This invention relates in general to the production of synthetic fibers and monofilaments. More particularly, it relates to novel fibers and monofilaments formed from isotactic polystyrene and to a novel melt spinning process for producing these fibers and monofilaments.

Recent developments, however, have led to the development of methods for producing isotactic polystyrene, i.e., styrene homopolymer chains which are sterically regular along substantially the entire chain length or at least along a considerable portion thereof. Isotactic polystyrene, because of its inherent ability to crystallize, offers several outstanding properties desirable in fibers or filaments for textile uses, such as high strength, high stiffness, and unusual chemical resistance. The isotactic polymer is useful for textile purposes only if methods are found to process the polymer raw material so that the products possess and/or maintain these useful properties, and at the same time overcome the problems incurred by the extremely low impact strength or Brittleness which characterize the isotactic polymer.

The method for forming fibers from conventional polymers generally referred to as melt spinning has heretofore not been adaptable to forming textile quality fibers of isotactic polystyrene. One of the major reasons has been the incompatibility of molecular orientation of the molecular chains in the fibers and dimensional stability at elevated temperatures. Especially has this been found to be true in applications relating to the textile art.

This general object and other more particular objects which will be apparent from the specification are accomplished in accordance with the present invention by the method which includes the steps of melt extruding an isotactic polystyrene having a melt index of between 1 and 20 through a fiber forming die at a temperature between about 230° C. and 330° C., hot drawing the fibers as they emerge from the forming die while maintaining the fibers at substantially the extrusion temperature, and thereafter cold drawing the fibers to impart a degree of stretch of from about 800 to 900 percent whereby a high degree of orientation is induced in said fiber. Several methods for polymerizing styrene to form the isotactic form of polystyrene have been proposed, but none of these was developed in a manner suitable for the polymerization autoclave has such an exceedingly high melt viscosity, i.e., very low melt index, that melt spinning of the un-
From here the product is extruded as a rod, and fed to the extruder provided with the spinneret die, or is passed through a quenching bath, and then to a dicer for pelletizing.

In a second method, the isotactic polystyrene is treated in a “heated mill” which continuously mills and heats the polymer. The essential feature in such a mill is the use of helically-threaded rolls which are rotated in opposite directions to draw the polystyrene into the bite of the rolls. These rolls are housed in such a manner that a heating jacket is provided and there is a chamber over at least part of the threaded portion of the roll whereby the material can be heat treated in the presence of an inert gas such as nitrogen or subjected to a vacuum during the thermal treatment. Under these operating conditions the polymer is repeatedly worked as it passes through the bite, blended to assure temperature uniformity, and conveyed along the rolls to the discharge end by the helical threads. Generally the polystyrene is preheated to about 300 °C before it enters the mill which is heated by passing hot liquids or vapors through the heating jacket. The ultimate temperature attained by the polystyrene, the period of time during which this temperature is maintained, and the initial melt viscosity of the polystyrene are interdependent factors which may be determined by routine experimentation to obtain the final pyrolyzed polystyrene product having the desired increased melt index.

The melt viscosity of the pyrolyzed isotactic polystyrene which is melt spun into fibers depends to a large extent upon the diameter of the orifices in the spinneret die since the polymer must be capable of being forced through the die orifices at a temperature which does not bring about any substantial degradation of the polymer. While the melt index range of the polystyrene found suitable for melt spinning according to the present process is therefore by no means critical, it has been found however that a melt index range of from about 1 to about 30 is generally suitable, with the preferred range being about 2 to about 20 at 250 °C. (ASTM 1258–52T).

Although isotactic polystyrene polymers having melt indices over a rather wide range may be melt spun, the temperature range for extrusion of these polymers through the die of the spinneret is quite narrow. The minimum extrusion temperature is, of course, at least as high as the first order transition temperature, and is as much higher than the first order transition temperature as practical limitations of the materials permit. The maximum extrusion temperature for the purposes of this invention is at least 230 °C. An extrusion temperature of about 250 °C. to about 300 °C. is particularly preferred.

The maximum extrusion temperature has as the sole limiting factor, in the case of isotactic polystyrene, thermal degradation of the polymer. At temperatures above about 330 °C. molecular degradation of the material in the spinneret is sufficient to seriously impair the physical properties of the spun fibers. For this reason the generally preferred extrusion temperature range is at least 230 °C. and not more than about 330 °C.

The isotactic polystyrene filaments as they are formed by the passing of the molten polymer mass through the spinneret die orifices are subjected to shearing stresses which cause a substantial degree of molecular orientation. Within the narrow range of temperatures found suitable for extrusion, the shear induced molecular orientation at the surface of the filament is not permitted to relax when the filament emerges from the spinneret into ambient room temperature because the chilling effect of room atmosphere is sufficient to cool the surface of the fiber to a point where relaxation is not possible. The internal portion of the filament, however, because of the relatively poor heat conductivity of the polystyrene, is sufficiently warm to permit relaxation of the stress induced orientation. Further, since the extruded filaments must be reduced in diameter for most textile uses by drawing down as they leave the spinneret, additional orientation would occur in the cooled outer portions of the filaments. Therefore, it is desired that the internal surface of the filaments be subjected to “cold stretching” for the purpose of inducing controlled uniform molecular orientation to increase the strength of the filaments, the molecules at the surface orient to their fullest extent before full orientation of the internal molecules occurs. Although such filaments can never be fully and uniformly oriented to the extent that they possess the requisite fiber strength, toughness, and crystallinity to ensure dimensional stability at elevated temperatures.

For this reason, in the process of this invention the isotactic polystyrene filaments are not chilled or permitted to become chilled as they leave the spinneret and are subjected to draw-down to bring about a size reduction. This is contrary to prior known melt spinning procedures involving other plastic materials including non-isotactic polystyrene in which a jet of cold air is conventionally directed across the filament at the point where it emerges from the spinneret. It is desired that at this point, however, it is vital that provision be made for maintaining the temperature of the filaments uniformly at the die temperature during the period of size reduction draw-down for a period of time sufficient to allow any oriented molecules at the surface of the filaments to relax whereby all molecules of the filaments are uniformly relaxed. This is accomplished in our invention by providing a heated zone immediately adjacent to the discharge end of the spinneret through which the emerging filaments pass during the size-reduction draw-down. The zone is of sufficient size so that the time required for the filaments to pass therethrough is such that complete molecular relaxation of the filaments may be brought about.

The physical apparatus utilized to create the heated zone are by no means critical. A heated fluid (liquid) bath containing a material inert to polystyrene and not a solvent therefor, or a heated gas stream have been found to be adequate. The preferred embodiment, however, is a cylinder-like chimney of metal or other refractory material capable of withstanding elevated temperatures and being provided with electrical or other heating means. The length of the chimney will depend to some extent on the draw rate of the filament which may vary from about 1 to about 1400 feet per minute, depending in turn upon the diameter of the filament of extrusion, and the diameter of the orifices in the spinneret. As a general rule, the time required for molecular relaxation from the orifice shear induced orientation is of the order of magnitude of 1 second at temperatures in the range of from 250 °C. to 330 °C.

After the filaments have been extruded and heat treated to remove the non-uniform orientation, they are permitted to cool under conditions which do not permit re-orientation of a non-uniform nature to occur. In this cold unoriented amorphous state the fibers are quite brittle and difficult to wind on a bobbin. It has been found that this difficulty can be overcome by heating the fibers, prior to the placement on bobbins, at a temperature not high enough to permit orientation. The temperature range of from about 75 °C. to about 100 °C. is generally suitable for this purpose. It is not necessary to the present process, however, that the fibers be stored on a bobbin prior to being stretched oriented. Even the cold brittle amorphous fibers are sufficiently flexible to permit winding of the fiber tow in a relatively large diameter drum for storage. Preferably, however, the amorphous fibers are neither wound on a bobbin nor coiled in a drum, but are passed without delay from the heat treating chimney to an orientation bath maintained at a temperature of about 120 °C. to about 140 °C. After the fibers have been heated in the orientation bath until the temperature of
the fibers is the same as that of the bath, they are passed to a set of godet rolls which impart stretch orientation in an amount of at least 800 percent in the fibers. This high degree of orientation has been found to be required to obtain isotactic polystyrene fibers which have heat stability at approximately 200° C. The rate of stretching found beneficial preferably should have a minimum value of at least 200 ft./min. and a maximum value of about 3000 ft./min.

The process of the present invention is better illustrated by consideration of the following detailed description of a preferred embodiment thereof in conjunction with the drawings, in which:

FIG. 1 is a schematic representation of one method of carrying out the process, and

FIG. 2 is a side elevation partially in section of a spinning head having a relaxing chimney attached thereto.

Referring now to FIG. 1, a conventional extrusion press indicated generally by letter "a" comprising a barrel having rotatably positioned therein an extrusion screw, means for driving said screw (screw and driving means not shown), and a hopper 10 for feeding particulate isotactic polystyrene to the channels of the extrusion screw, is provided with a conventional spinning head 12, preferably operated in conjunction with metering pump (not shown) and a relaxation chimney 14. Pre-polystyrene is fed into the extruder hopper 10 to the extruder barrel where the driving action of the screw forces it forward along the barrel to a heated zone 16 maintained at a temperature of about 230° C. to about 250° C. and then to heated zone 18 maintained at a temperature of about 250° C. to about 290° C. The combined shearing action of the screw and the heat transfer occurring in heated zones 16 and 18 flux the polystyrene to a viscous mass which is then delivered at a metered uniform rate to spinning head 12. The spinning head, or more particularly the die portion thereof, is maintained at a temperature of 230° C. to about 350° C. Under the pressure exerted by the metering pump, the molten polystyrene is forced through the die orifices of the spinning head at substantially the same temperature as the die itself. The fine fibers of the polymer issuing from the spinneret are maintained at the die temperature by means of heated chimney 14. The length of the chimney is dependent on the amount of thickness reduction to be accomplished by hot drawing and to a larger extent upon the rate of hot drawing which may vary from about 10 ft./min. to about 1400 ft./min. depending primarily upon the linear rate of extrusion of the filaments through the spinneret orifices. The length of the chimney must be in all events long enough to provide a heated zone maintained at the extrusion temperature sufficient to permit any molecular orientation induced in the filaments by the shearing stresses of forming and drawing to relax. After complete molecular relaxation is accomplished, the fibers emerge from the end of the chimney 14 and are collected as a fiber tow. The fiber tow is passed around pulley 20 at a temperature sufficient to prevent the fibers from being too brittle for handling, but at a temperature at which the polymer will not flow or permit orientation. Pulley 20 serves only as a direction changing means for the tow and may be replaced by any conventional equivalent means for accomplishing the same results. From the pulley 20, the tow passes to a pair of rolls 22 through which the force is applied to the fibers in the relaxing chimney to bring about the size reduction by hot drawing. The tow then passes to a constant temperature bath 24, advantageously of glycerine in which the amorphous fiber tow is brought to a temperature of about 125° C. to about 130° C. by the "polystyrene drawn" to impart uniform, maximum molecular orientation. Stretching of the fiber tow to induce orientation is conveniently accomplished by means of an orientation godet 26, although any means for stretching the tow is within the scope of the present invention. A stretch ratio of at least 9:1, i.e., 800 percent elongation, is required at 120° C. to 140° C. to form fibers having adequate dimensional stability and strength at room temperature upwards to about 200° C.

One embodiment of a spinning head in combination with a relaxing chimney is shown in detail in FIG. 2. Spinning head is attached to a conduit 28 which conducts the molten polymer stream from the extruder and metering pump into the head 30. The head is bored conventionally in such a way as to change the direction of flow of the molten polymer from horizontal to substantially vertical. The internal bore 31 channels the molten polystyrene to the top of a machined recess into which is fitted a manifold member 32 which serves to maintain uniform pressure and feed across the entire surface area of the multihole die forming member 34. Manifold member 32 and die member 34 are held securely in place in head 30 by means of bolts 36 and 38, ring 38. Constant temperature of the extruder head and die sufficient to maintain the flowing polystyrene in an extrudable condition is provided by electrical band heater 40. Chimney 42 is preferably attached by any suitable means to the spinning head 30 although it is by no means necessary that the chimney be in fact attached so long as the chimney is maintained close to the die orifices. Heater band 44 maintains the desired temperature in the central portion of the chimney, the temperature being conveniently measured by a thermocouple 46 extending through the side wall of the chimney. The individual fibers as they issue through the forming die and are drawn down within the chimney are caused to converge into a fiber tow at the bottom end of the chimney.

EXAMPLE 1

Isotactic polystyrene having a melt index of about 0.1 at 250° C. was pyrolyzed at a temperature of about 395° C. for a period of about 90 seconds to increase the melt index to 10 at 250° C. The pyrolyzed polystyrene in the form of ¾ inch pellets was fed at the rate of about 1 to 1½ lb/hr. to a 1 inch extruder provided with a spinning head having 50 orifices of 35 mil diameter. The polymer in the extruder barrel was advanced along the barrel by the action of the extrusion screw to a heated zone of the barrel maintained at 160° C. and then to a second zone heated to 260° C., the same temperature at which the spinneret was maintained. As the molten isotactic polystyrene was forced through the spinneret orifices, the resulting filaments were passed through a heated chimney attached to the spinning head and simultaneously hot drawn at the rate of 190 feet per minute. The chimney was maintained at 260° C. and provided a continuous heated passage 18 inches in length. At the draw rate of 190 ft./min., the filaments were reduced in size to about 3 mils in diameter and all shear induced molecular orientation dissipation. As the amorphous filaments emerged from the chimney into air at room temperature they were brought together to form a thread and coiled into a storage drum. The thread was constantly withdrawn from the storage drum at the rate of 20 feet per minute and fed at this rate into a glycerine bath maintained at a temperature of 130° C. to 132° C. The length of thread immersed was 4 feet. From the glycerine bath the thread was picked up by a godet roll travelling at about 190 feet per minute which induced a degree of stretch of about 50% to 90% percent. The final thread had a composite denier of 210, a tensile strength of 2.3 grams per denier, and an extension at break of about 25 percent. Several of these threads obtained as a product of the spinning were piled together to form a heavy knitting yarn. This yarn was textured by allowing a small degree of shrinkage at 135° C. The shrinkage of the individual fibers caused an overall fluffing of the yarn, which when knitted, produced a fabric with good hand and high bulk.
Fibers of crystallizable isotactic polystyrene having diameters of 20, 10 and 5 mils respectively were formed according to the general method described in Example I and using apparatus similar to that shown in FIG. 1 of the drawings.

(a) 20 mil fiber:
- Melt index of pyrolyzed polymer: 2.5.
- Extruder conditions:
  - First barrel zone: 190°C.
  - Second barrel zone: 260°C.
  - Die (single orifice): 250°C.
- Rate of draw down through chimney: 21 ft./min.
- Orientation stretch (rate at 155°C): 210 ft./min.
- Degree of orientation: 950%.
- Annealing after orientation: 10 min. at 135°C.

(b) 10 mil fiber:
- Melt index of pyrolyzed polymer: 2.5.
- Extruder conditions:
  - First barrel zone: 190°C.
  - Second barrel zone: 250°C.
  - Die (single orifice): 250°C.
  - Heated zone (chimney): 285°C.
- Rate of draw down through chimney: 27 ft./min.
- Orientation stretch (rate at 155°C): 125 ft./min.
- Degree of orientation: 950%.
- Annealing after orientation: 10 min. at 135°C.

(c) 5 mil fiber:
- Melt index of pyrolyzed polymer: 2.5.
- Extruder conditions:
  - First barrel zone: 190°C.
  - Second barrel zone: 250°C.
  - Die (6 hole spinning head): 250°C.
  - Heated zone (chimney): 295°C.
- Rate of draw down through chimney: 30 ft./min.
- Orientation stretch (rate at 155°C): Constant tension.
- Degree of orientation: 950-990%.
- Annealing after orientation: 10 min. at 135°C.

The following tables show physical property data of the fibers prepared according to Example II.

Table I

<table>
<thead>
<tr>
<th>Sample</th>
<th>Example II-a</th>
<th>Example II-b</th>
<th>Example II-c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (mils)</td>
<td>20</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Tensile Strength (lbs./sq. in.)</td>
<td>30,000-35,000</td>
<td>45,000-50,000</td>
<td>46,000-45,000</td>
</tr>
<tr>
<td>Extension at break</td>
<td>25</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>Tensile Modulus (lbs./sq. in.)</td>
<td>500,000</td>
<td>500,000</td>
<td>500,000</td>
</tr>
<tr>
<td>Modulus (p.s.i.)</td>
<td>900</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>at 25°C</td>
<td>900</td>
<td>900</td>
<td>900</td>
</tr>
<tr>
<td>at 100°C</td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>at 150°C</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>at 200°C</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

The following solvents were found to have no effect on the fibers after 18 hours immersion at 25°C. as determined by tensile strength, tensile modulus, and extension at break:
- Xylene
- Turpentine
- Ethylene glycol monooethyl ether
- Isopropyl alcohol
- Mineral spirits

Table II

| Effect on Tensile Strength, Tensile Modulus, and Extension of Solvent Immersion |
|-----------------------------|--------------|--------------|
| Before Imersion | 18 hrs. in Ethyl Acetate | 18 hrs. in Isobutyl Acetate |
| Tensile Strength (p.s.i.) | 48,000 | 46,000 | 45,000 |
| Tensile Modulus (p.s.i.) | 900,000 | 900,000 | 700,000 |
| Extension (percent) | 25 | 35 | 25 |

1 Fiber prepared in Example II-b.

Table III

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Tensile Strength (grams)</th>
<th>Extension at Break (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>2.7</td>
<td>16</td>
</tr>
<tr>
<td>45</td>
<td>2.3</td>
<td>15</td>
</tr>
<tr>
<td>60</td>
<td>2.0</td>
<td>18</td>
</tr>
<tr>
<td>80</td>
<td>1.8</td>
<td>20</td>
</tr>
<tr>
<td>100</td>
<td>1.4</td>
<td>25</td>
</tr>
<tr>
<td>120</td>
<td>1.0</td>
<td>20</td>
</tr>
<tr>
<td>140</td>
<td>1.0</td>
<td>20</td>
</tr>
</tbody>
</table>

Whereas the foregoing description and examples have been set forth with a certain degree of particularity it is not intended that the scope of the invention be thereby limited.

For instance, the term fiber as used herein is intended to include monofilaments having diameters of up to 20 mils or more, even though an arbitrary distinction is sometimes made in the art between fibers and monofilaments based on diameter size for the sake of convenience.

Since in terms of the present process the critical considerations in producing fibers of less than about 1 mil diameter are substantially the same as in producing monofilaments of greater than about 1 mil diameter, the distinction is not necessary.

What is claimed is:

1. The method for producing isotactic polystyrene textile fibers having uniform molecular orientation which comprises extruding isotactic polystyrene having a melt index of between about 1 and 30 through a die at a temperature between about 230°C. and 330°C. to form a continuous fiber, hot drawing the fiber as it emerges from the die while maintaining the temperature of said fiber substantially at the extrusion temperature until all the molecules of the fiber are completely relaxed, and thereafter cooling the fiber to a temperature of about 120°C. to 140°C. and cold drawing the fiber to impart a degree of stretch of from about 800 to 900 percent whereby a high degree of molecular orientation is induced in said fiber.

2. The method for producing isotactic polystyrene textile fibers having uniform molecular orientation which comprises pyrolyzing isotactic polystyrene at a tempera-
ture between about 325°C and 425°C. to obtain a polymer having a melt index in the range of about 1 to about 30, extruding the polymer through a die at a temperature between about 230°C and 330°C to form a continuous fiber, hot drawing the fiber as it emerges from the die while maintaining the temperature of said fiber substantially at the extrusion temperature until all the fiber molecules are completely relaxed, and thereafter cold drawing the fiber at a temperature in the range of 120°C to 140°C to a degree sufficient to impart in said fiber a degree of stretch of about 850 to 900 percent.

3. The method for producing isotactic polystyrene textile fibers having uniform molecular orientation which comprises pyrolyzing isotactic polystyrene at a temperature between about 325°C and 425°C to obtain a polymer having a melt index in the range of about 2 to about 20, extruding the polymer through a die at a temperature between about 250°C and 300°C to form a continuous fiber, hot drawing the fiber as it emerges from the die through a heated zone maintained at a temperature at least as high as the extrusion temperature and not higher than 330°C without permitting the temperature of the fiber to fall below the extrusion temperature until all the fiber molecules are completely relaxed, and thereafter cold drawing the fiber at a temperature in the range of 120°C to 140°C to stretch said fiber a degree of about 850 to 900 percent whereby a high degree of molecular orientation is induced therein.

4. The method according to claim 3 in which the cold drawing is carried out at a temperature in the range of 125°C to 135°C.

5. The method for producing isotactic polystyrene textile fibers having uniform molecular orientation which comprises pyrolyzing isotactic polystyrene having a melt index of from about 0.01 to about 1.0 at a temperature of between about 325°C and 425°C to obtain a polymer having a melt index in the range of about 2 to about 20, extruding the polymer through a die at a temperature between about 250°C and 300°C to form a continuous fiber, hot drawing the fiber as it emerges from the die through a heated zone maintained at a temperature at least as high as the extrusion temperature and not higher than 330°C without permitting the temperature of the fiber to fall below the extrusion temperature until all of the fiber molecules are completely relaxed, and thereafter cold drawing the fiber at a rate between 200 ft./min. and 3000 ft./min. and at a temperature of about 135°C to stretch said fiber a degree of about 850 to 900 per cent whereby a high degree of molecular orientation is induced therein.

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