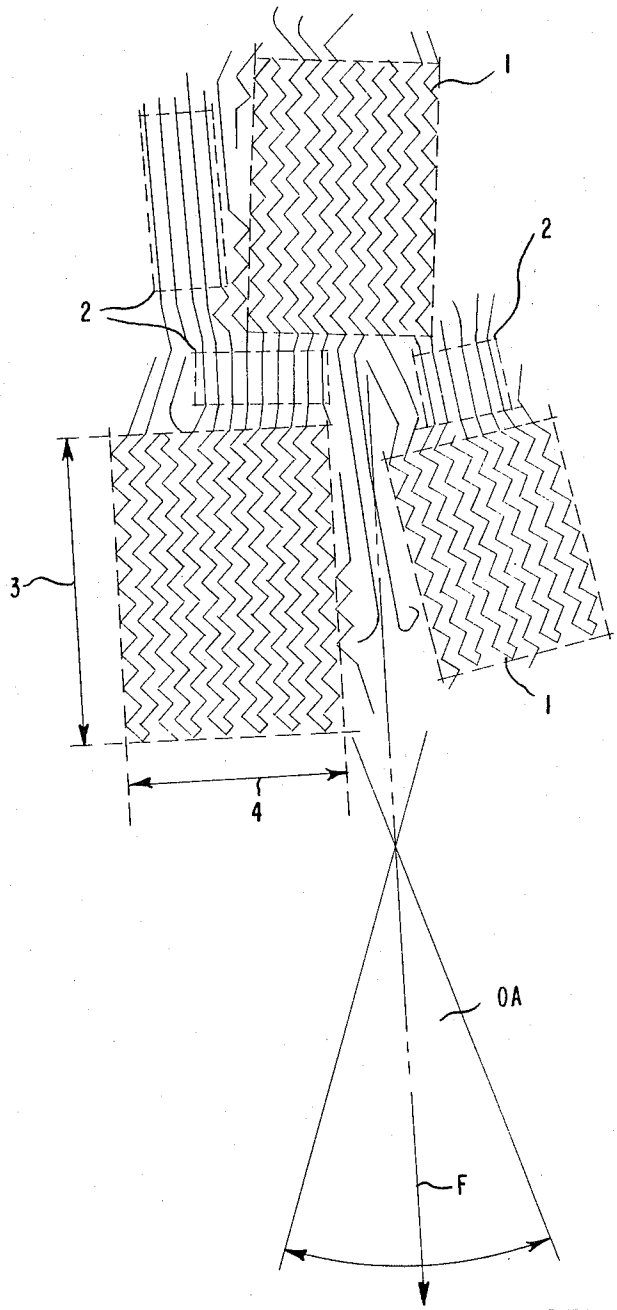
Jan. 17, 1967 F. W. KNOBLOCH ETAL 3,299,171

FIBERS OF MODIFIED POLYPIVALOLACTONE

Filed April 20, 1964 3 Sheets-Sheet 1

FIG. 1



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FIBERS OF MODIFIED POLYPIVALOLACTONE

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FIG. 2

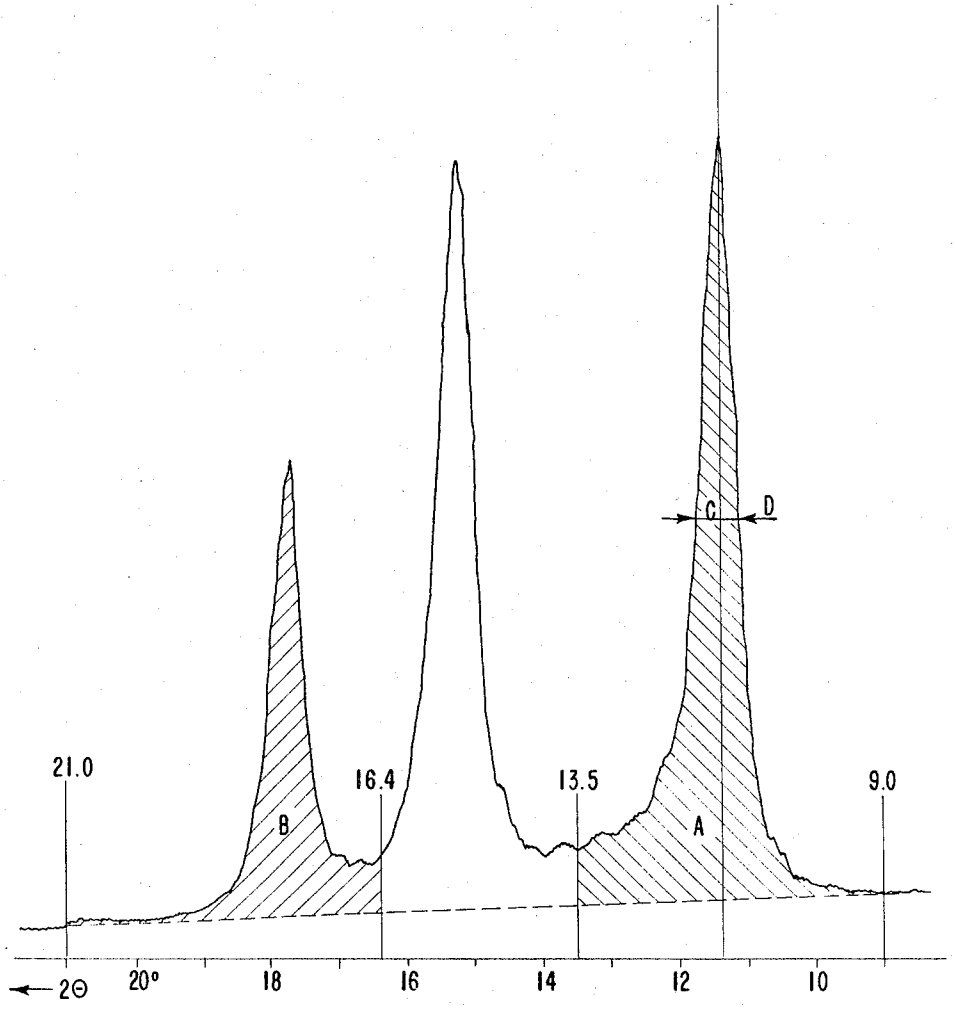

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FIG. 3

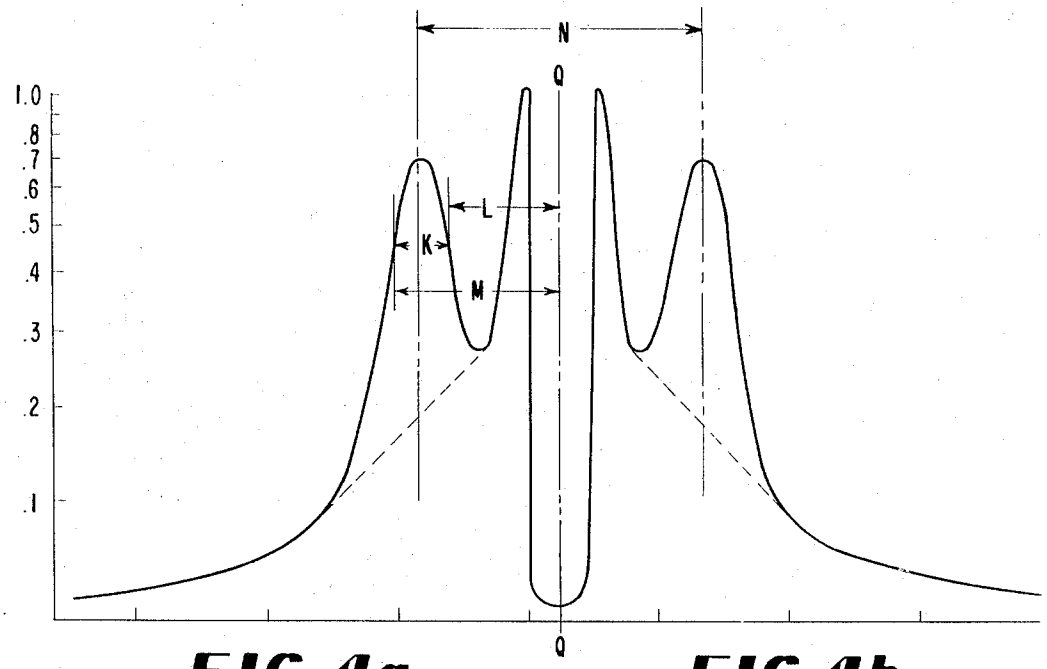


FIG. 4a

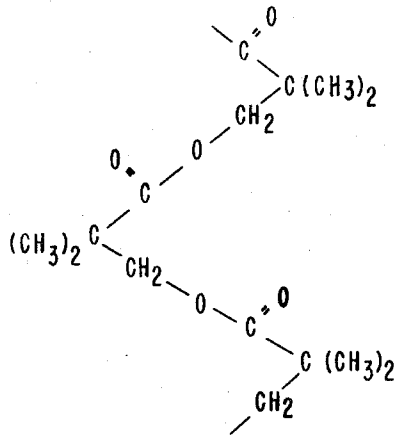
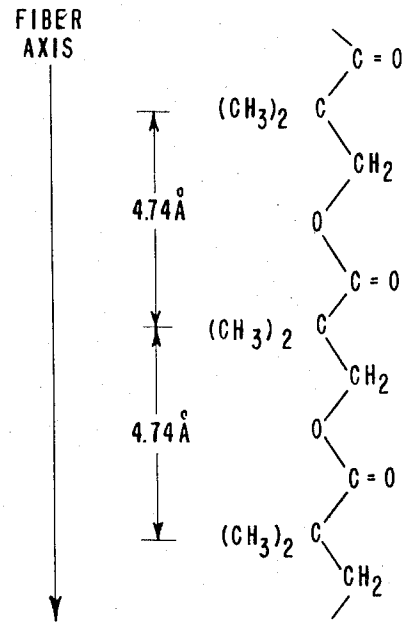


FIG. 4b



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3,299,171

FIBERS OF MODIFIED POLYPIVALOLACTONE

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8 Claims. (Cl. 260—857)

This invention relates to novel fibers exhibiting exceptionally high levels of work recovery and tensile recovery, and to a novel process for making the new high recovery fibers.

For many uses the performance of a textile fiber is related to its ability, when deformed by the application of stress, to return to its initial configuration when the stress is removed. Thus, the fibers in a carpet are required to recover rapidly from compression; otherwise, the carpets exhibit footprints and other marks. Limited ability of fibers to recover from deformation in fabrics results in wrinkles when the fabrics are creased or otherwise deformed.

A measure of the ability of a fiber to recover from deformations ordinarily encountered in textile applications is its work recovery from 5% elongation, designated herein by the symbol WR_5. As shown by Beste and Hoffman (Textile Research Journal, vol. XX, No. 7, July 1950, pages 441–453), the ability of a fabric to recover from creasing is dependent upon the work recovery of the fibers from which it is made. Although most fibers exhibit only a relatively low level of work recovery, with WR_5 values of less than 50%, a few fibers having higher work recovery are known. Drawn polypivalolactone fibers prepared as described by Alderson in his United States Patent 2,658,055 and Reynolds and Vickers in their British Patent 766,347 have a WR_5 up to about 74%. Values as high as 75% have been reported for nylon (Hoffman, Textile Research Journal, vol. XVIII, No. 3, March 1948, page 145), and the polyurethane prepared from N,N′-diphenyl-p-phenylenediamine and hydroquinone bis-chloroformate yields a fiber having a WR_5 of about 75%. However, even at this level of work recovery, there is still a 25% loss of energy when the fiber recovers from deformation, a significant loss for certain applications. Textile fibers exhibiting still higher WR_5 values have been greatly desired, but up to the present time such fibers have not been considered attainable.

A fiber has now been produced which exhibits WR_5 values up to 90% and higher. The new high recovery fiber comprises a polypivalolactone fiber having a novel physical structure. The structural elements in terms of which the novel fiber is characterized are discussed fully hereinbelow, but in summary they are as follows:

(1) The molecular weight of the polypivalolactone, a measure of which is given by the *inherent viscosity*.

(2) The orientation of the fiber, as characterized by its *orientation angle*.

(3) The relative amounts of the polymer existing in the two crystalline forms of which polypivalolactone has been found to be comprised: the α crystalline form, in which a sharp layer line having a 5.97 A. spacing appears on the wide angle X-ray diffraction pattern, and the β crystalline form, in which a diffuse layer line appears having a spacing of 4.74 A.; a measure of the relative amounts being given by the *α ratio*.

(4) The apparent width of the α crystallites, or average width of ordered regions of α crystalline form across the fiber, as characterized by the *α crystallite size transverse to the fiber axis*.

(5) The apparent length variation of the α crystalline domains in the direction parallel to the fiber axis, a measure of which is given by the *radial breadth of the low angle meridional X-ray peak*.

Briefly described, the novel fiber comprises a highly oriented polypivalolactone fiber predominantly in the α crystalline form and particularly characterized by the high order of length of its α crystallites parallel to the fiber axis, as measured by a value of not more than 0.40° for the radial breadth of the low angle meridional X-ray peak. The novel fiber thus differs fundamentally in structure from the previously known types of polypivalolactone fibers: (A) a substantially unoriented polypivalolactone fiber in the α crystalline form, in which both the length and width of the α crystallites are of relatively low order, and (B) an oriented polypivalolactone fiber which has a substantial degree of β crystalline structure, the latter fiber being obtained by orientation of the former.

More specifically, the high recovery fiber of the invention comprises a highly crystalline polypivalolactone fiber having an inherent viscosity, η_{inh}, of at least about 0.75; said fiber being highly oriented as characterized by an orientation angle less than the numerical value given by the expression,

$$10(\eta_{inh}+1)$$

said fiber being predominantly in the α crystalline form, in which a sharp layer line having a 5.97 A. spacing appears on the wide angle X-ray diffraction pattern, the α ratio as defined by the quotient of the area A of an equatorial intensity trace of the diffraction pattern between the angles of 9° and 13.5° and the area B of the intensity trace between the angles of 16.4° and 21.0° being at least 1.70; the α crystallite size transverse to the fiber axis being at least 85 A.; said fiber being particularly characterized by its highly ordered α crystalline character parallel to the fiber axis as measured by a value of not more than 0.40° for the radial breadth of the low angle meridional X-ray peak.

The novel fiber of the invention exhibits WR_5 values ranging from 80% as a minimum to more than 90%. The novel fiber also exhibits outstanding tensile recovery at 5% elongation, designated herein by the symbol TR_5. Values for TR_5 range from about 92% up to about 98%.

The high recovery fiber of the invention is produced by a novel process which comprises heating an oriented polypivalolactone fiber having an inherent viscosity, η_{inh}, of at least about 0.75 and an orientation angle, determined from its X-ray diffraction pattern, having a numerical value less than

$$8\eta_{inh}+15$$

to a temperature of at least 135° C. until its α ratio is at least 1.70, its α crystallite size transverse to the fiber axis is at least 85° A., and the radial breadth of its low angle meridional X-ray peak is reduced to a value of not more than 0.40°. Preferably, the oriented polypivalolactone fiber is heated to a temperature of at least 150° C.

The fibers to which the process of the invention is applied are readily prepared by conventional melt-spinning techniques with orientation of the fibers to an orientation angle having a numerical value less than

$$8\eta_{inh}+15$$

The required orientation may be developed during the spinning step alone simply by taking up the fibers on a forwarding roll or windup roll at a high spin-stretch factor, i.e., with a ratio of spinning speed at windup to the jet speed of the polymer stream issuing from the capillary orifice sufficient to orient the fiber to the desired extent. The orientation of the spun fibers is readily increased (lower orientation angle) by drawing

them immediately following the spinning step. The spun fibers usually have a high degree of α crystalline character as shown by a high α ratio, frequently even when they have received substantial orientation by spinning at a high spin-stretch factor, although the length of the α crystallites is low, and the α crystallite size transverse to the fiber axis is also low. The drawn fibers typically have a substantial degree of β crystalline structure, as characterized by an α ratio less than 1.70.

The conditions required for conversion of oriented polypivalolactone fibers to the novel fibers of the invention exhibiting high levels of work recovery vary somewhat, depending upon the method used to prepare the oriented fibers. In general, optimum results are achieved by heating within the temperature range of 170–200° C. The fibers may be free of tension, but best results are obtained by holding them taut. The minimum heating time is of the order of one second or less, especially at higher temperatures; although this statement is not intended to be limiting owing to the difficulty in estimating the time required for the fiber to reach the desired temperature when heat is applied and the rapidity of cooling when the heat treatment is stopped. For highest work recovery values the heating step is prolonged, and if desired may be prolonged for several hours or days. If desired, the steps of orienting and heating the fiber may be combined, with the fiber being heated hot enough for a sufficient exposure time during and immediately following orientation to achieve the structure of the novel fiber of the invention exhibiting high work recovery.

In some instances, the novel high recovery fiber of the invention may be produced by heating the initial oriented fiber at a temperature of 135° C. for about an hour, although for other samples of oriented polypivalolactone fiber a minimum heating temperature of 150° C. may be required. The temperature reached within the fiber during the application of heat should, of course, be maintained below the melting point of the polymer, preferably at least 10° C. below the melting point of the polymer. The melting point of polypivalolactone, in the absence of any copolymeric modifiers, is 238° C.

If desired, the heating may be carried out in two or more stages. In fact, when the fibers are intended for conversion into fabrics, it is preferred that achievement of the maximum degree of the high-recovery structure be deferred until the fibers are in fabric form. In a typical instance, the oriented polypivalolactone fibers may be heated at 150° C. for one minute to convert them to the high-recovery structure, after which the fibers may be processed to fabric form and given a further heat treatment at 170° C. or higher for a more prolonged period to develop further their α crystalline character and increase their level of work recovery. If desired, the initial heat treatment may be omitted, and the fabric may be prepared first with a subsequent heating step to convert the fibers to the novel high-recovery structure.

Owing to their marked ability to recover from creasing or compression, the fibers of the invention give excellent performance in both woven and nonwoven fabrics. They are highly useful in making carpets and as stuffing materials or reinforcing materials in pillows, sleeping bags, seat cushions, and other articles. The ability of the fibers to conserve energy applied during deformation and to return it in the form of work to recover their initial shape, without requiring the application of additional work to help them recover their shape, makes them of high utility for many diverse uses.

The discovery that oriented fibers of polypivalolactone can be converted from their previously known structural form to a new structural form exhibiting work-recovery behavior superior to any previously known textile fiber was highly unexpected. Extensive previous work with various polymeric lactones such as poly(α-ethyl-α-methylpropiolactone) and poly(α,α-diethylpropiolactone) failed to produce or even suggest the possibility of such high levels of work recovery. The maximum WR_5 values for fibers of these polymers appear to be in the 50–60% range. Evidence of a structural form exhibiting elastic recovery from high elongation was also lacking in fibers of these polymers.

ELASTIC FIBERS

In a variation of the novel polypivalolactone fibers having the structure described above and characterized by exceptionally high work recovery, the invention extends to comprehend fibers exhibiting good tensile recovery at very high elongation. At an elongation of 50%, such fibers exhibit a tensile recovery greater than 60% (tensile recovery from 50% elongation, measured on the second cycle after holding the fibers at 50% elongation for one minute, is designated herein by the symbol $TR_{50/1/2}$). The fibers are thus elastic in character. The novel elastic fibers exhibit an exceptional degree of "power," or modulus in the elongated state (measured on the second cycle at 50% elongation). This means that the novel elastic fibers have a high resistance to additional stretch in the elongated state, and correspondingly a high retractive force. The power of the novel elastic fibers is actually more than twenty times the power of rubber and about ten times the power of commercially available spandex (segmented polyurethane elastomeric) fibers.

Briefly described, the novel elastic fiber comprises an oriented polypivalolactone fiber exhibiting α crystalline character to a very high degree and particularly characterized by the high order of width of its α crystallites across the fiber axis, as measured by a minimum α crystallite size transverse to the fiber axis of at least 140 A. A portion of the entire range of novel fiber structures exhibiting elastic behavior coincides with the structural requirements defined above for high WR_5 fibers, and these fibers exhibit elastic behavior as well as exceptional work recovery. Fibers in the remainder of the structural region associated with elastic behavior exhibit somewhat lower levels of work recovery, although still high as compared with most previously known fibers.

More specifically, the elastic fiber of the invention comprises a highly crystalline polypivalolactone fiber having an inherent viscosity, η_{inh}, of at least about 0.75; said fiber being oriented as characterized by an orientation angle less than the numerical value given by the expression

$$10(2\eta_{inh}+1)$$

said fiber having α crystalline character to a very high degree as characterized by an α ratio of at least 2.15 and well ordered in the direction of the fiber axis as measured by a value of not more than 0.50° for the radial breadth of the low angle meridional X-ray peak; and said fiber being particularly characterized by the high order of width of its α crystallites across the fiber axis, as measured by a minimum α crystallite size transverse to the fiber axis of at least 140 A.

The novel elastic fiber exhibits $TR_{50/1/2}$ values ranging from 60% as a minimum to 90% and above. Owing to their high degree of power, they find utility in core spun yarns for use in automobile seat covers and other stretchable fabrics, in which the novel elastic fibers are employed as the elastic core surrounded by a sheath of cotton, rayon, or other staple fibers. The novel elastic fibers also exhibit high capacity to absorb energy, i.e., the amount of work required to break the fibers is of high order, for which reason the fibers find utility in the preparation of seat belts and other textile products requiring the ability to absorb large amounts of energy.

Elastic fibers exhibiting high work recovery.—As defined by the present invention, a class of elastic fibers which also exhibits excellent work recovery comprises a highly crystalline polypivalolactone fiber having an inherent viscosity, η_{inh}, of at least about 0.75; said fiber being highly oriented as characterized by an orientation

angle less than the numerical value given by the expression

$$10(\eta_{inh}+1)$$

said fiber having a crystalline character to a very high degree as characterized by an α ratio of at least 2.15; said fiber being particularly characterized by the high order of both the length and width of its α crystallites as measured by a minimum α crystallite size transverse to the fiber axis of at least 140 A. and a value of not more than 0.40° for the radial breadth of the low angle meridional X-ray peak.

The novel high-recovery, elastic fibers defined above exhibit WR_5 values ranging from 80% to more than 90%, TR_5 values ranging from about 92% up to 98% and $TR_{50/1/2}$ values ranging from 60% to more than 90%.

The high-recovery, elastic fibers are produced by a process which comprises heating an oriented polypivalolactone fiber having an inherent viscosity, η_{inh}, of at least about 0.75 and an orientation angle less than the numerical value given by the expression

$$8\eta_{inh}+15$$

to a temperature of at least 150° C. until its α ratio is at least 2.15, its α crystallite size transverse to the fiber axis is at least 140 A., and the radial breadth of its low angle meridional X-ray peak is reduced to a value of not more than 0.40°. The preferred temperature range is 170–200° C., optimum results being achieved by heating at about 190° C., at which temperature an exposure of only about a second, or at most a few seconds, is required.

Other elastic fibers.—As defined by the present invention, a class of fibers which has excellent elastic behavior, but generally exhibits a somewhat lower level of work recovery than the exceptional level shown by the class of fibers defined just above, comprises a highly crystalline polypivalolactone fiber having an inherent viscosity, η_{inh}, of at least about 0.75; said fiber being oriented as characterized by an orientation angle at least equal to the numerical value given by the expression

$$10(\eta_{inh}+1)$$

and less than the numerical value given by the expression

$$10(2\eta_{inh}+1)$$

said fiber having α crystalline character to a very high degree as characterized by an α ratio of at least 2.15 and well ordered in the direction of the fiber axis as measured by a value of not more than 0.50° for the radial breadth of the low angle meridional X-ray peak; and said fiber being particularly characterized by the high order of width of its α crystallites across the fiber axis, as measured by a minimum α crystallite size transverse to the fiber axis of at least 140 A.

The novel elastic fibers defined in the preceding paragraph exhibit $TR_{50/1/2}$ values ranging from 60% to more than 90% and WR_5 values ranging from about 50% to about 80%. They are produced by a process which comprises selecting an oriented polypivalolactone fiber having an inherent viscosity of at least about 0.75 and an orientation angle having a numerical value at least equal to the numerical value given by the expression

$$8\eta_{inh}+15$$

and less than the numerical value given by the expression

$$15\eta_{inh}+17$$

and heating said fiber to a temperature of at least 150° C. until its α ratio is at least 2.15, its α crystallite size transverse to the fiber axis is at least 140 A., and the radial breadth of its low angle meridional X-ray peak is reduced to a value of not more than 0.50°. The preferred temperature range is 170–200° C.

ILLUSTRATIVE DRAWINGS AND DEFINITIONS

The nature of the invention will be more fully understood by reference to the accompanying drawings, in which

FIGURE 1 is a schematic representation of the structure of a portion of a high recovery polypivalolactone fiber, taken in cross section along a plane containing the fiber axis;

FIGURE 2 is a typical X-ray diffractometer scan, or equatorial intensity trace of the X-ray diffraction pattern, of the fiber of FIGURE 1, illustrating the method of determining the α ratio and the α crystallite size transverse to the fiber axis;

FIGURE 3 is a typical radial photometer intensity trace of a low angle X-ray diffraction pattern of the fiber of FIGURE 1, illustrating the method of determining the radial breadth of the low angle meridional X-ray peak;

FIGURE 4*a* is a representation of a proposed conformation of two repeating units of the polypivalolactone molecule in the α crystalline form; and

FIGURE 4*b* is a representation of a proposed conformation of two repeating units of the polypivalolactone molecule in the β crystalline form.

Turning now to the figures, FIGURE 1 is a schematic representation of the structure of a portion of a high recovery polypivalolactone fiber in a plane which includes the fiber axis F. In the figure, crystallites of α crystalline form **1** are exemplified as aligned with the fiber axis F within the orientation angle O. Crystallites of the β crystalline form **2** are shown dispersed within the fiber material. A measure of the variation in length **3** of the α crystallites or, ordered regions of α crystalline form parallel to the fiber axis, is given by the radial breadth of the low angle meridional X-ray peak. The α crystallite size, identified as **4** in FIG. 1, represents the width of the α crystallite transverse to the fiber axis. The structural parameters by which the fiber is characterized are illustrated schematically in the figure, and quantitative values for the parameters are determined by the various X-ray procedures described in detail below. It is to be understood that the invention is defined in terms of the quantitative values for the parameters, and that the schematic interpretation of the parameters is not intended to be taken as limiting.

In the fiber of the invention, the crystalline regions of the polypivalolactone are comprised of two forms: the α crystalline form, in which a sharp layer line having a 5.97 A. spacing appears on the wide angle X-ray diffraction pattern, and the β crystalline form, in which a diffuse layer line having a 4.74 A. spacing appears. A measure of the relative amount of the two forms is given by the α ratio. A suitable method for determining the α ratio involves the use of a reflection technique to record an equatorial intensity trace of the X-ray diffraction pattern with an X-ray diffractometer (employing a goniometer with a 17 cm. focusing circle; Philips Electronic Instruments, type 42273/0). Approximately 1.5 meters of yarn are wound around a notched sample holder upon the bottom of which is cemented a sheet of lead foil across the rectangular hole so that the X-ray beam is diffracted only by the fibers on top of the holder. When the determination is made on staple fibers, the fibers are placed across the face of the sample holder and taped to each edge of the holder. Using CuKα radiation and 0.5° divergence and scatter slits, an equatorial intensity trace is recorded from 7° to 22°, 2θ, at a scanning speed of 1°, 2θ per min., a chart speed of 1 inch per min., and a time constant of 1; 2θ being the angle between the undiffracted beam and the diffracted beam. The full scale deflection of the recorder is set so that the peak with maximum intensity is at least 70% of the scale, which is a linear scale. The diffraction peak located at 11.5°, 2θ, is due entirely to diffracted radiation from the α crystal structure and is the maximum peak for samples of high α content. The diffraction peak located at approximately 17.8°, 2θ, is due

to diffracted radiation from both α and β crystal structure and is the maximum peak for the samples of high β content. To calculate the α ratio, a base line is first established on the diffractometer scan by drawing a straight line between the points on the curve at 9.0° and 21.0°, 2θ. Vertical lines are then drawn from points on the curve at 13.5° and 16.4°, 2θ, to the base line. FIGURE 2 illustrates a typical diffractometer scan and the guide lines drawn on it for calculation of the α ratio. Using a planimeter, the area A of the diffraction peak between 9.0° and 13.5°, 2θ, is measured and recorded. The area B of the diffraction peak between 16.4° and 21.0°, 2θ, is similarly determined. The α ratio is then calculated from the equation

$$\alpha \text{ Ratio} = \frac{A}{B}$$

Values for the α ratio as low as 0.2 are observed, but for the purposes of the present invention should be at least 1.70 for high work recovery fibers and at least 2.15 for elastic fibers. Observed values for the α ratio range up to about 4.1.

The α crystallite size transverse to the fiber axis is the degree of order of α crystalline character, or apparent average width of ordered regions of α crystalline form, transverse to the fiber axis; simply stated, it is the average width of the α crystallites. It is determined from the same diffractometer scan employed to calculate the α ratio, using the general method described by Klug and Alexander in their book, "X-ray Diffraction Procedures," published by John Wiley & Sons, Inc., New York, 1954, pp. 491–538. A vertical line is dropped from the peak in the vicinity of 11.5°, 2θ, to the base line, and the midpoint C of the line between the peak and the base line is ascertained. A horizontal line across the peak through C is drawn and the half-maximum peak breadth D is taken as the length of the horizontal line between its two intercepts on the curve, measured to the nearest 0.005 inch and converted to degrees (1 inch=1 degree). The α crystallite size is then calculated from the equation

$$\alpha \text{ Crystallite size, A.} = \frac{H}{0.01745[D^2 - I^2]^{1/2} \cos\theta}$$

where

D=breadth at half-maximum peak height in degrees
θ=the Bragg angle=5.75°
H=wavelength of radiation
=1.5418 A. where CuKα radiation is used
I=breadth at half-maximum peak height in degrees when calibrated by a metallic silicon standard (instrumental broadening).

Values for the α crystallite size as low as 30 A. are observed, but for the purposes of the present invention should be at least 85 A. for high work recovery fibers and at least 140 A. for elastic fibers. Observed values for the α crystallite size range up to about 300 A.

A measure of the degree of order of α crystalline character parallel to the fiber axis, or the apparent variation in the average length of ordered regions of α crystalline form in the direction of the axis, is given by the radial breadth of the low angle meridional X-ray peak, briefly designated herein as the "radial breadth." The radial breadth is measured by making a low angle X-ray diffraction pattern (transmission pattern), using a camera of the type described by W. O. Statton for use in small angle studies and shown in Figure VI–1, page 233, of his chapter in the book, "Newer Methods of Polymer Characterization," edited by Bacon Ke and published by Interscience Publishers, New York, 1964, of a fiber sample 40 mils thick, perpendicular to the axis of the fibers using CuKα radiation collimated by two 15-mil pinholes spaced 6 inches apart, and a 32-cm. sample-to-film distance. A radial photometer intensity trace of the discrete diffraction spots is made along the meridian at the rate of 1 centimeter of the chart paper for each millimeter of film. FIGURE 3 illustrates a typical intensity trace, in which the diffraction spots are symmetrical. A vertical center line Q is drawn between the peaks. The center line is conveniently established by folding the trace so that the centers of the diffraction spots are superimposed and then creasing the trace at the position which is centered between these two peaks. A straight base line is drawn beneath each peak. A vertical line is dropped from one peak to the base line and the mid-point K between the peak and the base line is ascertained, determined logarithmically if the intensity scale is logarithmic, as in FIGURE 3. A horizontal line across the peak through K is drawn and the distance L in mm. from the creased center line to the nearest peak edge is measured and recorded. Also the distance M in mm. from the creased center line to the farther peak edge is measured and recorded. The corresponding diffraction angles θ_1 and θ_2 are calculated, and their difference yields a value for the radial breadth;

$$\text{Tan } \theta_1 = L/3200$$
$$\text{Tan } \theta_2 = M/3200$$
$$\text{Radial breadth} = \theta_2 - \theta_1$$

Measurements are repeated for the other peak, and the average value is reported as the radial breadth. If the discrete diffraction spots are not symmetrical, the distance N between the two peaks is measured in mm. The diffraction angle θ_3 is calculated and a value for the radial breadth is then calculated according to the following equations:

$$\text{Tan } R_3 = N/6400$$
$$\text{Radial breadth} = 2(\theta_2 - \theta_3)$$

A second calculation is made, using the value for θ_2 determined from the other peak, and the average value is reported as the radial breadth. Radial breadth values ranging up towards 1° may be observed in some samples, but in accordance with the present invention it has been found that 0.50° is a critical radial breadth upper limit for fiber structures exhibiting elastic behavior and that 0.40° is a critical radial breadth upper limit for fiber structures exhibiting high work recovery. Radial breadth values down to about 0.15° are observed. The radial breadth values determined in accordance with the method described above are reproducible, employing the instrumental settings described.

The orientation angle of the fiber is determined by the general method described by Krimm and Tobolsky, Textile Research Journal, vol. 21, pp. 805–22 (1951). A wide angle X-ray diffraction pattern (transmission pattern) of the fiber is made, using CuKα radiation, a fiber-sample thickness of 20 mils, a sample-to-film distance of 2.2 cm., and an exposure time of 5 minutes. The fibers are aligned perpendicular to the X-ray beam. Crimped fibers are placed under sufficient tension to straighten the fibers, taking care not to impart additional orientation by drawing them. An azimuthal scan is made and the arc length in degrees at the half-maximum intensity of the first equatorial diffraction spot, which is located at 11.5°, 2θ, is measured and taken as the orientation angle of the sample. As indicated above, the diffraction peak located at 11.5°, 2θ, is due entirely to diffracted radiation from the α crystal structure; therefore, the orientation angle measured by this technique is a measure of the orientation of the α crystallites. Since the intensity trace is an essentially Gaussian curve and the measurement is made at half-maximum intensity, the physical meaning of the orientation angle given by the determination is that approximately 77% of the α crystallites are aligned within this angle about the fiber axis.

As disclosed above, the orientation angle should be less than the quantity, $10(2\eta_{inh}+1)$, for useful elastic fibers; otherwise, the fibers are too brittle. For fibers exhibiting high work recovery, the orientation angle should be less than the quantity, $10(\eta_{inh}+1)$. Decreasing orientation angles are indicative of increasing orientation of

the polymer molecules in the fiber. Orientation angles as low as about 20°, measured as described above, are indicative of a high degree of orientation. Values as low as about 12° are observed.

FIGURES 4*a* and 4*b*, although not intended to be taken as limitative, are proposed conformations of the polypivalolactone molecule in the α and β crystalline forms. In each case two full repeating structural units, plus certain adjacent groups, are shown. The repeat distance of 4.74 A. is close to that which would be expected (4.9 A.) for an extended planar zig-zag, and it is therefore hypothesized that in the β crystalline form of polypivalolactone the atoms comprising the main polymer chain lie substantially in a single plane, with only slight distortion. The 5.97 A. repeat distance observed in the α crystalline form is too large to be accounted for by a single repeating structural unit, and for two repeating structural units to be compressed to this distance it appears that the polymer chain must be folded or buckled in some nonplanar manner, perhaps into a type of spiral configuration.

The term "inherent viscosity," as used herein, is defined as the polymer property determined in accordance with the following relationship:

$$\eta_{inh} = \frac{\ln \eta_{rel}}{c}$$

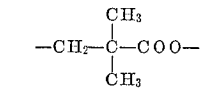
wherein the relative viscosity, η_{rel}, is calculated by dividing the flow time in a capillary viscometer of a dilute solution of the polymer by the flow time for the pure solvent, trifluoroacetic acid. The concentration (c) used in the examples is 0.5 gram of polymer per 100 ml. of solution, and the measurements are made at 30° C. A decrease in the inherent viscosity of a polymer is frequently noted when the polymer is extruded at high temperature through capillary orifices to form fibers. It has been found that there is a minimum inherent viscosity requirement of 0.75, measured when the polymer is already in fiber form, for both the elastic fibers of the invention and those exhibiting high work recovery. Inherent viscosity values up to 3 and higher are observed.

TR_5, tensile recovery from 5% elongation, is a measure of the extent to which a fiber or yarn recovers its original length after being stretched, as determined from a stress-strain curve. In this test the sample is stretched at the rate of 10% of its test length per minute until it has reached approximately 5% elongation, after which it is held at this elongation for 30 seconds and then allowed to retract at a controlled rate of 10% per minute, based on its original test length. The extension during elongation and the recovery during retraction are measured along the elongation axis. TR_5 is then calculated as the percentage ratio of the amount of fiber retraction to the amount of its elongation.

WR_5, work recovery from 5% elongation, is a measure of the freedom from permanent re-alignment of the polymer molecules following stretching of the fiber or yarn. The ratio of the work done by the polymer molecules in attempting to return to their original alignment following stretching to a predetermined elongation to the work done on the sample during stretching is termed the work recovery. The work recovery is determined from the same stress-strain curve employed to measure the tensile recovery at 5% elongation. WR_5 is calculated as the percentage ratio of the area under the controlled relaxation curve to the area under the stretching curve.

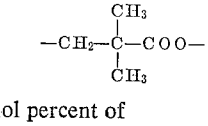
In running the stress-strain curve for determination of $TR_{50/1/2}$, the fiber sample is stretched at the rate of 100% of its test length per minute until it has reached approximately 50% elongation, after which it is held at this elongation for one minute and then allowed to retract at the rate of 100% per minute, based on its original test length. The sample is reclamped to remove any slack. A second cycle is then carried out wherein the fiber sample is elongated at the rate of 100% per minute until it has reached approximately 50% elongation, held for one minute, and then allowed to retract at the rate of 100% per minute. The extension during elongation and the recovery during retraction are measured along the elongation axis. $TR_{50/1/2}$ is then calculated as the percentage ratio of the amount of fiber retraction to the amount of its elongation.

By the term "polypivalolactone" is meant a linear condensation polyester consisting essentially of recurring ester structural units of the formula

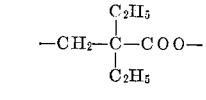


Alternative names for the polyester include poly(hydroxypivalic acid), poly(β-oxypivaloyl), poly(2,2-dimethylhydracrylate), and poly(2,2-dimethyl-3-hydroxypropionic acid) or poly(2,2-dimethyl-3-oxypropionoyl). The polyester is readily prepared by the polymerization of hydroxypivalic acid or its esters as disclosed by Alderson in his U.S. Patent 2,658,055; or by the polymerization of pivalolactone, the intramolecular ester of hydroxypivalic acid, as disclosed by Reynolds and Vickers in their British Patent 766,347. In a typical procedure, 25 g. of pivalolactone is added to a refluxing mixture of 250 ml. of n-hexane, 2.5 ml. of ethyl alcohol, 0.25 g. of triethylenediamine, 0.025 g. of 2,2-bis(4-hydroxyphenyl)propane and 0.075 g. of finely divided TiO_2. Refluxing is continued, with stirring, for 4 hours, during which time the delustered polypivalolactone polymer precipitates from the boiling mixture. The solid polymer is subsequently filtered off from the hexane solvent. Other procedures for preparing equivalent polymer are described by Alderson and by Reynolds and Vickers in the references mentioned above.

As used herein, "a fiber consisting essentially of polypivalolactone" refers not only to fibers wherein the sole fiber-forming polymeric constituent is polypivalolactone but also to fibers formed from certain copolymers or polymer blends as indicated below. Thus, copolymeric components may be present in amounts of up to about 10 mol percent and in some instances as high as 25 mol percent so long as they do not prevent the fiber from assuming high orientation with well developed α crystalline character. At the upper amounts of copolymer component content, it is preferred that the copolymeric units be grouped in sequences alternating with long polypivalolactone sequences to form a segmented or block copolyester. As copolymer components, the lactones or hydroxyacids are particularly suited and especially β-propiolactones such as disclosed by Etienne and Fischer in French Patent 1,231,163. For example, copolymers consisting essentially of the following units



With up to 25 mol percent of



as derived from copolymerization of pivalolactone and α,α-diethylpropiolactone are herein contemplated. Blends of polypivalolactone with up to about 10 percent or more by weight of polyamides as illustrated in Example XI or other polymers that do not materially affect the properties of the polypivalolactone are also suitable in the invention. Of course, conventional additives as dyes, pigments, stabilizers, etc. may be present in the fibers.

The following examples will serve to illustrate the scope of the invention; however, they are not intended to be limitative. The abbreviation "elong." is used for "break elongation" and the abbreviation "mod." for "modulus" in some of the data tabulations in the examples.

Example I.—High work recovery, elastic fiber

Molten polypivalolactone having an inherent viscosity of 2.6 and containing 0.1% 2,2-bis(4-hydroxyphenyl) propane by weight is extruded at 260° C. from a spinneret having a single orifice, 0.020 inch in diameter. The extruded filament is passed through a cylindrical annealing tube 3 inches in diameter and 6 inches long having a surface temperature of 300° C., after which it is quenched by passing it through room temperature air. After passing it over a feed roll operated at 611 y.p.m. and drawing it at a draw ratio of 2.5× over a 190° C. hot plate with a 3-foot contact length, the filament is wound up. It has a denier of 10.3. The inherent viscosity of the polymer comprising the filament is 2.2. A sample of the drawn filament wound taut on a bobbin is heated for 16 hours at 175° C. and is then "boiled off" by immersing it, free of tension, in boiling water containing 0.1% detergent for 30 minutes. After the heat treatment, the yarn has a WR_5 of 92% and a $TR_{50/1/2}$ of 94%.

As characterized by X-ray measurement, the high work recovery, elastic heat-treated yarn has an α ratio of 3.27, an α crystallite size of 219 A., a radial breadth of 0.30°, and an orientation angle of 21°. Its tenacity is 2.5 g.p.d., its break elongation 76%, its initial modulus 28 g.p.d. and its TR_5 96%.

Example II.—High work recovery, elastic fiber

Polypivalolactone having an inherent viscosity of 1.54 is melt-extruded at 280° C. from a spinneret containing 15 orifices, each 0.009 inch in diameter. The extruded filaments are passed through a vertical water-quench tube continuously fed by water maintained at 6° C. from a cylindrical pan surmounting the tube and maintained full of water. The filaments are passed through a convergence guide and the yarn so formed is taken up by a roll at 900 y.p.m. and then passed to a draw roll at 1133 y.p.m. for a draw ratio of 1.26×, after which the yarn is wound up at 1128 y.p.m. The inherent viscosity of the polymer comprising the yarn is 1.23. A sample of the drawn yarn wound taut on the bobbin is heated for 16 hours at 175° C. and is then boiled off for 30 minutes. After the heat treatment, the yarn has a WR_5 of 90%. The $TR_{50/1/2}$ of a sample of heat-treated yarn is 72%.

As characterized by X-ray measurement the high work recovery, elastic heat-treated yarn has an α ratio of 2.26, an α crystallite size of 163° A., a radial breadth of 0.32°, and an orientation angle of 15°. Its tenacity is 4.36 g.p.d., its break elongation 85%, its initial modulus 34 g.p.d. and its TR_5 94%.

Example III.—Illustration of critical structural limits

Polypivalolactone having an inherent viscosity of 2.5 is extruded at 265° C. from a spinneret having 15 orifices, each 0.007 inch in diameter. The extruded filaments are quenched by passing them through room temperature air and passed through a convergence guide, after which the yarn so formed is wound up. The spinning speed is 200 y.p.m. The yarn is subsequently oriented by drawing it at a draw ratio of 3.72× around a hot pin maintained at 130° C., after which it is again wound up. The inherent viscosity of the polymer comprising the yarn is 1.44. In Table 1 are listed the structural parameters of the drawn yarn as determined by X-ray characterization, as well as the physical properties of the yarn.

A sample of the drawn yarn wound taut on a bobbin is converted to a high work recovery yarn by heating it for two minutes at 170° C., after which the heat-treated yarn is boiled off for 30 minutes. A second sample of the drawn yarn wound taut on a bobbin is converted to a high work recovery, elastic yarn by heating it for 16 hours at 170° C., after which the yarn is boiled off for 30 minutes. As a control, a third sample of the drawn yarn is boiled off for 30 minutes without previously heating the yarn at 170° C. The structural parameters of each of these yarns as determined by X-ray characterization, as well as the physical properties of the yarns, are listed in Table 1.

TABLE 1.—COMPARISON OF FIBER STRUCTURES AND PROPERTIES

[Air quenched yarn spun at 200 y.p.m. and pin drawn 3.72× at 130° C.; before and after various heat treatments]

	Drawn Fiber	High WR_5 Fiber	Elastic, High WR_5 Fiber	Control
Heat treatment applied to drawn fiber		(1)	(2)	(3)
WR_5, percent	68	81	82	65
$TR_{50/1/2}$, percent	23	50	80	24
Fiber η_{inh}	1.44	1.44	1.44	1.44
α Ratio	1.63	2.19	2.26	2.12
α Crystallite size, A.	93	123	171	116
Radial breadth, degs.	0.52	0.37	0.31	0.50
Orientation angle, degs.	24.5	21	22	23
Tenacity, g.p.d.	3.5	4.0	3.1	3.3
Elongation, percent	90	81	96	102
Modulus, g.p.d.	27	26	26	21
TR_5, percent	90	94	95	90

[1] 170° C. for 2 min.; 30 min. boil-off.
[2] 170° C. for 16 hr.; 30 min. boil-off.
[3] 30 min. boil-off.

As shown in the table the drawn fiber has a relatively low degree of order of α crystalline character parallel to the fiber axis as illustrated by a radial breadth of 0.52°, and its WR_5 is only 68%. Its radial breadth value and work recovery are relatively unchanged upon boil-off. When the drawn yarn is heated for 2 minutes at 170° C. and boiled off, however, its radial breadth value drops to 0.37° and the WR_5 rises to 81%. The α crystallite size of this yarn is only 123 A. and the yarn is not considered elastic, the $TR_{50/1/2}$ value being only 50%. Upon prolonged heating at 170° C., however, the α crystallite size rises to 171 A. and the $TR_{50/1/2}$ value rises to 80%.

Example IV.—Additional illustration of critical structural limits

Polypivalolactone having an inherent viscosity of 1.61 and containing 0.1% TiO_2 is extruded at 275° C. from a spinneret having 15 orifices, each 0.009 inch in diameter. The extruded filaments are quenched by passing them through a cold water quench-tube and formed into a yarn by passage through a convergence guide. The yarn is taken up by a feed roll operated at a peripheral speed of 900 y.p.m., passed to a draw roll at a draw ratio of 1.3×, and then wound up. The inherent viscosity of the polymer comprising the yarn is 1.35. In Table 2 are listed the structural parameters of the drawn yarn as determined by X-ray characterization, as well as the physical properties of the yarn.

A sample of the drawn yarn wound taut on a bobbin is converted to a high work recovery yarn by heating it for 5 minutes at 175° C. A second sample of the drawn yarn wound taut on a bobbin is converted to a high work recovery, elastic yarn by heating it for 5 minutes at 200° C. X-ray data as well as physical properties for each of these yarns, determined in this instance on yarn samples not subjected to boil-off treatment, are listed in Table 2. Data are also listed for a control comprising a third sample of the drawn yarn boiled off for 30 minutes without previously heating the yarn.

TABLE 2.—COMPARISON OF FIBER STRUCTURES AND PROPERTIES

[Water quenched yarn spun at 900 y.p.m. and drawn 1.3×; before and after various heat treatments]

	Drawn Fiber	High WR_5 Fiber	Elastic, High WR_5 Fiber	Control
Heat treatment applied to drawn fiber		[1]	[2]	[3]
WR_5, percent	44	80	83	69
$TR_{50/1/2}$, percent	[4]	25	77	16
Fiber η_{inh}	1.35	1.35	1.35	1.35
α Ratio	0.19	2.10	2.18	2.26
α Crystallite size, A	33	114	150	82
Radial breadth, degs		0.39	0.37	0.59
Orientation angle, degs	16	16	16	21
Tenacity, g.p.d	5.3	5.3	6.2	3.9
Elongation, percent	39	73	80	97
Modulus, g.p.d	71	27	32	29
TR_5, percent	72	95	94	90

[1] 175° C. for 5 min.
[2] 200° C. for 5 min.
[3] 30 min. boil-off.
[4] Breaks.

As shown in the table the drawn fiber has a low α ratio and α crystallite size. The X-ray pattern for radial breadth is too faint to be measured. Upon boil-off the α ratio and α crystallite size are greatly enhanced; however, the fiber has only a low degree of order of α crystalline character parallel to the fiber axis as illustrated by a radial breadth of 0.59°. The WR_5 is only 69%. When the drawn yarn is heated for 5 minutes at 175° C., the radial breadth value drops to 0.39° and the WR_5 rises to 80%. However, the α crystallite size is only 114 A. and the $TR_{50/1/2}$ is only 25%. Upon heating the drawn yarn for 5 minutes at 200° C., however, the α crystallite size rises to 150 A. and the $TR_{50/1/2}$ value rises to 77%.

Example V.—Criticalness of the orientation angle

Polypivalolactone having an inherent viscosity of 1.25 is extruded at 260° C. from a spinneret having 15 orifices, each 0.005 inch in diameter, the extruded filaments being quenched by passing them through room temperature air. The yarn is wound up at a spinning speed of 650 y.p.m. The inherent viscosity of the spun yarn is 1.10, and its structural and physical properties are as follows:

WR_5, percent	36
$TR_{50/1/2}$, percent	23
α Ratio	2.06
α Crystallite size, A.	83
Radial breadth, degrees	0.77
Orientation angle, degrees	33
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	1.1/295/24
TR_5, percent	64

A sample of the spun yarn is converted to an elastic yarn by heating it, free of tension, for 1 minute at 197° C. After the relaxed heat treatment, the yarn has the following structural and physical properties:

WR_5, percent	73
$TR_{50/1/2}$, percent	81
α Ratio	2.52
α Crystallite size, A.	152
Radial breadth, degrees	0.40
Orientation angle, degrees	27
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	1.1/268/19
TR_5, percent	94

Although this yarn is an elastic yarn, it will be noted that it is not a high work recovery yarn. Its radial breadth value is at the limit for high work recovery yarns, and its orientation angle is above the limit for high work recovery yarns as calculated by the expression

$$10(\eta_{inh}+1)=10(1.1+1)=21°$$

The critical nature of the orientation angle for high work recovery yarns will be further appreciated by comparing the 27° orientation angle of the above yarn with the 16° orientation angle of the elastic yarn of Example IV, which exhibits a WR_5 value of 83%. The latter yarn, which exhibits substantially the same α crystallite size as the above yarn and generally similar values for α ratio and radial breadth, is made by a process which introduces greater orientation into the yarn.

Another sample of the spun yarn is converted to an elastic yarn by heating it, free of tension, for 35 minutes at 197° C. After the relaxed heat treatment, the yarn has the following structural and physical properties:

WR_5, percent	76
$TR_{50/1/2}$, percent	94
α Ratio	2.65
α Crystallite size, A.	180
Radial breadth, degrees	0.41
Orientation angle, degrees	31
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	1.0/248/21
TR_5, percent	95

The above yarn, while exhibiting a high degree of elastic recovery, also exhibits some tendency towards brittleness. Brittleness becomes quite marked above the critical limit $10(2\eta_{inh}+1)$, which has a value of 32° in the present example.

For the purposes of comparison, a sample of the spun yarn is boiled off for one hour without the 197° C. heat treatment. The boiled-off yarn has the following structural and physical properties:

WR_5, percent	53
$TR_{50/1/2}$, percent	22
α Ratio	2.36
α Crystallite size, A.	97
Radial breadth, degrees	0.62
Orientation angle, degrees	33
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	0.6/241/21
TR_5, percent	78

Even after an 8-hour boil-off, the yarn has a $TR_{50/1/2}$ of only 21%.

Example VI.—High work recovery fibers

Polypivalolactone having an inherent viscosity of 2.6 is extruded at 280° C. from a spinneret having 15 orifices, each 0.007 inch in diameter. The filaments are passed through a cold water quench-tube at a spinning speed of 550 y.p.m. and through a convergence guide, after which the yarn so formed is taken up by a feed roll, passed to a draw roll at a draw ratio of 1.25×, and then wound up. The inherent viscosity of the polymer comprising the yarn is 1.36. The structural and physical properties of the drawn fiber are as follows:

WR_5, percent	53
$TR_{50/1/2}$	[1] Low
α Ratio	0.60
α Crystallite size, A.	36
Radial breadth, degree	0.54
Orientation angle, degrees	20
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	4.7/55/35
TR_5, percent	78

[1] Est. as 20%.

A sample of the drawn yarn wound taut on a bobbin is converted to a high work recovery yarn by heating it for one minute in 170° C. air; however, the rate of heating is such that the temperature of the bobbin surface rises

above 150° C. only after about 30 seconds of the heating time have elapsed. After the one-minute heat treatment, the yarn is boiled off for 30 minutes. The structural and physical properties of the heat-treated fiber are as follows:

WR_5, percent	81
$TR_{50/1/2}$, percent	19
α Ratio	1.72
α Crystallite size A.	92
Radial breadth, degree	0.40
Orientation angle, degrees	90
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	5.9/68/30
TR_5, percent	95

By comparison, a sample of the drawn yarn boiled off for 30 minutes without treatment in air at 170° C. has a relatively low degree of order of α crystalline character parallel to the fiber axis. Its structural and physical properties are summarized below:

WR_5, percent	72
$TR_{50/1/2}$, percent	18
α Ratio	1.62
α Crystallite size, A.	74
Radial breadth, degree	0.52
Orientation angle, degrees	21.5
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	4.5/96/27
TR_5, percent	91

A sample of the drawn yarn heated at 125° C. for 2 minutes similarly has a WR_5 of only 71% and a relatively low degree of order of α crystalline character parallel to the fiber axis.

Example VII.—High work recovery, elastic fiber

A sample of the drawn yarn of Example VI is heated, free of tension, at 170° C. for 16 hours to convert it to a high work recovery, elastic yarn. The structural and physical properties of the fiber after this relaxed heat treatment are as follows:

WR_5, percent	87
$TR_{50/1/2}$, percent	81
α Ratio	2.28
α Crystallite size, A.	157
Radial breadth, degree	0.36
Orientation angle, degrees	22.5
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	3.6/91/28
TR_5, percent	97

Another sample of the drawn yarn of Example VI is wound taut on a bobbin and converted to a high work recovery elastic yarn by heating it for 64 hours in 170° C. air, followed by treatment in boiling water for 30 minutes. The structural and physical properties of this fiber are:

WR_5, percent	88
$TR_{50/1/2}$, percent	72
α Ratio	2.50
α Crystallite size, A.	148
Radial breadth, degree	0.30
Orientation angle, degrees	16
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	5.5/88/31
TR_5, percent	97

Example VIII.—Compressional recovery of staple pellets

Molten polypivalolactone having an inherent viscosity of 1.82 is extruded at 285° C. from a spinneret containing 15 orifices, each 0.009 inch in diameter. The extruded filaments are passed through a vertical water quench tube continuously fed by water maintained at 13° C. from a cylindrical pan surmounting the tube and maintained full of water. The filaments are passed through a convergence guide and the yarn so formed is taken up by a roll at 1,000 yards per minute and then passed to a draw roll at 1,100 y.p.m. for a draw ratio of 1.1×, after which the yarn is wound up. The inherent viscosity of the polymer comprising the yarn is 1.5. The yarn is plied (30 ends) at 70 yards per minute and heat set by passing it at the same speed over a roll heated to 175° C., the contact time being 0.5 second. The yarn is then padded with a 5% aqueous solution of an anionic textile finishing agent, the pick-up of finishing agent on the yarn being about 1%, after which a sheet of 23 plied ends is fed into a stuffer box crimper and crimped. The crimped yarn is cut to give 3-inch staple fibers, which are then scoured for one hour at 35° C. in a 0.1% detergent solution, rinsed, and air-dried. The staple fibers so prepared are designated as "Control Sample A." A portion of Control Sample A is heated, free of tension, for 10 minutes at 175° C., and the resulting staple fibers are designated as "Control Sample B." A second portion of Control Sample A is heated, free of tension, for 16 hours at 175° C., and the resulting staple fibers are designated as the "Test Sample." The structural parameters of each of these yarns as determined by X-ray characterization, as well as the physical properties of the yarns, are listed in Table 3.

TABLE 3.—PROPERTIES OF STAPLE YARNS

	Control Sample A	Control Sample B	Test Sample
WR_5, percent	67	78	86
$TR_{50/1/2}$, percent	20	36	89
α Ratio	2.12	2.23	2.39
α Crystallite size, A	75	105	168
Radial breadth, degs	0.56	0.45	0.32
Orientation angle, degs	23	23	19
Tenacity, g.p.d	4.0	4.0	4.1
Elongation, percent	80	91	84
Modulus, g.p.d	22	23	25
TR_5, percent	83	85	94

Samples of the staple fibers are shaped by hand into stable pellets and subjected to the standard Busse compressional recovery test. The Busse compressional recovery test measures the ability of a pellet or plug of staple fibers to recover from compressional forces and is expressed in percent. The apparatus used in the Busse test is described in Textile Research Journal, 23, 84 (1953). The test is performed at 65% relative humidity and at 70° F. A tuft of staple fibers weighing 0.3 gram is taken from a sliver or batt and placed in a metal cylinder which is 0.8 square inch in area. The tuft of staple is formed into a loose pellet by compressing it with a light wooden rod at approximately 0.2 p.s.i. The initial height of the loose pellet is then measured under this load. The wooden rod is then replaced with a steel rod and a loading force of 10,000 p.s.i. is applied to the pellet for one minute. This compressed pellet of fiber is then removed from the cylinder and allowed to recover. The recovery in percent is calculated from the ratio of the recovered pellet height to the initial pellet height. Because of the removal of the rod before the final measurement, the recovery may be greater in some cases than the initial height.

For comparison, a sample of standard, semidull, normal tenacity, polyethylene terephthalate staple fiber (standard polyethylene terephthalate staple produced by E. I. du Pont de Nemours and Company, Inc. as type 54) is heated, free of tension, for 4 hours at 175° C. The resulting staple fibers, which have a WR_5 of 31%, are also subjected to the Busse compressional recovery test. The results of these tests are listed in Table 4.

TABLE 4.—BUSSE COMPRESSIONAL RECOVERY TEST

Staple Sample	WR_5, percent	Recovery (Immediate), percent	Recovery (15 min.), percent
Polyethylene terephthalate	31	13	19
Polypivalolactone fibers:			
Control Sample A	67	27	53
Control Sample B	78	38	65
Test Sample	86	78	102

As a check on the work recovery level of the polyethylene terephthalate sample, a sample of filamentary polyethylene terephthalate yarn is spun and drawn 2.46× at a draw speed of 2,750 y.p.m. through an aqueous bath maintained at a temperature of 90° C. and a draw roll temperature of 101° C. in accordance with the process described by Dusenbury in his U.S. Patent 3,091,805. A sample of the drawn yarn boiled off for 30 minutes while held taut has a WR_5 of 35%. A sample boiled off free of tension for 30 minutes has a WR_5 of 28%. Another sample heated at 170° C. for 30 minutes while held taut and then boiled off free of tension for 30 minutes has a WR_5 of 33%.

Example IX.—High work recovery copolyester fiber

Thirty ml. of benzene is refluxed in a 500-ml. three-necked flask equipped with stirrer and condenser with 1.0 ml. of a 0.1 N solution of the tetrabutylammonium salt of hexyldimethylacetic acid (mixture of C_9–C_{11} trialkylacetic acids available commercially as "Versatic" acid from Shell Development Co.) in benzene. To this is added 1.92 g. of α,α-diethylpropiolactone. Refluxing is continued for 20 minutes, during which time highly swollen polymer precipitates. An additional 65 ml. of benzene is added and brought to reflux, after which 8.5 g. of pivalolactone is added and a vigorous exothermic polymerization occurs. After 20 minutes another 30 ml. of benzene is added and brought to reflux, whereupon a second 1.92 g. portion of α,α-diethylpropiolactone is introduced. Refluxing is continued for 20 minutes, after which 65 ml. more of benzene is added, the mixture brought back to the boil, and a second 8.5 g. portion of pivalolactone is added. The mixture is refluxed a final 1.5 hours and allowed to cool. The resulting copolymer, poly-(pivalolactone/α,α-diethylpropiolactone) (85/15 mol percent), is then coagulated by adding 200 ml. of alcohol, collected by filtration using more alcohol to wash the copolymer, and dried in a vacuum oven at 100° C. The yield is 20.6 g. and the inherent viscosity is 1.47. A plug of the copolymer is extruded at 250° C. from a single orifice having a diameter of 0.012 inch. The filament is quenched in ice water and wound up at 1600 yards per minute. A sample of the filament heated at 170° C. for 3.5 hours has the following structural and physical properties:

WR_5, percent	83
$TR_{50/1/2}$, percent	35
α Ratio	2.03
α Crystallite size, A.	97
Radial breadth, degree	0.30
Orientation angle, degrees	16
TR_5, percent	94

Tenacity/elongation/modulus values of 5.2 g.p.d./76%/26 g.p.d. are measured on a sample of the same filament heated taut at 175° C. for only 2 hours.

Example X.—High work recovery, elastic copolyester fiber

A mixture of 400 g. of pivalolactone and 13.4 g. of α,α-diethylpropiolactone is added to a refluxing solution of 4.1 g. of triethylenediamine and 0.41 g. of finely divided TiO_2 in 1650 ml. of hexane. An exothermic reaction occurs, after which refluxing is continued for 2 hours. The resulting copolymer, poly(pivalolactone/α,α-diethylpropiolactone) (97.5/2.5 mol percent) is collected by filtration and dried. The yield is 92% and the inherent viscosity is 1.5. A sample of the copolymer is spun and drawn in general accordance with the procedure of Example II. The inherent viscosity in yarn form is 0.94. A sample of the drawn yarn wound taut on the bobbin is heated for 16 hours at 170° C. and is then boiled off for 30 minutes. After the heat treatment, the yarn has the following structural and physical properties:

WR_5, percent	84
$TR_{50/1/2}$, percent	61
α Ratio	2.25
α Crystallite size, A.	140
Radial breadth, degree	0.39
Orientation angle, degrees	15
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	3.9/79/36
TR_5, percent	96

Example XI.—High work recovery, elastic fiber of polypivalolactone/copolyamide melt blend

A copolyamide derived from 10.96 g. of hexamethylenediamine, 9.04 g. of adipic acid, 10.22 g. of sebacic acid, and 16.80 g. of caprolactam by slowly heating at 215°–245° C. with a final polycondensation step at 245° C. for one hour at 1 mm. of mercury has a molecular weight of 2450 by end group titration. To 90 parts of powdered polypivalolactone is added 10 parts of the copolyamide, dissolved in a quantity of a solvent comprising 4 parts of ethanol and 3 parts of chloroform. The solvent is removed by heating, and a plug of the 90/10 wt. percent blend is molded. The blend is then melt spun from a press spinner at 230° C. and a spinning speed of 500 y.p.m. to form a filament which is then drawn 1.64× on a 155° C. hot plate. The inherent viscosity of the polymer blend comprising the filament is 1.4. A sample of the filament wound taut on a bobbin is heated for 2 hours at 170° C. and is then boiled off for 30 minutes. The heat-treated filament has the following structural and physical properties:

WR_5, percent	82
$TR_{50/1/2}$, percent	74
α Ratio	2.17
α Crystallite size, A.	144
Radial breadth, degree	0.28
Orientation angle, degrees	17
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	3.8/76/32
TR_5, percent	94

Example XII.—Comparative example

Following the procedure of Alderson in his U.S. Patent 2,658,055 (Example 4), hydroxypivalic acid is polymerized to form a polymer having an inherent viscosity of 1.13. Filaments of the polymer are extruded at 250° C. and quenched in a bath of kerosene maintained at 15° C., the spinning speed being 300 y.p.m. The yarn is drawn 3.5X and wound up. The inherent viscosity of the polymer comprising the yarn is 0.81. The structural and physical properties of the yarn are as follows:

WR_5, percent	51
$TR_{50/1/2}$	(Breaks)
α Ratio	1.55
α Crystallite size, A.	64
Orientation angle, degrees	22
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	2.22/69/25
TR_5, percent	82

A sample of the drawn yarn boiled off for 30 minutes has the following structural and physical properties:

WR_5, percent	71
$TR_{50/1/2}$, percent	27
α Ratio	2.34
α Crystallite size, A.	90

Radial breadth, degree	0.68
Orientation angle, degrees	21
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	2.3/72/28
TR_5, percent	89

The degree of α crystalline character parallel to the fiber axis of the above yarn is of low order, as evidenced by the radial breadth value far above the limits for either a high work recovery yarn or an elastic yarn. In addition, the orientation angle of 21° is above the limit for a high work recovery yarn as calculated by the expression

$$10(\eta_{inh}+1)=10(1.81)=18.1°$$

Even when treatment in boiling water is continued for 8 hours, the WR_5 of the yarn is only 73% and the $TR_{50/1/2}$ only 28%, with an α crystallite size of 92 A. and an α ratio of 2.14.

The orientation angles in the above example are determined by measurement of the diffraction spot at 11.5°, 2θ, as previously described. This diffraction spot is due entirely to diffraction radiation from the α crystalline structure and the technique accordingly yields the desired measure of the orientation of the α crystallites alone. The orientation angle for the sample of drawn yarn in the above example is additionally determined by measurement of the diffraction spot at 17.9°, 2θ, and this value is 18°. This value corresponds well with the 17° value observed by Alderson, who did not specify the diffraction spot employed. The 17.9°, 2θ, diffraction spot yields a mixed measure of α and β orientation.

Example XIII.—Comparative example

Polypivalolactone having an inherent viscosity of 2.5, corresponding to a logarithmic viscosity number of 160 (1% solution at 25° C. in a 60:40 mixture of phenol and o-chlorophenol), is extruded at 265° C. from a spinneret having 15 orifices, each 0.007 inch in diameter. The extruded filaments are quenched by passing them through air at room temperature, the spinning speed being 300 y.p.m. Following the procedure of Reynolds and Vickers in their British Patent 766,347 (Example 7), the spun filaments are drawn over a 125° C. hot pin and wound up. The draw ratio is 3.6×. The inherent viscosity of the polymer comprising the yarn is 1.44. The structural and physical properties of the drawn yarn are as follows:

WR_5, percent	74
$TR_{50/1/2}$	(Breaks)
α Ratio	1.29
α Crystallite size, A.	84
Radial breadth, degree	0.45
Orientation angle, degrees	18
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	4.04/74/27
TR_5, percent	92

A sample of the drawn yarn boiled off for 30 minutes has the following structural and physical properties:

WR_5, percent	71
$TR_{50/1/2}$, percent	21
α Ratio	1.47
α Crystallite size, A.	82
Radial breadth, degree	0.42
Orientation angle, degrees	20
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	3.9/74/32
TR_5, percent	92

The degree of α crystalline character parallel to the fiber axis of the drawn yarn, both before and after boil-off, is of relatively low order as evidenced by radial breadth values of 0.45° and 0.42°, too high for high work recovery yarns. Similarly, the α crystallite size is far below the limit in each instance for elastic yarns. Even after an 8-hour boil-off, the WR_5 and $TR_{50/1/2}$ values are only 73% and 23%, respectively, radial breadth estimated value of 0.42° and an α crystallite size of 118 A.

Example XIV.—High work recovery, elastic fiber

A sample of the drawn yarn of Example XIII wound taut on the bobbin is converted to a high work recovery, elastic yarn by heating it for 16 hours at 170° C. and then boiling it in water for 30 minutes. After the heat treatment, the yarn has the following structural and physical properties.

WR_5, percent	88
$TR_{50/1/2}$, percent	88
α Ratio	2.31
α Crystallite size, A.	152
Radial breadth, degrees	0.35
Orientation angle, degrees	19
Tenacity (g.p.d.)/elong. (percent)/mod. (g.p.d.)	4.2/90/27
TR_5, percent	97

Example XV.—Comparative example: Fibers of poly (α,α-diethylpropiolactone) and poly(α-ethyl-α-methylpropiolactone)

To a refluxing mixture of 8 liters of ethyl acetate, 3 g. of dried TiO_2, and 1 g. of tetrabutylammonium hydroxide is added 1026 g. of α,α-diethylpropiolactone. Refluxing is continued for 2.5 hours, after which the mixture is diluted with 8 l. of methanol and the precipitate is filtered, washed with methanol, and dried under vacuum. The product, poly-(α,α-diethylpropiolactone), is obtained in a yield of more than 90% and has an inherent viscosity of 1.42.

A sample of the polymer is extruded at 278° C. from a spinneret containing 14 orifices, each 0.009 inch in diameter. The extruded filaments are passed through a vertical water-quench tube continuously fed by water maintained at a temperature of not more than 12° C. from a cylindrical pan surmounting the tube and maintained full of water. The filaments are passed through a convergence guide and the yarn so formed is taken up by a roll at 400 y.p.m and then passed to a second roll at 700 y.p.m., after which the yarn is wound up. The yarn is subsequently passed from a feed roll operated at a peripheral speed of 54 y.p.m. across a plate maintained at 165° C. to a draw roll operated at 116 y.p.m., after which it is again wound up. A sample of the drawn yarn, when boiled off for 30 minutes, has a WR_5 of 53%. Its tenacity is 7.3 g.p.d., its break elongation 8%, its initial modulus 133 g.p.d. and its TR_5 72%. A sample of the drawn yarn wound taut on a bobbin is heated for 16 hours at 170° C. and is then boiled off for 30 minutes. After the heat treatment, the yarn has a WR_5 of 51%. Another sample of the drawn yarn wound taut on a bobbin and heated for 24 hours at 130° C. followed by a 30-minute boil-off has a WR_5 of 55%.

a mixture of 11.4 g. α-ethyl-α-methylpropiolactone, 140 ml. hexane, 0.068 g. dioctadecyldimethylammonium acetate, and 0.022 g. dihexadecyldimethylammonium acetate is refluxed for 3 hours. The resulting polymer, poly(α-ethyl-α-methylpropiolactone), is purified by dissolving it in a mixture of methanol and chloroform, reprecipitating the polymer by adding water, washing with ethanol, and drying it under vacuum. The yield is 97% and the inherent viscosity is 0.90.

A sample of the polymer is extruded at 130° C. from a press spinner through an orifice 0.009 inch in diameter and quenched in cold water. The spinning speed is 400 y.p.m. The filament is drawn 1.5× at 90° C. It has a WR_5 of 50%, a tenacity of 3.3 g.p.d., an elongation of 17% and an initial modulus of 42 g.p.d. The filament melts when heated to about 125° C.

Example XVI

Polypivalolactone having an inherent viscosity of 1.5 is melt extruded at 280° C. from a spinneret containing 30 orifices, each 0.007 inch in diameter. The extruded filaments are passed through a vertical water quench tube continuously fed by water maintained at 14° C. The filaments are passed through a convergence guide and the yarn so formed is taken up by a roll at 700 y.p.m. and is then passed to a draw roll at 816 y.p.m. for a draw ratio of 1.17×, after which the yarn is wound up. The drawn yarn has a denier of 70. The inherent viscosity of the polymer comprising the yarn is 1.06.

Plain weave taffeta fabric having a finished construction of 120 ends and 75 picks is woven from this yarn. One sample of the fabric, designated "Test Fabric," is heated at 170° C. for sixteen hours; and a second sample of the fabric, designated "Control Fabric," is heated in boiling water for one hour. Filaments removed from the warp and filling of the Test Fabric are found to have a WR_5 of 85%, while filaments similarly removed from the warp and filling of the Control Fabric are found to have a WR_5 of 75%. The Test Fabric exhibits superior recovery from wrinkling, under both wet and dry conditions, as compared with the Control Fabric.

Example XVII

Polypivalolactone having an inherent viscosity of 1.6 is extruded at 280° C. from a spinneret having 25 orifices, each comprising three 0.003 inch x 0.012 inch slots intersecting in a Y configuration. The filaments are quenched by a cross-flow stream of air at room temperature, supplied at the rate of 100 cubic feet per minute, after which they are gathered as a yarn and taken up by a forwarding roll at the rate of 800 y.p.m. The yarn is then passed continuously under a draw pin immersed in a bath of water maintained at 90° C. and out of the bath via a pair of guides to a pair of draw rolls maintained at 100° C. and operated at a peripheral speed of 1,800 y.p.m. The inherent viscosity of the polymer comprising the yarn is 1.5.

The yarns have a tenacity of 2.7 g.p.d., an elongation of 50%, an initial modulus of 40 g.p.d., and a WR_5 of 65%. The yarn is woven to form a taffeta fabric having a construction of 104 ends and 76 picks per inch. The griege fabric is scoured at 35° C. and dried at room temperature. One sample of the fabric is labelled "Control Sample"; while a second sample is heat set in a 175° C. oven for one hour, allowing 5% shrinkage in the fill direction, and designated as the "Test Sample." Filaments removed from the warp and fill of the Control Sample have an average WR_5 of 67%, while filaments removed from the warp and fill of the Test Sample have an average WR_5 of 89%.

A wrinkle recovery test is carried out on both the Control Sample and the Test Sample. In this test a fabric sample is wrapped around a cylindrical form consisting of a coiled spring covered with a plastic-coated cloth so that the form is compressible in the direction perpendicular to the base of the cylinder. The wrapped cylinder is compressed to one-half its original height and is held in this way for four minutes. Pressure is removed and the fabric sample is hung vertically and is photographed at intervals while recovering from the wrinkling imparted during testing. The Test Fabric has a markedly lower degree of imparted wrinkling than the Control Fabric; while the rate and degree of recovery from wrinkling of the Test Fabric is markedly superior to that of the Control Fabric. The Test Fabric is also markedly superior in this test to a fabric of similar construction prepared from polyethylene terephthalate yarn.

Example XVIII

Polypivalolactone having an inherent viscosity of 1.91 is extruded at 280° C. from a spinneret having 3 orifices, each 0.007 inch in diameter. The extruded filaments are quenched by passing them through air at room temperature to a guide located sixty inches below the spinneret, after which they are passed to a wind-up at 600 yds./min. The resulting 3-filament yarn has an inherent viscosity of 1.65, and the individual filaments have an average denier of 5.5. The structural and physical properties of the spun yarn is as follows:

WR_5, percent	35
$TR_{50/1/2}$, percent	23
α Ratio	2.36
α Crystallite size, A.	77
Radial breadth	(1)
Orientation angle, degrees	31
Tenacity (g.p.d.)/elong. (percent)/ mod. (g.p.d.)	1.2/210/21
TR_5, percent	65

[1] Too faint to measure.

A sample of the spun yarn is converted to an elastic yarn by passing fifty wraps of the yarn at low tension between a roll maintained at 180° C. and a separator roll. The yarn speed is 105 yds./min. and the contact time on the heated roll is 27 seconds. After the heat treatment, the yarn has the following structural and physical properties:

WR_5, percent	54
$TR_{50/1/2}$, percent	93
α Ratio	2.42
α Crystallite size, A.	228
Radial breadth, degrees	0.31
Orientation angle, degrees	31
Tenacity (g.p.d.)/elong. (percent)/ mod. (g.p.d.)	1.3/180/14
TR_5, percent	78

As shown by the above properties, the heat-treated yarn is an elastic yarn, although not a high work recovery yarn. The yarn exhibits extraordinarily high power, as shown by the following modulus values in the elongated state (measured on the second cycle at the indicated elongation). The power of a commercially available 40 denier, continuous filament spandex yarn (Du Pont "Lycra" spandex yarn) is also measured and the results are shown below for the purpose of comparison:

[Power (modulus) in g.p.d.]

Elongation	50%	60%	75%	90%
Polypivalolactone Yarn	1.30	1.36	1.30	1.31
Spandex Yarn	0.14	0.135	0.16	0.395

Core-spun stretch yarns are prepared by the process of Humphreys in his U.S. Patent No. 3,038,295, using as core yarns the polypivalolactone yarns described above. The process is carried out on a conventional spinning frame. Roving having a weight of one pound per 840-yard hank and comprised of 70% acrylic bicomponent staple (Du Pont "Orlon" acrylic type 24 fiber) and 30% acrylic staple (Du Pont "Orlon" acrylic type 42 fiber) is spun to a 259 denier (20/1 cotton count) yarn twisted 18.2 turns per inch in the S direction with the introduction of the core yarn to which a draft of 1.8 is applied. The final wind-up speed is 10.6 yards per minute. In applying the process to the spun polypivalolactone yarn as the core yarn, it is observed that the spun yarn is drawn during the drafting step and the product is a nonelastic core-spun yarn. The heat-treated polypivalolactone yarn yields an elastic core-spun yarn having a core content of 5.5% and a modulus of 0.39 g.p.d. at 90% elongation. The elastic core-spun yarn so prepared is useful for the preparation of stretchable fabrics.

What is claimed is:

1. A high work recovery fiber consisting essentially of polypivalolactone, said fiber having an orientation angle

less than the numerical value given by the expression

$$10(\eta_{inh}+1)$$

where η_{inh} is the inherent viscosity of the polymer of the fiber, said viscosity being determined at a concentration of 0.5 gm. of polymer per 100 ml. of solution in trifluoroacetic acid, and at a temperature of 30° C. and is at least 0.75, the said fiber having an α ratio of at least 1.70, an α crystallite size transverse to the fiber axis of at least 85 A. and a radial breadth of not more than 0.40°.

2. The fiber of claim 1 wherein the α crystallite size transverse to the fiber axis is at least 140 A., and the α ratio is at least 2.15.

3. A novel fiber consisting essentially of polypivalolactone, said fiber having an orientation angle less than the numerical value given by the expression

$$10(2\eta_{inh}+1)$$

where η_{inh} is the inherent viscosity of the polymer of the fiber, said viscosity being determined at a concentration of 0.5 gm. of polymer per 100 ml. of solution in trifluoroacetic acid, and at a temperature of 30° C. and is at least 0.75, the said fiber having an α ratio of at least 2.15, an α crystallite size transverse to the fiber axis of at least 140 A. and a radial breadth of not more than 0.50°.

4. An elastic fiber of high elongation consisting essentially of polypivalolactone, said fiber having an orientation angle that is greater than the numerical value given by the expression

$$10(\eta_{inh}+1) \text{ but less than } 10(2\eta_{inh}+1)$$

where η_{inh} is the inherent viscosity of the polymer of the fiber, said viscosity being determined at a concentration of 0.5 gm. of polymer per 100 ml. of solution in trifluoroacetic acid, and at a temperature of 30° C. and is at least 0.75, the said fiber having an α ratio of at least 2.15, an α crystallite size transverse to the fiber axis of at least 140 A. and a radial breadth of not more than 0.50°.

5. The fiber of claim 1 wherein the polymer contains up to 25 mol percent of repeating units derived from α,α-diethylpropiolactone.

6. The novel fiber of claim 1 containing minor amounts of a polyamide blended with the said polypivalolactone.

7. A process comprising incorporating oriented fibers into a fibrous structure, said fibers consisting essentially of polypivalolactone having an inherent viscosity η_{inh} of at least about 0.75, said viscosity being determined at a concentration of 0.5 gm. of polymer per 100 ml. of solution in trifluoroacetic acid, and at a temperature of 30° C. and an orientation angle having a numerical value less than $8\eta_{inh}+15$, and heating said fibrous structure at a temperature of at least 150° C. until the fibers have an α ratio of at least 1.70, an α crystallite size of at least 85 A. and a radial breadth of not more than 0.40°.

8. A process comprising incorporating oriented fibers into a fibrous structure, said fibers consisting essentially of polypivalolactone having an inherent viscosity η_{inh} of at least about 0.75, said viscosity being determined at a concentration of 0.5 gm. of polymer per 100 ml. of solution in trifluoroacetic acid, and at a temperature of 30° C. and an orientation angle having a numerical value less than $15\eta_{inh}+17$, and heating said fibrous structure at a temperature of at least 150° C. until the fibers have an α ratio of at least 2.15, an α crystallite size of at least 140 A. and a radial breadth of not more than 0.50°.

References Cited by the Examiner

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FOREIGN PATENTS

766,347	1/1957	Great Britain.
1,231,163	9/1960	France.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,299,171 January 17, 1967

Fred W. Knobloch et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 54, for "85° A." read -- 85 A. --; column 8, line 31, for "tan R_3" read -- tan θ_3 --; column 9, line 25, for "$\eta inh = \frac{in\ \eta rel}{C}$" read -- $\eta inh = \frac{ln\ \eta rel}{C}$ --; column 11, line 47, for "163° A." read -- 163 A. --; column 15, line 10, for "90°" read -- 19° --; column 19, line 22, for "diffraction" read -- diffracted --; column 22, line 51, for "0.395" read -- 0.195 --.

Signed and sealed this 26th day of September 1967.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents