

DYEABLE POLYPROPYLENE FIBERS CONTAINING POLYMERS OF VINYL PYRIDINES

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This invention relates to polypropylene fibers. More particularly, this invention relates to substantially crystalline polypropylene fibers which exhibit excellent dye affinity and fastness properties as well as good resistance to oxidation and weathering. In a more specific aspect, this invention relates to polypropylene fibers which are modified with polymeric vinyl pyridines and certain of their derivatives.

It is well-known that polypropylene, particularly the polypropylene which is partially or completely crystalline, can be melt spun into synthetic fibers having unusual physical properties. This polymer is, however, subject to inherent disabilities which greatly restrict its utility in the fabrication of general purpose fibers. For example, a high-molecular-weight, fiber forming, crystalline polyolefin such as polypropylene, is a relatively insoluble, chemically inert, hydrophobic material. Since it is not readily permeable to water, it cannot be dyed satisfactorily by the ordinary dyeing procedures. Since it is relatively inert chemically, it cannot be permanently dyed even with hydrocarbon soluble dyestuffs. Furthermore, substantially crystalline polypropylene yarns and fibers cannot be dyed readily with a wide variety of dispersed, premetallized and acid-type dyes nor can such yarns and fibers be dyed to deep shades having good light and gas fastness. Moreover, the susceptibility of polypropylene fibers to oxidative degradation, instability toward ultraviolet light and poor weathering characteristics have further limited their utility. Hence, it is most desirable to obtain fibers free from the above-mentioned disabilities in order to increase their value in the textile field.

The problem of obtaining polypropylene fibers having the high tenacity, low elongation and other excellent properties characteristic of such fibers without the accompanying undesirable limitations described above, has plagued prior art workers in this field for many years. However, with the development of the instant invention, we have been able to furnish such a polypropylene fiber.

Accordingly, it is an object of this invention to provide polypropylene fibers having improved dye affinity.

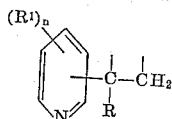
Another object of this invention is to provide polypropylene yarns and textile fibers with greatly improved dyeing characteristics so that they can be dyed readily with a wide variety of dispersed, premetallized and acid-type dyes which normally will not dye unmodified polypropylene.

Another object is to provide partially or completely crystalline polypropylene yarn and fibers which can be dyed to deep shades with excellent light and gas fastness.

Still another object of this invention is to provide polypropylene yarns and fibers having greatly improved resistance to oxidation and weathering in addition to excellent physical properties.

Further objects of the invention will become apparent throughout the following description.

In accordance with this invention it has been found that polymeric blends of polypropylene and an effective concentration of one or more of the vinyl pyridine units, in polymeric form, having the following structure:



wherein R is hydrogen or methyl, R¹ is a lower alkyl group, desirably containing 1–4 carbon atoms and n is an integer from 0 to 4, can be spun into high strength fibers and yarns which exhibit excellent dye affinity for dispersed, premetallized and acid-type dyes. The dye materials obtained thereby exhibit excellent light and gas fastness and unexpectedly good oxidative stability.

The invention provides melt extruded polypropylene articles and melt spun polypropylene textile fibers of excellent dye affinity containing a polymeric modifier which is either a homopolymer of a vinyl pyridine monomer, a copolymer of one or more vinyl pyridine monomers, or a copolymer of one or more vinyl pyridine monomers and one or more N-substituted acrylamide monomers. The amount of the polymeric modifier is preferably from 1 to 25% by weight based on the polypropylene, and more preferably from 5 to 15%.

The discovery that certain polymeric blends of crystalline polypropylene with polymers of the vinyl pyridines can be spun into high strength fibers and yarns having excellent affinity for dispersed, premetallized and acid-type dyes as well as excellent light and gas fastness was quite surprising since it could not have been predicted from the prior art. According to the prior art, it would have been predicted that melt spinning temperatures would cause appreciable degradation of the modifier. For example, fiber-forming polyesters such as polyethylene terephthalate when modified with poly(2-methyl-5-vinyl pyridine) undergoes severe degradation on melt spinning.

Although unmodified polypropylene shows virtually no affinity for dyestuffs, it can be dyed with some dyes to weak shades having, however, very poor fastness properties as mentioned hereinbefore. Surprisingly, it has been found that the shades produced by a given dye on the unmodified polypropylene yarn and on the modifiers themselves was quite different from the shades produced by the same dye on the modified polypropylene yarns of this invention. This unpredictable result indicates that the fibers spun from the polymeric blends described above possess characteristics which ordinarily would not have been expected in fibers spun from simple mixtures of polymeric materials. In this connection, it was also discovered that the modified polypropylene fibers described herein were more resistant to oxidative degradation than fibers obtained from unmodified polypropylene.

The modified polypropylene fibers of this invention are also more stable toward ultraviolet light and weathering conditions than unmodified polypropylene fibers. The reason for the increased stability of the modified polypropylene fibers toward oxidation, light and weathering is not completely understood. It is possible, however, that free radicals generated from the polymeric modifiers combine with free radicals produced from the polypropylene to prevent chain reactions which would otherwise result in rapid deterioration of the polyolefin. It is possible that the polymeric modifiers may also be effective in absorbing actinic radiant energy which otherwise could activate free-radical mechanism of decomposition in the polypropylene.

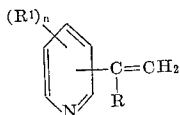
The modified polypropylene fibers and yarns may be further stabilized against thermal breakdown and weathering with any of the conventional stabilizers for polyolefins. It is usually convenient to add such stabilizers to the polymeric blends before spinning into fibers.

The modified polypropylene fibers of this invention may be drawn to give yarns having the same high tenacities, low elongations and other excellent properties found in unmodified polypropylene fibers and yarn. This is quite surprising, since the polymers of vinyl pyridines are substantially non-crystalline when prepared by conventional methods and, as a result, give fibers which possess

low tenacities, high shrinkage properties, and no commercial value. It would have been predicted, contrary to fact, that these materials, when used to modify polypropylene for fibers and yarn, would have deleteriously affected the properties of the yarn.

Another unpredictable feature of this invention is the fact that the polymeric vinyl pyridines used to modify polypropylene could not be used satisfactorily to modify polyolefin fibers in general. For example, when these modifiers were incorporated into high density or into conventional polyethylene, they were found to be substantially incompatible. Thus, a blend of polyethylene (90 parts) and poly(2-methyl-5-vinyl pyridine) (10 parts) on melt spinning gave fibers which were badly segmented. When these fibers were drafted, fibrillation resulted, giving a substantially useless product in contrast to the polypropylene fibers of our invention which showed no fibrillation when drafted.

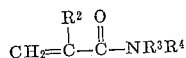
According to the practice of the invention, the monomers which are suitable for polymerization into the useful polymeric compositions for blending with polypropylene in accordance with this invention are those represented by the generic formula:



wherein R is hydrogen or methyl, R¹ is a lower alkyl group, desirably containing 1-4 carbon atoms and n is an integer from 0 to 4.

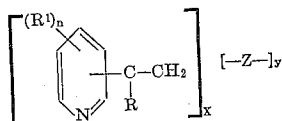
The monomeric units which are described herein can be present either in the form of a homopolymer or in the form of a copolymer of the desired vinyl pyridine with another vinyl pyridine or with N-substituted acrylamides, as hereinafter described.

Useful copolymers then can be composed of two or more different vinyl pyridine units, as set forth hereinbefore, or of these units and one or more monomeric units as described hereinafter. Monomeric units of the latter type are those derived from N-substituted acrylamides having the formula:



wherein R² is hydrogen or a lower alkyl group, desirably containing 1 to 4 carbon atoms, R³ is hydrogen or an alkyl, cycloalkyl, aralkyl or aryl group desirably containing 1 to 18 carbon atoms and R⁴ is a member selected from the group consisting of alkyl, cycloalkyl, aralkyl and aryl groups containing 1 to 18 carbon atoms. These monomers include N-isopropylacrylamide, N-isopropylmethacrylamide, N,N-dimethylacrylamide, N-phenylacrylamide, N-cyclohexylacrylamide, N-butylacrylamide, N,N-diethylacrylamide, N-ethylacrylamide, N-methylacrylamide, N-methyl-N-phenylacrylamide, N-dodecylacrylamide, N-propylacrylamide, N-benzylacrylamide and N-α-naphthylacrylamide.

Hence, the polymeric modifiers may also be described as polymers containing recurring units having the general structure:



wherein R, R¹ and n are as defined above, Z is the residue of an unsaturated polymerizable N-substituted acrylamide as defined hereinbefore and x and y are integers which will provide a homo- or copolymer having a molecular weight of at least 1000. It is obvious that the nature of the polymerizable, monoethylenically unsaturated N-substituted acrylamide which is copolymerized with the vinyl pyridine to form the modifier is subject to wide varia-

tion. The truly important feature of the modifier is that vinyl pyridine units of the type described above be present therein, preferably in amounts of from 25 to 100 mole percent.

Those radicals which can be present in the pyridine group, as described by R¹ in the above formulas, include any of the conventional lower alkyls as exemplified by methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and t-butyl.

The monomeric units described above may comprise less than 25 mole percent, e.g., 20, 10 or even 5 mole percent of the polymeric modifier, but mole percentages of 25 to 100 percent are preferred, particularly where affinity for acid-type dyes is especially desired.

It has been found that blends of crystalline polypropylene with the polymeric modifiers described can be melt spun into high strength yarns which can be dyed to deep, light and gas fast shades by means of dispersed, premetalized and acid-type dyes. The dyeing process can be carried out using conventional procedures either with or without carriers. The polypropylene blends can contain from 1% or less to 25% or more by weight, of the homo or copolymeric modifier, although the preferred concentration of modifier is from 5 to 15%. However, there are special situations which may warrant the use of 30 or perhaps even 40% by weight based on the polypropylene, of certain of the copolymeric modifiers disclosed. Furthermore, even though as little as 1% by weight based on the polypropylene, of the specified polymeric modifiers will impart dye affinity to the fibers, it is preferred that amounts of at least 5% be employed, particularly where deep shades are desired. Polypropylene blends of this type can be melt spun at temperatures ranging from 25 to 50° C. lower than are necessary to melt spin pure polypropylene.

Some specific modifiers useful in the practice of this invention are:

- Poly(2-vinyl pyridine)
- Poly(3-vinyl pyridine)
- Poly(4-vinyl pyridine)
- Poly(5-ethyl-2-vinyl pyridine)
- Poly(2-methyl-5-vinyl pyridine)
- Poly(2-methyl-6-vinyl pyridine)
- Poly(2,4-dimethyl-6-vinyl pyridine)
- Poly(5-propyl-2-vinyl pyridine)
- 75/25 copolymer 2-methyl-5-vinyl pyridine/N,N-dimethylacrylamide
- 75/25 copolymer N-isopropylacrylamide/2-methyl-5-vinyl pyridine
- 85/15 copolymer N-methylmethacrylamide/2-methyl-5-vinyl pyridine
- 93/7 copolymer N,N-dimethylacrylamide/2-methyl-6-vinyl pyridine
- 80/15/5 copolymer N-isopropylacrylamide/N-tert-butylacrylamide/2-methyl-5-vinyl pyridine
- 70/10/15 copolymer N-isopropylacrylamide/N,N-dimethylacrylamide/2-methyl-5-vinyl pyridine
- 80/10/10 copolymer N-isopropylacrylamide/2-methyl-5-vinyl pyridine/2-vinyl pyridine
- 75/17/8 copolymer N-methylacrylamide/2-methyl-5-vinyl pyridine/3-vinyl pyridine

Blends of crystalline polypropylene with one or more of the polymeric modifiers may be prepared in any desired manner, whether it be mechanical mixing, coprecipitation or other blending method, e.g., they can be prepared at elevated temperatures on rolls, in a banbury mixer or any other suitable type of processing equipment or they can be prepared by multiple extrusion techniques. The polymeric modifiers can have a molecular weight of 1000 and higher depending on the particular blend properties desired and the blending method employed. It is

NOTE.—The integers given to indicate the copolymer composition are based on mole percent here and throughout the specification.

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to be understood, of course, that any polymeric modifier having a molecular weight in excess of 1000 which is capable of introducing the specified percent by weight, based on polypropylene, of the described vinyl pyridine units into the blend is within the scope of our invention.

Usually, it is preferable to prepare the modified polypropylene compositions from polypropylene having a conditioned density above 0.90 and an inherent viscosity in tetralin at 145° C. of from 0.9 to 1.2. Conditioned density, as used herein, refers to the density determined on a sample which has been annealed in an attempt to obtain maximum crystallinity. A conventional annealing procedure involves placing the sample in a tube, heating under high vacuum or in a nitrogen atmosphere to just below the softening point, and allowing the sample to cool slowly. Polypropylene having inherent viscosities above 1.2 can be used in preparing the modified compositions, but then it is usually necessary to degrade these compositions thermally to a lower viscosity in order to realize optimum melt spinning characteristics and fiber properties. The temperatures required for this degradation are usually above 300° C. and often result in an appreciable degradation of the modifier. Polypropylene of inherent viscosity less than 0.9 can be used in preparing modified compositions for melt spinning, but it does not afford fibers having optimum physical properties.

The modified polypropylene compositions described herein may be melt spun into fibers having the desired characteristics by conventional melt spinning procedures or melt extruded into articles by extrusion through a suitable die. Furthermore, these modified polypropylene compositions can be formed into the various cross-sections, e.g., cloverleaf, Y-section etc., by employing spinnerettes or dies having appropriately shaped orifices.

The following examples are introduced to illustrate but not necessarily to limit our invention.

Example 1

Several compositions comprising crystalline polypropylene (inherent viscosity=1.0 and density=0.912) and poly(2-methyl-5-vinyl pyridine) are prepared by mechanically blending pellets of the two polymeric materials followed by melt extrusion and repelleting of the resulting compositions. These compositions are then melt spun into 34 filament yarns having the properties shown in the table below. Knit tubes prepared from these yarns all dye to deep shades with 4-(4'- β -hydroxyethyl-anilino)-5-nitro-1,8 dihydroxy anthraquinone Isolan Red B, a neutral dyeing premetallized dye (Colour Index, volume 4, second edition (1956), page 4326), and Wool Fast Blue BL (Colour Index 833) in the aqueous dye baths at boil for 1 hour. Even deeper shades are obtained by using carriers such as benzyl n-butyrate. All samples show excellent fastness to ultraviolet light in a fadeometer for 20 hours or more.

	I	II	III	IV	V
Percent Polypropylene.....	100	95	90	85	80
Percent Poly(2-methyl-5-vinyl pyridine).....	0	5	10	15	20
Yarn Viscosity.....	0.93	0.97	0.95	0.99	0.93
Total Denier.....	223	237	248	230	209
Tenacity, g./den.....	7.33	7.24	6.50	5.80	7.24
Elongation, percent.....	18	19	18	15	17
Elastic modulus, g./den.....	63	74	65	62	64

Similar results are obtained with a 75/25 2-methyl-5-vinyl pyridine/N,N-dimethylacrylamide copolymer used in place of the poly(2-methyl-5-vinyl pyridine).

Example 2

A mixture of 9 parts of crystalline polypropylene (inherent viscosity=1.05 and density=0.914) and 1 part of poly(2-methyl-6-vinyl pyridine) is prepared by evaporating a toluene solution of the latter onto pellets of the polypropylene in a conical mixer under vacuum. The

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solvent-free mixture is then melt extruded into 1/8-in. rod and then is chopped into pellets having a length of about 1/8-in. The resulting composition is readily melt spun into 34 filament yarn at a spinning temperature of 265° C.

The unmodified polypropylene requires a melt spinning temperature of 280° C. for optimum spinning characteristics. The modified polypropylene yarn obtained above is knitted into a "sock" or tube which is used in dyeing tests. Excellent dye affinity for dispersed and premetallized dyes is demonstrated by the deep shades with Isolan Red B, a neutral dyeing premetallized dye (Color Index, volume 4, second edition (1956), page 4326), Wool Fast Blue BL (Colour Index 833) and 4-(4'- β -hydroxyethyl-anilino) - 5 - nitro - 1,8 - dihydroxyanthraquinone.

Other polymeric modifiers which, when used in place of the poly(2-methyl-6-vinyl pyridine) as above, give similar results, are poly(2-vinyl pyridine), poly(4-vinyl pyridine) and poly(5-isobutyl-2-vinyl pyridine).

Example 3

Blends of crystalline polypropylene with poly(2,4-dimethyl-6-vinyl pyridine) are prepared by melt extrusion of the mechanical mixtures of the two resins. These blends are then melt spun into 34 filament yarns. Knit tubes fashioned from these yarns are readily dyed with 4 - (4' - β - hydroxyethyl-anilino) - 5 - nitro - 1,8 - dihydroxy-anthraquinone and Isolan Red B, a neutral dyeing premetallized dye (Color Index, volume 4, second edition (1956), page 4326), as well as with Wool Fast Blue BL (Colour Index 833) and Du Pont Milling Red SWG (1952 "Technical Manual Yearbook of the American Association of Textile Chemists and Colorists," volume XXVIII, page 205). Deep shades which are both light and gas fast are readily obtained.

Poly(5-ethyl-2-vinyl pyridine) or poly(5-propyl-2-vinyl pyridine), when used in place of the above polymer, give similar results.

Example 4

Several compositions comprising crystalline polypropylene (inherent viscosity 1.0 and density 0.912) and 75/25 copolymer 2-methyl-5-vinyl pyridine/N,N-dimethylacrylamide are prepared by mechanically blending pellets or granules of the two polymeric materials followed by melt extrusion and repelleting of the resulting compositions. These compositions are then melt spun into 34 filament yarns. Knit tubes prepared from these yarns all dye to deep shades with 4-(4'- β -hydroxyethyl-Blue BL (Colour Index 833) and Du Pont Milling Red B, a neutral dyeing premetallized dye (Color Index, volume 4, second edition (1956), page 4326), and Wool Fast Blue BL (Colour Index 833) in the aqueous dye baths at boil for 1 hour. Even deeper shades are obtained using carriers such as benzyl n-butyrate. All samples show excellent fastness to ultraviolet light in a fadeometer for 20 hours or more.

Suitable vinyl pyridine copolymers which can give similar results include 2-vinyl pyridine/3-vinyl pyridine copolymers, 2-methyl-5-vinyl pyridine/5-ethyl-2-vinyl pyridine copolymers, 2-methyl-6-vinyl pyridine/2-methyl-5-vinyl pyridine copolymers and 5-propyl-2-vinyl pyridine/2,4-dimethyl-6-vinyl pyridine copolymers.

Thus, by means of this invention, substantially crystalline polypropylene yarns and fibers having improved dye affinity, excellent light and gas fastness and increased stability may be obtained. The improved polypropylene fibers of this invention may be used in the same manner as conventional polypropylene fibers; for example, they can be woven into wool-like blankets or used in the production of automobile seat covers and marine hawsers that are as strong as nylon and somewhat cheaper.

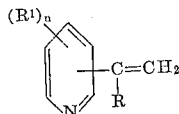
The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations

and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A melt spun polypropylene textile fiber exhibiting excellent dye affinity, light and gas fastness, resistance to oxidation and weathering, said fiber containing a polymeric modifier selected from the group consisting of:

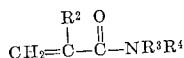
(a) homopolymers of vinyl pyridine monomers having the formula:



wherein R is a member selected from the group consisting of hydrogen and methyl, R¹ is a lower alkyl group, and n is an integer from 0 to 4,

(b) copolymers of at least two vinyl pyridine monomers having said formula (a), and

(c) copolymers of vinyl pyridine monomers having said formula (a) with N-substituted acrylamide monomers having the formula:



wherein R² is a member selected from the group consisting of hydrogen and lower alkyl, R³ is a member selected from the group consisting of hydrogen, alkyl, cycloalkyl, aralkyl and aryl groups containing 1-18 carbon atoms, and R⁴ is a member selected from the group consisting of alkyl, cycloalkyl, aralkyl and aryl groups containing 1-18 carbon atoms.

2. A melt spun polypropylene textile fiber according to claim 1 wherein the polymeric modifier is present in an amount of from 1-25% by weight based on the polypropylene.

3. A melt spun polypropylene textile fiber according to claim 2 wherein said polymeric modifier is a homopolymer of a vinyl pyridine monomer.

4. A melt spun polypropylene textile fiber according to claim 2 wherein said polymeric modifier is a copolymer of at least two vinyl pyridine monomers.

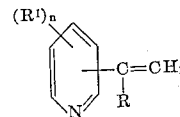
5. A melt-spun polypropylene textile fiber according to claim 2 wherein said polymeric modifier is a copolymer of vinyl pyridine and N-substituted acrylamide monomers.

6. A melt-spun polypropylene textile fiber according to claim 3 wherein said vinyl pyridine monomer is selected from the group consisting of 2-vinyl pyridine, 3-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, 5-ethyl-2-vinyl pyridine, 2-methyl-6-vinyl pyridine, 2,4-dimethyl-6-vinyl pyridine, and 5-propyl-2-vinyl pyridine.

7. A melt-spun polypropylene textile fiber according to claim 4 wherein at least one of said vinyl pyridine monomers is selected from the group consisting of 2-vinyl pyridine, 3-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, 5-ethyl-2-vinyl pyridine, 2-methyl-6-vinyl pyridine, 2,4-dimethyl-6-vinyl pyridine, and 5-propyl-2-vinyl pyridine.

8. A melt-extruded polypropylene article exhibiting excellent dye affinity, light and gas fastness, resistance to oxidation and weathering, said article containing a polymeric modifier selected from the group consisting of:

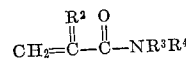
(a) homopolymers of vinyl pyridine monomers having the formula:



wherein R is a member selected from the group consisting of hydrogen and methyl, R¹ is a lower alkyl group, and n is an integer from 0 to 4,

(b) copolymers of at least two vinyl pyridine monomers having said formula (a), and

(c) copolymers of vinyl pyridine monomers having said formula (a) with N-substituted acrylamide monomers having the formula:



wherein R² is a member selected from the group consisting of hydrogen and lower alkyl, R³ is a member selected from the group consisting of hydrogen, alkyl, cycloalkyl, aralkyl and aryl groups containing 1-18 carbon atoms, and R⁴ is a member selected from the group consisting of alkyl, cycloalkyl, aralkyl, and aryl groups containing 1-18 carbon atoms.

9. A melt-extruded polypropylene article according to claim 8 wherein the polymeric modifier is present in an amount of from 1-25% by weight based on the polypropylene.

10. A melt-extruded polypropylene article according to claim 9 wherein the polymeric modifier is a homopolymer of a vinyl pyridine monomer.

11. A melt-extruded polypropylene article according to claim 9 wherein said polymeric modifier is a copolymer of at least two vinyl pyridine monomers.

12. A melt-extruded polypropylene article according to claim 9 wherein said polymeric modifier is a copolymer of vinyl pyridine and N-substituted acrylamide monomers.

13. A melt-extruded polypropylene article according to claim 10 wherein said vinyl pyridine monomer is selected from the group consisting of 2-vinyl pyridine, 3-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, 5-ethyl-2-vinyl pyridine, 2-methyl-6-vinyl pyridine, 2,4-dimethyl-6-vinyl pyridine, and 5-propyl-2-vinyl pyridine.

14. A melt-extruded polypropylene article according to claim 11 wherein at least one of said vinyl pyridine monomers is selected from the groups consisting of 2-vinyl pyridine, 3-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine, 5-ethyl-2-vinyl pyridine, 2-methyl-6-vinyl pyridine, 2,4-dimethyl-6-vinyl pyridine, and 5-propyl-2-vinyl pyridine.

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