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**PROCESS FOR PREPARING FILAMENTS FROM
POLY-β-LACTAMS**

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ABSTRACT OF THE DISCLOSURE

A process for preparing filaments of poly-β-lactams, especially of poly-4-methyl-azetidin-2-one, by spinning solutions of formic acid of the polymers in an aqueous precipitating bath containing, in addition to formic acid, one or several formiates of the alkaline earth metals and, if necessary or required, other alkaline earth metal and alkali metal salts.

The present invention relates to a process for preparing filaments from poly-β-lactams.

Filaments and fibers obtained from poly-β-lactams may be employed in many fields. It is known that some poly-β-lactams, in particular the poly-4,4-dimethyl-azetidin-2-one, are soluble in a methanolic calcium thiocyanate solution and may be spun from such a solution into filaments in a precipitating bath of distilled or deionized water (French Patent 1,416,414). However, the spinning process proceeds only with said poly-β-lactams disubstituted in 4,4-position in an unobjectionable manner for a prolonged period of time and also in this case only under certain conditions, for example while maintaining the temperature of the precipitating bath constant at ±1° C.

It is also known that the poly-β-lactams readily dissolve in a variety of inorganic and organic acids, of which especially the concentrated formic acid has proved useful. Spinning solutions of formic acid of the polymer are spun in precipitating baths which consist mainly of flowing water and which may contain inorganic salts, such as sodium chloride, zinc chloride, zinc sulfate or sodium sulfate to enhance the coagulating effect. Relatively good results were obtained, for example, with the use of sodium chloride solutions of 15 percent concentration by weight (French Patents, 1,432,966 and 1,432,967). However, it was found that the sodium chloride concentration is critical and may not be less than 15 percent, since otherwise a flocculent precipitate deposits in the precipitating bath which causes serious disturbances during the spinning operation.

Now I have found that these disadvantages can be avoided and filaments of poly-β-lactams, especially of poly-4-methylazetidin-2-one, be obtained by spinning solutions of formic acid of the polymers, when aqueous precipitating baths are used which contain formiates of the alkaline earth metals in addition to formic acid. Although, fundamentally, all formiates of the alkaline earth metals may be used according to the process of the present invention, beryllium and radium have gained no importance for carrying out the process of the present invention on an industrial scale for reasons easy to understand. Of the remaining alkaline earth metals magnesium and calcium are preferred, but also with the use of strontium and barium good results are obtained. The concentration of the formiates of the alkaline earth metals in the precipitating bath may vary within wide limits up to that concentration at which the precipitating bath is saturated with the formiate of the alkaline earth metal at the respective

temperature of the precipitating bath. The concentration to be used in each case depends on the nature of the polymer to be coagulated, especially on its viscosity. In general, concentrations of 8 to 15 percent by weight, preferably of 9 to 12 percent by weight, are sufficient. The proportion of the free formic acid in the precipitating baths is 0.5 to 4 percent by weight, preferably 1 to 2 percent by weight. It has proved to be advantageous to add free formic acid to the precipitating baths from the beginning and to maintain the portion of free formic acid entrained into the bath during the spinning process as constant as possible. This can be achieved by introducing a fresh, neutral solution of the formiates of the alkaline earth metals into the precipitating bath or by neutralizing the formic acid by means of hydroxides of the alkaline earth metals.

The advantage of the precipitating baths containing formiates of the alkaline earth metals is that the filament is slowly precipitated in these precipitating baths and that the completely coagulated filament remains soft and elastic for a long time and can thus be processed without disturbances. Another advantage of the precipitating baths according to the present invention is that they can easily be prepared and that the salts used can be recovered. The formiates of the alkali earth metals are relative difficultly soluble and can, therefore, already be separated by partial evaporation of the exhausted precipitating baths which is very advantageous for recovering the formic acid from the precipitating bath. The enriched formic acid can be neutralized without difficulty by conversion with the corresponding oxides or hydroxides of the alkaline earth metals, and the salts formed can be isolated together with the coagulation salts.

It could not be expected that soft and elastic filaments could be obtained by the process of the present invention when spinning solutions of formic acid of poly-β-lactams in precipitating baths containing formiates of the alkaline earth metals, especially in view of the fact that there is only required a relatively low concentration of the formiates of the alkaline earth metals in the precipitating bath, for the coagulating effect of sodium chloride, zinc chloride, zinc sulfate or sodium sulfate is considerably lower than that of the formiates of the alkaline earth metals. As mentioned already, it has been found that with the use of sodium chloride, with which relatively good results are obtained, in precipitating baths in a concentration below 15 percent by weight a flocculent precipitate forms in the precipitating bath which, especially in the vicinity of the spinneret-openings, mechanically injures the still very soft, freshly coagulated capillary filaments whereby highly fluffy filaments are obtained whose quality is of no use. Apparently the coagulating strength of these precipitating baths does not suffice to precipitate the polymer rapidly enough so that portions of low viscosity of the polymer dissolve out from the filament and precipitate in the form of fine flocks. The nitrogen analysis and the determination of the relative viscosity of the isolated precipitate showed that it was a fraction of medium viscosity of the dissolved polymer. If the concentration of sodium chloride was increased in order to avoid these disadvantages, the coagulation of the freshly spun filaments commenced very rapidly in the case of a concentration of from 22 to 25 percent by weight of sodium chloride in the precipitating bath; however, the drawability of the filaments was diminished thereby and the tendency to form fluffs increased.

The use of pure sodium chloride baths, moreover, has the disadvantage that the recovery of the amounts of formic acid, of which a low percentage had been entrained into the precipitating baths, by evaporating the exhausted precipitating baths is uneconomic due to the comparatively

high content of sodium chloride. The same applies to the use of sodium sulfate, ammonium sulfate, zinc sulfate, aluminum sulfate and the primary and secondary alkali metal phosphates.

The advantages gained with the use of formiates of the alkaline earth metals according to the process of the present invention are surprising above all for the reason that own tests have shown that alkali metal formiates do not have these advantages when used as coagulation salts in precipitating baths. The rapid coagulating effect of precipitating baths of formic acid which contain alkali metal formiates and/or ammonium formiate has proved to be harmful to the quality of the filaments. Already with the use of low concentrations of from 5 to 12 percent by weight of alkali metal formiates there are obtained brittle filaments with an elongation at break of only 5 to 11 percent. With higher concentrations of alkali metal formiates this phenomenon increases further and may result in a total embrittlement of the filaments, which can then no longer be drawn and break off in the immediate vicinity of the spinneret-openings even if the draw-off speed into the precipitating bath is extremely low.

When working according to the process of the present invention there may be used precipitating baths containing an alkaline earth metal salt of formic acid or a mixture of several formiates of the alkaline earth metals. This is especially advantageous when spinning concentrated spinning solutions of high viscosity whose period of fall of the ball is situated above 800 seconds, as well as for spinning polymeric β -lactams with relative viscosities of from 8 to 13. The coagulating strength of these precipitating baths containing formiates of the alkaline earth metals, whose total salt concentration is relatively low, suffices to produce filaments with good properties from such spinning solutions of high viscosity.

However, it is also possible to use, in addition to the formiates of the alkaline earth metals in the precipitating baths, other inorganic alkali metal or alkaline earth metal salts, for example $MgCl_2$, $MgSO_4$, $CaCl_2$, $NaCl$ or Na_2SO_4 , especially alkali metal formiates. The concentration of these additionally employed salts should not exceed 18 percent by weight and should amount preferably to 5 to 10 percent by weight. Such salt combinations are preferably used for spinning poly- β -lactams whose relative viscosity only amounts to 3.2 to 3.6. In spite of the high total salt concentration which, with the use of the usual amounts of up to 15 percent by weight of formiates of the alkaline earth metals, amounts up to 33 percent by weight, but may also be higher, the dreaded phenomenon of a supercoagulation does not occur as observed, for example, with the use of high-percent pure sodium chloride in the precipitating baths, and which entails an intolerable embrittlement of the spun filaments. This phenomenon is due to the extraordinarily favorable coagulating effect of the formiates of the alkaline earth metals, whose mild and slow coagulating action on the filaments of poly- β -lactams is distinctly perceptible also in the presence of other salts. The combination of formiates of the alkaline earth metals with magnesium sulfate, for example 12 percent by weight of magnesium formiate and 10 percent by weight of magnesium sulfate, has proved to be especially advantageous. Precipitating baths of a corresponding composition, for example 2 percent by weight of formic acid, 11.2 percent by weight of magnesium formiate and 8.9 percent by weight of sodium formiate, remained entirely clear in spinning tests conducted over long periods of time.

However, the advantages of the process according to the present invention are not limited to the non-occurrence of turbidity phenomena in the precipitating baths used according to the present invention or to the prevention of the fluffiness resulting therefrom. Since the precipitation of the filament takes place gradually and, for this reason, the filament remains elastic in the precipitating bath, it can be drawn off more rapidly without breaking. In this manner it is possible to increase the final draw-off rate to

90 m./minute and thereby to raise the production. For the reasons stated above also the drawability of the spun filaments is distinctly improved. High strength values can be obtained at sufficiently high elongations. Further advantages of the process according to the present invention result when spinning a coarse capillary titer whose production has not been possible heretofore with the use of sodium chloride precipitating baths. The process of the present invention enables filaments having individual titers of from 3 to 5 deniers to be spun without difficulty in, for example, calcium- or magnesium formiate precipitating baths, said filaments having good textile properties.

It has already been mentioned that it is easy to recover the formiates of the alkaline earth metals from the precipitating baths. It has proved useful to employ a corresponding working method also in the case of precipitating baths which contain, in addition to formiates of the alkaline earth metals, still other salts. After these baths have been concentrated by partial evaporation, the difficultly soluble formiates of the alkaline earth metals are present in a preponderant amount in the deposited salt mixture, which formiates may be recovered together with the neutralized formic acid.

The filaments or fibers obtained by the process of the present invention find many applications in the textile industries. The filaments have a pleasant, silk-like feel and, with a relative atmospheric moisture of 65 percent, absorb 9 percent of water which is 3 percent more than in the case of poly- ϵ -caprolactam. Knitted or woven fabrics may be produced from the continuous filaments, said fabrics withstanding a boiling wash. Staple fibers produced from the spun filaments are employed in the worsted yarn industries.

The following examples serve to illustrate the invention. The relative viscosity was measured in a solution of 1 percent concentration by weight of the polymer in 98 percent sulfuric acid at 20° C. The viscosity of the spinning solution was measured at 20° C. according to the falling ball test by means of a steel ball (diameter 3 millimeters) with a vertical falling distance of 20 cm.

EXAMPLE 1

Poly-4-methyl-azetidin-2-one having a relative viscosity of 3.3 was dissolved in a 98% formic acid so that a solution of 30.2% concentration by weight was obtained. The viscosity of the spinning solution measured according to the falling ball test corresponded to a period of fall of the ball of 160 seconds.

This spinning solution was spun at the rate of 0.33 ml./minute by means of a gear pump through a tantalum spinneret having 40 openings of a diameter of 0.2 mm. each into an aqueous precipitating bath which had a length of 105 cm., a temperature of 23° C. and which contained 2.6% by weight of formic acid, 10.9% by weight of magnesium formiate and 6.2% by weight of magnesium sulfate. The coagulated filament was drawn off at the rate of 6.6 m./minute by means of a trio-roller and drawn in a ratio of 1:4.4 in a water bath which had a temperature of 24° C. and a length of 35 cm. by means of another trio-roller turning at the rate of 30 m./minute. In an associated washing bath which had a length of 80 cm., the remaining formic acid was washed out with flowing wash water which had a temperature of approx. 20° C., the filament was squeezed off between two rollers, provided with the required sizing agents on a sizing roller, the excess amount being again squeezed off. Finally, the filament was dried in a hot-air tunnel dryer having a length of 100 cm. at 230° C., and the finished fiber was wound on a bobbin. The precipitating bath remained entirely clear during a prolonged period of service.

The filament obtained had a total titer of 40 deniers and an individual titer of 1.0 denier. The ultimate tensile strength of the filament was 2.60 g./denier at an elongation of break of 17%.

EXAMPLE 2

Poly-4-methyl-azetid-2-one having a relative viscosity of 8.0 was dissolved with formic acid so that a spin-

which became turbid during the period of the test, and the textile properties of the filaments obtained therewith:

TABLE

Composition of the precipitating bath (percent by weight)	Total titer den.	Indiv. titer den.	Ultim. tensile strength, g./den.	Elongation at break, percent
(4) 2.8 HCOOH+9.0 Mg(OOCH) ₂ +8 MgSO ₄ -----	40	1.0	2.80	31
(5) 3.0 HCOOH+14.9 Ca(OOCH) ₂ -----	41	1.0	2.28	38.2
(6) 2.9 HCOOH+10.2 Ca(OOCH) ₂ +5.2 NaCl-----	40	1.0	3.02	19.6
(7) 2.7 HCOOH+8.8 Mg(OOCH) ₂ +8.5 NaCl-----	41	1.0	3.16	17.0
(8) 2.3 HCOOH+11.2 Sr(OOCH) ₂ -----	40	1.0	2.70	25.0
(9) 3.0 HCOOH+19.5 Ba(OOCH) ₂ -----	41	1.0	3.30	19.0
(10) 2.6 HCOOH+9.0 Mg(OOCH) ₂ +11.0 sodium formiate-----	39	1.0	3.20	15.0

ning solution of 25.8% concentration by weight was obtained which had a falling ball viscosity of 700 seconds. In a manner analogous to that described in Example 1, this spinning solution was spun, at a rate of 0.493 ml./minute, into an aqueous precipitating bath which had a length of 120 cm., a temperature of 27° C. and which contained 2.8% by weight of formic acid and 11.7% by weight of magnesium formiate.

In a water bath having a length of 30 cm. and a temperature of 28° C., the filament was drawn to 4.5 times it original length. The precipitating bath remained entirely clear during this test.

When working in this manner a filament was obtained which had a total titer of 63 deniers and an individual titer of 1.6 deniers. Its ultimate tensile strength was 2.85 g./den. at an elongation of break of 13.0%. If the drawing was carried out in a ratio of 1:5.4 in a steam pipe having a length of 20 cm. instead of in a water bath, a filament was obtained which had a total titer of 56 deniers and an individual titer of 1.4 deniers. The ultimate tensile strength of such a filament was 4.85 g./den. at an elongation of break of 6.0%.

EXAMPLE 3

A spinning solution which corresponded to that used in Example 2 was spun by means of a spinneret having 15 openings each having a diameter of 0.3 mm. and processed in the manner described in Example 1. The filament obtained had a total titer of 60 deniers and an individual titer of 4.0 deniers; its ultimate tensile strength was 3.08 g./den. at an elongation of break of 26%.

EXAMPLES 4 to 10

In the manner described in Example 1, poly-4-methyl-azetid-2-one having a relative viscosity of 8.0 was spun at a rate of 0.465 ml./minute in the form of a spinning solution of 21% concentration by weight in formic acid with a falling ball viscosity of 222 seconds. The following table shows the precipitating baths used, none of

I claim:

1. In the process for preparing filaments of poly-β-lactams by spinning formic acid solutions of the lactams in an aqueous precipitating bath, the improvement which comprises spinning said solutions in an aqueous precipitating bath which contains about 8 to 15% by weight of an alkaline earth metal formiate and from about 0.5 to 4% by weight of formic acid.
2. The process according to claim 1 wherein the lactam is poly-4-methyl-azetid-2-one.
3. The process according to claim 1 wherein the bath contains up to 18 percent by weight of another salt selected from the group consisting of inorganic salts of the alkaline earth metals, inorganic alkali metal salts and alkali metal formiates.
4. The process according to claim 3 wherein the lactam is poly-4-methyl-azetid-2-one.
5. The process according to claim 1 wherein the additional salt is magnesium sulfate.
6. The process according to claim 5 wherein the lactam is poly-4-methyl-azetid-2-one.
7. The process according to claim 1 wherein the additional salt is MgCl₂, MgSO₄, CaCl₂, NaCl, Na₂SO₄ or alkali metal formiate.

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