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(57) Abstract

The invention pertains to an alternating polyketone polymer composed of ethene and carbon monoxide units having a melting point above 240 °C and an intrinsic viscosity in the range of 0.3 to 2.5 dl/g, which was found to be so stable without additives that, after heating to above the melting point and cooling to room temperature, at least 40 % of the crystalline phase in the polymer has the α structure. Preferably, such a polymer is obtained by making use of a palladium complex-containing catalyst in the presence of methanol, and the obtained polymer is washed in methanol and/or 2,4-pentanedione, and/or converted to the crystallised form in a solvent that is inert toward the polymer. Preferably, the reactants are added to the lower half of the contents in the reactor, in particular near or at the bottom of the reactor. In particular, the polymers according to the invention are highly suitable for making products by melt-processing. The invention accordingly relates to melt-processed films and fibres of polyketone polymer of which at least 40 % of the crystalline phase has the α form, and to products manufactured using such films and fibres.

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POLYKETONE POLYMER, POLYKETONE PRODUCTS, AND A PREPARATIVE PROCESS

The invention pertains to an alternating polyketone polymer composed of carbon monoxide and ethene units having a melting point above 240°C and an intrinsic viscosity in the range of 0.3 to 2.5 dl/g, to a process for its production, to products made thereof, and to a process for making such products by melt processing.

Such a polymer, product, and process as mentioned above are known from US Patent Specification 4,892,697, where an alternating copolymer of carbon monoxide and ethene is heated in vacuo to 270°C and moulded to form a film. In the description of the experiment it is mentioned that the polymer film is formed by working in vacuo to attempt to reduce degradation.

EP 310 171 discloses a process for melt spinning an alternating polyketone polymer composed of carbon monoxide and ethene units, but fails to provide any information on the implementation of any such process.

EP 360 358 discloses fibres which have been melt spun from an ethene/CO copolymer. However, information on the polymer, the preparative process, the manufacture of the fibres, and the outcome is wholly lacking.

There has now been found a polymer composed of alternating carbon monoxide and ethene units which in its pure form suffers only minor degradation or none at all when exposed to temperatures between its melting point and 285°C and in addition has such a molecular structure that products made by melt processing will possess very favourable properties.

This polymer of alternating carbon monoxide and ethene units has a melting point above 240°C and an intrinsic viscosity value in the range of 0.3 to 2.5 dl/g and is characterised in that, after heating to at least 257°C for 60 seconds followed by cooling to room temperature, at least 40% of the structure of the crystalline phase in the pure polymer has the α form.

The α form of polyketone-c2 has been described by B.J. Lommerts, E.A. Klop, and J. Aerts in the Journal of Polymer Science: Part B, Vol.31 (1993), 1319-1330.

Polymer of the type indicated in the preamble of the claims is referred to hereinbelow as polyketone-c2. Although the polymer of the present invention can advantageously comprise additives such as stabilisers, fillers, or the like, when it does not comprise any such additives and, thus, is in its pure form, it will exhibit at least 40% of α structure in its crystalline phase. By pure polymer is meant here, polyketone-c2 which contains no additives such as stabilisers or other polymers, although substances foreign to the polymer remaining from the polymer preparation, e.g., remaining catalyst or solvent, may be present still in the pure polyketone-c2 described here. As a rule, such substances are present in very minute amounts, i.e., of less than 100 ppm; preferably, they are entirely absent. Some solvent can still be present in the polymer. Preferably, less than 2 wt.% or less than 1 wt.%, or no solvent at all is present.

Thus, the polymer is tested according to the following method in its pure form. The proportion of α structure in the crystalline phase is determined by X-ray analysis of the pure polymer. To this end, two hotplates are heated about 5 degrees above the temperature at which the polymer is to be heated, which is at least 257°C. Then, 5 g of polymer are heated between the two hotplates for 60 seconds, either in one go or for twice 30 seconds to allow deaeration between the 30-second periods. After said heating, the polymer is cooled in air to

room temperature. The thus obtained product has its X-ray pattern determined in the manner disclosed below. If substances foreign to the polymer such as solvents are present, the X-ray pattern of the substance to be examined is determined, after which the X-ray patterns of the substances foreign to the polymer are deducted from the X-ray pattern of the substance to be examined in a manner familiar in itself. The remaining pattern is the polymer's.
For describing the X-ray patterns use is made of the five-line Pearson VII model described in H.M. Heuvel and R. Huisman, "Five-Line Model for the Description of Radial X-Ray Diffractometer Scans of Nylon 6 Yarns," Journal of Polymer Science: Polymer Physics Edition, Vol. 19 (1981), 121-134.

Next, it is examined whether and, if so, how much of the crystalline portion of the polymer has the α structure.
The α structure referred to here is obtained from peak intensities having 2ϑ values in the ranges of 21.43° to 21.73° (the 110 reflection), 25.30° to 26.00° (the 200 reflection), and 30.75° to 31.55° (the 210 reflection). The percentage having the α form can be calculated by determining the percentage of area under the peaks corresponding to the 200 and 210 reflections of the α structure vis-à-vis the area under the peaks corresponding to the 200 and 210 reflections of the α and β structures combined.
This β structure is obtained from peak intensities having 2ϑ values in the ranges of 21.50° to 21.80° (the 110 reflection), 21.60° to 23.00° (the 200 reflection), and 28.60° to 29.70° (the 210 reflection).

As a greater percentage of the polymer's crystalline phase has the α structure, it is more suitable for being processed into a polymer product. Preferably, at least 55% of the crystalline phase of the polymer will have the α form, more particularly at least 65%, and most preferably, over 90% will have the α form.
Advantageously, the polyketone polymer still exhibits at least 40%, in

particular at least 65% or over 90%, of α form crystalline phase structure after the polymer has been heated to at least 270°C, in particular to at least 275°C for 60 seconds and cooled down to room temperature.

The new polymer is hardly subject to degradation when heated up to or above its melting point and so is highly suitable for making products by means of melt processing. The polymer now found can be turned into products by being heated up to or above its melting point and then, in its molten form, shaped by moulding, compression moulding, extruding, calandering, and other moulding techniques known in the polymer processing field.

Alternating polyketone, where the α structure is not displayed by at least 40% of the crystalline phase, was found less suitable for melt processing into products as its mechanical and other properties are insufficiently high to allow the products of such a polymer to be used.

The polymer according to the invention can be prepared by polymerising a mixture of carbon monoxide and ethene in the presence of a palladium-containing catalyst such as described in, int. al., EP 121 965, EP 181 014, and EP 391 579. Appropriate catalysts for preparing the polymer contain a complex obtained by reacting a metal salt of palladium, nickel, or cobalt, preferably a palladium salt such as palladium acetate, with an anion of an acid having a pKa of less than 2, and a phosphine bidentate. Particularly suitable for the production of polyketone-c2 according to the present invention were found to be those catalysts containing a bidentate ligand selected from 1,3-bis(diphenylphosphino)propane and 1,3-bis[di(2-methoxyphenyl)phosphino]propane and, as anion of said acid, any one of para-toluene sulphonic acid, trifluoroacetic acid, or a boric acid derivative such as described in, e.g., EP 314 309.

Preferably, however, the use of any strong Brönsted acids is avoided. Very favourable polymers according to the present invention are obtained when the solvent used in preparing the polymer is methanol or acetic acid.

The polymerisation process is favourably carried out at a pressure in the range of 1000 to 7000 kPa, more particularly in the range of 2000 to 6000 kPa, and a temperature in the range of 20° to 120°C, more particularly in the range of 50° to 100°C. Although the speed of reaction can be improved by increasing the pressure, it is found that working at very high pressures is less economical in view of the increase of the costs.

A significant improvement of the reaction yield is found if use is made of a process in which the ethene and carbon monoxide gases are added to the lower half of the contents in the reactor. Optimum results are obtained if the inlet for the reactants is near or at the bottom of the reactor. By that method, the ethene and carbon monoxide gas bubbles whirl through the polymer and catalyst comprising slurry which is present in the reactor, and the gas can be further distributed throughout the slurry by means of vigorous stirring. It was found that by this method no reduction of polymerisation velocity occurs, although the viscosity of the suspension increases to a high level.

It has been found that the stability of the polymer product, and of the amount of α structure in the polymer, is significantly improved if use is made of this process. Also, the molecular weight distribution of the polymer obtained is reduced as compared with the common process where gas is added only at the top of the reactor or just below the level of the suspension in the reactor. Moreover, the molecular weight of the polymer can be increased significantly by use of the improved process. A further improvement of the process and the advantages resulting therefrom can be had by circulating the ethene and the carbon monoxide continuously through the slurry. To this end, the gas mixture is removed from the top of the reactor, e.g., by pumping, and subsequently injected at the bottom of the reactor. In the recirculation process it is preferred that the total gas flow pumped through the slurry is at least five times the amount of gas consumed by the polymerisation reaction.

To maintain the pressure in the reactor, ethene and/or carbon monoxide or a gas causing chain transfer reactions or a gas which is inert to the reaction mixture or mixtures thereof can be added separately or together with the recycling gas mixture. The better the dispersion of the gas through the slurry in the reactor is, the greater the improvements mentioned above will be.
Preferably, a slight excess of ethene gas is used if the molecular weight of the polymer is desired to be above an intrinsic viscosity of 0.5 dl/g.

In another preferred embodiment, the reaction process is carried out as a continuous process. Examples thereof are found in the use of a tube reactor means, a loop reactor means, a cascade of continuously stirred tank reactors, or other means. It was found that very stable polymers comprising a very high portion of α structure in the crystalline phase after having been heated to temperatures of 265°C for 60 seconds and cooled down to room temperature are obtained if use is made of a continuous process consisting of a cascade of reactor means which have the gas inlet pipe near or at the bottom of the reactor.

According to a preferred embodiment of the process for preparing the polymer according to the present invention, there is the fullest possible removal of contaminants from the polymer after it has been taken from the autoclave. To this end, it may be washed thoroughly with methanol of 0° to 80°C, preferably of 0° to 40°C, or with

2,4-pentanedione of 80° to 140°C, preferably of 80° to 120°C. Alternatively, there may be washing with a mixture of these compounds at a temperature in the range of 0° to 120°C, depending on the composition of the washing agent. More favourable results still can be obtained when several washing steps using any one or a combination of said washing liquids are carried out. The washing may take place immediately after the polymer is obtained from the reaction, or at a later time.

By another method, good results are attained when the polymer, after it has been washed or not, is recrystallised from an appropriate medium inert to the polymer, such as benzyl alcohol or propylene carbonate. This method is in particular suitable for polymer material of the present invention of which the stability is not as high as desired for a particular purpose, say, for polymer material having less than 55% in the α form.

After washing and/or recrystallisation or, if there is no washing, after filtering off from the reactor, the polymer is dried, preferably under vacuum or nitrogen. The polymer can be dried advantageously at a temperature in the range of 0° to 80°C, preferably in the range of 0° to 40°C. It was found that the optimum drying temperature is dependent on the purity of the polymer to be dried.

The intrinsic viscosity of the employed polyketone is between 0.3 and 2.5 dl/g, more particularly between 0.5 and 2.3 dl/g, preferably between 0.8 and 2.0 dl/g.

The intrinsic viscosity of the polymer, which is also indicated as $[\eta]$, is determined by the equation

$$[\eta] = \lim_{c \to 0} \frac{\eta spec}{c} = \lim_{c \to 0} \frac{t - t_o}{t_o . c}$$

and so represents the ratio between the flow times t and t_o, with t_o and t standing for the flow times of the solvent and the polymer-containing solution, respectively, in a capillary viscometer at 25°C. In this determination c stands for the polymer concentration in meta-cresol, expressed in grams per deciliter.

Of the alternating polyketone composed of ethene and carbon monoxide units according to the prior art, 0-100% of the crystalline part of the polymer can exhibit the α structure, but said α structure, if present at all, does not reappear upon cooling after the polymer has been heated up to or above its melting point. It was found that the α structure is no longer formed as the polymer is cooled to room temperature when the molecular chains display defects; such defects result from degradation of the polymer through heating up to or above its melting point, the melting point for polyketone-c2 as a rule being above 240°C and generally in the range of 252° to 260°C. With polymers according to the art, such degradation was found to occur even with a good stabiliser present.

In most cases, the objectionable structure of the crystalline phase of the polymer found when there is mild degradation of the polymer after heating and cooling to room temperature, will be the β structure. Likewise, the crystal structure of the chain will be so disturbed by the presence of units other than ethene/CO, e.g., propene/CO units, that it is incapable of forming an α structure upon melt crystallisation. Polyketone-c2 according to the invention will not contain more than 2 to 3% of propene units, calculated on the amount of ethene units present in the polymer. The presence of a greater quantity of propene units in the polymer so disturbs the molecular chains that the polymer structure will hardly have the α form anymore.

Obviously, the addition of an appropriate stabiliser will cause still less degradation to occur when the polymer is heated up to or above its melting point. Of a polymer to which a stabiliser such as an anti-oxidant, an acid scavenger, some other appropriate stabiliser, or mixtures thereof, has been added, a greater percentage will consequently have the α form after it has been heated to above its melting point.

Suitable as stabilisers are those according to the general formula $M_{10}(PO_4)_6(OH)_2$, wherein M stands for barium, strontium or calcium, anti-oxidants and/or other acid scavengers.

Examples of suitable stabilisers for the polymers according to the invention are calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) to which at least one or more acid scavengers and/or one or more anti-oxidants have been added in small quantities. Examples of suitable stabilisers are those which in addition to calcium hydroxyapatite contain acid scavengers such as epoxide compounds, e.g., resins such as Epon Resin DPS-14 ex Shell or DEN 444 ex Dow Chemical and/or anti-oxidants of hindered phenols, e.g., Irganox 1010, Ethanox 330 or Ethanox 398; combinations of hindered phenols and phosphites such as Irganox B 215 (Ciba-Geigy); or combinations of hindered phenols, phosphites, and epoxide compounds; alkylated diphenyl amines such as Naugard 445 ex Uniroyal Chemical or aromatic polycarbodiimides such as Staboxol P ex Rhein Chemie Corp. Very favourable results may be obtained by the addition of 0.5-4 wt.% of calcium hydroxyapatite, 0-1 wt.% of Irganox B 215, and 0-1 wt.% of DEN 444.

In addition, to improve particular properties other adjuvants may be added to the polymer. Preferably, the polymer contains less than 10 wt.%, more particularly less than 5 wt.%, of non-polymeric substances.

Using a polymer according to the invention, optionally in the presence of a stabiliser, makes it possible to manufacture products by moulding the polymer at a temperature of 265°C or higher, with at least 40% of the crystalline phase of the polymer retaining the α form after the obtained product has been cooled to room temperature. Preferably,

products are melt processed at a temperature of 270°C or higher, with at least 40% of the crystalline phase of the polymer from which the products have been made having the α form. It has been found that heating the polymer to a temperature of 265°C, more particularly of 270°C, will cause any polymeric nuclei for crystallisation present to virtually disappear, in particular when shear is applied. This is found to be advantageous in particular with respect to the tensile properties of the product in the solid state, such as fibres made from the polymer.
The most desired polymer is found if the polymer has at least 80% in the α form after being heated to 270°C for at least 60 seconds, with the heating means having a starting temperature of 5°C above said temperature.

Because the polyketone-c2 polymer according to the invention can be melt processed into products having good physical properties, the polymer is especially suited to be melt processed into products of which at least on dimension is of very small size. Examples of such products include films, tapes, hollow fibres, and fibres.
For instance, it has been found that, in terms of strength and modulus, melt processed polyketone-c2 products of which the dimension in at least one direction is less than 200 μm and at least 40% of the crystalline phase is in the α form are significantly superior to products with a lower percentage in the α structure.

In consequence, the invention also pertains to products of a polyketone polymer of alternating carbon monoxide and ethene units of which the dimension in at least one direction is less than 200 μm and having an intrinsic viscosity in the range of 0.3 to 2.5 dl/g, which polymer has been obtained by being moulded at a temperature higher than or equal to its melting point, and is characterised in that at least 40% of the crystalline phase of the polymer is in the α form.

Products having a dimension of less than 60 μm in two directions, such as fibres, which are melt processed from polymers of which at least 40% of the crystalline phase is in the α form are of particular importance. Although there has been a clear need for products of such dimensions made by melt processing, it has been impossible to make them up to now.

It is now possible to make such products by heating a suitable polyketone-c2 polymer to a temperature at or above its melting point and below 285°C, preferably of about 270°C, using a spinning pump to force it through a plate provided with a number of small orifices, and cooling the resulting extrudates, optionally before or after their being drawn. It was found that, in a number of cases, the proportion of polymer in the α structure will increase as a result of the drawing, at the expense of the polymer in the β structure.
The drawn products preferably have an initial modulus, at an elongation of less than 0.2%, in the range of 1.10 to 26.5 N/tex, more particularly in the range of 3.8 to 19 N/tex, and a tenacity in the range of 250 to 1500 mN/tex, more particularly in the range of 500 to 1500 mN/tex. In a preferred embodiment, the product is a fibre filament which has a strength of at least 600 mN/tex, in particular a fibre having an initial modulus of at least 5.5 N/tex, or at least 6.9 N/tex.

A superior process still is achieved by drawing the product resulting from the practice of the above-described process to at least thrice its original length. The drawing is preferably carried out at elevated temperatures, with the heat transfer medium during drawing preferably being set at a temperature between 180° and 250°C for the first drawing step. The melting temperature of the obtained product is increased as a result of the drawing. The drawing temperature for any further drawing steps is determined by the melting temperature of the product to be further drawn and will preferably be in the range of

180°C to the melting temperature of the product to be drawn minus 10°C. It is preferred for the maximum drawing temperature not to be in excess of 265°C. Preferably, the product is drawn in at least three steps. By drawing the polymer at least five times, and preferably more than nine times, fibres are obtained with better properties still for industrial application. When the crystalline phase of the polymer of which such fibres are mostly composed is analysed, at least 55%, more particularly 70%, more particularly still 80%, and preferably more than 94% of it, exhibits the α-structure.

Polyketone-c2 products having one or two dimensions of very small size, such as fibres, films, or tapes, where the polymer from which they are made wholly has the α structure, are known in themselves. Such products were made by dissolving polymer of alternating ethene and carbon monoxide units in an appropriate solvent, without the polymer being heated to a temperature equal to or higher than its melting point. However, the wet-spin or wet casting process employed is attended with drawbacks of a predominantly economical nature, which result in the obtained products being too expensive for many major industrial application areas.

It was found that, because of the combination of favourable properties, such as the polyketone-c2 polymer's superior adhesion to rubber and polyvinyl chloride, and the economically advantageous manufacturing process, the products according to the invention with dimensions of less than 200 μm in at least one direction are particularly suited for use as reinforcing material, e.g., in laminates, and more particularly for flexible composites, int. al., mechanical rubber goods such as car tyres, conveyor belts, and rubber hose, and, e.g., composites containing polyvinyl chloride. The very favourable price/performance ratio of the reinforcing material also makes for an improved price/performance ratio of mechanical rubber goods so reinforced, e.g., car tyres.

The invention will be further illustrated with reference to the following examples. In these examples, tenacity, initial modulus (IM), and maximum modulus (MM) were obtained by breaking a single filament on an Instron tester. The gauge length for single broken filaments was about 100 mm. The test elongation rate was 10% per minute.
The tenacity, elongation, and initial modulus as defined in ASTM D 2256-88, published April, 1988, were obtained from the load-elongation curve. The maximum tangential modulus was determined as the maximum angle of inclination of the stress-strain curve for elongation in excess of 0.2%. Where the drawing rates are indicated, 100% per minute means that drawing took place at a rate of 30 mm/min.

EXAMPLE I

A catalyst mixture was prepared by dissolving 36.8 mg of palladium(II)-acetate, 68.8 mg of 1,3-bis-diphenyl-phosphino-propane, and 63.4 mg of para-toluene-sulphonic acid in 100 ml of methanol at room temperature and with continuous shaking.

The preparation of alternating polyketone copolymer was as follows:
The catalyst mixture was charged to a 6.4 l autoclave, whereupon 3400 ml of methanol were added. The reactor was flushed three times by alternately having pressures of 500 kPa N_2 and atmospheric.
After the final flushing the reactor pressure was brought to about 4100 kPa by adding a mixture of CO and C_2H_4 (molar ratio 1:1).
Next, the reactor contents were heated to 85°C and kept at 83°C for 16 hours, during which time, with stirring, the reaction between the carbon monoxide and the ethene took place. The pressure in the reactor was 4730 kPa at the outset of the reaction and about 3510 kPa at its conclusion. The pressure in the reactor was regulated by controlling the amount of CO and ethene mixture added. The molar ratio of the carbon monoxide and the ethene in the mixture was 1:1 at all times.

On conclusion of the reaction the reactor contents were cooled to about 30°C and the gaseous shield was blown off. The reactor was flushed with nitrogen three times, and its milky contents were transferred to a beaker and then immediately filtered. The filter cake which was left on the filter was then washed with about 3 l of methanol of approximately room temperature. Next, the filter cake was dried in vacuo at about 70°C. The drying period was 60 hours.

Part of the polymer was washed with methanol again, by rinsing methanol and polymer in a weight ratio of 10 in an Erlenmeyer at room temperature for 12 hours. The polymer was drained off on a filter and subsequently dried in vacuo at 65°C for 6 hours.

Obtained in this way were 600 g of polyketone-c2 polymer having an intrinsic viscosity of 0.57 dl/g and a bulk density of 380 kg/m^3.

The thus obtained washed, but unstabilised polyketone-c2 polymer was moulded between two 257°C hotplates. Next, the moulded film was released from the plates and slowly cooled in air. The resulting product had a milky white colour, which is considered to indicate the absence of polymer degradation.
The obtained film had a thickness of 120 μm. This film was cut up into strips of 3 mm by 60 mm, which were then subjected to X-ray analysis.

X-ray analysis as specified hereinbefore gave the following peaks:

TABLE I

Peak area rel.%	peak position °2ϑ	halfwidth °2ϑ	hkl-α		hkl-β
45.0	20.76	8.10		amorph.	
31.0	21.69	0.41		110	
9.4	22.45	0.59			200
3.1	24.68	0.74		111	
6.9	25.71	0.64	200		
2.3	29.30	0.54			210
2.1	31.34	0.94	210		

The proportion of the crystalline phase of the polymer having the α form thus was 0.435, which corresponds to 43.5%.

The polyketone-c2 strips were drawn at 245°C to about eight times their original length. The tenacity measured on the resulting product was found to be 620 mN/tex, the initial modulus was 6.8 N/tex, and the elongation at break 14%.
The product did not suffer discolouration.

X-ray analysis of the drawn fibres gave the following peaks:

TABLE II

Peak area rel.%	peak position °2ϑ	halfwidth °2ϑ	hkl-α		hkl-β
23.0	21.90	9.50		amorph.	
48.0	21.61	0.74		110	
2.7	22.46	0.84			200
2.9	24.82	1.83		111	
16.7	25.81	1.17	200		
1.7	29.31	0.89			210
4.8	31.26	1.19	210		

The proportion of the crystalline phase of the polymer having the α form thus was 0.83, which corresponds to 83%.

In other words, the percentage of polymer with a crystalline phase having the α form had increased from 43.5% to 83% as a result of the drawing.

EXAMPLE II

A catalyst mixture was prepared by dissolving 12.8 mg of palladium(II)-acetate, 24.6 mg of 1,3-bis(diphenylphosphino)propane, and 25.0 mg of para-toluene-sulphonic acid in 20 ml of methanol at room temperature and with continuous shaking.

The preparation of alternating polyketone copolymer was as follows:
Charged into a 1.8 l stainless steel reactor were 660 g of 99-100%-acetic acid. Next, with stirring, the oxygen present was removed by alternately raising the pressure in the reactor to 500 kPa using nitrogen and then creating a vacuum. This procedure was repeated twice.
The catalyst solution was charged to the reactor with the aid of the reactor vacuum. Next, the pressure in the reactor was raised to about 2000 kPa by adding a mixture of CO and C_2H_4 in a molar ratio of 1:1.
The reactor contents were then heated to 80°C, after which the pressure was set at 5400 kPa using a 1:1 gas mixture of CO and C_2H_4. After two hours the reactor pressure was found to have decreased to 3800 kPa, and the reactor was cooled.
The excess pressure was blown off, and the contents of the reactor were filtered off and washed with 1 l of water. Next, the filter contents were deprived of as much water as possible and then dried in vacuo at 50°C for 48 hours. In this way 27 g of polymer with an intrinsic viscosity of 2.3 dl/g were obtained.

Of this polymer, 5.46 g were then dissolved in 100 ml of propylene carbonate at 206°C under an atmosphere of nitrogen and using an oil bath. The resulting solution was slightly cloudy and had a greyish/beige colour.

Next, with stirring, the solution was cooled to room temperature, with polymer crystallisation occurring. The mixture was passed through a filter, and 200 ml of methanol were added to the filter contents. This mixture was vigorously stirred and then filtered. Such washing with methanol was repeated twice more, with the polymer being left to stand in the methanol for about 14 hours prior to being filtered off during the third washing. The polymer was then dried at 40°C for one hour at a pressure of 11 mbar and subsequently subjected to additional drying _in vacuo_ at 40°C for four hours. The obtained polymer had a melting temperature of 257°C.

A portion of the thus obtained unstabilised polymer was then moulded between two 260°C hotplates for five minutes. Next, the moulded film was released from the plates and slowly cooled in air. The resulting product was transparent and had a very pale brownish/green colour. There was found not to have been any gas evolution.

The obtained film had a thickness of 160 μm. This film was cut up into strips of 2 mm by 60 mm, which were then subjected to X-ray analysis.

X-ray analysis as specified hereinbefore gave the following peaks:

TABLE III

Peak area rel.%	peak position °2ϑ	halfwidth °2ϑ	hkl-α		hkl-β
0.77	20.40	7.50		amorph.	
0.09	21.66	0.47		110	
0.09	22.04	0.81			200
0.02	24.66	0.92		111	
-- *	--*	---*	200		
0.01	29.25	0.60			210
0.01	31.77	0.37	210		

* could not be distinguished.

The proportion of the crystalline phase of the polymer having the α form was 0.50, calculated on the area under the peaks corresponding to the 210 reflections (α:(α+β)). This is therefore consistent with 50% of α structure. It is clear from this data that even with exposure to temperatures above the polymer's melting point for a lengthy period, a substantial proportion of the crystalline phase of the polymer still had the α structure.

The strips of polyketone-c2 were drawn at a temperature of 245°C. Some of the strips were drawn to about 4.5 times their original length, others to about 9.5 times their original length. The tenacity measured on the product drawn 4.5 times was found to be 300 mN/tex, the initial modulus was 2.27 N/tex, and the elongation at break 18.4%.
The tenacity measured on the product drawn 9.5 times was found to be 590 mN/tex, the initial modulus was 8.33 N/tex, and the elongation at break 7.2%.
The product was transparent and, as regards colour, practically clear to very pale brownish/green.

Since polymerisation microscopy failed to show any clear spherulitic structure, it may be concluded that persistent nuclei were not present at all or only present in a very minute amount.

X-ray analysis of the fibres drawn 4.5 times gave the following peaks.

TABLE IV

Peak area rel.%	peak position °2ϑ	halfwidth °2ϑ	hkl-α		hkl-β
0.20	21.29	5.1		amorph.	
0.55	21.72	0.4		110	
0.06	22.38	0.1			200
--*	----*	--*		111	
0.13	25.77	1.7	200		
0.05	29.28	0.5			210
0.02	31.25	0.2	210		

* could not be distinguished.

The proportion of the crystalline phase of the polymer having the α form thus was 0.58, which corresponds to 58%.

X-ray analysis of the product drawn ten times gave the following peaks.

TABLE V

Peak area rel.%	peak position °2ϑ	halfwidth °2ϑ	hkl-α		hkl-β
0.20	21.50	5.50		amorph.	
0.49	21.80	0.78		110	
0.13	22.25	1.03			200
---*	----*	---*		111	
0.10	25.84	1.37	200		
0.07	29.36	0.97			210
0.02	31.35	1.17	210		

* could not be distinguished.

The proportion of the crystalline phase of the polymer having the α form thus was 0.38, which corresponds to 38%.

EXAMPLE III

Preparation of the polymer

The preparation of alternating polyketone copolymer was as follows: A 170 l stainless steel reactor was equipped with an inlet at the bottom of the reactor, via which the gases, int. al., ethene and carbon monoxide, were added to the reactor, and a gas circulation system. Charged into the reactor were 125 l methanol and 500 g polyketone-c2 with an intrinsic viscosity of 1.1 dl/g. Next, the oxygen present was removed by alternately raising the pressure in the reactor to 500 kPa using nitrogen and then creating a vacuum. This procedure was repeated three times.

The reactor was pressurized by adding carbon monoxide via the inlet in such a manner that the pressure was 50 kPa. Using this reduced pressure in the reactor, a catalyst solution of 0.645 g of palladium(II)-acetate, 1.503 g of 1,3-bis-diphenyl-phosphino-propane, and 1.510 g of para-toluene-sulphonic acid in 500 ml trifluoroethanol were added. Carbon monoxide and ethene were added such that an excess of 3.2 kg of ethene was added to the reactor via the inlet and the pressure in the reactor was raised to about 1500 kPa. The reactor contents were then heated to 60°C, the pressure being kept at 2100 kPa using a 1:1 gas mixture of CO and C_2H_4. The pressure and the temperature were maintained for 72 hours. Using the gas circulation system the gas from the top of the reactor was circulated through the slurry in the reactor via the inlet at the bottom. Including the 100 to 150 m^3 of gases added and reacted per hour, 17000 m^3 per hour were circulated. It was found that there was an increase in productivity in the reactor despite the increased viscosity of the suspension in the reactor.

Subsequently, the contents of the reactor were filtered off using a filter with a diameter of 1 m and then washed with 125 l of methanol. The product from the filter was dried in a Nauta mixer for about 70

hours at a temperature of 60°C and a pressure of 0.10 kPa.
About 14 kg of polyketone-c2 product were obtained with an intrinsic viscosity of 1.82 dl/g and a melting temperature of 250°C. The polymer comprised less than 22 ppm of Pd.

Preparation of fibres
A portion of the thus obtained unstabilised polymer was then moulded between two hotplates for 60 seconds by use of a force of 50 kN. The temperature of the hotplates at the moment the polymer was added to the plates was 270 °C for sample III A and 275 °C for sample III B. During the pressing, the plates lost some heat - the temperature drop being no more that about 5°C - due to the polymer and the polymer support plates absorbing the heat of the plates. Next, the moulded film was released from the support plates and cooled in air. The resulting products were transparant and clearly white, no discolouration being observed.

The films so obtained had a thickness of about 100 μm, and were cut up into several small strips. These strips were then subjected to X-ray analysis. The III A sample in the undrawn form showed that 67 % of the crystalline phase of the polymer had the α structure. The III B sample in the undrawn form showed that 54% had the α structure.

Next, the samples were drawn at an initial drawing rate of 100% per minute at a temperature of 225°C to a draw ratio indicated as λ in TABLE VI, and the percentage of the crystalline phase showing the α structure was determined by X-ray analysis. A sample III A was drawn to λ being 8.0, and 48% of the crystalline phase showed the α structure. A film strip of sample III B was drawn under the same conditions, resulting in λ being 5.7 and 63% of the crystalline phase of the fibre obtained showing the α structure. The results are indicated below.

TABLE VI

Sample no.	tenacity [mN/tex]	el. at break [%]	IM [N/tex]
III A	734	9.5	6.5
III A	672	9.6	6.3

EXAMPLE IV

Preparation of the polymer

The preparation of alternating polyketone copolymer was as follows: Charged into a 170 l stainless steel reactor were 125 l methanol and 500 g polyketone-c2 with an intrinsic viscosity of 1.1 dl/g. The reactor was equipped with an inlet at the bottom of the reactor, via which the gases, int. al., ethene and carbon monoxide, were added to the reactor. Next, the oxygen present was removed by alternately raising the pressure in the reactor to 500 kPa using nitrogen and then creating a vacuum. This procedure was repeated three times.

The reactor was pressurized by adding carbon monoxide via the inlet in such a manner that the pressure was 50 kPa. Using this reduced pressure in the reactor, a catalyst solution of 0.645 g of palladium(II)-acetate, 1.510 g of 1,3-bis-diphenyl-phosphino-propane, and 1.512 g of para-toluene-sulphonic acid in 500 ml trifluoroethanol was added. Carbon monoxide and ethene were added such that an excess of 1.6 kg of ethene was added to the reactor via the inlet and the pressure in the reactor was raised to about 1500 kPa. The reactor contents were then heated to 60°C, the pressure being kept at 2100 kPa using a 1:1 gas mixture of CO and C_2H_4. The pressure and the temperature were maintained for 72 hours. After the reaction, the pressure was kept at a constant level for four hours by the use of ethene, after which the gas inlet was closed.

After a further 65 hours, the contents of the reactor were filtered off using a filter with a diameter of 1 m and then washed with 100 l of methanol. 78.8 kg of slurry were obtained from the filter.

Of the filter product, about 52.5 kg were dried in a Nauta mixer for about 70 hours at a temperature of 60°C and a pressure of 0.15 kPa. About 10.5 kg of polyketone-c2 product were obtained with an intrinsic viscosity of 1.49 dl/g and a melting temperature of 253°C. About 20% of the polymer obtained had the α structure. It was found that there was a significant increase in productivity in the reactor. After about 800 minutes, a gas consumption corresponding to a polymer production rate indicated as grams of polymer obtained per gram of Pd per hour of about 400 was observed. Hence, the reaction rate increased over time even though the viscosity of the formed methanol and polymer comprising slurry was increased significantly. After about 4200 minutes, a gas consumption corresponding to a polymer production rate of about 1100 was observed.

Preparation of the fibres

A portion of the thus obtained unstabilised polymer was then moulded between two hotplates for 60 seconds. The temperature of the hotplates at the moment the polymer was added to the plates is indicated in the table below. During the pressing, the plates lost some heat - the temperature drop being no more that about 5°C - due to the polymer and the support plates absorbing the heat of the plates. Next, the moulded film was released from the support plates and cooled in air. The resulting product was clearly white, no discolouration being observed.

The film so obtained was cut up into several strips having a linear density as indicated below, which strips were then subjected to X-ray analysis. The results are indicated below.

TABLE VII

Sample no	starting temperature [°C]	α form [%]	lin.dens. [dtex]
IV	as polymerized	20	powder
IV A	260	87	3029
IV B	265	87	2309
IV C	270	89	3057

The resulting samples were analysed for their physical properties. The results are as follows.

TABLE VIII

Sample no.	tenacity [mN/tex]	el. at break [%]	IM [N/tex]	MM [N/tex]
IV A	57	22	1.45	0.80
IV B	55	27	1.30	0.55
IV C	56	27	1.35	0.65

The fibres were subsequently drawn at initial drawing rates of 100% per minute to a draw ratio λ as indicated, and the physical properties of the drawn fibres were measured and are indicated in TABLE IX.

TABLE IX

Sample no.	λ	α form [%]	tenacity [mN/tex]	el. at break [%]	IM [N/tex]	MM [N/tex]
IV A	8.7	87	460	7.8	6.90	9.15
IV A	8.8	82	719	10.9	7.90	7.90
IV B *	9.3	95	373	7.5	5.90	8.50
IV C	8.9	77	520	7.8	7.30	7.45
IV C	8.6	84	605	9.7	6.95	8.30

* drawn at 120 % per minute

Other fibres of samples III A, B, and C were also drawn at initial drawing rates of 250% per minute, and the physical properties of the drawn fibres were measured and are indicated in TABLE X.

TABLE X

Sample no.	λ	α form [%]	tenacity [mN/tex]	el. at break [%]	IM [N/tex]	MM [N/tex]
IV A	8.2	59	768	10.6	8.80	8.20
IV A	8.0	56	668	9.5	8.10	8.10
IV B *	8.2	72	125	5.6	2.20	4.55
IV C	8.3	60	634	10.6	7.05	6.60

* drawn at 275% per minute

Other fibres of samples III A and C were drawn at initial drawing rates of 700% per minute, and the physical properties of the drawn fibres were measured and are indicated in TABLE XI.

TABLE XI

Sample no.	λ	α form [%]	tenacity [mN/tex]	el. at break [%]	IM [N/tex]	MM [N/tex]
IV A	8.0	44	573	8.6	7.90	8.95
IV A	8.3	47	555	8.6	6.90	7.40
IV C	7.7	44	644	11.7	6.10	6.40

Claims

1. An alternating polyketone polymer composed of carbon monoxide and ethene units having a melting point above 240°C and an intrinsic viscosity in the range of 0.3 to 2.5 dl/g, characterised in that after heating to at least 257°C for 60 seconds followed by cooling to room temperature, at least 40% of the structure of the crystalline phase in the pure polymer has the α form.

2. An alternating polyketone polymer according to claim 1, characterised in that after heating to at least 270°C for 60 seconds followed by cooling to room temperature, at least 40% of the structure of the crystalline phase in the pure polymer has the α form.

3. An alternating polyketone polymer according to either of claims 1 or 2, characterised in that at least 65% of the structure has the α form.

4. An alternating polyketone polymer according to claim 3, characterised in that at least 90% of the structure has the α form.

5. An alternating polyketone polymer according to any one of the preceding claims, characterised in that the polymer is made using a palladium complex-containing catalyst in the presence of methanol, and the obtained polymer is washed in methanol and/or 2,4-pentanedione.

6. An alternating polyketone polymer according to any one of claims 1-3, characterised in that the polymer is made using a palladium complex-containing catalyst in the presence of methanol, and the

obtained polymer is converted to the crystallised form by being dissolved in an appropriate solvent that is inert toward the polymer and subsequently crystallised.

7. A process for the production of an alternating polyketone polymer of carbon monoxide and ethene units by reaction of carbon monoxide and ethene in the presence of a catalyst and a solvent, characterised in that the process is carried out by adding the carbon monoxide and ethene gases to the lower half of the contents in the reactor.

8. A process according to claim 7, characterised in that the carbon monoxide and ethene gases are added near or at the bottom of the reactor vessel.

9. A product made of an alternating polyketone polymer composed of carbon monoxide and ethene units, characterised in that the product is made of a polymer according to any one of claims 1 through 6.

10. A product made of an alternating polyketone polymer composed of carbon monoxide and ethene units obtained by moulding the polymer at a temperature above its melting point, characterised in that the product is made by moulding at a temperature of at least 265°C and, after cooling of the polymer product to room temperature, at least 40% of the crystalline phase has the α form.

11. A product according to claim 10, characterised in that the product is made by moulding at a temperature of at least 270°C and, after cooling of the polymer product to room temperature, at least 40% of the crystalline phase has the α form.

12. A product according to any one of claims 9-11, characterised in that the product has a dimension of less than 200 μm in at least one direction.

13. A product according to claim 12, characterised in that the product has a size of less than 60 μm in two directions.

14. A product according to claim 13, characterised in that the product is a fibre filament which has a tenacity of at least 600 mN/tex.

15. A product according to either of claims 13 or 14, characterised in that the product is a fibre filament which has an initial modulus of at least 5.5 N/tex.

16. A product according to claim 15, characterised in that the fibre filament has an initial modulus of at least 6.9 N/tex.

17. A process for spinning a polyketone polymer, characterised in that the polymer to be spun is a polymer according to any one of claims 1-6 and the fibre is spun at a temperature at or above the polymer's melting point and lower than or equal to 285°C.

18. A reinforced mechanical article of rubber, such as a car tyre, which contains as reinforcing material a product according to any one of claims 12-16.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 94/00596

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08G67/02 D01F6/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08G D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 296 687 (SHELL) 28 December 1988 see claims 1-10; example 1 ---	1
Y	WO,A,90 14453 (STAMICARBON) 29 November 1990 see page 12, line 10 - page 13, line 9 see page 4, line 35 - page 5, line 18 see page 3, line 13 - line 23 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Stienon, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte. onal Application No
PCT/EP 94/00596

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