

## UNITED STATES PATENT OFFICE

2,628,886

PRODUCTION OF ARTIFICIAL FIBERS OF  
POLYMERIC MATERIALS

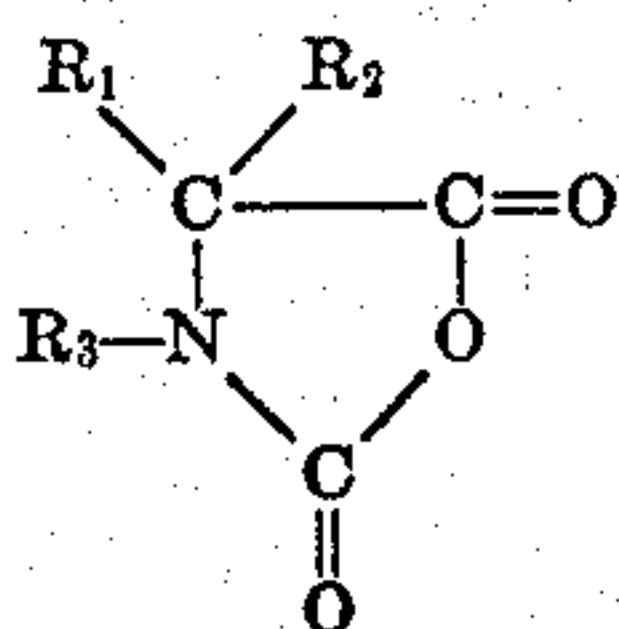
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7 Claims. (Cl. 18—54)

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This invention relates to the production of artificial fibres of polymeric compounds and particularly to the production of fibres of synthetic polypeptides by polymerising anhydrocarboxy-amino-acids having the general formula:



$R_1$ ,  $R_2$  and  $R_3$  being hydrogen atoms or alkyl, aryl or aralkyl groups, which may be substituted or unsubstituted.

The specification of application Serial No. 159,391 describes and claims a process for the production of fibres from synthetic polypeptides which comprises 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 acid or mixtures of these compounds. Examples of suitable solvents specified are meta-cresol, formic acid, dichloroacetic acid and trichloroacetic acid. It is stated in the specification of application Serial No. 159,391 filed May 1, 1950, or its continuation-in-part Serial No. 221,744, filed April 18, 1951, that fibres obtained using formic acid as solvent generally have a  $\beta$  configuration whereas fibres obtained using phenols, dichloroacetic acid and trichloroacetic acid as solvents have generally an  $\alpha$  configuration. A number of polypeptide fibres having an  $\alpha$  configuration tend to swell or even dissolve in benzene, carbon tetrachloride and similar non-polar organic liquids some of which find use as dry-cleaning agents.

The object of the present invention is to reduce the tendency for these polypeptide fibres to dissolve or swell in non-polar organic liquids.

According to the present invention, a process for the production of synthetic polypeptide fibres comprises extruding through a jet into a setting medium a solution of the polypeptide in a solvent giving an  $\alpha$  configuration, for example, meta-cresol, dichloroacetic acid or trichloroacetic acid and then treating the resultant thread with a bath comprising at least one aliphatic monocarboxylic acid containing from one to six carbon atoms per molecule or a like acid containing on the  $\alpha$  carbon atom a bromine, phenyl or mercaptan group, so that at least part of the fibres is converted into the  $\beta$  configuration. Examples of suitable monocarboxylic acids are formic acid,

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glacial acetic acid, propionic acid, n-butyric acid, iso-butyric acid, n-caproic acid, iso-caproic acid and crotonic acid. Examples of  $\alpha$ -substituted acids which may be used are bromoacetic acid, phenylacetic acid,  $\alpha$ -bromo propionic acid,  $\alpha$ -bromo butyric acid,  $\alpha$ -bromo-n-valeric acid and thioglycollic acid. Formic acid is the preferred acid. The extruded fibres while in the  $\alpha$  form may be stretched before being treated with the acid in accordance with the invention.

The polypeptide solutions may be wet spun, or they may be dry spun, for example into hot air. Suitable coagulant liquids for use in the invention are water, ethyl alcohol, methyl alcohol and aqueous alcohols as described in the specification of application Serial No. 159,391.

The treatment according to the invention may be effected by immersing the fibres for a short time, for example, from 1 to 3 minutes in a liquid acid at ordinary temperatures although in some cases a shorter time is effective; if the particular acid is solid at ordinary temperatures, such acid may be used in the form of an aqueous or alcoholic solution. When formic acid is used the acid bath may consist of 100 per cent formic acid or aqueous or alcoholic solutions of formic acid containing at least 75 per cent by volume of formic acid.

The present invention is illustrated by the following examples in which percentages are by weight unless otherwise stated.

## Example 1

A copolymer of DL- $\beta$ -phenylalanine and DL-leucine was prepared as described in the specification of application Serial No. 159,392 as follows:

60 millimols of anhydrocarboxy-DL-leucine and 60 millimols of anhydrocarboxy-DL- $\beta$ -phenylalanine were dissolved in approximately three times their total weight of nitro-benzene. 0.15 millimol of sarcosine dimethylamide in benzene solution was added as initiator and the mixture was allowed to stand for 3 days at 50° centigrade. At the end of this time polymerisation was substantially completed and evolution of carbon dioxide had substantially ceased. The polymer was precipitated by adding petroleum ether, the precipitate was filtered off, washed with petroleum ether and dried.

The copolymer obtained, which was soluble in benzene and in carbon tetrachloride, was dissolved in trichloroacetic acid containing 10 per cent of water to form a 15 per cent solution and the solution was extruded into a bath of water at ordinary temperature (20° centigrade). The



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fibres so produced, which had an  $\alpha$  configuration, were withdrawn from the bath of water, passed through a bath of formic acid at 20° centigrade, and dried at 100° centigrade.

The fibres obtained had a  $\beta$  configuration and were no longer soluble in benzene or carbon tetrachloride.

#### Example 2

A polymeric DL- $\beta$ -phenylalanine produced as described in Example 2 of the specification of application Serial No. 159,391 was dissolved in meta-cresol to form a 15 per cent solution and the solution was extruded into a bath of ethyl alcohol at 20° centigrade. The fibres so produced, which had an  $\alpha$  configuration, were withdrawn from the alcohol bath, passed through a bath of formic acid at 20° centigrade containing about 2 per cent by volume of water, and dried at 100° centigrade.

The fibres obtained had a  $\beta$  configuration.

#### Example 3

The copolymer of DL- $\beta$ -phenylalanine and  $\gamma$ -methyl-L-glutamate prepared as described in Example 1 of the specification of application Serial No. 159,391 was dissolved in dichloroacetic acid to form a 15 per cent solution and the solution was extruded into a bath of water at 20° centigrade. The fibres so produced, which had an  $\alpha$  configuration were withdrawn from the water bath, passed through a bath of formic acid at 20° centigrade containing 10 per cent by volume of water, and dried at 100° centigrade.

The fibres obtained had a  $\beta$  configuration.

#### Example 4

The copolymer of DL- $\beta$ -phenylalanine and DL-leucine as used in Example 1 was dry spun into hot air from a 30 per cent solution in methylene chloride. The resulting fibre was oriented by stretching 200 per cent in steam, passed through a bath of formic acid containing 10 per cent by volume of water, the bath being at 20° centigrade, and dried at 100° centigrade.

The fibres obtained had a  $\beta$  configuration.

#### Example 5

Fibres of the copolymer of DL- $\beta$ -phenylalanine+DL-leucine prepared as described in Example 1 were immersed for one minute in glacial acetic acid at 20° centigrade and then dried at 100° centigrade. The fibres obtained were insoluble in benzene whereas the fibres before treatment were readily soluble in benzene.

#### Examples 6 to 11

Fibres of the benzene soluble copolymer described in Example 1 were immersed for 3 minutes in one of each of the following baths at 20° centigrade:

Example 6.....	$\alpha$ -bromo-n-butyric acid.
Example 7.....	$\alpha$ -bromo-n-propionic acid.
Example 8.....	thioglycollic acid.
Example 9.....	$\alpha$ -bromo-n-valeric acid.
Example 10.....	80 percent aqueous bromo-acetic acid.
Example 11.....	Saturated solution of phenyl acetic acid in mixture of equal volumes of ethanol and water.

The fibres were then washed with ether and dried. The products obtained in each example were insoluble in benzene.

#### Examples 12 to 14

Fibres of the benzene-soluble copolymer described in Example 1 were immersed for 1 minute

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in one of each of the following baths at 20° centigrade:

Example 12.....	n-butyric acid.
Example 13.....	isobutyric acid.
Example 14.....	n-caproic acid.

The fibres were then washed with ether and dried. The products obtained in each example were insoluble in benzene.

#### Examples 15 to 17

A copolymer prepared from equimolecular proportions of DL- $\beta$ -phenylalanine, DL-leucine and  $\gamma$ -benzyl-DL-glutamate was prepared by the method described in application Serial No. 159,392 using  $\frac{1}{800}$  proportion of carcose dimethylamide as initiator. The product was spun into fibres from benzene solution using petroleum ether as coagulant bath.

Samples of the fibres were then treated as follows:

Example 15.....	Immersed for 1 minute in formic acid and then dried directly at 100° centigrade.
Example 16.....	Immersed for 3 minutes in glacial acetic acid, washed with ether and dried.
Example 17.....	Immersed for 1 minute in propionic acid and dried directly at 100° centigrade.

The products of each example were insoluble in benzene.

What we claim is:

1. A process for the production of fibres from fibre-forming polypeptides obtained by polymerising alpha - anhydrocarboxyamino-carboxylic acids comprising extruding through a jet into a setting medium a solution of the polypeptide in a solvent giving an  $\alpha$  configuration and then treating the resultant thread for a period of time not exceeding about 3 minutes in a bath comprising at least one acid chosen from the group consisting of aliphatic monocarboxylic acids containing from one to six carbon atoms per molecule and such acids containing on the  $\alpha$  carbon atom a radical chosen from the group consisting of bromide, phenyl and mercaptan groups, so that at least part of the fibres is converted into the  $\beta$  configuration.

2. A process for the production of fibres from fibre-forming polypeptides obtained by polymerising alpha - anhydrocarboxyamino-carboxylic acids comprising extruding through a jet into a setting medium a solution of the polypeptide in dichloroacetic acid and then treating the resultant thread for a period of time not exceeding about 3 minutes in a bath comprising at least one acid chosen from the group consisting of aliphatic monocarboxylic acids containing from one to six carbon atoms per molecule and such acids containing on the  $\alpha$  carbon atom a radical chosen from the group consisting of bromide, phenyl and mercaptan groups, so that at least part of the fibres is converted into the  $\beta$ -configuration.

3. A process for the production of fibres from fibre-forming polypeptides obtained by polymerising alpha - anhydrocarboxyamino-carboxylic acids comprising extruding through a jet into a setting medium a solution of the polypeptide in trichloroacetic acid and then treating the resultant thread for a period of time not exceeding about 3 minutes in a bath comprising at least one acid chosen from the group consisting of aliphatic monocarboxylic acids containing from one to six carbon atoms per molecule and such acids containing on the  $\alpha$  carbon atom a



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radical chosen from the group consisting of bromide, phenyl and mercaptan groups, so that at least part of the fibres is converted into the  $\beta$  configuration.

4. A process for the production of fibres from fibre-forming polypeptides obtained by polymerising alpha - anhydrocarboxyamino-carboxylic acids comprising extruding through a jet into a setting medium a solution of the polypeptide in a solvent given an  $\alpha$  configuration and then treating the resultant thread for a period of time not exceeding about 3 minutes in a bath comprising formic acid so that at least part of the fibres is converted into the  $\beta$  configuration.

5. A process for the production of fibres from fibre-forming polypeptides obtained by polymerising alpha - anhydrocarboxyamino-carboxylic acids comprising extruding through a jet into a setting medium a solution of the polypeptide in dichloroacetic acid and then treating the resultant thread for a period of time not exceeding about 3 minutes in a bath comprising formic acid so that at least part of the fibres is converted into the  $\beta$  configuration.

6. A process for the production of fibres from fibre-forming polypeptides obtained by polymerising alpha - anhydrocarboxyamino-carboxylic acids comprising extruding through a jet into a setting medium a solution of the polypeptide in trichloroacetic acid and then treating the resultant thread for a period of time not exceeding about 3 minutes in a bath comprising formic

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acid so that at least part of the fibres is converted into the  $\beta$  configuration.

7. A process for the production of fibres from fibre-forming polypeptides obtained by polymerising alpha - anhydrocarboxyamino-carboxylic acids comprising extruding through a jet into a setting medium a solution of the polypeptide in a solvent giving an alpha configuration, stretching the resultant thread and then treating the resultant thread for a period of time not exceeding about 3 minutes in a bath comprising at least one acid chosen from the group consisting of aliphatic mono-carboxylic acids containing from one to six carbon atoms per molecule and such acids containing on the alpha carbon atom a radical chosen from the group consisting of bromide, phenyl and mercaptan groups, so that at least part of the fibres is converted into the beta configuration.

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