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3,377,415

**ELASTIC POLYPROPYLENE YARN
AND PROCESS**

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11 Claims. (Cl. 264—210)

ABSTRACT OF THE DISCLOSURE

A high degree of elasticity is imparted to filaments of stereoregular polypropylene by incorporating therein a small amount of a polyfunctional azido compound, spinning at high temperatures and high draw-down ratios and then heat treating the finished filaments under substantially no tension.

This invention relates to yarns of stereoregular, or crystalline, polypropylene having a high degree of elasticity and to processes for the production thereof.

So-called "stretch yarns" are much in demand in the textile field at the present time. Such yarns are finding increasing application in the clothing industry in general in the manufacture of a wide variety of snug fitting garments. They are especially adaptable to the manufacture of such items as hosiery, corsets, gloves, stretch pants and the like, designed to fit a range of sizes.

The most obvious and familiar criterion for measuring the elastic properties of a yarn is its ability to recover its original length upon the release of an imposed stress. This property is referred to as "tensile recovery" or "elastic recovery" or more simply as "recovery." It is expressed as a percentage of the imposed elongation which is lost when the imposed stress is removed. Percent recovery (R) is calculated as:

$$\text{Percent } R = \frac{L_e - L_r}{L_e} \times 100$$

where L_e represents the distance the sample was elongated and L_r represents the portion of the elongation which is retained when the imposed stress is removed. The parameter L_r is also referred to as "permanent set." The percentage of permanent set is equal to 100 minus percent recovery. It should be obvious that higher values of recovery or, conversely, lower values of permanent set indicate greater elastic properties.

A number of stretch yarns of synthetic polymers are known to the trade. Many of these are based upon the plastic memory of the synthetic polymer from which they are made. The basis of manufacture of such stretch yarns is that the synthetic yarn is held in a crimped or folded condition by some means while at an elevated temperature so that upon cooling it remains crimped. If yarn that has been so crimped is pulled, the crimps straighten out, and the yarn extends in length. When the extending force is removed, the crimps reform, and the yarn contracts in length. Other types of synthetic stretch yarns depend upon the insertion of a high twist at some stage of their production. Still other types of stretch yarns are helically crimped. The common feature of all such yarns, however, is that stretchability is a result of the physical structure of the yarn rather than inherent elasticity of the synthetic polymer.

There are also known to the art stretch yarns which are truly elastic, i.e., they possess the ability to be stretched repeatedly and regain substantially their original length after removal of the elongating force due to the inherent elasticity of the material from which they are made. An example of elastic yarn is so-called spandex, which is made from a rubbery polyurethane.

Truly elastic yarns of crystalline polypropylene have

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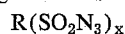
been found to be difficult to produce since this polymer has very little inherent elasticity. British Patent 935,809, assigned to E. I. du Pont de Nemours and Company, discloses highly crystalline polypropylene yarns which are said to have a high degree of elasticity. These yarns are characterized by "gamma orientation" and a heat stable orientation angle of 10 to 30°. The production of the yarns of that patent requires melt spinning the polymer under conditions which impart gamma orientation, or potential gamma orientation, to the yarn, orienting the yarn to such an extent as to give an orientation angle of 10 to 55°, and finally heat treating the yarn at a temperature of 105 to 160° C. under tension free conditions whereby the orientation angle of 10 to 30° is produced. The elastic yarns of the British patent are characterized by a tensile recovery from the second and succeeding cycles of 25% elongation of at least 85%.

Now, in accordance with this invention, it has been found that elastic polypropylene yarns having even higher tensile recovery can be prepared by the manipulative process outlined in the aforesaid British patent if there is added to the polypropylene prior to spinning an azido cross-linking agent in an amount sufficient to increase the melt viscosity of the polymer without affecting its solubility in perchloroethylene at 110° C. The amount required is ordinarily between 0.1 and 0.8 mole per mole of polypropylene. Thus, the actual quantity of the azido cross-linking agent present in any yarn is related to the functionality of the particular azido compound used, its molecular weight, and the molecular weight of the polypropylene. In a preferred embodiment of the invention, spun polypropylene yarn containing 0.1 to 0.8 mole of azido compound per mole of polypropylene is melt drawn about 10 to 100 to 1 and subjected in the relaxed state to a heat treatment at about 140 to 155° C. By the method of this invention, it has been possible to produce yarns showing a tensile recovery as high as 86% from elongations of up to about 150%.

The spinning of the polymer is conducted under conditions which produce the characteristic referred to in the British patent as gamma orientation. Basically, gamma orientation refers to an orientation of the molecules in a direction or in a plane not substantially parallel to the axis of the fiber. Such orientation is produced during the melt draw down of the polymer, its magnitude depending upon the viscosity of the polymer and the amount of such melt draw down. By melt draw down is meant a permanent elongation of the yarn in the molten state prior to any solidification thereof as it leaves the spinneret. The amount of such melt draw is expressed as the ratio of the diameter of the individual filaments to the diameter of the individual spinneret orifices. The presence of the azido cross-linking agent in the fibers of this invention permits the attainment of high levels of gamma orientation with less melt draw and substantially higher elasticity in the yarn than can be attained with unmodified polypropylene as in the British patent.

The improved elasticity of the polypropylene yarns of this invention is at its optimum when the melt draw ratio of the yarn is between 10 and 100 to 1. Above this level there is little further improvement in elasticity and frequent problems of yarn breakage are encountered. Below this level of melt draw, there is not sufficient gamma orientation to produce the desired elasticity.

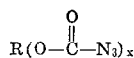
The azido cross-linking agents useful in the invention are exemplified by sulfonazides and azidoformates. The sulfonazides have the general formula:



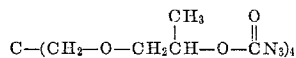
where R is an aliphatic or aromatic hydrocarbon radical inert to reaction with polypropylene and x is an integer from 2 to about 8. Exemplary sulfonazides are

1,5-pentane bis(sulfonazide),
 1,10-decane bis(sulfonazide),
 1,3-benzene bis(sulfonazide),
 1-octyl-2,4,6-benzene tris(sulfonazide),
 4,4'-diphenylmethane bis(sulfonazide),
 4,4'-diphenyl ether bis(sulfonazide),
 4,4'-bis-octadecyl biphenyl-3,5,3',5'-tetra(sulfonazide),
 4,4'-diphenyl disulfide bis(sulfonazide),
 1,6-bis(4'-sulfonazidophenyl) hexane,
 2,7-naphthalene bis(sulfonazide), etc.

Other sulfonazides having substituents such as halogen, carboxyl groups, carbonyl groups and the like on the organic radical R may be used so long as the substituent is inert to reaction with polypropylene. The azidoformates have the general structural formula:



where R is an organic radical inert to reactions with polypropylene and x is an integer from 2 to about 8. Exemplary of the azidoformates used are the alkyl azidoformates such as tetramethylene-bis(azidoformate), pentamethylene-bis(azidoformate); the cyclic alkyl azidoformates such as 1,4-cyclohexanedimethyl - bis(azidoformate); the aralkyl azidoformates such as α,α' -*p*-xylylene-bis(azidoformate); the aromatic azidoformates such as 2,2-isopropylidene-bis(*p,p'*-phenyl azidoformate); the azidoformate ethers such as 2,2'-oxydiethyl-bis(azidoformate), 2,2'-oxydipropyl-bis(azidoformate), 2,2'-ethylenedioxydiethyl - bis(azidoformate), the tetraazidoformate of pentaerythritol—propylene oxide adduct having the general formula:



the azidoformate thioethers such as 2,2'-thiodiethyl-bis(azidoformate), 4,4'-thiodibutyl-bis(azidoformate); etc. It will, of course, be obvious to those skilled in the art that still other azidoformates containing functional groups, which are inert to modification reactions, such as halogen,



etc., groups are included in the above definition.

It is known to cross-link polypropylene by the use of azido compounds such as the aforesaid sulfonazides and the azidoformates. Highly cross-linked or vulcanized compositions exhibit a much higher impact strength, durability, and stiffness than does normal polypropylene and are insoluble in perchloroethylene at 110° C. The values attained by these parameters are dependent upon the amount of the azido compound which is used to effect the cross-linking.

In order to improve elastic properties of the yarns of this invention, it is necessary that a small amount, and only a small amount of such cross-linking agent be present. That is, the amount should be sufficient to increase the melt viscosity of the polymer but insufficient to alter its solubility in perchloroethylene at 110° C. Generally, this amount of cross-linking agent is from about 0.1 to 0.8 mole per mole of polypropylene. When the amount of azido cross-linking agent materially exceeds this range, the polymer is too highly cross-linked to exhibit the desired elastic properties. When the amount is below the range, little or no benefits are realized.

The azido cross-linking agent reacts with the polypropylene under the influence of heat. The temperature required to effect this reaction depends largely upon the particular azido cross-linking agent being used, but will usually be between 100 and 250° C. This is easily effected by control of the extruder temperature. That is to say, the polymer containing the azido compound is extruded at a temper-

ature sufficiently high to cause the reaction to take place during the extrusion.

The azido cross-linking agent can be added to the polypropylene by any method commonly used to accomplish the addition of an additive to a polymer. These methods include, but are not limited to, deposition on the polymer flake from a solvent, mixing on a heated mill such as a Banbury mixer, and dry blending. Deposition from a solvent has been found to be another satisfactory means of incorporating the additive into the polymer.

The azido cross-linking agent-modified yarn which is formed by the extrusion and melt draw down as previously discussed has very little elasticity as it procured from the extrusion apparatus. The latent, potential elasticity must be fully developed by a tension-free heat treatment. This heat treatment is conducted at temperatures in the range of 140 to 155° C. for a minimum of about 2 minutes with the yarn fully relaxed. The treatment tends to relax any strains which have been set up in the yarn as a result of the melt draw down, causing about 2 to 8% shrinkage of the yarn. The resulting heat-treated yarn then exhibits the desired elasticity.

In order to permit the yarn to relax to the fullest extent possible, the heat treatment may conveniently be effected by collecting untreated yarn into skeins and heating these in an oven at the desired temperature. Alternatively, it may be conducted as a continuous process by feeding the yarn into an oven at the desired temperature and free of tension as soon as it has solidified and prior to any collection thereof into skeins or otherwise.

Following are examples of the invention. In these examples, the azido cross-linking agent was added to the polymer by wetting finely-divided polymer with a solution of the azido compound in acetone, evaporating the acetone by gentle heating under reduced pressure and extruding the polymer flake into pellets. The polymer pellets were then extruded into multifilament yarns according to the conditions specified in each example. Melt drawn down was effected by drawing the yarn away from the spinneret at a rate greater than the rate of extrusion.

Example 1

Stereoregular polypropylene having a reduced specific viscosity of 2.6 (determined on a 0.1% solution in decahydronaphthalene at 135° C.), which corresponds to a molecular weight of about 260,000, stabilized against light and heat and containing 30 mole percent of decamethylene disulfonazide (DSA) cross-linking agent was extruded through a spinneret having 8 holes of 20 mils diameter at a rate of 35 g./min. and a temperature of 287° C. to form a multifilament yarn which was subjected to a melt draw down of 20 to 1. Using the exact same spinning conditions, another batch of yarn was prepared but the decamethylene disulfonazide was omitted. This yarn was also subjected to the 20 to 1 melt draw down.

Skeins of both types of yarn were heat treated by placing on a metal grating in a forced draft oven. Heat treatment was conducted at 150° C. for 10 minutes. Both the yarn containing the decamethylene disulfonazide cross-linking agent and the control yarn exhibited gamma orientation.

Table 1 records the percent recovery of these yarns after being subjected to elongation to the various degrees specified. The yarn was held at the specified elongation for 10 minutes, and then allowed to recover for 5 minutes. The recovery is expressed as the percentage of the elongation which is not retained according to measurements taken after the cycle.

TABLE 1

	Percent Recovery (from indicated elong.)			
	10%	75%	100%	150%
Control.....	84	88	74	63
0.3% DSA.....	95	96	93	86

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As these data indicate, the yarn produced by the process of the invention is substantially more elastic than the control yarn.

Example 2

Employing the same procedure as that outlined in Example 1, sample yarn was spun containing 30 mole percent tetramethylene bis(azidoformate) (TBAF) as well as an unmodified control. Both yarns exhibited gamma orientation. The recovery of these yarns from imposed stress is presented in Table 2.

TABLE 2

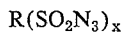
	Percent Recovery (from indicated elong.)					
	10%	15%	20%	75%	100%	150%
Control.....	86	86	83	83	70	62
0.3% TBAF.....	93	95	95	94	91	83

Here again, the improvement in elasticity effected by the process of the invention is apparent.

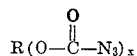
What I claim and desire to protect by Letters Patent is:

1. In manufacture of elastic yarns from stereoregular polypropylene wherein the yarn is spun under conditions to produce gamma orientation and heat treated, the improvement which comprises incorporating into the stereoregular polypropylene, prior to spinning, 0.1 to 0.8 mole of a polyfunctional azido cross-linking agent per mole of polypropylene.

2. The process of claim 1 where the azido cross-linking agent is selected from the group consisting of sulfonazides having the formula:



where R is an organic hydrocarbon radical inert to reaction with polypropylene and x is an integer from 2 to about 8, and azidoformates having the formula:



where R is an organic hydrocarbon radical inert to reaction with polypropylene and x is an integer from 2 to about 8.

3. The process of claim 1 where the azido cross-linking agent is decamethylene disulfonazide.

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4. The process of claim 1 where the azido cross-linking agent is tetramethylene bis(azidoformate).

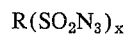
5. The process of claim 1 where the yarn is spun at 260 to 310° C.

6. The process of claim 1 where the yarn is subjected to a melt draw down of 10 to 100 to 1.

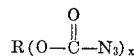
7. The process of claim 1 where the yarn is heat treated at 140 to 155° C.

8. The process for preparing elastic yarns from stereoregular polypropylene which comprises incorporating into the polymer 0.1 to 0.8 mole of a polyfunctional azido cross-linking agent per mole of stereoregular polypropylene, extruding the polymer into filaments at 260 to 310° C., melt drawing the thus formed filaments 10 to 100 to 1, and heat treating the filaments at 140 to 155° C. in the relaxed state.

9. The process of claim 8 where the azido cross-linking agent is selected from the group consisting of sulfonazides having the formula:



where R is an organic hydrocarbon radical inert to reaction with polypropylene and x is an integer from 2 to about 8, and azidoformates having the formula:



where R is an organic hydrocarbon radical inert to reaction with polypropylene and x is an integer from 2 to about 8.

10. The process of claim 8 where the azido cross-linking agent is decamethylene disulfonazide.

11. The process of claim 8 where the azido cross-linking agent is tetramethylene bis(azidoformate).

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