvents in an extractor of the Kumagawa type and for each solvent the extraction is continued until the percolating solvent does not contain any more appreciable quantities of extracted polymer.

The extracted fractions are isolated by re-

moving the solvent under vacuum in the hot. The following solvents are employed in succession: acetone, diethyl ether, n-heptane.

The acetone extract consists of oily, low molecular weight products and amounts to 2.8% of the solid polymer obtained.

The ether extract, corresponding to 39% of the solid polymer, consists of a rubbery, solid product having in tetrahydronaphthalene solutions at 135° C. an intrinsic viscosity equal to 1 (expressed in 100 ml/g). The ether extract obtained, examined by X-Rays analysis, appeared amorphous.

The heptane extract, corresponding to 19.9 % of the solid polymer, consists of a solid product which appears partially crystalline (for about 50%) under the X-Rays and shows in tetrahydronaphthalene solutions at 135° C. an intrinsic viscosity equal to 1.2.

The residue of the extraction with heptane consists of a powdery solid which softens at about 170° C. and appears completely crystalline under the X-Rays.

The residue insoluble in the three solvents of this Example shows a specific gravity of about 0.92, and an intrinsic viscosity determined in tetrahydronaphthalene solution of 3.33 (100 ml.g.). A 1% solution in tetrahydronaphthalene shows a specific viscosity of 0.374. Said residue starts to sinter at 120° C., loses its crystallinity at about 150° C. and at 170° C. is wholly converted into a transparent, very viscous mass.

By moulding it in a flat press at 140—150° C., plates are obtained which appear crystalline under the X-Rays, show a 700% elongation and a breaking load of 550 kg/sq.cm., referred to the original section. The product extruded when warm and then either warm or cold stretched appears very crystalline and has a very high breaking load. A cold stretched thread of 0.3 mm. diameter after stretching shows a breaking load of 32 kg/sq.mm. and an elongation of 40%.

Characteristics similar to those described above, with a lower tensile strength, are shown by the residue of the extraction with ether, which shows intermediate properties between those of the n-heptane extract and those of the n-heptane residue.

EXAMPLE 3.

The polymerisation was carried out as in the foregoing example, but in the cold (temperature 20° C.), by introducing into the autoclave 167 g. propylene, obtaining pressures of 3.9—3.6 atm. The polymerisation is much slower and less complete. In fact, only 32 g. of polymer were obtained, of which 21 g. consisting of solid polymer.

The solid polymer obtained is extractable to the extent of 7% with acetone in the hot, 40.5% with ether and 28% with heptane. After said extractions, 24% of the polymer obtained remains as residue.

The fractions thus obtained have properties similar to those described in the preceding example.

EXAMPLE 4.

Example 2 was repeated with the exception that 270 g. propylene were charged at once. The temperature was kept between 60° and 70° C. The autoclave was kept in motion until the pressure was reduced from 15 to about 11 atm. The vented gases contained 97.4 litres propylene and 0.4 litres ethylene. 3.5 litres propylene and 0.1 litres ethylene were further evolved during the decomposition of the catalyst which was carried out as in Example 2. 83 g. of polymer were obtained, which was subsequently purified as in Example 2.

The acetone extract of the polymer obtained, amounts to 7.1% and consists of oily products.

The ether extract corresponds to 43.9% and consists of an amorphous solid substance having in tetrahydronaphthalene solution an intrinsic viscosity equal to 1.0. The heptane extract corresponds to 17.8% and consists of a partially crystalline solid having an intrinsic viscosity of 1.31.

The residue which remains after said extractions corresponds to 31.2% and consists of a highly crystalline solid having a first-order transition point of about 160° C. and an intrinsic viscosity in tetrahydronaphthalene at 135° C. equal to 3.

EXAMPLE 5.

1 g. *isopropyl* alcohol is added to a solution of 5.7 g. triethyl-aluminium in 70 ml. petroleum. The mixture so obtained is then cooled to 0.5° and 1.8 g. titanium tetrachloride dissolved in 25 ml. petroleum are added to it dropwise. The solution is then diluted with 100 ml. petroleum and the so prepared catalyst is transferred into a 430 ml. autoclave. 95 g. propylene are then introduced and the autoclave is kept in motion heating to 65—70° C. After the pressure has fallen from 24 to 17 atm. further 21 g. propylene are introduced. The pressure rises up to 28 atm. and then falls to 15 atm. The unreacted gases are then vented collecting 9 N litres propylene. The catalyst is decomposed by introducing methanol into the autoclave and the reaction product made up of a solid mass drenched with petroleum and methanol is then discharged.

The polymer is purified by treatment with ether and hydrochloric acid in the hot and then coagulated completely with a large quantity of methanol. After filtration and hot drying under vacuum, the polymer amounts to 96 g. and consists of a white solid product which is fractionated by hot extraction with solvents.

The acetone extract corresponds to 9.30% of the polymer obtained and consists of oily, low molecular weight products.

The ether extract corresponds to 43.3% of the polymer obtained and consists of a rubbery, amorphous solid having in tetrahydronaphthalene solutions at 135° C. an intrinsic

viscosity of 0.8 (corresponding to a molecular weight of about 23,000).

The heptane extract corresponds to 18.7% of the polymer obtained and consists of a partially crystalline solid having an intrinsic viscosity equal to 1 (corresponding to a molecular weight of about 32,000).

The residue which remains after said extractions corresponds to 30.6% of the total polymer and consists of a powdery, highly crystalline solid having an intrinsic viscosity of 2.7 (corresponding to a molecular weight of about 150,000).

EXAMPLE 6.

In a stainless steel autoclave of 2150 ml. capacity, 600 ml. of solvent (heptane-*iso*-octane mixture) containing 11.4 g. triethyl aluminium are introduced. 325 g. of propylene are added and the mixture is heated up to 60° C; then 3.6 g. titanium tetrachloride dissolved in 50 ml. solvent are admitted into the autoclave. The temperature rises spontaneously in a few minutes up to 113° C. and then slowly decreases. When the temperature reaches 80° C., 1.8 g. titanium tetrachloride dissolved in 50 ml. petroleum are added. A further smaller temperature increase is then observed. The autoclave is kept in agitation for about two hours. It is then cooled to 60° C. and the residual gases are released.

The polymerising agent is decomposed by introducing into the autoclave 150 ml. methanol. After stirring for a few minutes, the reaction product, consisting of a solid mass drenched with methanol and petroleum, is then discharged The product is slurried in ether and treated with hydrochloric acid in order to remove most of the inorganic substances, and is then coagulated with methanol and filtered. Thus 282 g. of a white solid product are obtained whose softening point is about 130—140° C. The yield of solid propylene in respect of the introduced propylene is 87%; the yield in respect of the converted propylene is higher than 95%.

The polymer obtained is fractionated by hot extraction with solvents, employing successively acetone, diethyl ether and n-heptane.

The ether extract corresponds to 40.5% of the polymer obtained and consists of a rubbery, amorphous solid. In tetrahydronaphthalene solution at 135° C. it shows an intrinsic viscosity equal to 0.49 (corresponding to a molecular weight of about 11,000).

The heptane extract corresponds to 24.4% of the polymer obtained and consists of a partially crystalline solid having an intrinsic viscosity equal to 0.64. The residue which remains after said extractions amounts to 27.2% of the polymer obtained and consists of a powdery, highly crystalline solid having a first-order transition point of about 160° C. In tetrahydronaphthalene solutions at 135° it shows an intrinsic viscosity equal to 1.77 (corresponding to a molecular weight of about 78,000).

EXAMPLE 7.

Two steel balls, a glass vial containing 13 g. of titanium tetrabromide, and a solution of 11.4 g. of triethyl aluminium in 500 ml. of n-heptane are introduced under nitrogen into a shaking autoclave of 1750 ml. capacity. The autoclave is heated, keeping it motionless, up to 63° C. and at this point 280 g. of propylene are introduced into the equipment. Soon afterwards the autoclave is put into motion, causing in this way the breaking of the vial. The temperature rises now spontaneously in a short time up to 97° C. and drops then again down to 85° C. The autoclave is kept in agitation at this temperature for about 10 hours. The unreacted gases are vented and methanol is pumped into the autoclave.

The polypropylene is then purified in the usual manner; 249 g. of polymer are obtained, equal to a conversion of 89% of the monomer employed.

The acetone extract corresponds to 15.1% of the polymer obtained and consists of oily products.

The ether extract corresponds to 33% of the polymer obtained and consists of a rubbery, amorphous solid with intrinsic viscosity 0.53.

The heptane extract corresponds to 22.1% of the polymer obtained and consists of a partially crystalline solid having an intrinsic viscosity equal to 0.65.

The residue which remains after said extractions corresponds to 30.8% of the polymer obtained and consists of a highly crystalline solid having, in tetrahydronaphthalene solutions at 135° C., an intrinsic viscosity equal to 1.78.

EXAMPLE 8.

Two steel balls, a glass vial containing 17 g. of titanium tetraiodide, and a solution of 11.4 g. of triethyl aluminium in 500 ml. of heptane are introduced into a shaking autoclave of 2080 ml. capacity.

The autoclave is heated to 71° C. and at this temperature 150 g. of propylene are introduced and soon afterwards the autoclave is put into motion, causing in this way the breaking of the vial. The temperature rises spontaneously in a short time up to 100° C. and then drops again down to 90° C. At this moment 118 g. of propylene are added. The autoclave is kept in motion for about 6 hours and then the unreacted gases are vented, proceeding afterwards as described in the foregoing examples.

184 g. of propylene polymer are thus obtained, which are fractionated by hot extraction with solvents.

The acetone extract corresponds to 20.4% of the polypropylene obtained and consists of oily, low molecular weight products.

The ether extract corresponds to 22.7% of the polymer obtained and consists of an

amorphous solid having, in tetrahydronaphthalene solutions at 135° C., an intrinsic viscosity equal to 0.43.

The heptane extract corresponds to 22% of the polymer obtained and consists of partially crystalline solid with intrinsic viscosity 0.73.

The residue which remains after said extractions corresponds to 35% of the polymer obtained and consists of a powdery, highly crystalline solid having an intrinsic viscosity of 2.16.

EXAMPLE 9.

30 cc. air-free and sodium-distilled Fischer-Tropsch Diesel oil, which had been thoroughly freed from unsaturated products by hydrogenation, 17.1 g. aluminium triethyl and 11.7 g. zirconium tetrachloride were mixed in a small ball mill, or a vibrating ball mill of 150 cc. capacity, duly fitted up for working with nitrogen, and ground intensively for 24 hours. A thick, black suspension was produced, which was mixed with 1 litre of the same Diesel oil and poured under nitrogen into a 5 litre agitator autoclave. 590 g. propylene was then injected at room temperature, the agitator mechanism was set in motion and the temperature raised to 80°. In the course of 50 hours, the pressure dropped from an initial 23 atmospheres to 14.2 atmospheres. The reaction, which had still not quite finished, was now broken off. The excess propylene was left to cool and expand. 190 g. of propylene were recovered. The contents of the autoclave were a thick, black paste, which, after acetone had been added and a suction filtering process undergone, became colourless on contact with the air. The radicals of the catalyst were extracted by heating with alcoholic hydrochloric acid. After renewed washing out with acetone and drying, 400 g. of a white, flaky polypropylene, which is easily pressed into sheets and rolled out was obtained.

EXAMPLE 10.

Two steel balls, a glass vial containing 4.7 g. of zirconium tetrachloride, and a solution of 5.7 g. of triethyl aluminium in 100 ml. of n-heptane are introduced under nitrogen into a 435 ml. autoclave. The autoclave is heated keeping it motionless, up to 79° C. and at this temperature 106 g. of propylene are injected into the autoclave which is soon afterwards put in motion. The autoclave is kept in agitation for 15 hours at temperatures of 80 to 85° C. and then methanol is pumped into it; the reaction product is discharged and purified, proceeding as described in the foregoing examples. 22 g. of polypropylene are thus isolated, which are then fractionated with solvents in the hot.

The acetone extract corresponds to 60.4% of the polymer obtained and consists of semi-solid, low molecular weight products.

The ether extract corresponds to 11.6% of the polymer obtained and consists of an amorphous solid with intrinsic viscosity 0.49.

The heptane extract corresponds to 13.85% of the polymer obtained and consists of a partially crystalline solid having an intrinsic viscosity of 0.94.

The residue which remains after said extractions corresponds to 14.3% of the polymer obtained and consists of a highly crystalline solid with intrinsic viscosity 2.

EXAMPLE 11.

A solution of 5.7 g. of triethyl aluminium in 50 ml. of n-heptane is introduced under nitrogen into a 435 ml. autoclave, previously emptied of the air. 118 g. of propylene are then introduced into the equipment, which is heated, while agitating, up to a temperature of 80° C. At this temperature a solution of 4.3 g. of VCl_4 in 50 ml. of n-heptane is injected into the autoclave under nitrogen pressure. The autoclave is kept in agitation at temperatures between 80 and 83° C. and after said period of time methanol is pumped into it. The polymer is then purified proceeding as described in the preceding examples.

77 g. of a solid polypropylene are thus obtained, which are then fractionated by hot extraction with solvents.

The acetone extract corresponds to 10.0% of the polymer obtained and consists of oily, low molecular weight products.

The ether extract corresponds to 45.2% of the polymer obtained and consists of a rubbery, amorphous solid having in tetrahydronaphthalene solutions at 135° C. an intrinsic viscosity equal to 0.82 (corresponding to a molecular weight of about 24,000).

The heptane extract corresponds to 16.4% of the polymer obtained and consists of a partially crystalline solid having an intrinsic viscosity of 1.31 (molecular weight about 48,000).

The residue which remains after said extractions corresponds to 28.2% of the polymer obtained and consists of a highly crystalline solid having an intrinsic viscosity equal to 1.88 (molecular weight about 85,000).

EXAMPLE 12.

In a 2150 cc. autoclave are introduced under nitrogen 10 g. of a mixture containing 50% $MoCl_5$ and 50% $ZoCl_4$, and a solution of 11.4 g. triethyl-aluminium in 500 cc. n-heptane.

Thereafter 365 g. propylene are introduced and the autoclave is heated to 100° C., and maintained at this temperature under stirring for about 20 hours. The unreacted propylene is then vented, and the reaction product is extracted from the autoclave and purified by treatment with methanol and hydrogen chloride.

After evaporation of the solvents 115.3 g. polypropylene are obtained, which are fractionated by hot solvent extraction. The acetone extract corresponds to more than 90% of the total product and is formed of oily, low molecular weight products.

The residue after extraction with acetone

is formed by approximately 50% of a polypropylene, which is non-crystallisable and which is extractable with ether, while the rest is a propylene which appears crystalline at the X-Rays.

EXAMPLE 13.

530 ml. petroleum containing 15.6 g. tripropyl aluminium and 275 g. propylene are introduced into a 2150 ml. autoclave, which is then heated up to 70° C.; thereafter 3.6 g. titanium tetrachloride dissolved in petroleum are added. The temperature rises spontaneously to 95° C.; when it is down again to 80° C. a further addition of 1.8 g. titanium tetrachloride is made. The autoclave is then kept in agitation for four hours while keeping the temperature at 80° C. By operating as in example 6, 209 g. of solid polymer are obtained. The purified, unfractionated polymer begins to soften at 140° C. The yield is 76% on the introduced propylene, and higher than 95% on the converted propylene.

The acetone extract corresponds to 7.1% of the polymer obtained and consists of oily, low molecular weight products.

The ether extract corresponds to 32.4% of the polymer obtained and consists of a rubbery amorphous solid product having an intrinsic viscosity of 0.9.

The heptane extract corresponds to 19.1% of the polymer obtained and consists of a partially crystalline solid having an intrinsic viscosity of 0.95.

The residue which remains after said extractions corresponds to 41.4% of the polymer obtained and consists of a powdery solid product which appears highly crystalline when examined under the X-Rays and has an intrinsic viscosity of 4.6 and a softening point of about 180° C.

The mechanical properties of samples obtained from such products are, in accordance with the higher viscosity, better than those of samples obtained by the procedure described in example 6.

EXAMPLE 14.

500 ml. petroleum containing 12 g. diethyl aluminium monochloride, and 310 g. propylene are introduced into a 2150 ml. autoclave, which is heated to 60° C. Two portions of respectively 3.6 and 1.8 g. $TiCl_4$, dissolved in petroleum, are then added. The reaction proceeds as described in the foregoing examples.

The reaction product consists of 248 g. solid, white, polypropylene. The yield is 80% on the introduced propylene and about 95% on the converted propylene.

The acetone extract, consisting of oily products, corresponds to 25% of the polymer obtained.

The ether extract consisting of a rubbery, amorphous solid, corresponds to 44% of the polymer obtained and has an intrinsic viscosity of 0.4.

The heptane extract corresponds to 16.4% of the polypropylene obtained and consists of a partially crystalline solid with intrinsic viscosity 0.78.

The residue which remains after said extractions corresponds to 14.4% of the product obtained, has an intrinsic viscosity of 1.53 and appears highly crystalline when examined under the X-Rays.

EXAMPLE 15.

A solution of 8.2 g. of diethyl zinc in 100 ml. of n-heptane is introduced under nitrogen into a 435 ml. autoclave. 115 g. of propylene are then introduced and the whole is heated, while agitating, to 62° C. At this temperature a solution of 3.8 of titanium tetrachloride in 20 ml. of n-heptane is injected into the autoclave.

The autoclave is then kept in agitation for about 10 hours at temperatures between 60 and 70° C. After said period of time the unreacted gases are vented, methanol is pumped into the autoclave and the reaction product is discharged. The purification is carried out in a similar way as already described, by treatment with ether and hydrochloride acid in the hot, followed by a complete coagulation of the polymer with methanol.

After filtering and vacuum drying in the hot, the polypropylene amounts to 16 g. which are then submitted to a hot extraction with solvents.

The acetone extract, consisting of oily, low molecular weight products, corresponds to 41% of the polymer obtained.

The ether extract, corresponding to 20% of the polymer obtained, consists of an amorphous product and has an intrinsic viscosity of 0.23.

The heptane extract, corresponding to 20% of the polymer obtained, consists of a partially crystalline solid with intrinsic viscosity 0.41.

The residue which remains after said extractions corresponds to 19% of the polymer obtained and consists of a highly crystalline solid product with intrinsic viscosity 1.22.

EXAMPLE 16.

17.5 g. sodium triethylborohydride in 200 cc. toluene (produced by heating sodium hydride with triethylboron in toluene until the sodium hydride dissolves) and 7.5 g. of titanium tetrachloride are mixed under nitrogen in an agitator autoclave. Then 500 g. propylene are injected in the mixture heated to 70—80° and agitated. Within 30 hours, the pressure falls from 20 to 11 atmospheres. The product is worked up according to Example 9. The result is similar.

EXAMPLE 17.

In like manner as in Example 9, 23 g. magnesium-aluminium alloy of the composition Mg_3Al_2 (crudely pulverised) are intensively ground in 100 cc. hexane with 8.8 g. of titanium tetrachloride for 36 hours. After this time, there are no further signs of $TiCl_4$ in test samples of the clarified solution. The grey-

black catalyst suspension obtained is further treated in accordance with Example 9, with propylene. From 790 g. propylene, 660 g. of a synthetic plastic like polyproylene are obtained, in addition to 130 g. of unchanged propylene, the first-mentioned polypropylene being similar to the polymers obtained according to Examples 1 or 9.

EXAMPLE 18.

A solution of 11.4 g. triethyl aluminium in 500 ml. petroleum and 320 g. of a mixture propylene-propane (containing 15% propane) are introduced into a 2150 ml. autoclave. The mixture is heated to 71° C., and 3.6 g. titanium tetrachloride dissolved in 50 ml. petroleum are then added. The temperature rises spontaneously to 108° C., then goes slowly down again. After about 1 hour, further 1.8 g. titanium tetrachloride dissolved in petroleum are added and a further, smaller temperature increase is noticed. About three hours after the first addition of titanium tetrachloride, methanol is admitted into the autoclave and the unreacted gases are released. The reaction product purified as in example 6, consists of 200 g. of a solid white polymer. The yields are 73% on the introduced propylene and 93% on the converted propylene the propane remaining unpolymerised. The obtained polypropylene shows properties which are practically identical with those of the polymer obtained from pure propylene.

EXAMPLE 19.

Small amounts of ethylene contained in the propylene show that ethylene does not interfere with the polymerisation. It is observed however that ethylene polymerises more rapidly than propylene.

By employing in examples 3, 4 and 5 a propylene which contains 5% ethylene, it is observed that the polymerisation residual gases are impoverished in ethylene. The characteristics of the final products are however only slightly altered. Under the X-Rays they still show the typical polypropylene structure, even if accompanied by an amount of amorphous substances larger than in the polymers obtained from ethylene-free propylene.

EXAMPLE 20.

The procedure is according to Example 1 to begin with; however, by connection of the autoclave with a pressure ethylene storage container and careful adjustment of the valve, an ethylene partial pressure of 1—3 atmospheres is maintained additionally in the autoclave. It is advisable to check the composition of the fluid phase by taking small samples and by gas analysis. In the fluid, ethylene should be contained, preferably in a quantity a few percent of the propylene, as the ethylene polymerises more rapidly than propylene. In this experiment, too, a solid copolymer is obtained which can be pressed into sheets, the properties of which lie roughly between those of polyethylene and polypropylene.

EXAMPLE 21.

50 cc. Diesel oil, 3.5 g. diethyl aluminium monochloride and 0.44 g. titanium tetrachloride are used in the preparation of the catalyst in this case. The catalyst is dissolved under nitrogen in 2½ litres Diesel oil; a well-dried and oxygen-free mixture of 12 vol.% propylene and 88 vol.% ethylene, in the gaseous state, is introduced at atmospheric pressure. On heating to about 70° and, over a period of 8 hours, increasing the temperature gradually to 90 , an insoluble polymer, finely pulverulent, is precipitated, the contents of the agitator container becoming gradually thicker thereby. After 8 hours' reaction period, the experiment was interrupted and, after filtering off, 168 g. of a solid, colourless synthetic plastic substance were obtained, which, had essentially the properties of polyethylene, in which, however, propylene was also no doubt polymerised therewith, as could be seen from the infra-red spectrum. Figure 2 of the accompanying drawings shows alongside one another the absorption of a polymer obtained in like manner from ethylene alone and those of the copolymer according to this example, in the range 1382 cm^{-1}. At the point marked, the copolymer referred to in the figure as the mixed polymerizate has one absorption edge more, which is characteristic for the methyl branching. This absorption band is also found in the high pressure polymerised polyethylene, which has, as has been shown, a certain branching degree. The same inference, that in the presence of ethylene a copolymer forms, can also be drawn from a careful balancing of the substances, if the gases given off from the reaction container are recovered by deep freezing. It is easily ascertained that some 10% of propylene must be polymerised in the polymerisate.

EXAMPLE 22.

A solution of 11.4 g. triethyl aluminium in 500 ml. petroleum is introduced into a 2150 c. cm. autoclave. 267 g. propylene are then introduced and the autoclave is heated to 68° C.; then a solution of 6.8 g. isoprene in 100 ml. petroleum is introduced into the autoclave. Soon afterwards 3.6 g. titanium tetrachloride in 50 ml. petroleum are added. A temperature increase of about 10° C. is noticed. Two further additions of titanium tetrachloride are then made. About six hours from the start of the reaction, the catalyst is decomposed with 100 g. methanol and the residual gases are released. The polymer obtained is purified as in Example 6; 225 g. of a white solid product are obtained, which indicates a conversion of 82% on the total olefins and diolefins present. The product absorbs bromine; it has a lower crystallinity than the polymers obtained under the same conditions from propylene alone.

EXAMPLE 23.

The procedure is as for Example 1, but the propylene is replaced by a like quantity of a-

butylene (butene-1) or of a hydrocarbon fraction rich in α-butylene. The poly-butene-1 obtained is superficially similar to polypropylene, but is somewhat softer.

EXAMPLE 24.

160 ml. petroleum containing 5.7 g. triethyl aluminium, and 85 g. butene-1 (Philips technical grade) are introduced into a 435 ml. autoclave.

The autoclave is heated to 81° C, and 1.8 g. titanium tetrachloride dissolved in 35 ml. petroleum are then added. A spontaneous temperature increase of some degrees occurs.

After about one hour a further addition of titanium tetrachloride dissolved in petroleum is made; a spontaneous temperature increase of about 10° C. occurs. The autoclave is kept in agitation for some hours at a temperature of 90—98° C.

Operating as in the foregoing examples, 10 g. of a white solid product are obtained, which softens at 110° C. and appears crystalline under the X-Rays. The residue of the extraction with ether corresponds to 46% of the obtained polymer and shows an intrinsic viscosity, calculated from measurements similar to those described in example 6, of 1.44.

EXAMPLE 25.

400 ml. petroleum containing 11.4 g. triethyl aluminium, and 291 g. of a butene-2/butene-1 mixture (with 70% of butene-1) are introduced into a 2150 ml. autoclave. The autoclave is then heated to 71° C. and 3.6 g. titanium tetrachloride dissolved in petroleum are added; the temperature rises to 77° C.

After two hours a further addition of 3.6 g. titanium tetrachloride is made. The autoclave is kept in agitation for some hours at temperatures in the range 80—85° C. Operating as in the foregoing examples, 86 g. of white solid product are obtained. Said product shows characteristics similar to those described in example 24, and softens at 125° C. Fibres are readily obtained from this product by extrusion in a spinnerette under nitrogen pressure at temperatures close to the softening point. They show a mechanical strength of the same order of the fibres obtained from polypropylene but a higher elasticity.

The raw polymer obtained was fractionated by hot extraction with solvents. The acetone extract corresponds to 14% of the polymer obtained and consists of oily, low molecular weight products.

The ether extract, corresponding to 35.5% of the polymer obtained, consists of a rubbery, amorphous solid having an intrinsic viscosity equal to 0.35 (corresponding to a molecular weight of about 7,000).

The residue of the extraction with ether is completely extractable with n-heptane in the hot and consists of a highly crystalline solid having a melting point of 125° and an intrinsic viscosity of 1.02 (corresponding to a molecular weight of about 33,000).

EXAMPLE 26.

45 g. of pentene-1 and a solution of 5.7 of triethyl aluminium in 250 ml. of heptane are introduced under nitrogen into a 500 ml. flask fitted with a mechanical stirrer, a dropping funnel and a reflux condenser.

The whole is heated to 50° C. and at this temperature a solution of 3.8 g. of titanium tetrachloride in 20 ml. of n-heptane is dropped into the flask. A spontaneous increase of the temperature up to 70° C is at once observed. The mass is kept in agitation for 3 hours at this temperature, then the organo-metallic compounds present are decomposed with methanol.

The polymer obtained is purified as described in the preceding examples. 16.5 g. of polymer are thus obtained, and extracted with solvents in the hot.

The acetone extract corresponds to 47.8% of the polymer obtained and consists of oily products.

The extract obtained with ethyl acetate corresponds to 44.3% of the polymer obtained and consists of a rubbery, amorphous solid product.

The ether extract corresponds to 7.9% of the polymer obtained and consists of a solid polypentene which appears highly crystalline when examined under the X-Ray.

EXAMPLE 27.

25 g. of hexene-1 dissolved in 29 g. hexane, containing 5.7 g. triethyl aluminium, are heated under reflux in a 500 ml. flask fitted with a stirrer, under an atmosphere of nitrogen. 1.8 g. titanium tetrachloride dissolved in hexane are then added and the mixture is allowed to boil under reflux for 5 hours. The obtained solution is treated after cooling with methanol, then with diluted hydrochloric acid, and finally evaporated to dryness. The formed polymer corresponds to a conversion on the employed hexene higher than 50%. This polymer is soluble in petroleum and ether, very sparingly soluble however in methanol. The portion insoluble in methanol shows very marked viscous-elastic properties.

EXAMPLE 28.

91 g. styrene and 11.4 g. triethyl-aluminium dissolved in 500 cc. n-heptane are introduced into a 2150 cc. autoclave. 282 g. propylene are then introduced and the autoclave is heated to 62° C. At this temperature 3.8 g. $TiCl_4$ dissolved in 40 cc. heptane are injected into the autoclave under nitrogen pressure. The temperature rises spontaneously to 100° C., and falls then slowly to 72° C.; at this point a second addition of 3.8 g. $Ti Cl_4$ in 40 cc. heptane is made. After about 6 hours from the beginning of the run the reacted gases are vented and 24 Nl of propylene are recovered.

Methanol is now pumped into the autoclave and the obtained polymer is purified in the usual way.

299 g. of a solid, white β-polymer are

obtained, which is fractionally extracted with boiling acetone, ethyl ether and n-heptane, in succession. The acetone extract corresponds to 14.6% of the total obtained polymer and consists of oily products of low molecular weight. The ether extract is 32.8% of the total obtained α-polymer, and is a solid, amorphous product of rubberlike appearance.

The n-heptane extract, 19.8% of the total, is a solid which becomes plastic at 90° C. The extraction residue, 32.8% of the total obtained α-polymer, is a powdery solid; the X-Rays analysis reveals a content of crystalline polypropylene.

The U.V. Spectra of n-heptane solutions of the fractions obtained by extraction with ether and n-heptane indicate the presence of aromatic rings. The ether and n-heptane extracts contain therefore a copolymer propylene-styrene.

EXAMPLE 29.

A solution of 11.4 g. of triethyl aluminium in 400 ml. of n-heptane and 250 g. of monomeric styrene are introduced under nitrogen into a 2150 ml. autoclave. The autoclave is heated to 68° C. and at this temperature a solution of titanium tetrachloride in 50 ml. of heptane is injected under nitrogen into the autoclave. After 3 hours, during which period of time the temperature was kept between 68 and 70° C., a solution of 3.8 g. of titanium tetrachloride in 50 ml. of heptane is injected into the autoclave.

6 hours after the first addition of titanium tetrachloride, 100 ml. of methanol are pumped into the autoclave and then the reaction product is discharged, and appears as a viscous liquid containing in suspension a fine powder.

The reaction mass is then treated with hydrochloric acid in order to bring to solution the inorganic products present. By addition of a large quantity of methanol a polymer coagulates; this polymer is filtered off and is treated with acetone which becomes acid due to the presence of hydrochloric acid. In this way the amorphous polystyrene and the inorganic impurities, which are still present, are brought to solution and removed.

The residue which remains after said treatment with acetone is vacuum dried in the hot; 30 g. of polystyrene consisting of a white powder are thus obtained, and appear highly crystalline when examined under the X-Rays.

The crystalline polystyrene obtained has a molecular weight of about 2,800,000 (as calculated from viscosimetrical measurements in benzene at 25° C.), a density of 1.08 and a first-order transition point higher than 210° C.

The solvents employed in the purification and polymerisation are then vacuum concentrated in the hot to a small volume and finally treated with methanol. The amorphous polymer is thus precipitated. This polymer is isolated by filtration and vacuum dried in the hot. 50 g. of a solid, amorphous polymer, having a molecular weight of about 10,000, are thus obtained.

EXAMPLE 30.

The procedure is first as indicated in Example 21, but the mixture of Diesel oil and catalyst is mixed with 250 cc. 1-vinyl cyclohexene-4 (product of the thermal dimerisation of butadiene). Thereupon, pure ethylene is introduced. The experiment proceeds superficially in like manner to the production of polyethylene, but the ethylene absorption takes place noticeably more slowly. After 9 hours' duration of the experiment, 120 g. of a polymer had formed, which had the surface appearance of polyethylene, in which, though, according to results of infra-red analysis, a portion of vinyl-cyclohexene which cannot at first be accurately indicated had been polymerised in. This can be seen from the fact that a sheet 120—140 μ thick pressed out of the polymer has an infra-red absorption band at 658 cm^{-1}, which is to be found in the infra-red spectrum of the polymers to be obtained in like manner from ethylene alone. This band is also characteristic however for the double bond-linkage in the cyclohexene ring. That this infra red absorption band is not due to a residue of dissolved vinyl cyclohexene monomer can be seen from the fact that the infra-red spectrum of the polymer does not show the very characteristic bands of the vinyl group. This gives a genuine α-polymer of obviously largely ethylene with a little vinyl-cyclohexene. The copolymer, as opposed to the pure, analogously produced polyethylene, shows a distinctly increased strength and higher softening temperature.

WHAT WE CLAIM IS:—

1. A method of polymerising an alpha olefin of the general formula R—CH = CH_2 (R being an alkyl, cycloalkyl, cycloalkenyl or aryl group) or a mixture of such alpha olefins, either alone or with ethylene and/or other hydrocarbon having at least one vinyl double bond, wherein there is used a catalyst formed by contacting a halide (other than a fluoride) of a metal of Group IVa, Va or VIa of the Periodic Table as herein defined, with a metal of Group Ia or II of the said table or aluminium, or with an alloy of metals of Group Ia and/or II and/or aluminium, or with a hydride or organo-metallic compound of a said metal of Group Ia or II and/or of aluminium, or with a complex hydride or a complex organo-metallic compound of boron and a said metal of Group Ia or II, the choice of the constituents of the catalyst and the conditions of polymerisation being such that at least a part of the said metal of Group IVa, Va or VIa is present in the catalyst in a valency state lower than the maximum and that in substantially anhydrous and oxygen free conditions polymerisation of the said olefin results.

2. A method as claimed in claim 1, characterised in that the said metal of Group IVa,

obtained, which is fractionally extracted with boiling acetone, ethyl ether and n-heptane, in succession. The acetone extract corresponds to 14.6% of the total obtained polymer and consists of oily products of low molecular weight. The ether extract is 32.8% of the total obtained α-polymer, and is a solid, amorphous product of rubberlike appearance.

The n-heptane extract, 19.8% of the total, is a solid which becomes plastic at 90° C. The extraction residue, 32.8% of the total obtained α-polymer, is a powdery solid; the X-Rays analysis reveals a content of crystalline polypropylene.

The U.V. Spectra of n-heptane solutions of the fractions obtained by extraction with ether and n-heptane indicate the presence of aromatic rings. The ether and n-heptane extracts contain therefore a copolymer propylene-styrene.

EXAMPLE 29.

A solution of 11.4 g. of triethyl aluminium in 400 ml. of n-heptane and 250 g. of monomeric styrene are introduced under nitrogen into a 2150 ml. autoclave. The autoclave is heated to 68° C. and at this temperature a solution of titanium tetrachloride in 50 ml. of heptane is injected under nitrogen into the autoclave. After 3 hours, during which period of time the temperature was kept between 68 and 70° C., a solution of 3.8 g. of titanium tetrachloride in 50 ml. of heptane is injected into the autoclave.

6 hours after the first addition of titanium tetrachloride, 100 ml. of methanol are pumped into the autoclave and then the reaction product is discharged, and appears as a viscous liquid containing in suspension a fine powder.

The reaction mass is then treated with hydrochloric acid in order to bring to solution the inorganic products present. By addition of a large quantity of methanol a polymer coagulates; this polymer is filtered off and is treated with acetone which becomes acid due to the presence of hydrochloric acid. In this way the amorphous polystyrene and the inorganic impurities, which are still present, are brought to solution and removed.

The residue which remains after said treatment with acetone is vacuum dried in the hot; 30 g. of polystyrene consisting of a white powder are thus obtained, and appear highly crystalline when examined under the X-Rays.

The crystalline polystyrene obtained has a molecular weight of about 2.800.000 (as calculated from viscosimetrical measurements in benzene at 25° C.), a density of 1.08 and a first-order transition point higher than 210° C.

The solvents employed in the purification and polymerisation are then vacuum concentrated in the hot to a small volume and finally treated with methanol. The amorphous polymer is thus precipitated. This polymer is isolated by filtration and vacuum dried in the hot. 50 g. of a solid, amorphous polymer, having a molecular weight of about 10,000, are thus obtained.

EXAMPLE 30.

The procedure is first as indicated in Example 21, but the mixture of Diesel oil and catalyst is mixed with 250 cc. 1-vinyl cyclohexene-4 (product of the thermal dimerisation of butadiene). Thereupon, pure ethylene is introduced. The experiment proceeds superficially in like manner to the production of polyethylene, but the ethylene absorption takes place noticeably more slowly. After 9 hours' duration of the experiment, 120 g. of a polymer had formed, which had the surface appearance of polyethylene, in which, though, according to results of infra-red analysis, a portion of vinyl-cyclohexene which cannot at first be accurately indicated had been polymerised in. This can be seen from the fact that a sheet 120—140 μ thick pressed out of the polymer has an infra-red absorption band at 658 cm^{-1}, which is to be found in the infra-red spectrum of the polymers to be obtained in like manner from ethylene alone. This band is also characteristic however for the double bond-linkage in the cyclohexene ring. That this infra red absorption band is not due to a residue of dissolved vinyl cyclohexene monomer can be seen from the fact that the infra-red spectrum of the polymer does not show the very characteristic bands of the vinyl group. This gives a genuine α-polymer of obviously largely ethylene with a little vinyl-cyclohexene. The copolymer, as opposed to the pure, analogously produced polyethylene, shows a distinctly increased strength and higher softening temperature.

WHAT WE CLAIM IS:—

1. A method of polymerising an alpha olefin of the general formula R—CH = CH_2 (R being an alkyl, cycloalkyl, cycloalkenyl or aryl group) or a mixture of such alpha olefins, either alone or with ethylene and/or other hydrocarbon having at least one vinyl double bond, wherein there is used a catalyst formed by contacting a halide (other than a fluoride) of a metal of Group IVa, Va or VIa of the Periodic Table as herein defined, with a metal of Group Ia or II of the said table or aluminium, or with an alloy of metals of Group Ia and/or II and/or aluminium, or with a hydride or organo-metallic compound of a said metal of Group Ia or II and/or of aluminium, or with a complex hydride or a complex organo-metallic compound of boron and a said metal of Group Ia or II, the choice of the constituents of the catalyst and the conditions of polymerisation being such that at least a part of the said metal of Group IVa, Va or VIa is present in the catalyst in a valency state lower than the maximum and that in substantially anhydrous and oxygen free conditions polymerisation of the said olefin results.

2. A method as claimed in claim 1, characterised in that the said metal of Group IVa,

Va or VIa is titanium, or zirconium, or vanadium, or chromium, or molybdenum.

3. A method as claimed in claim 1 or claim 2, in which the said compound of aluminium is of the general formula

$$R^{I}R^{II}AlR^{III},$$

wherein R^{I} and R^{II} are hydrocarbon radicals, particularly alkyl radicals, and R^{III} is a hydrocarbon radical or hydrogen, or halogen, or an alkoxy group.

4. A method as claimed in claim 1 or claim 2, in which the said compound of a metal in Group Ia or II or aluminium is of the general formula

$$A[MR^{I}R^{II}XY]$$

wherein A is an alkali metal, M is aluminium or boron, R^{I} and R^{II} are hydrocarbon radicals, particularly alkyl radicals, and X and Y are hydrocarbon radicals or hydrogen.

5. A method as claimed in claim 1 or claim 2, characterised in that the said organo-metallic compound is of magnesium or zinc.

6. A method as claimed in claim 1 or claim 2, characterised in that a reaction product of an aluminium alkyl with a titanium halide (other than a fluoride) is used as a catalyst.

7. A method as claimed in claim 6, in which the aluminium alkyl is aluminium triethyl.

8. A method as claimed in claim 6 or claim 7, in which the titanium halide is titanium tetrachloride.

9. A method of preparing a polymer of an alpha olefin of the general formula

$$R—CH\ CH_2$$

(R being an alkyl group having not more than 4 carbon atoms, or a cyclohexenyl, or a phenyl group) or of a mixture of such alpha olefins, either alone or with ethylene and/or with a diolefin having at least one vinyl double bond, wherein there is used a catalyst formed by contacting a halide (other than a fluoride) of titanium, or zirconium, or vanadium with an aluminium alkyl compound, the choice of the constituents of the catalyst and the conditions of polymerisation being such that at least a part of the titanium, zirconium or vanadium is present in the catalyst in a valency state lower than the maximum and that in substantially anhydrous and oxygen free conditions polymerisation of the said olefin results.

10. A method as claimed in any one of the preceding claims, characterised in that a dispersion or solution of the said compound of a metal of Group IVa, Va or VIa in an inert solvent is brought together with a dispersion or solution of the compound of a said metal of Group Ia or II or aluminium in an inert solvent.

11. A method as claimed in any one of the preceding claims 1 to 2 or 6 to 10 characterised in that a quantity of 1 to 12 mols of an aluminium trialkyl compound is used to 1 mol of the said compound of a metal of Group IVa, Va or VIa, in the production of the catalyst.

12. A method as claimed in claim 11, save that a quantity of from 1 to 3 mols of an aluminium trialkyl compound is used to 1 mol of the said compound of a metal of Group IVa, Va or VIa, in the production of the catalyst.

13. A method as claimed in any one of the preceding claims, characterised in that the operation is carried out in the liquid phase, the catalyst being used in the presence of a solvent, preferably in the liquid olefin itself or in a solution of the latter in an inert solvent.

14. A method as claimed in any one of the preceding claims characterised in that the catalyst is produced in the presence of an olefin.

15. A method as claimed in claim 14 in which the olefin is the alpha olefin or a mixture of alpha olefins either alone or with other said olefins which is or are the subject of polymerisation.

16. A method as claimed in any one of the preceding claims, characterised in that the polymerisation is carried out at temperatures between 20 and 150° C., preferably between 50 and 100° C.

17. A method as claimed in any one of the preceding claims, characterised in that the polymerisation is carried out at elevated pressures of up to 30 atmospheres.

18. A method as claimed in claim 14 characterised in that a dispersion or solution of the said compound of the metal of Group IVa, Va or VIa in an inert solvent, or in a part of the olefin to be polymerised, is added gradually, preferably continuously, to a mixture of the fluid olefin and an organo-metallic compound of the said metal of Group Ia or II or aluminium, during the polymerisation.

19. A method as claimed in any one of the preceding claims, characterised in that both the said compounds of a metal of Group IVa, Va or VIa, in dispersion or solution form, and the solution of said organo-metallic compound of a metal of group Ia or II or of aluminium are introduced gradually, preferably continuously, during the polymerisation.

20. A method as claimed in any one of the preceding claims, in which a mixed polymer is obtained, characterised in that the polymer obtained is separated, after decomposition of the catalyst, into fractions which comprise polymers of different steric structures, by fractionation with solvents which do not swell the crystalline polymers, the fractionation being carried out at a temperature below the melting point of the polymer.

21. A method as claimed in claim 20, wherein the polymer is a mixture of crystalline and amorphous polypropylene, the fractionation being carried out by removing an amorphous fraction by means of boiling diethyl ether, then a partially crystalline fraction by means of boiling *n*-heptane, leaving a highly crystalline fraction as a residue.

22. A method of preparing polymers of alpha-olefins substantially in accordance with any one of the foregoing Examples.

23. A linear, essentially unbranched, head-to-tail polymer of an alpha-olefin of the general formula $R—CH=CH_2$, (R being an alkyl, cycloalkyl or cycloalkenyl group) or of a mixture of such alpha-olefins, either alone or with ethylene and/or with other unsaturated hydrocarbon having at least one vinyl double bond, the average molecular weight exceeding 10,000, as determined by the herein described viscosimetric method of measurement.

24. A linear, essentially unbranched, head-to-tail polymer of an alpha-olefin of the general formula $R—CH=CH_2$, (R being an alkyl group having not more than 4 carbon atoms, or a cyclohexenyl or phenyl group) or of mixtures of such alpha-olefins, either alone or with ethylene and/or with a diolefin having at least one vinyl double bond, the average molecular weight exceeding 10,000 as determined by the herein described viscosimetric method of measurement.

25. A linear, essentially unbranched, head-to-tail, crystalline or crystallisable polymer of an alpha-olefin of the general formula $R—CH=CH_2$, (R being an aryl group) either alone or with ethylene and/or other unsaturated hydrocarbon having at least one vinyl double bond, the average molecular weight exceeding 10,000 as determined by the herein described viscosimetric method of measurement.

26. A solid crystalline or crystallisable polymer according to claim 23 or claim 24 comprising a homo-polymer of isotactic structure having an average molecular weight of more than 20,000.

27. A solid crystalline or crystallisable styrene homo-polymer of isotactic structure having an average molecular weight of more than 20,000.

28. An amorphous, linear, essentially unbranched, head-to-tail polymer of an alpha-olefin of the general formula R—CH CH. (R being an alkyl, cycloalkyl or cycloalkenyl group) or of mixtures of such alpha-olefins, either alone or with ethylene, and/or with other unsaturated hydrocarbon having at least one vinyl double bond, in which the main chain asymmetric carbon atoms of the two possible steric configurations have a random distribution along the main chain, the average molecular weight being more than 2,000 as determined by the herein described viscosimetric method of measurement.

29. An amorphous, linear, essentially unbranched polymer in accordance with claim 28 in which R is an alkyl group having not more than 4 carbon atoms or a cyclohexenyl group.

30. A solid polymer as claimed in claim 26 in which R is a CH_3 group.

31. A solid crystalline or crystallisable propylene homo polymer of isotactic structure having an average molecular weight of more than 20,000 as determined by the herein described viscosimetric method of measurement.

32. A propylene homo-polymer according to claim 31, characterised in that it has, in the crystalline state, a regular, spiral structure which corresponds to an identity period of 6.4 Angstrom units or a multiple of that value.

33. A propylene homo-polymer according to claim 28 or claim 29, characterised in that it is soluble in boiling diethyl ether, has a density below 0.90, and viscous elastic properties like those of an unvulcanized elastomer.

34. A linear, head-to-tail propylene homo-polymer, characterized in that it is insoluble in boiling diethyl ether but soluble in *n*-heptane, and is partly crystalline, the crystallinity being retained to over 100° C. and completely disappearing only above 150° C., and which behaves like an elastomer at temperatures at which a part of the crystallinity has disappeared, and becomes very viscous and liquid only at still higher temperatures.

35. A linear, head-to-tail, propylene polymer having an average molecular weight of more than 20,000, as determined by the herein described viscosimetric method of measurement and which is substantially insoluble in boiling *n*-heptane.

36. A linear, head-to-tail propylene homo-polymer characterised in that it has a density between 0.90 and 0.94, and high crystallinity and is insoluble in boiling *n*-heptane, and can be spun into filaments at temperatures above 160° C.

37. A propylene polymer as claimed in any one of claims 31 to 36, but which contains such an amount of polymerised ethylene or other polymerised olefins as does not substantially change its properties.

38. A linear, head-to-tail butene-1 polymer having an average molecular weight of more than 20,000, as determined by the herein described viscosimetric method of measurement and which is substantially insoluble in boiling ether.

39. A filament of a propylene polymer as claimed in any one of claims 31, 32 and 36, characterisesd in that after cold stretching it has a breaking load exceeding 30 kg. per square millimetre, and at the same time has an elongation at break of at least 30%.

40. A filament according to claim 39 in which the breaking load exceeds 40 kg. per square millimetre, but does not exceed 70 kg. per square millimetre.

41. A polymer as claimed in claim 26 wherein R is a C_2H_5 group and which has a melting point of at least 125° C. and is crystalline, can be spun into a filament which can be cold stretched and has good insulating properties, is flexible and has high tensile strength and elastic extensibility.

42. An amorphous polymer as claimed in

claim 28 or 29 wherein R is a C_2H_5 group, characterised in that it is soluble in boiling diethyl ether.

43. A product, particularly a foil, fibre, or filament, consisting or containing polyolefins according to any one of claims 26, 27, 31, 32, 34, 35, 36, 37, 38, or 41.

44. An elastomeric product or composition consisting of, containing or derived from a polymer of propylene as claimed in claim 28 or 33.

45. A linear, essentially unbranched, head-to-tail polymer of an alpha-olefin of the general formula R—CH CH_2 (R being an alkyl, cycloalkyl or cycloalkenyl group) or a mixture of such alpha-olefins, either alone or with ethylene, and/or with other unsaturated hydrocarbon having at least one vinyl double bond, said polymer having an average molecular weight of more than 10,000 as determined by the herein described viscosimetric method of measurement, when produced according to any of claims 1 to 19.

46. A mixed polymer which consists substantially of two fractions, one of which consists mainly of an amorphous, linear, essentially unbranched, head-to-tail homo-polymer of an alpha-olefin which fraction has an average molecular weight of more than 2,000 and in which the asymmetric carbon atoms of the two possible steric configurations have a random distribution along the main chain, and the other fraction of which contains mainly a solid homo polymer of an alpha-olefin of isotactic structure and having an average molecular weight of more than 20,000, as determined by the herein described viscosimetric method of measurement, said polymers being produced by a method according to any of claims 1 to 19 and separable into fractions according to claim 20.

47. A solid, crystalline or crystallisable propylene polymer of isotactic structure and having an average molecular weight of more than 20,000, as determined by the herein described viscosimetric method of measurement, said polymer having been produced by a method according to any of claims 1 to 19 followed by separation according to claim 21.

48. A mixed propylene polymer, consisting of three fractions, of which the first contains a propylene polymer which is soluble in boiling diethyl ether, has a density below 0.90 and viscous-elastic properties of the type of an unvulcanised elastomer; the second contains a propylene polymer which is insoluble in boiling diethyl ether but soluble in *n*-heptane, is partly crystalline, the crystallinity of which is retained to over 100° and completely disappears only above 150° C., and which behaves like an elastomer at temperatures at which a part of the crystallinity has disappeared and becomes very viscous and liquid only at still higher temperatures; and the third contains a highly crystalline propylene polymer insoluble in boiling *n*-heptane, having a melting point above 160° C. and a density of 0.90 to 0.94, said mixed polymer being produced by a method according to any of claims 1 to 19 and separable according to claim 21.

49. A polymer of butene-1, which is crystalline, has a melting point of a least 125° C., can be spun into a filament, can be stretched in the cold state, has good insulating properties, is very flexible, has high tensile strength, and elastic extensibility, and was produced by a method according to any of claims 1 to 19 followed by separation according to claim 20.

50. An amorphous polymer of butene-1, which is soluble in boiling ether, produced by a method according to any of claims 1 to 19, followed by separation according to claim 20.

51. A solid crystalline or crystallisable styrene homo-polymer of isotactic structure and having an average molecular weight exceeding 10,000 as determined by the herein described viscosimetric method of measurement, said polymer being produced by a method according to any of claims 1 to 19, followed by separation according to claim 20.

52. A copolymer of alpha-olefins of the type CH_2 - CHR with one another and/or with ethylene or with other unsaturated hydrocarbon having at least one vinyl double bond, produced according to any of claims 1 to 19.

53. A polymer of alpha-olefins having at least three carbon atoms in the molecule, or mixtures thereof with one another and/or with ethylene, and/or with other unsaturated hydrocarbons having at least one vinyl double bond, when produced by the method described and ascertained in any one of the foregoing Examples or by an obvious chemical equivalent thereof.

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