

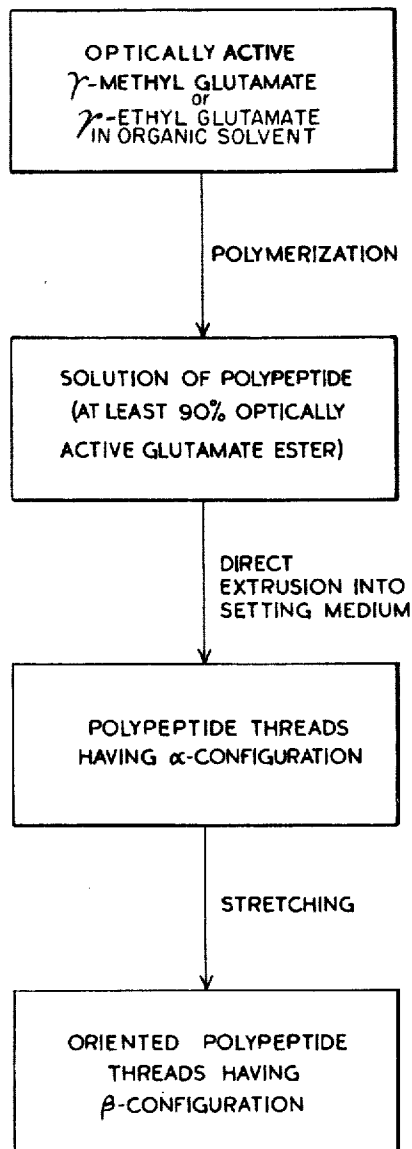
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PRODUCTION OF ARTIFICIAL THREADS

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## PRODUCTION OF ARTIFICIAL THREADS

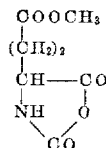
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This invention relates to the production of artificial threads and is particularly concerned with the production of threads from the polypeptides poly-gamma-methyl-L-glutamate and poly-gamma-methyl-D-glutamate. The term "threads" is used generally to include all filamentary forms such as fibres, threads, filaments, monofilaments, staple fibres and the like. This application is a division of my copending application Serial No. 94,069, filed March 7, 1961. Said application Serial No. 94,069 is itself a continuation-in-part application of my applications Serial Numbers 805,180, filed April 9, 1959, 9,153, filed January 22, 1960, and 27,260, filed May 6, 1960. Said applications Serial Nos. 805,180, 9,153 and 27,260 were copending with said application Serial No. 94,069 but have now been abandoned.

It is known that N-carboxy-amino-acid anhydrides in the presence of suitable initiators undergo polymerisation with the loss of carbon dioxide to form polypeptides. Among the N-carboxy-amino-acid anhydrides which may be used are those of the optically active forms of gamma-methyl-glutamate which have the formula:



In the Bamford and Hanby Patent No. 2,697,085 a process is disclosed for producing threads from synthetic polypeptides by extruding through a jet into a setting medium a solution of the polypeptide in a solvent consisting of or comprising a monohydric phenol, a lower aliphatic carboxylic acid, a halogen substituted lower aliphatic carboxylic acid, or mixtures of these compounds. The setting medium may be a coagulating bath such as water, a lower alcohol, aqueous alcohols and ether or petroleum ether alone or mixed with an alcohol.

The present invention provides a method for making novel threads having desirable textile properties consisting essentially of units derived from one only of the optically-active forms of gamma-methyl or gamma-ethyl glutamic esters, namely poly-gamma-methyl-L-glutamate, poly-gamma-methyl-D-glutamate, poly-gamma-ethyl-L-glutamate.

The new fibres of the present invention are crystalline fibres consisting essentially of poly-gamma-methyl-L- or D-glutamate or poly-gamma-ethyl-L- or D-glutamate substantially in the  $\beta$  configuration and exhibiting a substantial amount of orientation as determined by X-rays, and having characteristic X-ray diagrams and infra-red spectra as indicated below; cross-sections of the fibres generally closely resemble those of natural silk.

The fibres of this invention preferably consist of homopolymers of poly-gamma-methyl-L- or D-glutamate or of poly-gamma-ethyl-L- or D-glutamate but the advantages of this invention can be substantially obtained using copolymers of one of the esters consisting essentially of units of one optically-active form only, that is to say copolymers containing at least 90 percent by weight of

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gamma-methyl-L- or D-glutamate units or of gamma-ethyl-L- or D-glutamate units with not more than 10 percent by weight of one or more other N-carboxy anhydrides such as the anhydrides of leucine, phenylalanine, norleucine, isoleucine, gamma-benzyl-glutamate. It is also possible to use a mixture of the optically-active forms of poly-gamma-methyl-glutamate or of poly-gamma-ethyl-glutamate provided that at least 90 percent by weight of the mixture consists of one optically active form only.

The  $\alpha$  configuration is one in which the polypeptide chains are folded in a regular manner, and in which all the hydrogen bonds joining together CO and NH groups of different amino acid residues are intra-chain in character. The  $\beta$  form has no specific or regular folds, the polypeptide chains being fully extended or coiled in a random manner; hydrogen bonds between CO and NH groups are formed between suitably placed groups, irrespective of whether these are located in the same polypeptide chain or not. As a rule, the hydrogen bonds are inter-chain in character in the  $\beta$  form.

The process in accordance with this invention for making the new fibres comprises forming a polymer consisting essentially of gamma-methyl-L- or D-glutamate or of gamma-ethyl-L- or D-glutamate in solution by polymerisation of gamma-methyl-L- or D-glutamate N-carboxylic anhydride or the corresponding ethyl derivative in an organic liquid or mixture of liquids which is a solvent for the polypeptide so produced, extruding a solution of the polypeptide which has been maintained in the solvated state so that the polypeptide is in the  $\alpha$  configuration on extrusion, and stretching the resultant threads whereby the polypeptide is substantially converted into the  $\beta$  configuration and the fibre is substantially oriented along its axis. The polypeptide solution may be dry spun or wet spun, that is to say the setting medium may be a gas such as air which may be heated, or may be a coagulating bath which is a non-solvent for the polypeptide but is a solvent for the polypeptide solvent.

The fibres made according to this invention are produced from polymers consisting essentially of gamma-methyl-L- or D-glutamates or of gamma-ethyl-L- or D-glutamates and having a reduced viscosity of at least 1.4 so that the resultant threads obtained will have adequate tensile properties for normal textile purposes; the polymers based on the methyl glutamates preferably have a reduced viscosity of at least 2.0 and for those based on the ethyl glutamates, the reduced viscosity is preferably at least 2.5. In this specification reduced viscosity is defined as  $\eta_{sp}/c$  where  $\eta_{sp}$  is the specific viscosity of a solution having a concentration of c. grams per 100 cc. of solution.

The infra-red spectrum of a bundle of oriented, crystalline poly-gamma-methyl-L- or D-glutamate fibres made according to this invention has a marked absorption band in the region 4520–4540  $\text{cm}^{-1}$  which shows the presence of the extended chain or  $\beta$  polypeptide configuration. For the corresponding polyethyl glutamate fibres the marked absorption band is in the region 4510–4530  $\text{cm}^{-1}$ . When polarised radiation is used to observe the infra-red spectrum, both bands show marked parallel dichroism, being strong when the electric vector is parallel to the fibres, but vanishingly weak in the perpendicular direction, which shows that these  $\beta$  polypeptide chains are highly oriented. The predominance and orientation of the  $\beta$  form is also shown by the parallel dichroism seen in a band at 4850–4875  $\text{cm}^{-1}$ , for the methyl glutamate fibres and at 4840–4860  $\text{cm}^{-1}$ , for the ethyl glutamate fibres. The behaviour of both of those bands in polarised radiation is qualitatively the same in stretched fibres of poly-gamma-methyl-L- or D-glutamate or the corresponding ethyl glutamate fibres and in fibres of *Bombyx mori* silk and is evidence of the similarity of the chain configuration in all these

types of fibres. Oriented polypeptide fibres in a folded configuration (for example wool or hair fibres) may be distinguished from  $\beta$  fibres by the perpendicular dichroism of the 4850–4875  $\text{cm}^{-1}$  or 4840–4860  $\text{cm}^{-1}$  bands, as well as by a band near 4600  $\text{cm}^{-1}$  instead of the 4520–4540  $\text{cm}^{-1}$  or 4510–4530  $\text{cm}^{-1}$  bands.

The X-ray diffraction photograph of the oriented polygamma-methyl-L- or D-glutamate fibres of this invention is characterised by two equatorial arcs at about 11 Å. and 4.7 Å. and by layer lines spaced at about 7 Å. and 3.5 Å. For the corresponding ethyl glutamate fibres the equatorial arcs are at about 12.5 Å. and 4.7 Å., the layer lines being also spaced at about 7 Å. and 3.5 Å. The repeat of pattern may be accurately determined from the sixth order meridional arc which gives a fibre repeat of  $6.9 \pm 0.1$  Å. In all cases the diffraction pattern is therefore typical of a  $\beta$ -polypeptide in which the polypeptide chains are almost fully extended. The diffraction photograph also contains regions of diffuse blackening due to disordered material and in addition there is a small amount of material in the  $\alpha$  or folded configuration. The crystalline portion of the fibres is, however, predominantly in the  $\beta$  form.

The extent to which the stretching process has substantially oriented the crystallites of the  $\beta$ -polygamma-methyl-L- or D-glutamate or the corresponding polyethyl glutamate may be measured from the angular spread of the two equatorial arcs. This is conveniently done by finding the spread at half-peak intensity. The angle measured is the angle subtended at the centre of the pattern by the point of maximum intensity on the arc and the point at which the intensity is one-half that at the maximum.

For a perfectly oriented fibre the angular spread at half-peak intensity should be zero and it will increase with increasing disorientation. In practice, the angular spread as measured from an X-ray photograph will always be greater than zero owing to the finite size of the sample and the X-ray beam. Tests carried out on oriented, crystalline fibres produced according to this invention have produced remarkably consistent results with the semi-angular spread for the arc at 11 Å. for the polymethyl glutamate fibre and for the 12.5 Å. for the polyethyl glutamate fibre never greater than  $15^\circ$  and for the arcs for both types of fibre at 4.7 Å. never greater than  $10^\circ$ .

For the wet or dry spun polymethyl glutamate fibres which have been stretched from 70 to 100 percent, the semi-angular spread for the 11 Å. arc is more usually in the range of  $10^\circ$  to  $12^\circ$ , the corresponding figures for the 4.7 Å. arc being usually from  $5^\circ 30'$  to  $6^\circ 30'$ . Similar ranges are obtained with the semi-angular spreads for the 12.5 Å. and 4.7 Å. arcs with the corresponding polyethyl glutamate fibres. However, by using particular stretching conditions, for example by stretching wet spun fibres 100 percent while saturated with cold water or by stretching dry spun fibres 100 percent while saturated with steam, even lower figures for the semi-angular spreads may be obtained; thus the semi-angular spread may be as low as  $7^\circ 30'$  for the 11 Å. arc and as low as  $5^\circ \pm 10'$  for the 4.7 Å. arc, these particular figures indicating that the fibre is practically in the pure  $\beta$  form.

The measurements referred to in the previous paragraph were measured from flat-film photographs taken in vacuo using nickel-filtered copper radiation and a collimator 50 mm. long by 0.5 mm. diameter. The sample was a bundle of parallel filaments of oriented crystalline fibres according to the invention having a denier between 650 and 750. The exposure was arranged to give a peak optical density on the photograph of about 1.0, that is, on the linear part of the X-ray film characteristic curve and the half intensity position on the arc was determined after drawing a straight-line under the tails of the arc to remove background intensity. For eight samples of oriented crystalline polymethyl glutamate fibres produced

according to this invention, the following results were obtained:

	Stretch, percent	Semi-Angular Spread (11 Å. arc)	Semi-Angular Spread (4.6 Å. arc)
Sample 1	80	$11^\circ 50'$	$6^\circ 20'$
Sample 2	90	$10^\circ 0'$	$5^\circ 50'$
Sample 3	90	$10^\circ 10'$	$6^\circ 10'$
Sample 4	90	$10^\circ 0'$	$6^\circ 0'$
Sample 5	70	$11^\circ 40'$	$6^\circ 0'$
Sample 6	70	$11^\circ 40'$	$6^\circ 20'$
Sample 7	100	$9^\circ 10'$	$4^\circ 50'$
Sample 8	100	$7^\circ 30'$	$5^\circ 0'$

In these results no correction has been made for the finite beam or sample size, but it is considered to be less than  $1^\circ$ . Similar results are obtained using corresponding polyethyl glutamate fibres according to this invention.

The accompanying drawing shows in FIGURE 1 part of the cross-section of oriented crystalline polygamma-methyl-L-glutamate filaments in a twisted yarn. FIGURE 2 is a corresponding cross-section for real silk filaments.

In describing the properties of the fibres of this invention above, I have dealt at some length with the X-ray and infra-red properties of the fibres since these constitute the most efficient way of demonstrating conclusively the very substantial predominance of the  $\beta$  form in the fibres.

The fibres of this invention, mainly I believe as a result of the predominance of the  $\beta$  form in the fibre, have very desirable textile properties whereas the only partially converted  $\beta$  fibres obtained hitherto were unsuitable as textile fibres because of their low mechanical strength and solubility characteristics. Thus fibres can be produced with filament deniers as low as 1 and the fibres generally have dry tenacities of from 2 to 3.5 grams/denier or even rather higher with dry extensibilities at break of the order of 10 to 20 percent. The corresponding wet properties are only slightly inferior to the dry properties. The fibres are therefore well suited from all the normal uses of textile fibres.

This invention is based on the observation that when a polymer consisting essentially of polygamma-methyl-L- or D-glutamate or of polygamma-ethyl-L- or D-glutamate is prepared by polymerising gamma-methyl-L- or D-glutamate N-carboxy anhydride or the corresponding ethyl compounds in the presence of an organic liquid or a mixture of liquids in which the polymer is soluble, the polypeptide produced is in the  $\alpha$  configuration in which form it is soluble in a number of organic solvents. If the polymer is precipitated from the solution and separated, I have found that it has a marked tendency to pass into the  $\beta$  configuration in which form it is generally insoluble in those organic liquids in which the polymer with the  $\alpha$  configuration is readily soluble. Even the normal handling which the separated polymer receives in filtration, drying and transportation is sufficient to convert at least part of the  $\alpha$  configuration polymer into the  $\beta$  configuration. However, if the polymer is kept in the solvated state until it is required for spinning, that is to say, it is never permitted to dry out but remains in the swollen state either in solution or in the form of a gel, the polymer remains in the  $\alpha$  configuration and a thread in the  $\alpha$  configuration can be formed by wet or dry spinning and the polymer, in thread form, can be readily converted into the  $\beta$  configuration. Such conversion can be effected to some extent merely by bending or flexing the thread but it is conveniently effected substantially completely in a short time by the stretching which the thread receives during the subsequent processing.

Examples of suitable solvents for the polymer in the spinning solution are neutral solvents, particularly the chlorinated aliphatic hydrocarbons preferably those containing not more than 4 carbon atoms, and containing least 2 chlorine atoms in the molecule. Specific examples

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of such preferred solvents are methylene chloride, 1,2-dichlorethane, trichlorethane, dichlorethylene, ethylidene dichloride and chloroform. Other solvents may, however, be used for example N,N-dimethyl formamide. Mixtures of any of these solvents may also be used. The solvent may also contain liquids such as dioxane which, although they can strictly be described as solvents for the polymer when used alone since they maintain the polymer in the solvated state, give in fact only very viscous solutions or gels which are not suitable for spinning. Esters such as ethyl acetate, methyl acetate and methyl propionate may also be used as diluents instead of dioxane, with the advantage that such esters are not so toxic as dioxane. A diluent which is non-solvent for the polymer may also be present provided the proportion used does not appreciably impair the solvent powers of the solvent so that the polymer as it is formed remains in the solvated state. Acetone is an example of such a diluent.

In the preferred form of carrying out the process of this invention, the polymerisation of the gamma-methyl-L- or D-glutamate N-carboxy anhydride or of the corresponding ethyl compounds is effected in the solvent which is to be used in the spinning operation. Methylene chloride is the preferred solvent for the polymerization as polymers with reduced viscosities of the order of 2.5 are readily obtained with this solvent. Thus, when methylene chloride is used as solvent, a spinning solution can be readily prepared by polymerising, in the presence of an initiator, a solution containing for example 5 to 20 percent of gamma-methyl-L- or D-glutamate N-carboxy anhydride or one of the corresponding ethyl compounds in methylene chloride. However, it is possible to polymerise the N-carboxy anhydride in a solvent such as dioxane which produces gels in which the polymer is still in the solvated state. Such gels are not suitable for use as spinning solutions but by adding a solvent such as methylene chloride in sufficient quantity, a solution of a concentration and a viscosity suitable for spinning can be produced. The polymerisation solvent may in fact be removed entirely and replaced by another solvent, for example by polymerising in dioxane, adding methylene chloride and removing all the dioxane as an azeotrope, sufficient methylene chloride being used or added as required to keep the polymer in the solvated state. It is also possible to carry out the polymerisation in a liquid which is not a solvent for the N-carboxy anhydride but is a solvent for the polymer which therefore passes into solution as it is formed. It is also possible to add to a gel such as is obtained with dioxane, a solvent such as dichloroacetic acid or trifluoroacetic acid, which, on account of its strongly acidic character, cannot be used as polymerisation solvent.

In general for the present invention a tertiary amine type of initiator such as tri-n-butyl amine is preferred, although other forms of initiator may be used as described for example in the Hanby et al. Patent No. 2,598,372.

It is to be understood that in the above description reference to the polymerisation of gamma-methyl-L- or D-glutamate N-carboxy anhydride or the corresponding ethyl compounds includes homopolymerisation of such anhydrides and also copolymerisation of at least 90 percent by weight of such anhydride with up to 10 percent by weight of one or more other N-carboxy anhydrides.

When threads are formed by wet spinning, the coagulant liquid used must be miscible with the spinning solvent and must be a non-solvent for the polymer. It is also preferably miscible with water for reasons which will appear. The preferred coagulant when using chlorinated hydrocarbons as solvent in the spinning solution is acetone but other liquids such as methyl ethyl ketone, methanol and ethanol or mixtures of coagulating liquids may be used. The coagulant bath may also contain a little water but the proportion of water in the bath should not be higher than about 5 percent by volume for the polymethyl gluta-

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mate fibres and not higher than about 10 percent by volume for the polyethyl glutamate fibres.

The wet-spun thread obtained by the present invention leaves the coagulating bath swollen with the organic liquid used in the coagulating bath. This liquid is removed from the thread by immediately washing it in a bath of water, preferably using a counter-current flow of water. The thread leaving the wash bath is saturated with water and it is with the thread in this condition that the substantially complete conversion of the  $\alpha$  to  $\beta$  configuration and the attendant orientation of the fibre are preferably effected by stretching. After the stretching operation the thread is dried. The thread is preferably stretched about 70 to 100 percent. The dried, stretched thread obtained is no longer soluble in any of the solvents mentioned above and it can therefore be safely cleaned with many of the usual dry-cleaning solvents. As is to be expected, the stretching also increases the tensile strength of the thread. Threads obtained according to this invention generally have a high wet tenacity which is only a little below the dry tenacity. The use of a water bath as described above is highly desirable as it eliminates or considerably reduces the risk of obtaining stuck filaments in the final thread.

Instead of stretching the water-saturated thread, the thread may be first dried and then stretched at ordinary or elevated temperatures. Similarly, when the thread is formed by dry-spinning, the dried thread may be stretched after it has left the spinning cell. The steps of dry stretching, like the wet-stretching, also completes the conversion of the  $\alpha$  to  $\beta$  configuration, and orientates the fibre, with the attendant change in solubility characteristics and improved tensile properties. Dry spun threads may be stretched in the dry state at ordinary or elevated temperatures, in the wet state when saturated with cold or hot water, or in steam.

FIGURE 3 of the accompanying drawings is a flow diagram of a process according to this invention.

In carrying out a wet spinning process in accordance with this invention, it is undesirable to allow the polymer solvent content of the coagulating bath to build up above 10 percent. The bath may be rectified as desired by withdrawing part of the bath, suitably fractionating it to recover the polymer solvent and then returning the coagulating liquid to the bath.

It will be seen that an essential step in the process of my invention is that the polypeptide is prepared in solution in the  $\alpha$  form and is kept in the solvated state and consequently in the  $\alpha$  form right up to the moment of extrusion so that the stretching to effect the  $\alpha$  to  $\beta$  transformation is carried out on the substantially pure  $\alpha$  form of fibre to produce an almost pure  $\beta$  form of fibre having valuable textile properties. I am aware that it is known that an  $\alpha$  to  $\beta$  transformation in polypeptides can be effected by a stretching operation but, as stated on pages 302-4 of the book "Synthetic Polypeptides" (1956) by Bamford et al., such conversions with polymethyl glutamates have hitherto only been partial and the transformation has been far from complete. In fact the fibre referred to in the book on the pages quoted is an  $\alpha$  polypeptide fibre containing some  $\beta$  polypeptide whereas the fibres of my invention are substantially pure  $\beta$  polypeptide. This has been particularly true of the polymethyl glutamate fibres made hitherto by the standard technique of forming the polymer, dissolving it in a solvent and spinning the solution; Bamford et al. state that only a partial conversion is obtained because of the presence of the large, practically non-polar side chains in the polypeptide. In view of the known effect of the large methyl and ethyl glutamate side chains in the polypeptide used in the invention it was surprising to find that by the solvent polymerization technique evolved in this invention with these polypeptides, it was possible to obtain an almost complete conversion from the  $\alpha$  to  $\beta$  form.

The threads obtained by the process of this invention

have an appearance and a scroopy handle closely resembling those of natural silk and give X-ray diffraction photographs and infra-red spectra as described above. The fibres all have semi-angular spreads of the 11 A. (or 12.5 A. for the polyethyl fibres) and 4.7 A. arcs which are not greater than 15° and 10° respectively, these figures indicating clearly the substantial orientation of the fibre. The threads can be readily knitted or woven by standard methods to form fabrics which have a very high ironing point. Thus a woven fabric consisting entirely of threads made from fibres according to this invention can be safely ironed at a temperature at which linen immediately scorches.

The invention is illustrated by the following examples in which the reduced viscosity figures quoted are in all cases obtained with a concentration c. of 0.5 gram/100 cc. and the solvent used for the methyl glutamate, Examples 1-9, was dichloroacetic acid and for the ethyl glutamate, Examples 10 to 18, a 1:9 mixture by volume of trifluoroacetic acid and dichloroacetic acid. Parts and percentages are by weight unless otherwise stated.

#### Example 1

9.8 parts of gamma-methyl-L-glutamate N-carboxy anhydride were dissolved in 100 parts of a mixture of 80 volumes of methylene chloride and 20 volumes of dioxane and polymerized at ordinary temperature by the addition of 0.16 part of tri-n-butyl amine to form a 7.5 percent solution of a poly-gamma-methyl-L-glutamate, reduced viscosity 2.62.

The solution obtained was then wet spun in a conventional viscose spinning machine in which the solution after being filtered twice, was fed under pressure at a rate of 16.8 metres/minute to a gear pump and thence to the jet having 60 3 mil holes. The coagulant bath used was acetone containing about 5 percent by volume of water. The concentration of methylene chloride in the coagulating bath was maintained throughout at less than 10 percent by volume. The bundle of filaments formed was withdrawn from the coagulating bath by means of a godet and passed, at 16.8 metres/minute, through a water bath which removed all the acetone. The filaments were withdrawn from the water bath by means of a reel round which the filaments were passed several times and they were then stretched 90 percent between godets while still wet, dried on a steam-heated godet and collected on a ring spinner as a thread with 1.6 twists per inch.

The thread obtained, which correspond to sample 2 in the table of semi-angular spreads given above, contained no stuck filaments and all the filaments had a circular cross-section. It has a chalk-white appearance with a pronounced lustre. Its general physical properties were as follows:

Denier (per filament) .....	1.7.
Dry tenacity .....	3.1 grams per denier.
Wet tenacity .....	2.7 grams per denier.
Dry elongation .....	11.8 percent.
Wet elongation .....	15.0 percent.
Fibre elastic recovery .....	80.0 percent.
Water imbibition .....	11.0 percent.

The filaments when cut into staple lengths had a warm feed and a pronounced scroopy handle usually associated with natural silk.

The thread was no longer soluble in methylene chloride or any of the other chlorinated hydrocarbons in which the  $\alpha$ -form of the polymer is soluble. The infra-red spectrum of a bundle of the filaments in the thread had a marked absorption band in the 4520-4540  $\text{cm}^{-1}$  band and showed parallel dichroism in the 4850-4875  $\text{cm}^{-1}$  band. The X-ray diffraction photographs were characterised by two equatorial arcs at about 11 A. and 4.7 A. and by layer lines at about 7 A. and 3.5 A. The semi-angular spread of the 11 A. arc was 10°0' and of the

4.7 A. arc 5°50'. The cross-section photographs were almost identical with those of natural silk.

The threads were woven into a fabric which had a silk-like appearance and a resistance to creasing similar to that of silk. It was safely ironed at a temperature which scorched linen.

Sample 5 referred to in the table of semi-angular spreads was obtained as described in the above example but with a 70 percent stretch in place of the 90 percent stretch. The angular spreads were then 11°40' and 6°0' respectively for the 11 A. and 4.7 A. arcs.

#### Example 2

500 grams of gamma-methyl-L-glutamate N-carboxy anhydride were polymerised at ordinary temperature in 5340 grams of methylene chloride and 1033 grams of dioxane using 8.35 grams of tri-n-butylamine to initiate the polymerisation. After 5 hours, polymerisation was complete and a clear solution containing 380 grams of poly-gamma-methyl-L-glutamate, corresponding to a 7.5 percent weight/volume solution was obtained. The solution was spun through a 60 x 3 mil jet into methyl ethyl ketone at room temperature at a linear velocity of 16.8 metres/minute. The concentration of methylene chloride in the spin bath was kept below 10 percent by volume. The filaments were transferred at the same speed to a wash bath of water and were then stretched while saturated with water, dried and twisted as described in Example 1.

The thread corresponding to sample 3 referred to in the table of semi-angular spreads above was essentially similar to that described in Example 1 but with a less pronounced lustre. Its physical properties were as follows:

Denier (per filament) .....	1.87.
Dry tenacity .....	2.25 grams per denier.
Dry elongation .....	10.2 percent.

The X-ray photographs were substantially the same as those obtained with the thread of Example 1, the semi-angular spreads being 10°10' and 6°10' respectively for the 11 A. and 4.7 A. arcs.

#### Example 3

A solution of poly-gamma-methyl-L-glutamate prepared as described in Example 2 was extruded into methanol at room temperature using a 60 x 3 mil jet. The extrusion rate was equivalent to a linear velocity of 16.8 metres/minute and the filaments were removed from the coagulating bath at 24 metres/minute. The methylene chloride concentration in the coagulating bath was maintained below 10 percent by volume. The filaments were washed with water, stretched while saturated with water, dried and collected as a thread as described in Example 1.

The thread produced, corresponding to sample 4 referred to in the table of semi-angular spreads above, had no stuck filaments and was similar in appearance to that described in Example 1 and gave an X-ray photograph and infra-red spectrum as characterised for the same thread. The semi-angular spreads were 10°0' and 6°0' respectively for the 11 A. and 4.7 A. arcs. The physical properties of the thread were as follows:

Denier (per filament) .....	2.62.
Dry tenacity .....	2.25 grams per denier.
Dry elongation .....	12.3 percent.

#### Example 4

The procedure described in Example 3 was repeated using ethanol in place of methanol in the coagulating bath. The thread obtained was essentially similar to the product of Example 3, giving the same X-ray figures and having the following physical properties:

Denier (per filament) .....	2.72.
Dry tenacity .....	1.94 grams per denier.
Dry elongation .....	14.0 percent.

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## Example 5

A solution of poly-gamma-methyl-L-glutamate was prepared by the polymerisation at ordinary temperature of 8 parts of gamma-methyl-L-glutamate N-carboxy anhydride using 0.15 part of tri-n-butyl amine as initiator in 100 parts of methylene chloride (60 percent by volume) and acetone (40 percent by volume); the polymer had a reduced viscosity of 2.1 and its concentration in the solution was 6.1 percent.

This solution was extruded following the procedure described in Example 1 with the only exception that the filaments were stretched 100 percent when saturated with cold water. The thread obtained, corresponding to sample 8 in the table of semi-angular spreads given above, was without stuck filaments and very similar to that described in Example 1. Its tensile properties were as follows:

Denier (per filament)----- 1.32.  
Dry tenacity----- 2.7 grams per denier.  
Dry elongation----- 10.0 percent.

Like the fibre of Example 1, the infra-red spectrum of a bundle of filaments had a marked absorption band in the 4520-4540  $\text{cm}^{-1}$  band and showed parallel dichroism in the 4850-4875  $\text{cm}^{-1}$  band. The X-ray diffraction photographs were characterized by two equatorial arcs at about 11 A. and 4.7 A. The semi-angular spread of the 11 A. arc was  $7^{\circ}30'$  and for the 4.7 A. arc was  $5^{\circ}0'$ , indicating that the fibre was practically in the pure  $\beta$  form.

## Example 6

9.8 parts of gamma-methyl-L-glutamate N-carboxy anhydride were dissolved in 100 parts of dioxane and polymerised at ordinary temperature by the addition of 1.6 parts of tri-n-butyl amine to form a 7.5 percent solution of a poly-gamma methyl-L-glutamate, reduced viscosity 2.07. This solution was in a gelled condition. Direct isolation of the poly-gamma-methyl-L-glutamate by evaporation of the solvent from the macerated gel and drying was found to be unsatisfactory for the production of threads since the dried polymer dissolved in methylene chloride with difficulty. Instead, the gel was dissolved in methylene chloride and the resulting solution was concentrated by evaporation. By repeating this process three times, a satisfactory spinning solution which contained 7.5 percent of polymer in 70 volumes of methylene chloride and 30 volumes of dioxane was obtained.

The solution was wet spun into diethyl ether at a rate of 16.8 metres/minute using a jet having one 5 mil hole. The resulting monofil was removed from the spin bath at the same rate and dried in a warm stream of air and then cold drawn 90 percent. The tensile properties of the monofil were as follows:

Denier ----- 1.6.  
Dry tenacity ----- 2.70 grams per denier.  
Dry elongation ----- 21.0 percent.

The semi-angular spread of the 11 A. arc was  $13^{\circ}0'$  and of the 4.7 A. arc  $6^{\circ}0'$ .

## Example 7

95.5 parts of gamma-methyl-L-glutamate N-carboxy anhydride, 180.4 parts of ethyl acetate, 1072 parts of methylene chloride and 0.512 part of trimethylamine were mixed to form a solution which was allowed to stand at room temperature for polymerisation to take place; the polymerisation was complete after 5 hours. The solution containing 5.7 percent of polymer was filtered, deaerated and extruded by means of a standard viscose spinning unit through a 60 x 3 mil hole jet into acetone. The resultant fibres were washed with water, stretched 80 percent at room temperature while still wet, dried on a steam-heated reel and collected as a twisted thread on a ring-spinning machine.

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The thread obtained, corresponding to sample 1 referred to in the table of semi-angular spreads given above, was an oriented crystalline thread with a semi-angular spread for the 11 A. arc of  $11^{\circ}50'$  and for the 4.7 A. arc  $6^{\circ}20'$  so that it consists mainly of the  $\beta$  polypeptide form; it was no longer soluble in methylene chloride.

## Example 8

15.2 parts of gamma-methyl-L-glutamate N-carboxy anhydride were dissolved in 100 parts of a mixture of 70 volumes of methylene chloride and 30 volumes of ethyl acetate, which contained less than 0.5 percent of water, and was polymerised at ordinary temperature by addition of 0.25 part of tri-n-butyl amine to form an 11.5 percent solution of a poly-gamma-methyl-L-glutamate, reduced viscosity 2.52.

The solution obtained was deaerated, heated to  $65^{\circ}\text{C}$ . under 60 lb./in.<sup>2</sup> pressure and extruded through a 19 x 0.003 inch jet at an equivalent linear velocity of 183 metres/minute into the top of a heated spinning cell. The air in this cell was at a temperature of  $75$  to  $80^{\circ}\text{C}$ . and was displaced at a rate of 63 litres per minute. The cell was 3 metres long and its diameter was 0.15 metre. At the bottom of the chamber was a winding apparatus which collected the filaments untwisted at 180 metres per minute.

The filaments collected were stretched 100 percent in three different ways, (1) cold and dry; (2) saturated with cold water; (3) saturated with steam. The table below sets out the mechanical properties of the filaments obtained by these drawing processes:

	Denier	Tenacity, Grams/ denier	Extensibility, percent
Undrawn-----	90.5	0.84	129
(1) Drawn 100 percent cold and dry-----	45.2	2.32	17.5
(2) Drawn 100 percent saturated with cold water-----	45.8	2.57	9.5
(3) Drawn 100 percent saturated with steam-----	45.7	2.62	5.0

Examination of these three types of drawn filaments by X-ray and infra-red methods showed that all three methods of drawing give filaments which were principally  $\beta$ -poly-gamma-methyl-L-glutamate. The semi-angular spreads of the three fibres are given in the following table:

Fibre	Semi-angular spread	
	11 A. arc	4.7 A. arc
(1)-----	$11^{\circ}30'$	$8^{\circ}50'$
(2)-----	$10^{\circ}20'$	$5^{\circ}40'$
(3)-----	$9^{\circ}10'$	$4^{\circ}50'$

Fibre 3 corresponds to sample 7 referred to in the table of semi-angular spreads given above.

## Example 9

10 parts of gamma-methyl-L-glutamate N-carboxy anhydride were dissolved in 100 parts of a mixture of 70 volumes of methylene chloride and 30 volumes of ethyl acetate, which contained less than 0.5 percent of water, and polymerised in the manner described in Example 8 to form a 7.5 percent by weight solution of poly-gamma-methyl-L-glutamate having a reduced viscosity of 2.50.

The solution obtained was deaerated and dry-spun in the manner described in Example 8, the filaments being stretched 100 percent cold and dry. The tenacity of the filaments was 2.2 grams/denier and the extensibility 26 percent. The semi-angular spread of the 11 A. arc was  $13^{\circ}40'$  and the 4.7 A. arc  $7^{\circ}0'$ .

In all of the above examples the optically-active L-form of the polymethyl glutamate may be replaced by the cor-

## 11

responding optically active D-form with the same results; the fibres of both forms produced in the same way have identical X-ray photographs and infra-red spectra. The L-form of the polymer is generally preferred for economic reasons. Similarly, although it is preferred to use homopolymers of the gamma-methyl glutamates, small amounts of other amino acid anhydrides may be included in the polymerisation solution provided that the ultimate fibre produced contains at least 90 percent of one optically-active form of the glutamate ester.

*Example 10*

10 parts of gamma-ethyl-L-glutamate N-carboxy anhydride were dissolved in 100 parts of a mixture of 70 volumes of methylene chloride and 30 volumes of ethyl acetate and polymerised at ordinary temperature by the addition of 0.05 part of tri-n-butylamine to form a 7.5 percent solution of poly-gamma-ethyl-L-glutamate. The viscosity of the solution was 183 poises and the reduced viscosity of the polymer was 2.5.

The solution obtained, after being filtered twice, was wet spun horizontally through a 20 x 3 mil hole jet in a conventional viscose spinning machine into a coagulating bath 36 inches long at 20° C. consisting of a 1:1 by volume mixture of ether and methanol. The extrusion speed was 8 metres/minute. The filaments were withdrawn from the bath by a godet from which they were passed through a water wash bath to a reel; the filaments were passed twenty times round this reel before being passed to a second reel to stretch them 110 percent. The filaments were finally dried on a heated reel and collected on a ring spinner as a twisted thread.

The general tensile properties of the thread were as follows:

Denier	1.47 per filament.
Dry tenacity	2.9 grams/denier.
Dry elongation	8.3 percent.

The thread gave an X-ray photograph which was typical of a  $\beta$ -polypeptide. The X-ray diffraction photographs were characterised by two equatorial arcs at about 12.5 Å. and 4.7 Å. and by layer lines at about 7 Å. and 3.5 Å. The infra-red spectrum of a bundle of the filaments had a marked absorption band in the 4510–4530  $\text{cm}^{-1}$  region and showed parallel dichroism in the 4840–4860  $\text{cm}^{-1}$  band.

*Example 11*

The same spinning solution as in Example 10 was extruded also as described in Example 10 but the filaments from the wash bath were passed to a drying reel and were then drawn 93 percent at ordinary temperature. The tensile properties of the thread were as follows:

Denier	1.61 per filament.
Dry tenacity	2.5 grams/denier.
Dry elongation	15.8 percent.

*Example 12*

The solution as used in Examples 10 and 11 was extruded downwards through a 20 x 3 mil hole jet into a vertical tube 26 inches long and containing a 70:30 by volume mixture of ethanol and acetone. The extrusion rate was 4 metres/minute. From the bottom of the tube the bundle of swollen filaments was passed first round a godet having a peripheral speed of 8.0 metres/minute and then through a bath of cold water to a thread-advancing drying reel. The dried filaments from the reel were stretched 75 percent at ordinary temperature.

Tensile properties of the thread were as follows:

Denier	0.87 per filament.
Dry tenacity	2.43 grams/denier.
Dry elongation	27.2 percent.

*Example 13*

The spinning solution as used in Examples 10, 11 and

## 12

12 was extruded downwards through a 21 x 3.5 mil hole jet into a vertical tube containing a 60:40 by volume mixture of ethanol and acetone. The linear extrusion rate was 3.34 metres/minute. The filaments were withdrawn from the coagulating bath by a godet having a peripheral speed of 8.0 metres/minute, washed in water and, after being passed 20 times round a thread-advancing reel, wet-stretched 86 percent, and dried.

Tensile properties of the thread were as follows:

Denier	1.00 per filament.
Dry tenacity	2.7 grams/denier.
Dry elongation	19.1 percent.

*Example 14*

10 parts of gamma-ethyl-L-glutamate N-carboxy anhydride were dissolved in 30 parts of ethyl acetate and polymerised by adding 0.055 part of tri-n-butylamine. The resultant solution containing about 20 percent of poly-gamma-ethyl-L-glutamate, reduced viscosity 3.8, was extruded by a gear pump through a jet having 20 x 3 mil holes into a horizontal bath containing a mixture of 90 volumes of acetone and 10 volumes of water. After an immersion of 36 inches the highly swollen filaments were passed around a godet which had a peripheral speed of 8 metres/minute and then through a bath of cold water. The filaments were withdrawn from this bath at the same speed by a thread-advancing reel round which they were passed 10 times and then stretched 75 percent between godets. The filaments were collected under tension on a bobbin on which they were dried. Fibre properties were as follows:

Denier	3.13 per filament.
Dry tenacity	2.36 grams/denier.
Dry elongation	17 percent.

*Example 15*

A 20 percent solution of poly-gamma-ethyl-L-glutamate as used in Example 14 was extruded horizontally as described in Example 14 into a coagulant bath consisting of a mixture of equal volumes of ether and ethanol. The filaments were washed in water, passed to a thread-advancing reel, stretched while wet 87 percent, dried and collected as a twisted thread.

Fibre properties were as follows:

Denier	3.25 per filament.
Dry tenacity	2.71 gram/denier.
Dry elongation	10.5 percent.

*Example 16*

The spinning solution as used in Examples 14 and 15 was extruded through a 20 x 3 mil hole jet at 8.0 metres/minute into a horizontal bath 28 inches long and consisting of methoxy ethanol. The filaments were washed in cold water, stretched while wet 86 percent, collected on a bobbin and dried on the bobbin as described in Example 14.

Fibre properties were as follows:

Denier	3.34 per filament.
Dry tenacity	2.41 grams/denier.
Dry elongation	9 per cent.

*Example 17*

A 7.5 percent solution of poly-gamma-ethyl-L-glutamate in methylene chloride (70)/ethyl acetate (30) as used in Example 1 was extruded horizontally at 8.0 metres/minute through a 20 x 3 mil hole jet into ether. After an immersion of 36 inches the filaments were passed first through a bath of methanol and then through a bath of water; they were then stretched 110 percent while wet.

Fibre properties were as follows:

Denier	1.49 per filament.
Dry tenacity	2.1 grams/denier.
Dry elongation	16 percent.



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## Example 18

A 20 percent solution of poly-gamma-ethyl-L-glutamate, relative viscosity 3.0, prepared in a manner similar to that described in Example 14 was heated to 75° C. and was extruded downwardly through a jet containing 3 mil holes into a heated spinning cell 3 metres long into which air at 90° C. was fed. The filaments leaving the cell were collected and stretched 100 percent at room temperature between godets. The filaments were no longer soluble in the spinning solvent used.

The X-ray characteristics and infra-red spectra of the threads produced in Examples 11 to 18, that is both wet and dry spun threads, are substantially the same as those of the product of Example 10.

In all of the above Examples 10 to 18 the optically-active L-form of the poly-L-ethyl-glutamate may be replaced by the corresponding optically active D-form with the same results; the fibres of both forms produced in the same way have identical X-ray photographs and infra-red spectra. The L-form of the polymer is generally preferred for economic reasons.

What I claim is:

1. A process for the manufacture of fibres composed of polymers consisting essentially of units of an optically active form of a glutamic ester chosen from the group consisting of gamma-methyl-glutamate and gamma-ethyl-glutamate which comprises polymerising an optically active N-carboxy anhydride chosen from the group consisting of the N-carboxy anhydrides of gamma-methyl-glutamate and gamma-ethyl-glutamate in an organic liquid medium which is a solvent for the polypeptide formed, the polypeptide being composed of at least 90 percent by weight of units of the optically active glutamic ester, extruding a solution of the polypeptide while it is still in the solvated state into a setting medium so that the polypeptide is in the  $\alpha$  configuration on extrusion, and stretching the resultant threads thereby converting the polypeptide substantially into the  $\beta$  configuration and substantially orienting the fibre along its axis.

2. A process for the manufacture of fibres composed of a homopolymer of an optically active form of a glutamic ester chosen from the group consisting of gamma-methyl-glutamate and gamma-ethyl-glutamate which comprises homopolymerising an optically active N-carboxy anhydride chosen from the group consisting of the N-carboxy anhydrides of gamma-methyl-glutamate and gamma-ethyl-glutamate in an organic liquid medium which is a solvent for the polypeptide formed and which contains at least a major proportion of a chlorinated aliphatic hydrocarbon and the molecule of which contains not more than 4 carbon atoms and at least two chlorine atoms, extruding the polypeptide solution so formed into a setting medium so that the polypeptide is in the  $\alpha$  configuration on extrusion, and stretching the threads so formed thereby converting them substantially into the  $\beta$  configuration and substantially orienting the fibre along its axis.

3. A process as claimed in claim 2 wherein the organic liquid medium consists of a major proportion of methylene chloride and a minor proportion of dioxane.

4. A process as claimed in claim 2 wherein the organic liquid medium consists of a major proportion of methylene chloride and a minor proportion of ethylene acetate.

5. A process for the manufacture of fibres composed of a homopolymer of an optically active form of gamma-

## 14

methyl-glutamate which comprises homopolymerising an optically active gamma-methyl-glutamate N-carboxy anhydride in a solvent mixture for the resultant polypeptide consisting essentially of a mixture of a major proportion of methylene chloride and a minor proportion of a further solvent chosen from the group consisting of dioxane, ethyl acetate, methyl acetate and methyl propionate, extruding the polypeptide solution so formed into a coagulating liquid which is miscible with both water and the spinning solvent and which is a non-solvent for the polymer to form fibres in the  $\alpha$  configuration, washing the fibres with water to remove coagulating liquid, stretching the thread while still wet thereby converting them substantially into the  $\beta$  configuration and substantially orienting the fibres along their axes and drying the fibres.

6. A process as claimed in claim 5 wherein the coagulating bath consists of acetone containing not more than 5 percent by volume of water.

7. A process for the manufacture of fibres composed of a homopolymer of an optically active form of gamma-methyl-glutamate which comprises homopolymerising an optically active gamma-methyl-glutamate N-carboxy anhydride in a solvent mixture for the resultant polypeptide consisting essentially of a mixture of a major proportion of methylene chloride and a minor proportion of a further solvent chosen from the group consisting of dioxane, ethyl acetate, methyl acetate, and methyl propionate, extruding the polypeptide solution so formed into a heated evaporative atmosphere to form a thread in the  $\alpha$  configuration and stretching the resultant thread, thereby converting the polypeptide into the  $\beta$  configuration and substantially orienting the thread along its axis.

8. A process as claimed in claim 7 wherein the optically active N-carboxy anhydride used is gamma-methyl-L-glutamate N-carboxy anhydride.

9. A process for the manufacture of fibres composed of a homopolymer of an optically-active form of gamma-ethyl-glutamate which comprises homopolymerising an optically active gamma-ethyl-glutamate N-carboxy anhydride in an organic liquid medium which is a solvent for the polypeptide formed and which contains a major proportion of methylene chloride and a minor proportion of ethyl acetate, extruding the polypeptide solution so formed into a setting medium so that the polypeptide is in the  $\alpha$  configuration and then stretching the resultant fibres thereby converting them substantially into the  $\beta$  configuration and substantially orienting the fibre along their axes.

10. A process for the manufacture of fibres composed of a homopolymer of an optically active form of gamma-ethyl-glutamate which comprises homopolymerising an optically active gamma-ethyl-glutamate N-carboxy anhydride in a solvent mixture for the resultant polypeptide consisting essentially of a mixture of a major proportion of methylene chloride and a minor proportion of ethyl acetate, extruding the polypeptide solution so formed into a coagulating liquid which is miscible with both water and the spinning solvent and which is a non-solvent for the polymer to form fibres in the  $\alpha$  configuration, washing the fibres with water to remove coagulating liquid, stretching the fibres while still wet converting them substantially into the  $\beta$  configuration and substantially orienting the fibres along their axes, and drying the fibres.

No references cited.