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3,156,743

DYEABLE POLYPROPYLENE FIBERS CONTAINING ACRYLATE AND METHACRYLATE UNITS IN POLYMERIC FORM

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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 acrylic or methacrylic esters.

It is well known that polypropylene, particularly the polypropylene which is partially or completely crystalline, can be 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 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.

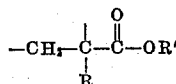
Still another object of this invention is to provide polypropylene yarns and fibers having greatly improved resistance to oxidation and weathering in addition to excellent physical properties.

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 about 1 to about 25% and more preferably about 5 to about 15%, by weight based on the polypropylene, of one or more of the acrylate or meth-

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acrylate units, in polymeric form, having the following structure:



wherein R is hydrogen or methyl and R' is an alkyl, alkoxyalkyl, cycloalkyl, aralkyl or aryl radical desirably containing 1 to 12 carbon atoms, can be spun into high strength fibers and yarns having the same percentage composition which exhibit excellent dye affinity for dispersed, premetallized and acid-type dyes. The dyed materials obtained thereby exhibit excellent light and gas fastness and unexpectedly good oxidative stability.

The discovery that certain polymeric blends of crystalline polypropylene with polymers of acrylic or methacrylic esters can be spun into high strength fibers and yarns having excellent affinity for dispersed and premetallized 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, poly(methylmethacrylate), when used as a modifier for acrylic fibers, such as acrylonitrile fibers, imparts only a low affinity for dispersed dyes and, even so, the dyed materials obtained thereby exhibit very poor light fastness.

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 were 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 from 3 to 4 times 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.

These 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.

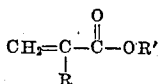
The modified polypropylene fibers and yarns of this invention may be drawn to give the same high tenacities, low elongations and other excellent properties found in unmodified polypropylene fibers and yarn. This is quite surprising, since the polymers of acrylic and methacrylic esters are substantially 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, con-

trary 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 acrylic and methacrylic esters 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(methylmethacrylate) (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.

A still further unpredictable feature of this invention is the fact that the nitriles and amides of the acrylates and methacrylates employed in this invention failed to impart the desired characteristics to polypropylene yarns and fibers. Thus, ineffective modifiers for polypropylene fibers included polymethacrylonitrile, polyacrylamide and polymethacrylamide.

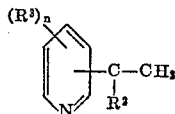
According to the practice of the invention, the monomers which are suitable for polymerization into the useful polymeric compositions for blending with polypropylene in accordance with this invention are those represented by the generic formula:



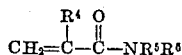
wherein R is hydrogen or methyl and R' is an alkyl, alkoxyalkyl, cycloalkyl, aralkyl or aryl radical desirably containing 1 to 12 carbon atoms.

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 acrylate or methacrylate with another acrylate or methacrylate or with a vinyl pyridine or N-substituted acrylamide as hereinafter defined.

Useful copolymers then, can be composed of two or more different acrylate or methacrylate units, as set forth hereinbefore, or of these materials and one or more vinyl pyridine or N-substituted acrylamide units, as hereinafter described. Monomeric units of the latter type are those derived from (1) vinyl pyridines having the formula:

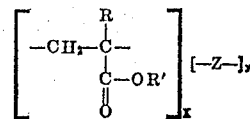


wherein R² is hydrogen or methyl, R³ is a lower alkyl group desirably containing 1 to 4 carbon atoms, n is an integer from 0 to 4, and (2) N-substituted acrylamides having the formula:



wherein R⁴ is hydrogen or a lower alkyl group desirably containing 1 to 4 carbon atoms; R⁵ is hydrogen or an alkyl, cycloalkyl, aralkyl or aryl group desirably containing 1 to 18 carbon atoms and R⁶ is an alkyl, cycloalkyl, aralkyl or aryl group desirably containing 1 to 18 carbon atoms. Suitable monomers include 2-vinyl pyridine, 3-vinyl pyridine, 4-vinyl pyridine, 5-ethyl-2-vinyl pyridine, 2-methyl-5-vinyl pyridine, 2-methyl-6-vinyl pyridine, 2,4-dimethyl-6-vinyl pyridine, 5-propyl-2-vinyl pyridine, 5-isobutyl-2-vinyl pyridine, 2-isopropenyl pyridine, N-isopropylacrylamide, N-isopropylmethacrylamide, N,N-dimethylacrylamide, N-phenylacrylamide, N-cyclohexylacrylamide, N-butylacrylamide, N,N-diethylacrylamide, N-ethylacrylamide, N-methylacrylamide, N-methyl-N-phenylacrylamide, and N-dodecylacrylamide.

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



wherein R and R' are as defined above, Z is the residue of an unsaturated, polymerizable vinyl pyridine or N-substituted acrylamide, as described above, 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 unsaturated, polymerizable vinyl pyridine or N-substituted acrylamide units are subject to wide variation. The truly important feature of the modifier is that acrylate or methacrylate units of the type described above be present therein, preferably in amounts of from 50 to 100 mole percent.

Those radicals which can be present in the ester group of the monomeric acrylate or methacrylate, as described by R' in the above formulas, are subject to wide variation and include, for example: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, 2-ethylhexyl, nonyl, lauryl, dodecyl, cyclopentyl, cycloheptyl, cyclohexyl, trimethylcyclohexyl, benzyl, phenylhexyl, phenyl, trimethylphenyl, diphenyl, methoxyethyl, ethoxybutyl, methoxylauryl and ethoxyethyl.

The monomeric units described above may comprise less than 50 mole percent, e.g., 40, 30, 20, or even 10 mole percent of the polymeric modifier, but mole percentages of 50 to 100 percent are preferred particularly where good dye affinity for dispersed dyes is 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 and pre-metallized 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 blend, of certain of the copolymeric modifiers disclosed. Furthermore, even though as little as 1% by weight based on the blend, 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 65° C. lower than are necessary to melt spin pure polypropylene.

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

- Poly(methyl methacrylate)
- Poly(ethyl methacrylate)
- Poly(isopropyl methacrylate)
- Poly(n-propyl methacrylate)
- Poly(n-butyl methacrylate)
- Poly(isobutyl methacrylate)
- Poly(tert-butyl methacrylate)
- Poly(n-hexyl methacrylate)
- Poly(lauryl methacrylate)
- Poly(cyclohexyl methacrylate)
- Poly(benzyl methacrylate)
- Poly(phenyl methacrylate)
- Poly(methyl acrylate)
- Poly(n-propyl acrylate)
- Poly(n-butyl acrylate)
- Poly(2-methoxyethyl acrylate)
- Poly(2-ethoxyethyl acrylate)
- Poly(2-ethylhexyl acrylate)

75/25 copolymer methyl acrylate/ethyl methacrylate
 20/80 copolymer ethyl acrylate/N-tert-butylacrylamide
 25/75 copolymer methyl methacrylate/N,N-dimethylacrylamide
 50/50 copolymer methyl methacrylate/2-methyl-5-vinyl pyridine
 75/25 copolymer ethyl acrylate/2-methyl-6-vinyl pyridine
 50/50 copolymer 2-vinyl pyridine/ethyl acrylate
 50/50 copolymer methyl methacrylate/3-isopropenyl pyridine
 60/30/10 copolymer N,N-dimethylacrylamide/N-isopropenyl acrylamide/methyl methacrylate

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

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 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 acrylate or methacrylate 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 loss of modifier through depolymerization. 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 spun into fibers having the desired characteristics by the conventional spinning procedures, e.g., melt spinning, dry spinning, wet spinning or 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(methyl methacrylate) were prepared by mechanically blending pellets of the two polymeric materials followed by melt extrusion and repelleting of the resulting compositions. These compositions were then melt spun into 34 filament yarns having the properties shown in the table below. Knit tubes prepared from these yarns all dyed to deep shades with 4-(4'- β -hydroxyethyl-anilino)-5-nitro-1,8 dihydroxy anthraquinone and Isolan Red B,

a neutral dyeing premetalized dye [Color Index, volume 4, Second Edition (1956), page 4326], in the aqueous dye baths at boil for 1 hour. Even deeper shades were obtained by using carriers such as benzyl n-butyrate. All samples showed excellent fastness to ultraviolet light in a fadeometer for 20 hours.

	I	II	III	IV	V
Percent Polypropylene.....	100	95	90	85	80
Percent Poly(methyl methacrylate).....	0	5	10	15	20
Yarn Viscosity.....	0.93	0.97	0.91	0.85	0.89
Total Denier.....	223	196	164	153	162
Tenacity, g./den.....	7.33	5.23	7.25	6.80	7.25
Elongation, percent.....	18	28	17	18	14
Elastic modulus, g./den.....	63	62	71	59	79

Example 2

Although the methyl esters of acrylic and methacrylic acid are preferably used, the other alkyl esters as defined herein can be used with excellent results. Thus, a mixture of 9 parts of crystalline polypropylene (inherent viscosity=1.05 and density=0.914) and 1 part of poly(n-butyl methacrylate) was prepared by evaporating a toluene solution of the latter onto pellets of the polypropylene in a conical mixer under vacuum. The solvent-free mixture was then melt extruded into 1/8 in. rod and then was chopped into pellets having a length of about 1/8 in. The resulting composition was readily melt spun into 34 filament yarn at a spinning temperature of 230° C. The unmodified polypropylene required a melt spinning temperature of 280° C. for optimum spinning characteristics. The modified polypropylene yarn obtained above was knitted into a "sock" or tube which was used in dyeing tests. Excellent dye affinity for dispersed and premetalized dyes was demonstrated by the deep shades with Isolan Red B, a neutral dyeing premetalized dye [Color Index, volume 4, Second Edition (1956), page 4326], 4-anilino-3-nitrobenzenesulfonamide, 4-(4'-methyl-2'-nitrobenzene)-3-methyl-5-pyrazolene, 4-[4'-(benzeneazo)-benzeneazo]-phenol, 1'-amino-4-hydroxy-2-phenoxy-anthraquinone, 4-(4'-nitrobenzeneazo)-N-ethyl-N- β -hydroxyethyl aniline, 1-methylamino-4- β -methylethylamino-anthraquinone and 4-(4'- β -hydroxyethyl-anilino)-5-nitro-1,8-dihydroxyanthraquinone.

Other polymeric modifiers which, when used in place of the poly(n-butyl methacrylate) as above, gave similar results, were poly(ethyl methacrylate), poly(ethyl acrylate), poly(isobutyl methacrylate), poly(2-ethylhexyl acrylate), poly(lauryl methacrylate) and poly(2-methoxyethyl acrylate).

Example 3

Acrylate and methacrylate homopolymers are conveniently used, but copolymers, as described herein, are also suitable in the amounts and proportions also defined herein. The procedure of Example 2 was followed except that the poly(n-butyl methacrylate) was replaced with a 50/50 copolymer n-butyl/isobutyl methacrylate. The resulting yarn had a tenacity of 5.2 g./den., an elongation of 27% and an elastic modulus of 40g./den. Knit tubes of this yarn dyed to deep shades with 4-(4'- β -hydroxyethyl-anilino)-5-nitro-1,8 dihydroxy-anthraquinone and Isolan Red B, a neutral dyeing premetalized dye [Color Index, volume 4, Second Edition (1956), page 4326], in the aqueous dye baths at boil for 1 hour. A sample of the unmodified polypropylene in the form of a knit tube showed comparatively little or no tendency to take up these dyes. When a carrier was used, the unmodified yarn dyed to light shades with poor fastness properties which showed distinct differences in actual color when compared with the corresponding samples of dyed modified yarn.

Other copolymers which gave similar results when used in place of the N-butyl/isobutyl methacrylate copolymer as above were 75/25 copolymer methyl acrylate/ethyl methacrylate, 50/50 copolymer methyl/n-butyl methacry-

late, 80/20 copolymer methyl methacrylate/ethyl acrylate and a 60/40 copolymer methyl/cyclohexyl methacrylate. In these instances, the amount of modifier was selected to give an effective concentration of 1% to 25% of acrylate or methacrylate based on the polypropylene. 5

Example 4

A mixture of 9 parts of crystalline polypropylene (inherent viscosity 1.05 and density 0.914) and 1 part of 50/50 copolymer methyl methacrylate/3-isopropenyl pyridine was prepared by evaporating a toluene solution of the latter onto pellets of the polypropylene in a conical mixer under vacuum. The solvent-free mixture was then melt extruded into 1/8 in. rod and then chopped into pellets having a length of about 1/8 in. The resulting composition was readily melt spun into 34 filament yarn at a spinning temperature of 265° C. The unmodified polypropylene required a melt spinning temperature of 280° C. for optimum spinning characteristics. The modified polypropylene yarn obtained above was knitted into a "sock" or tube which was used in dyeing tests. Excellent dye affinity for dispersed, premetallized and acid dyes was demonstrated by the deep shades obtained with Isolan Red B, a neutral dyeing premetallized dye, [Color Index, volume 4, Second Edition (1956), page 4326], Wool Fast Blue (Color Index 833) and 4-(4'-β-hydroxyethyl-anilino)-5-nitro-1, 8 - dihydroxy - anthraquinone. 10 15 20 25

Similar results were obtained when a 60/30/10 copolymer 2-methyl-5-vinyl pyridine/3-vinyl pyridine/n-butyl methacrylate was used in place of the 50/50 copolymer methyl methacrylate/3-isopropenyl pyridine, as above. 30

Example 5

The procedure of Example 4 was followed except that the 50/50 copolymer methyl methacrylate/3-isopropenyl pyridine was replaced with a 75/25 copolymer ethyl acrylate/2-methyl-6-vinyl pyridine. The resulting yarn had a tenacity of 7.0 g./den., an elongation of 20% and an elastic modulus of 81 g./den. Knit tubes of this yarn dyed to deep shades with 4-(4'-β-hydroxyethyl-anilino)-5-nitro-1,8-dihydroxy anthraquinone and Wool Fast Blue BL (Color Index 833) in aqueous dye baths at boil for 1 hour. A sample of the unmodified polypropylene in the form of a knit tube showed comparatively little or no tendency to take up these dyes. When a carrier was used, the unmodified yarn dyed to light shades with poor fastness properties which showed distinct differences in actual color when compared with the corresponding samples of dyed modified yarn. 35 40 45 50

Similar results were obtained when a 50/50 copolymer 2-vinyl pyridine/ethyl acrylate was used in place of the 75/25 copolymer ethyl acrylate/2-methyl-6-vinyl pyridine, as above. 55

Example 6

Blends of crystalline polypropylene with a 50/50 copolymer methyl methacrylate/2-methyl-5-vinyl pyridine were prepared by melt extrusion of the mechanical mixtures of the two resins. These blends were then melt spun into 34 filament yarns having the properties shown below. 60

	I	II	III
Polypropylene, percent.....	92	83	75
50/50 copolymer methyl methacrylate/2-methyl-5-vinyl pyridine, percent.....	8	17	25
Yarn Viscosity.....	0.86	0.89	0.85
Total Denier.....	152	162	184
Tenacity, g./den.....	7.24	7.25	6.82
Elongation, percent.....	15	14	21
Elastic modulus, g./den.....	81	79	60

Knit tubes fashioned from these yarns were readily dyed with 4-(4'-β-hydroxyethyl-anilino)-5-nitro-1,8-dihydroxy-anthraquinone as well as with Wool Fast Blue BL (Color Index 833) and Du Pont Milling Red SWG (1952 75

Technical Manual and Yearbook of the American Association of Textile Chemists and Colorists, volume XXVIII, page 205). Deep shades were both light and gay fast and were readily obtained.

Example 7

Several compositions comprising crystalline polypropylene (inherent viscosity 1.0, density 0.912) and a 20/80 copolymer ethyl acrylate/N-tert-butylacrylamide were prepared by mechanically blending granules of the two polymeric materials followed by melt extrusion and repelleting of the resulting compositions. These compositions were then melt spun into 34 filament yarns. Knit tubes prepared from these yarns all dyed to deep shades 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], in aqueous dye baths at boil for 1 hour. The knit fabric also dyed well with Wool Fast Blue BL (Color Index 833) and Du Pont Milling Red SWG (1952 Technical Manual and Yearbook of the American Association of Textile Chemists and Colorists, volume XXVIII, page 205) under similar conditions. Even deeper shades were obtained by using carriers such as benzyl n-butyrate. All samples showed excellent fastness to ultraviolet light in a fadeometer for 20 hours. A sample of the unmodified polypropylene showed comparatively little tendency to take up these dyes.

Example 8

A mixture of 9 parts of crystalline polypropylene (inherent viscosity 1.05 and density 0.914) and 1 part 50/30/20 copolymer N,N-dimethylacrylamide/N-isopropyl-acrylamide/methyl methacrylate was prepared by mechanically blending granules of the two polymers. The mechanical blend was then melt-extruded into 1/8 in. rod and then was chopped into pellets having a length of about 1/8 in. The resulting composition was readily melt spun into 34 filament yarns at a spinning temperature of 265° C. The unmodified polypropylene required a melt spinning temperature of 280° C. for optimum spinning characteristics. The modified polypropylene yarn obtained above was knitted into a sock, or tube, which dyed to deep shades 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], in aqueous dye baths at boil for 1 hour. A sample of the unmodified polypropylene in the form of a knit tube showed comparatively little or no tendency to take up these dyes. When a carrier was used, the unmodified yarn dyed to light shades with poor fastness properties, which showed distinct differences in actual color when compared with the corresponding samples of dyed modified yarn. 35 40 45 50 55

Example 9

Blends of crystalline polypropylene with a 25/75 copolymer methyl methacrylate/N,N-dimethylacrylamide were prepared by melt extrusion of the mechanical mixture of the two resins. These blends were then melt spun into 34-filament yarns having the properties shown below. 60

	I	II	III
Propylene, percent.....	97	82	75
25/75 copolymer methyl methacrylate/N,N-dimethylacrylamide, percent.....	3	18	25
Yarn Inherent Viscosity.....	1.01	0.93	0.85
Total Denier.....	148	178	176
Tenacity, g./den.....	8.55	6.97	6.74
Elongation, percent.....	16	20	23
Elastic modulus, g./den.....	102	71	62

Knit tubes fashioned from these yarns were 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

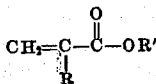
(1956), page 43261 as well as with other dispersed and premetalized dyes. Good dyeability was noted also when these materials were subjected to dyeing with acid and direct dyes. Deep shades which were both light and gas fast were readily obtained.

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 almost as strong as nylon and somewhat cheaper.

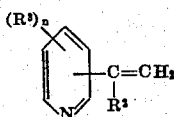
The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

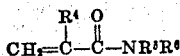
1. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness, resistance to oxidation and weathering, said fiber containing a polymeric modifier selected from the group consisting of homopolymers of (1) a monomer having the formula:



wherein R is a member selected from the group consisting of hydrogen and methyl and R' is a member selected from the group consisting of alkyl, alkoxyalkyl, cycloalkyl, aralkyl and aryl radicals containing 1-12 carbon atoms, and copolymers of a monomer having said formula with a member selected from the group consisting of (A) different monomers having said formula and (B) vinyl pyridine monomers having the formula:

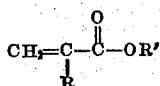


wherein R² is a member selected from the group consisting of hydrogen and methyl and R³ is a lower alkyl group containing 1-4 carbon atoms, n being an integer from 0 to 4, and (C) N-substituted acrylamide monomers having the formula:



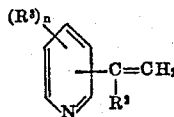
wherein R⁴ is a member selected from the group consisting of hydrogen and lower alkyl groups containing 1-4 carbon atoms, R⁵ is a member selected from the group consisting of hydrogen, alkyl, cycloalkyl, aralkyl and aryl groups containing 1-18 carbon atoms and R⁶ is a member selected from the group consisting of alkyl, cycloalkyl, aralkyl and aryl groups containing 1-18 carbon atoms.

2. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness, resistance to oxidation and weathering, said fiber containing about 1 to about 25%, by weight, based on polypropylene, of a polymeric modifier selected from the group consisting of homopolymers of (1) a monomer having the formula:

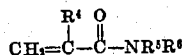


wherein R is a member selected from the group consisting of hydrogen and methyl and R' is a member selected from the group consisting of alkyl, alkoxyalkyl, cycloalkyl, aralkyl and aryl radicals containing 1-12 carbon atoms, and copolymers of a monomer having said formula with a member selected from the group consisting of (A)

different monomers having said formula and (B) vinyl pyridine monomers having the formula:



wherein R² is a member selected from the group consisting of hydrogen and methyl and R³ is a lower alkyl group containing 1-4 carbon atoms, n being an integer from 0 to 4, and (C) N-substituted acrylamide monomers having the formula:



wherein R⁴ is a member selected from the group consisting of hydrogen and lower alkyl groups containing 1-4 carbon atoms, R⁵ is a member selected from the group consisting of hydrogen, alkyl, cycloalkyl, aralkyl and aryl groups containing 1-18 carbon atoms and R⁶ is a member selected from the group consisting of alkyl, cycloalkyl, aralkyl and aryl groups.

3. The fiber of claim 2 which contains about 5 to about 15%, by weight, based on polypropylene, of the polymeric modifier.

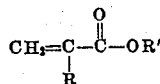
4. The fiber of claim 2 in which the polymeric modifier is a homopolymer of (1).

5. The fiber of claim 2 in which the polymeric modifier is a copolymer of a monomer (1) with a monomer (A).

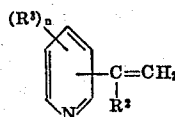
6. The fiber of claim 2 in which the polymeric modifier is a copolymer of a monomer (1) with a monomer (B).

7. The fiber of claim 2 in which the polymeric modifier is a copolymer of a monomer (1) with a monomer (C).

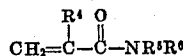
8. A blend comprising solid polypropylene and about 1 to about 25%, by weight, based on polypropylene, of a polymeric modifier selected from the group consisting of homopolymers of (1) a monomer having the formula:



wherein R is a member selected from the group consisting of hydrogen and methyl and R' is a member selected from the group consisting of alkyl, alkoxyalkyl, cycloalkyl, aralkyl, and aryl radicals containing 1-12 carbon atoms, and copolymers of a monomer having said formula with a member selected from the group consisting of (A) different monomers having said formula and (B) vinyl pyridine monomers having the formula:



wherein R² is a member selected from the group consisting of hydrogen and methyl and R³ is a lower alkyl group containing 1-4 carbon atoms, n being an integer from 0 to 4, and (C) N-substituted acrylamide monomers having the formula:



wherein R⁴ is a member selected from the group consisting of hydrogen and lower alkyl groups containing 1-4 carbon atoms, R⁵ is a member selected from the group consisting of hydrogen, alkyl, cycloalkyl, aralkyl and aryl groups containing 1-18 carbon atoms and R⁶ is a member selected from the group consisting of alkyl, cycloalkyl, aralkyl and aryl groups containing 1-18 carbon atoms.

9. The blend of claim 8 which contains about 5 to

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about 15%, by weight, based on polypropylene, of the polymeric modifier.

10. The blend of claim 8 in which the polymeric modifier is a homopolymer of (1).

11. The blend of claim 8 in which the polymeric modifier is a copolymer of a monomer of (1) with a monomer of (A)₁₀.

12. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness, resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of poly(methyl methacrylate). 10

13. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness, resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of poly(cyclohexyl methacrylate). 15

14. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness, resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of poly(benzyl methacrylate).

15. Polypropylene fiber exhibiting excellent dye affinity, light and gas fastness and resistance to oxidation and weathering, said fiber containing about 1 to about 25% by weight, based on the fiber, of poly(2-methoxyethyl acrylate). 20

16. A blend comprising solid polypropylene and about 1 to about 25% by weight, based on the polypropylene, of poly(methyl methacrylate). 25

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17. A blend comprising solid polypropylene and about 1 to about 25% by weight, based on the polypropylene, of poly(cyclohexyl methacrylate).

18. A blend comprising solid polypropylene and about 1 to about 25% by weight, based on the polypropylene, of poly(benzyl methacrylate). 5

19. A blend comprising solid polypropylene and about 1 to about 25% by weight, based on the polypropylene, of poly(2-methoxyethyl acrylate).

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