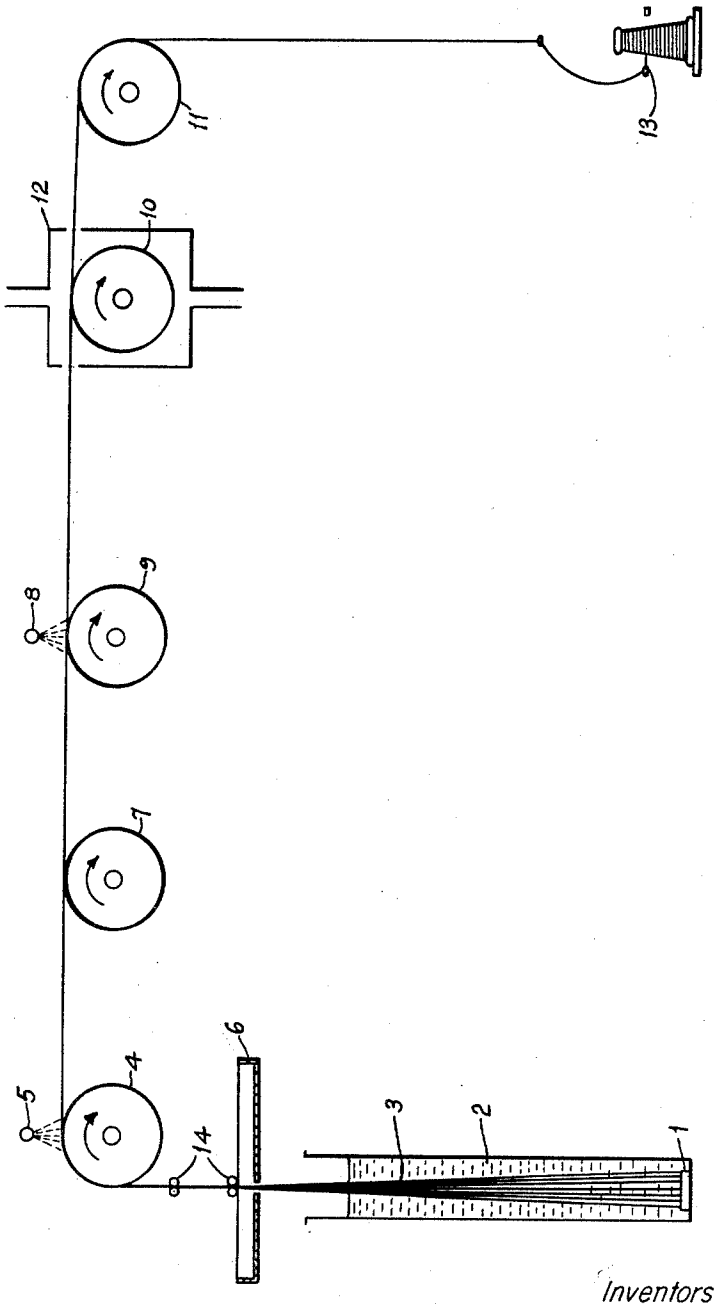
Feb. 18, 1964 D. G. H. BALLARD ETAL 3,121,766

WET SPINNING OF BIREFRINGENT SOLUTIONS OF OPTICALLY ACTIVE POLYPEPTIDE

Filed May 8, 1962



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United States Patent Office 3,121,766 Patented Feb. 18, 1964

3,121,766

WET SPINNING OF BIREFRINGENT SOLUTIONS OF OPTICALLY ACTIVE POLYPEPTIDE

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Filed May 8, 1962, Ser. No. 193,667
Claims priority, application Great Britain May 9, 1961
7 Claims. (Cl. 264—202)

This invention relates to the production of artificial threads from polypeptides, and is particularly concerned with the production of threads composed essentially of the optically active forms of poly-gamma-methyl glutamate as obtained by the polymerisation of gamma-methyl glutamate N-carboxy anhydrides.

The Ballard patent application Serial Number 94,069 filed March 7, 1961 (a continuation-in-part application of applications Serial Numbers 805,180 filed April 9, 1959, 9,153 filed January 22, 1960 and 27,260 filed May 6, 1960 all now abandoned) describes and claims new crystalline polypeptide fibres of which at least 90 percent by weight is composed of units of an optically active form of gamma-methyl glutamate (or of the corresponding ethyl glutamates) said fibre being substantially in the beta configuration and exhibiting a substantial amount of orientation as determined by X-rays and said polymer having a reduced viscosity of at least 1.4. Such fibres are produced by a process such as claimed in the Ballard application Serial Number 161,762 filed December 1, 1961, now Patent No. 3,089,749 and divided out of Serial Number 94,069, the process comprising polymerising an optically active gamma-methyl glutamate N-carboxy anhydride 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 glutamate ester, extruding a solution of the polypeptide while it is still in the solvated state into a setting medium, for example a coagulating bath, so that the polypeptide is in the alpha configuration on extrusion and stretching the resultant fibre while it is still in the alpha configuration thereby converting the polypeptide substantially into the beta configuration and orienting the fibre along its axis. The polymerisation processes described in the said applications Serial Numbers 94,069 and 161,762 produce spinning solutions of poly-gamma-methyl glutamates generally containing from 6 to 9 percent of the polypeptide.

The process of wet spinning the poly-gamma-methyl glutamate solution can be carried out readily for example using standard viscose machinery and the fibres obtained have very satisfactory textile properties. However, extrusion speeds in wet spinning with poly-methyl glutamates as described in said applications Serial Numbers 94,069 and 161,762 have been rather low, for instance speeds of 16.8 metres per minute are described in the examples, and it has not proved possible with the solutions described therein to improve the spinning speeds materially above about 70 metres/minute. The term "spinning speed" is used in this specification to mean the linear speed at which the extruded filaments are withdrawn from the coagulating bath by the first godet, reel or roller to which the filaments are passed when they leave the spinning bath.

From an economic point of view, it is clearly desirable that the output of each spinning unit should be as high as possible. This is particularly true of wet-spinning units which are appreciably more expensive than dry-spinning units. However, other technical considerations may make it desirable to use wet-spinning processes. In order to increase the output of a particular spinning machine, it is desirable to increase the spinning speed as far as possible subject generally to the two provisos that satisfactory and stable spinning conditions can be achieved and that the textile properties of the fibres obtained are satisfactory.

The present invention is directed particularly to the problem of increasing the spinning speed in the production of polypeptide fibres. By the present invention we have been able to achieve spinning speeds in the polypeptide field of 140 to 300 metres per minute and even higher to produce commercially satisfactory textile fibres.

Investigations which we have carried out have shown that dilute solutions of poly-gamma-methyl glutamates obtained as described in the above-mentioned application Serial Number 94,069 are isotropic, that is to say that when a flat layer of the solution is placed between two crossed Nicol prisms or "Polaroid" plates with a source of light beyond one of the prisms or plates, there is no transmission of light.

By carrying out the solvent polymerisation of the gamma-methyl glutamate N-carboxy anhydride at an elevated temperature, and with an appropriate concentration of the gamma-methyl glutamate N-carboxy anhydride in the solvent medium, it has been found possible to produce more concentrated solutions, for example solutions containing 14 percent by weight or more of the poly-methyl glutamate. Unlike the dilute solutions referred to in the previous paragraph, these concentrated solutions are birefringent, that is to say, they transmit light between two crossed prisms or plates. We have found that the birefringent solutions can be extruded at high speeds, namely at least 140 metres per minute.

The difference in optical properties described in the preceding paragraph may be illustrated by the fact that the 7.5 percent solution obtained as described in Example 1 of application Serial Number 94,069 is isotropic whereas both the 15 and 16 percent solutions described in Example 1 below in this specification are birefringent. As a result of our investigations it is apparent that there is a range of solutions of these polypeptides, which are those containing up to about 10 percent by weight of the polypeptides, which are substantially isotropic and a range of solutions, which we believe to be those containing more than about 12 percent by weight of the polypeptide, which are substantially birefringent, the solutions with concentrations in between these two limits being a mixture of the two types of solution.

In its widest aspect, therefore, the present invention comprises a process for the production of fibres composed of polymers consisting of at least 90 percent by weight of units of an optically active form of gamma-methyl glutamate comprising extruding a birefringent solution of the polymer into a liquid coagulating bath at a spinning speed, as hereinbefore defined, of at least 140 metres per minute, and stretching the resultant fibre while the polymer is still in the alpha configuration thereby converting the polymer substantially into the beta configuration and substantially orienting the fibre along its axis.

Our investigations have further shown that under certain preferred spinning conditions, which are discussed more fully below, the birefringent solutions can be wet spun at very high speeds, that is to say at speeds of 140 to 300 metres per minute, preferably 180 to 260 metres per minute, to produce textile fibres having particularly desirable tensile properties which we define in this specification as those having dry tenacities of at least 2 grams per denier and a dry extensibility of at least 10 percent.

The present invention is applicable to the optically-active form of the polypeptides prepared from either of the optically-active gamma-methyl glutamates, both homopolymers and copolymers containing at least 90 percent by weight of one of the optically-active glutamate

esters as described in the above-mentioned Ballard applications. For convenience, however the invention will now be described with particular reference to the homopolymer of gamma-methyl-L-glutamate.

Gamma-methyl-L-glutamate can be readily polymerised in a solvent mixture such as methylene chloride-ethyl acetate at elevated temperature as described above to produce birefringent solutions containing, for example, from 14 to 20 percent by weight of the polypeptide. These solutions can be wet spun for example into acetone or ethyl acetate or a mixture of the two liquids to form threads.

The fibres according to this invention are produced from polymers consisting essentially of gamma-methyl-L- or D-glutamates 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 preferably have a reduced viscosity of at least 2.0. In this specification reduced viscosity is defined as

$$\frac{\eta_{sp}}{C}$$

where η_{sp} is the specific viscosity of a solution having a concentration of C grams per 100 cc. of solution. The solvent used for all the reduced viscosity measurements given in this specification was a 1 to 9 volume by volume mixture of trifluoroacetic acid and trichloroacetic acid.

When carrying out high speed spinning using the birefringent type of solutions as described herein it has been found highly desirable in order to obtain the desirable tensile properties as defined to have regard to two factors namely (*a*) the viscosity of the spinning solution, (*b*) the pull-off ratio used in the spinning process.

As regards the viscosity of the spinning solutions, we have carried out spinning trials with birefringent solutions of the polypeptide having viscosities ranging as far apart as from 56 to 10,000 poises. Viscosities throughout this specification are measured at 25° C. When using pull-off ratios known to be suitable for high speed spinning as described below, the solution having the viscosity of 56 poises could be spun at high speeds to produce stretched fibres but the tensile properties of the fibres deteriorated as the speed increased. On the other hand, solutions having viscosities ranging from 70 to as high as 10,000 poises were found to be suitable for spinning at high speeds consistent with the production of fibres having the desirable tensile properties. However it is possible to obtain useful fibres by using a spinning solution having viscosities from 50 to 70 poises if care is taken to ensure that the spinning speed and pull-off ratio are suitable, but the properties of the fibers may deteriorate as the spinning speeds are increased.

We have observed that even when using apparently identical conditions for the polymerisation step with identical quantities of the same reagents, the spinning solutions obtained have had widely different viscosities, and even when polymerising a stock solution in two or more parts under identical conditions the resulting spinning solutions are likely to have widely differing viscosities. However, for the purposes of the invention the actual value of the viscosity is immaterial provided that, in order to obtain the tensile properties as defined above, the viscosity of the actual solution is at least 50 poises and preferably at least 70 poises.

In wet spinning, the pull-off ratio is defined as the rate at which the filaments are withdrawn from the spinning bath by the first godet or other draw-off device divided by the linear rate of extrusion, both rates being generally expressed as metres per minute. In general, we have found that birefringent solutions of the polypeptide of suitable viscosity as explained above can be wet spun at speeds of as high as 260 metres per minute but that the tensile properties of the threads obtained after the required stretching operation depend markedly on the pull-off ratio used. At pull-off ratios of less than 1.0 the dry tenacity of the fibres obtained is usually less than 2.0 grams/denier and there is a linear decrease in the tenacity as the spinning speed increases. At a pull-off ratio of 1.0 there is no reduction in tensile properties until speeds of about 180 metres per minute are reached but beyond this speed fibre properties deteriorate markedly. However at a pull-off ratio of 1.2 the fibre properties are maintained at speeds up to 260 metres per minute and at a pull-off ratio of 1.5 spinning speeds of as high as 300 metres per minute may be used to produce high tenacity textile fibres. Accordingly, in carrying out this invention, the pull-off ratio is preferably at least 1.2 so that spinning speeds of 180 to 260 metres per minute may be used.

The present invention therefore includes a process for the production of fibres having a tenacity of at least 2 grams per denier, and an extensibility of at least 10 percent composed of polymers consisting of at least 90 percent by weight of units of an optically active form of gamma-methyl glutamate comprising extruding a birefringent solution of the polypeptide having a viscosity of at least 50 poises and preferably at least 70 poises, the reduced viscosity of the polymer being at least 1.4 and preferably at least 2, into a liquid coagulating bath at a spinning speed, as hereinbefore defined, of at least 140 metres per minute, and at a pull-off ratio of at least 1.0, and preferably at least 1.2, and stretching the resultant fibre while it is still in the alpha configuration thereby converting the polypeptide substantially into the beta configuration and substantially orienting the fibre along its axis.

The polymerisation solvent used is preferably a methylene chloride-ethyl acetate mixture containing a major proportion of methylene chloride, but other solvents or solvent mixtures as described in application Serial Number 94,069 may be used. When solvents containing a major part of methylene chloride are used in the polymerisation, the polymerisation step may conveniently be carried out at or near the boiling point (40° C.) of methylene chloride, for example under refluxing conditions. The preferred coagulating liquid is acetone. The extrusion of the solution may be either vertical or horizontal, and may also be carried out according to the procedure known as tube-spinning as used in viscose spinning.

One form of apparatus suitable for spinning at high speeds according to the process of this invention is illustrated diagrammatically in the accompanying drawing. As shown, the spinning solution is extruded vertically upwards through a jet **1** by means of the usual type of metering pump (not shown) into a liquid coagulating bath **2**. The resulting filaments **3** are withdrawn from the bath by means of a thread advancing reel **4** on which they are washed with acetone from a feed pipe **5**, the acetone wash running down into the spinning bath via a trough **6**. The filaments are then passed round a second reel **7**, and washed with water supplied by a pipe **8** on a third reel **9**. They are then passed to another reel **10** and are stretched between the reels **9**, **10**. Reel **10** is partly enclosed in a container **12** to which warm air is supplied in order to dry the filaments. The filaments pass by way of a final reel **11** for collection on a conventional ring spinner **13**. The peripheral speeds of reels **4**, **7** and **9** are substantially the same; the speed of reel **4** determines the spinning speed.

The reel **4** may be replaced by a godet which will then determine the spinning speed and the acetone wash effected on reel **7**.

It is desirable when carrying out high speed spinning to provide one or more suitable guides **14** for the filaments above the surface of the coagulant in order to prevent excess carry-over of the coagulant, contaminated with solvent, by the filaments on to the first godet or reel.

For convenience in setting up, the reels and the meter-

ing pump are preferably all driven together through a single infinitely variable gear box so that the whole spinning line can be set up at a low speed at which the filaments can be manipulated conveniently, and the speed of all the reels can then be increased to the desired high speed in unison.

The invention is illustrated by the following examples in which percentages are by weight.

Example 1

24.5 parts of gamma-methyl-L-glutamate N-carboxy anhydride were dissolved in 100 parts of a mixture of 12 volumes of methylene chloride and 5 volumes of ethyl acetate. The solution was heated under a reflux condenser to 40° C. and polymerisation was effected at 40° C. by adding 0.16 part of tri-n-butylamine. The resultant polymer solution contained approximately 15 percent by weight of poly-gamma-methyl-L-glutamate. On degassing its concentration increased to 16 percent.

The solution which had a viscosity of 140 poises was then extruded vertically upwards into acetone as illustrated in the accompanying drawing. The solution was fed to a 20 x 2 mil hole jet by a metering pump and the resultant filaments, after an immersion of 46 centimetres, were passed round a godet, and then on to a first thread-advancing reel where the filaments were washed in acetone and then to a second reel where the filaments were given a water wash; both the reels had the same peripheral speed as the godet. The pull-off ratio was 1.216 and the spinning speed, i.e. the peripheral speed of the godet, was 260 metres per minute.

From the second reel the filaments were passed to a third reel and between these reels they were stretched 80 percent in air to convert the polypeptide into the beta configuration. The filaments were dried on the third reel and collected on a ring spinner. The dry tenacity of the fibres was 2.8 grams/denier.

Using the same solution and the spinning conditions set out in this example with (*a*) a spinning speed of 180 metres per minute and a stretch of 80 percent and (*b*) an extrusion speed of 220 metres per minute and a stretch of 80 percent, the tensile strengths of the fibres obtained were (*a*) 2.85 grams/denier and (*b*) 2.9 grams/denier.

Example 2

The same solution as used in Example 1 was extruded at an extrusion speed of 260 metres per mintue to form fibres which were washed, stretched 80 percent and dried as described in Example 1 with the exception that the pull-off ratio used was 1.52. In this case the tensile strength of the fibres was 2.9 grams/denier.

Using spinning speeds of 140, 180 and 220 metres per minute, similar fibres to those of Example 1 were obtained in all three cases.

Example 3

A solution of poly-gamma-methyl-L-glutamate prepared as described in Example 1 had a viscosity of 950 poises. It was extruded into acetone as described in Example 1 but with horizontal spinning at a spinning speed of 300 metres per minute through the jet positioned just below the surface of the coagulant, the fibres being withdrawn from the bath by way of a guide placed just above the surface of the acetone and 48 cms. from the jet.

The dry tenacity of the fibres obtained after stretching 80 percent was 2.5 grams/denier. At spinning speeds of 180, 220 and 260 metres respectively, the corresponding tenacity figures were 2.35, 2.65 and 2.65 grams/denier.

Example 4

A solution of poly-gamma-methyl-L-glutamate prepared as described in Example 1 had a viscosity of 3,400 poises. The solution was then extruded vertically upwardly into ethyl acetate through a 20 x 2 mil hole jet using a metering pump. After an immersion path of 40 cms. in the ethyl acetate bath, the resulting fibres were passed over a series of thread-advancing reels as shown in the drawing, the stretch being 80 percent. The pull-off ratio was 1.22 and the speed of the filaments on the first reel was 180 metres per minute. The filaments had a dry tenacity of 2.36 grams per denier.

Example 5

A solution of poly-gamma-methyl-L-glutamate prepared as described in Example 1 had a viscosity of 93 poises. The spin bath and spinning equipment were the same as those used in Example 1, except that a 60 x 2 mil hole jet was used. The spinning speed was 180 metres per minute. The pull-off ratio was 1.36. The fibres were stretched 70 percent and then dried using air at 50° C. The dry tenacity of the filaments was 2.75 grams/denier and the extensibility was 14.7 percent.

Example 6

A solution of poly-gamma-methyl-L-glutamate prepared as described in Example 1 had a viscosity of 1,400 poises. The spinning bath and equipment were the same as those used in Example 1. The spinning speed was 140 metres per minute. The pull-off ratio was 1.26. The fibres were stretched 73 percent and then dried using air at 66° C. The resulting filaments had a dry tenacity of 3.31 grams per denier and an extensibility of 15.6 percent.

What we claim is:

1. A process for the production of polypeptide fibres consisting of at least 90 percent by weight of units of an optically active form of gamma-methyl glutamate comprising extruding a birefringent solution of the polymer into a liquid coagulating bath at a spinning speed of at least 140 metres per minute and stretching the resultant fibre while the polymer is still in the alpha configuration thereby converting the polymer substantially into the beta configuration and substantially orienting the fibre along its axis.

2. A process as claimed in claim 1 wherein the polymer used is a homopolymer of gamma-methyl-L-glutamate.

3. A process for the production of polypeptide fibres having a tenacity of at least 2 grams per denier and an extensibility of at least 10 percent, consisting of at least 90 percent by weight of units of an optically active form of gamma-methyl glutamate, comprising extruding a birefringent solution of the polymer having a viscosity of at least 50 poises, the reduced viscosity of the polymer being at least 1.4, into a liquid coagulating bath at a spinning speed of at least 140 metres per minute and at a pull-off ratio of at least 1.0, and stretching the resultant fibre while the polymer is still in the alpha configuration thereby converting the polymer substantially into the beta configuration and substantially orienting the fibre along its axis.

4. A process for the production of polypeptide fibres having a tenacity of at least 2 grams per denier and an extensibility of at least 10 percent, consisting of at least 90 percent by weight of units of an optically active form of gamma-methyl glutamate, comprising extruding a birefringent solution of the polymer having a viscosity of at least 70 poises, the reduced viscosity of the polymer being at least 1.4, into a liquid coagulating bath at a spinning speed of at least 180 metres per minute and at a pull-off ratio of at least 1.2, and stretching the resultant fibre while the polymer is still in the alpha configuration thereby converting the polymer substantially into the beta configuration and substantially orienting the fibre along its axis.

5. A process for the production of polypeptide fibres having a tenacity of at least 2 grams per denier and an extensibility of at least 10 percent, consisting of at least 90 percent by weight of units of an optically active form of gamma-methyl glutamate, comprising extruding a birefringent solution of the polymer having a viscosity of at least 70 poises, the reduced viscosity of the polymer be-

ing at least 2.0, into a liquid coagulating bath at a spinning speed of at least 180 metres per minute and at a pull-off ratio of at least 1.2, and stretching the resultant fibre while the polymer is still in the alpha configuration thereby converting the polymer substantially into the beta configuration and substantially orienting the fibre along its axis.

6. A process for the production of polypeptide fibres consisting essentially of a homopolymer of gamma-methyl-L-glutamate having a tenacity of at least 2 grams per denier and an extensibility of at least 10 percent, comprising extruding a birefringent solution of the polymer having a viscosity of at least 70 poises, the reduced viscosity of the polymer being at least 1.4, into a liquid coagulating bath at a spinning speed of at least 180 metres per minute and at a pull-off ratio of at least 1.2, and stretching the resultant fibre while the polymer is still in the alpha configuration thereby converting the polymer substantially into the beta configuration and substantially orienting the fibre along its axis.

7. A process for the production of polypeptide fibres

consisting essentially of a homopolymer of gamma-methyl-L-glutamate having a tenacity of at least 2 grams per denier and an extensibility of at least 10 percent, comprising extruding a birefringent solution of the polymer having a viscosity of at least 70 poises, the reduced viscosity of the polymer being at least 2.0, into a liquid coagulating bath at a spinning speed of at least 180 metres per minute and at a pull-off ratio of at least 1.2, and stretching the resultant fibre while the polymer is still in the alpha configuration thereby converting the polymer substantially into the beta configuration and substantially orienting the fibre along its axis.

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