United States Patent Office 3,035,031 Patented May 15, 1962

3,035,031

ACRYLONITRILE COPOLYMERS

Robert D. Evans, West Chester, Pa., assignor to American Cyanamid Company, New York, N.Y., a corporation of Maine

No Drawing. Continuation of application Ser. No. 610,646, Sept. 18, 1956. This application Feb. 24, 1960, Ser. No. 10,555

2 Claims. (Cl. 260—85.5)

This invention relates to the production of new synthetic materials having valuable and characteristic properties that make them especially suitable for use in industry. More particularly, the invention is concerned with multi-component polymers of acrylonitrile (commonly known as "acrylonitrile copolymers"), and especially with such polymers that are fiber-formable, that is, are capable of being made into fibers or filaments. The scope of the invention also embraces products comprising an oriented fiber or filament comprised of a fiber-formable acrylonitrile copolymer of the invention, as well as method features.

One of the deficiencies of textiles comprised of synthetic fibers made from the prior polymers of acrylonitrile has been their relatively poor "comfort" factor. Although "comfort" is a very complicated response, there is valid reason to believe that it may be associated closely with the moisture-regain properties of the fiber. Thus, textiles comprised of fibers having good moisture-regain properties are more likely to feel warm and comfortable to the touch than those comprised of fibers having poor moisture-regain properties. In other words, if the moisture-regain properties of the fibers are low, as is the case with fibers made from certain condensation polymers, textile materials comprised of such fibers may feel wet, clammy and uncomfortable. Although no exact figures are available as to the amount of water that must be absorbed before some improvement in comfort is noticeable, it is believed that the minimum amount should be of the order of about 5% by weight of the fiber at 65% relative humidity.

Parenthetically it may here be pointed out that improvement in one property of a fiber frequently can be obtained only at the expense of some other property. One of the valuable attributes of fibers made from the usual polymers of acrylonitrile resides in the fact that such fibers normally have the ability to impart dimensional stability and wrinkle resistance to fabrics and garments made therefrom. Inherently, these and other desirable characteristics of polyacrylonitrile fibers are a direct result of their low water absorption. If the ability to absorb water is substantially increased by suitable modification of the polymer composition, then those characteristics that presently make polyacrylonitrile fibers so attractive in the textile field may be excessively diminished.

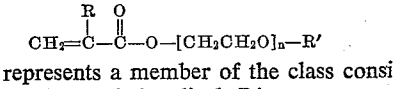
Another serious deficiency encountered in the spinning of polyacrylonitrile fibers into yarns, and also in actual service uses of garments made therefrom, is their pronounced tendency to accumulate static charges of electricity; in other words, they have poor antistatic properties. This difficulty has been obviated or minimized in spinning yarns from the fibers by applying a relatively large amount of an antistatic finishing agent to the fibers prior to spinning. However, such antistatic-finishing treatments are not permanent; and, in service uses, garments and other textiles made from fibers comprised of an acrylonitrile polymer frequently accumulate excessive static charges of electricity and cause complaints on the part of the user or customer. Some efforts to solve this problem heretofore have been made by modification of the acrylonitrile polymer so as to "build into" the polymer molecule substantially permanent antistatic characteristics which were

carried through into fibers made from the modified polymer.

Prior efforts on the part of other investigators to solve the problems described briefly above have generally resulted in adversely affecting the other useful properties of the acrylonitrile polymer and of fibers made therefrom, particularly the sticking temperature. Usually, when the polymer composition was modified so as to make it possible to produce fibers that were more hydrophilic (and consequently having, for instance, improved moisture-regain and/or improved antistatic properties) than those fibers made from, for example, homopolymeric acrylonitrile, then the sticking point or temperature of the fiber was excessively lowered. This lowering of the sticking point had obvious disadvantages from the standpoint of convenience of ironing of fabrics and other textiles made from such fibers of low sticking point.

The present invention is based on my discovery of a suitable and convenient means whereby fibers having improved hydrophilic properties can be produced without adversely affecting (if at all) other desirable properties, e.g., sticking temperature, to a point where the fiber would be unsuited for the usual textile applications. Specifically, the aforementioned useful results flowing from the invention are secured by the production of a new and novel fiber-formable copolymer by polymerization of a mixture of particular proportions of copolymerizable ingredients including (1) acrylonitrile and (2) a compound or substance represented by the general formula

(I)



$$CH_2{=}C(R)-C(=O)-O-[CH_2CH_2O]_n-R'$$

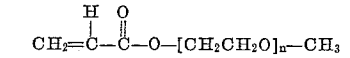
wherein R represents a member of the class consising of hydrogen and the methyl radical, R′ represents an alkyl radical containing from 1 to 4 carbon atoms, inclusive (specifically methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec.-butyl and tert.-butyl radicals), and *n* represents a positive integer having an average value which is at least 5 and not more than about 20. Advantageously *n* represents a positive integer having an average value between about 7 and about 16. The compound of (2) constitutes from 1 to 15 mole percent of the total amount of copolymerizable ingredients which are present in the aforesaid mixture. The copolymerizable substance of (2) and the mole percent thereof (within the aforementioned range) are critical in producing the fiber-formable copolymers of this invention and in attaining the desired results.

The acrylontrile polymers of this invention are comprised of a backbone chain of acrylonitrile units with infrequent long chains of the relatively high-molecular-weight comonomer dangling from the backbone. The copolymers of the invention are, in effect, graft polymers, and hence the method features of this invention constitute an indirect method of producing graft polymers. Because of the higher molecular weight of the comonomer of (2), as compared with those which are commonly copolymerized with acrylonitrile, it is possible to keep the mole percent constant while holding the weight percent at a much higher level. Since other useful fiber properties such as moisture-regain, dyeability and antistatic characteristics may be a function of weight percent, the present invention provides means whereby one can obtain fibers having combined therein the desirable property of high sticking point and, also, the other improved properties which are normally associated with a high degree of copolymerization of acrylonitrile with a hydrophilic monomer. Furthermore, the new oriented fibers produced from the copolymers of this invention, either in the form of continuous filament or as staple, may be readily processed with conventional equipment with little evidence of the accumulation of static charges of electricity (if any)

to give yarns and fabrics with improved moisture-regain properties, improved dyeability and with sticking points which are sufficiently high to make these fibers suitable for the usual textile applications.

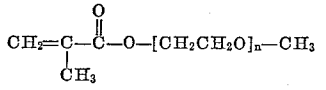
With further reference to Formula I it will be noted that, when R represents hydrogen and R′ represents the methyl radical, the compound is the acrylic ester of a methoxy polyethylene glycol and may be represented by the formula

(II)



and, when R and R′ each represents the methyl radical, the compound is the methacrylic ester of a methoxy polyethylene glycol and may be represented by the formula

(III)



In Formulas II and III *n* has the same meaning as given above with reference to Formula I.

Further modification of the properties of the fiber-formable copolymers of this invention can be attained by polymerizing a mixture of copolymerizable ingredients including (1) from 75 to 99 mole percent of acrylonitrile, (2) from 1 to 15 mole percent of a compound or substance embraced by Formula I, and (3) up to 10 mole percent of at least one different (e.g., one, two, three, four or any higher desired number of different) monoethylenically unsaturated substance or substances which are copolymerizable (conjointly polymerizable) with the other ingredients. Thus, the different monoethylenically unsaturated substance of (3) may include, for example, a vinylpyridine (e.g., 2-methyl-5-vinylpyridine), vinyl acetate, or both a vinylpyridine and vinyl acetate, or other different monoethylenically unsaturated substance, numerous examples of which hereinafter are given.

Improvements in dye receptivity toward acid dyes are obtained when the different monoethylenically unsaturated substance is a vinylpyridine. In such cases the fiber-formable copolymer is produced by polymerization of a mixture of copolymerizable ingredients including (1) from 75 to 98 mole percent of acrylonitrile, (2) from 1 to 15 mole percent of a compound or substance embraced by Formula I, and from 1 to 10 mole percent of a vinylpyridine, e.g., 2-methyl-5-vinylpyridine alone, or a mixture of vinylpyridines which includes 2-methyl-5-vinylpyridine.

Any suitable method can be used in preparing the compounds or substances embraced by Formula I. One suitable method comprises effecting reaction between acrylyl or methacrylyl chloride and an alkoxy polyethylene glycol represented by the general formula

(IV) $R'—[OCH_2CH_2]_n—OH$

where R′ and *n* have the same meanings as given above with reference to Formula I. Or, alternatively, the alkoxy polyethylene glycol reactant may be represented by the general formula

(V) $R'—O—CH_2—(CH_2OCH_2)_n—CH_2—OH$

where R′ has the same meaning as given above with respect to Formula I and *n* represents a positive integer having an average value which is at least 4 and not more than about 19.

The acrylyl or methacrylyl chloride is preferably used in molar excess (e.g., from 5% to 30% in excess of equal molar proportions) over the molar amount of alkoxy polyethylene glycol employed; and the reaction is effected in the presence of a suitable hydrohalide acceptor, e.g., triethyl amine. The hydrohalide acceptor and the acrylyl or methacrylyl chloride are commonly used in equal molar proportions. The reaction advantageously may be effected in a suitable inert liquid medium, e.g., acetonitrile.

Alkoxy polyethylene glycols of the kind embraced by Formulas IV and V are available from established chemical manufacturers. The more common grades are listed below, together with their average molecular weights:

Name:	Average molecular weight
Methoxy Polyethylene Glycol 350	330–370
Methoxy Polyethylene Glycol 550	525–575
Methoxy Polyethylene Glycol 750	715–785

These methoxy polyethylene glycols, and others, are available from, for instance, Carbide and Carbon Chemicals Company, 30 East 42nd Street, New York 17, New York. Such alkoxy polyethylene glycols yield acrylic and methacrylic esters wherein the average value for *n* (Formula I) ranges between about 7 and about 16 or 17. Methoxy polyethylene glycols wherein *n* has an average value of 5 or 6 can be fractionally separated in known manner from Methoxy Polyethylene Glycol 350, supra; while those wherein *n* has an average value of from 18 to 20, inclusive, can be fractionally separated in known manner from Methoxy Polyethylene Glycol 750, supra. Or, methoxy polyethylene glycols where *n* has the aforementioned lower average values (5–6) or higher average values (18–20) can be collected, as such, by the manufacturer during the process of manufacture.

Heat, light or heat and light can be used to effect or to accelerate polymerization of the mixture of comonomers, although under such conditions the rate of polymerization may be relatively slow. Hence, it is usually preferred to accelerate the polymerization by employing a polymerization catalyst accompanied by heat, light or heat and light. Ultraviolet light is more effective than ordinary light.

Any of the polymerization catalysts which are suitable for use in polymerizing compounds containing an ethylenically unsaturated grouping, specifically a vinyl grouping, can be employed. Among such catalysts are the inorganic peroxides, e.g., hydrogen peroxide, barium peroxide, magnesium peroxide, etc., and the various organic peroxy catalysts, illustrative examples of which latter are: the dialkyl peroxides, e.g., diethyl peroxide, dipropyl peroxide, dilauryl peroxide, dioleyl peroxide, distearyl peroxide, di-(tert.-butyl) peroxide and di-(tert.-amyl) peroxide, such peroxides often being designated as ethyl, propyl, lauryl, oleyl, stearyl, tert.-butyl and tert.-amyl peroxides; the alkyl hydrogen peroxides, e.g., tert.-butyl hydrogen peroxide (tert.-butyl hydroperoxide), tert.-amyl hydrogen peroxide (tert.-amyl hydroperoxide), etc.; symmetrical diacyl peroxides, for instance peroxides which commonly are known under such names as acetyl peroxide, propionyl peroxide, lauroyl peroxide, stearoyl peroxide, malonyl peroxide, succinyl peroxide, phthaloyl peroxide, benzoyl peroxide, etc.; fatty oil acid peroxides, e.g., coconut oil acid peroxides, etc.; unsymmetrical or mixed diacyl peroxides, e.g., acetyl benzoyl peroxide, propionyl benzoyl peroxide, etc.; terpene oxides, e.g., ascaridole, etc.; and salts of inorganic per-acids, e.g., ammonium persulfate, sodium persulfate, potassium persulfate, sodium percarbonate, potassium percarbonate, sodium perborate, potassium perborate, sodium perphosphate, potassium perphosphate, etc. Catalysts which accelerate polymerization as the result of the liberation of a free radical, e.g., sym.-dicyanotetra-methylazomethane and similar known diazo polymerization catalysts, can be employed. Various reduction-oxidation ("redox") catalyst systems also can be used advantageously in many instances. Other examples of organic peroxide and of other catalysts that can be employed are given, for example, in Drechsel and Padbury Patent No. 2,550,652 dated April 24, 1951.

The concentration of the catalyst employed is usually small, that is, for the preferred catalysts from, by weight, about 0.5 to 1 part of catalyst per thousand parts of the polymerizable composition to be polymerized to about 3 or 4 or more parts of catalyst per 100 parts of the mixture of comonomers.

If desired, the mixed monomers can be polymerized in emulsion or in solution state to yield a copolymer.

In the latter case, various inert organic solvents may be employed, depending upon the particular comonomer used, e.g., toluene, xylene, dioxane, ethers (e.g., dibutyl ether), esters (e.g., butyl acetate), chlorobenzene, ethylene dichloride, ketones (e.g., methyl ethyl ketone), tertiary alcohols, for instance tertiary-butyl alcohol, tertiary-amyl alcohol, tertiary-hexyl alcohol, etc., as well as others. When the reaction is effected in solution state, then a temperature at or approaching the boiling temperature of the solution generally is used. The copolymer can be separated from the liquid medium in which copolymerization was effected by any suitable means, e.g., by filtration, centrifuging, solvent extraction, etc.

The polymerization also can be effected by conventional bulk polymerization technique, in the presence or absence of a solvent capable of dissolving the monomeric mixture and in which the latter preferably is inert; or in solution in a solvent in which the monomeric mixture is soluble but the copolymer is insoluble; or by conventional bead polymerization methods. The polymerization of the mixture of monomers can be effected by a continuous process as well as by a batch operation. In one method of copolymerization, which is generally satisfactory, the monomers are copolymerized in an aqueous medium, with the aid of a polymerization catalyst, and the resulting copolymer is then isolated by any suitable means, e.g., by filtration, centrifuging, etc., from the aqueous medium in which polymerization has been effected.

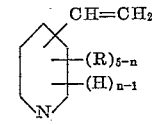
The temperature of polymerization of the polymerizable composition, at atmospheric or slightly above atmospheric pressure and in the presence or absence of a polymerization catalyst, can be varied over a wide range, up to and including or slightly above the boiling point (at atmospheric pressure) of the monomeric mixture (or of the lowest boiling component thereof), but in all cases is below the decomposition temperature of the monomeric materials. In most cases the polymerization temperature will be within the range of 20° C. to 100° C., more particularly within the range of about 30° C. to about 90° C., depending, for example, upon the particular mixture of monomers employed, the particular catalyst, if any, used, the rapidity of polymerization wanted, and other influencing factors.

The properties of the fundamental polymers made from acrylonitrile and esters of the kind embraced by Formula I can be modified, as desired or as may be required, by additionally including in the polymerizable mixture one or more other monoethylenically unsaturated substances which are different from the aforesaid ingredients, for instance one or more other and different compounds containing a $CH_2=C<$ grouping that are conjointly polymerizable with the other ingredients of the polymerizable mixture.

Illustrative examples of such different substances are the different vinyl compounds (that is, vinyl compounds which are different from the other ingredients of the polymerizable mixture), including the vinyl aromatic compounds, more particularly the vinyl aromatic hydrocarbons (e.g., styrene and the various dialkyl styrenes), other aliphatic compounds containing a $CH_2=C<$ grouping, e.g., the various substituted acrylonitriles (e.g., methacrylonitrile, ethacrylonitrile, phenylacrylonitrile, etc.), the various acrylamides (e.g., acrylamide itself, methacrylamide, ethacrylamide, the N-monoalkyl and -dialkyl acrylamides and methacrylamides, e.g., N-monomethyl, -ethyl, -propyl, -butyl, etc., and N-dimethyl, -ethyl, -propyl, -butyl, etc., acrylamides and methacrylamides, N-monoaryl and -diaryl acrylamides and alkacrylamides, e.g., N-monophenyl and -diphenyl acrylamides and methacrylamides, etc.), monoethylenically unsaturated monocarboxylic acids, e.g., acrylic acid, methacrylic acid, ethacrylic acid, cinnamic acid, etc., vinyl esters, e.g., vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl valerate, etc., esters of an acrylic acid including acrylic acid itself and the various alpha-substituted acrylic acids, e.g., methacrylic acid, ethacrylic acid, phenylacrylic acid, etc.) that are different from those embraced by Formula I, more particularly the alkyl esters of an acrylic acid, e.g., the ethyl, propyl, isopropyl, n-butyl, isobutyl, sec.-butyl, tert.-butyl, amyl, hexyl, heptyl, octyl, decyl, dodecyl, etc., esters of acrylic, methacrylic, ethacrylic, phenylacrylic, etc., acids including the alkyl acrylates containing not more than four carbon atoms in the alkyl grouping, examples of which are given above.

Additional examples of different monoethylenically unsaturated substances that can be added to the polymerizable mixture of copolymerizable ingredients include the various vinylpyridines, which are vinyl-substituted heterocyclic tertiary amines (sometimes designated as vinyl-substituted tertiary heterocyclic amines), and more particularly vinylpyridines represented by the general formula

(VI)



wherein R represents a lower alkyl radical, and n represents an integer from 1 to 5, inclusive. Examples of radicals represented by R are the methyl, ethyl, propyl (including n-propyl and isopropyl) and butyl (including n-butyl, isobutyl, sec.-butyl and tert.-butyl) radicals. Examples of vinylpyridines embraced by the above formula are 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, 2-methyl-3-vinylpyridine, 3-vinyl-4-methylpyridine, 3-vinyl-5-methylpyridine, 2-vinyl-3-methylpyridine, 2-vinyl-4-methylpyridine, 2-vinyl-5-methylpyridine, 2-vinyl-6-methylpyridine, 2-methyl-4-vinylpyridine, 3-methyl-4-vinylpyridine, 2-vinyl-4,6-dimethylpyridine and 2-vinyl 4,6-diethylpyridine.

Other examples of vinyl-substituted heterocyclic tertiary amines that can be used are the various isomeric vinylpyrazines, vinylquinolines (including the 2- and 4-vinylquinolines), vinyloxazoles, vinylimidazoles and vinylbenzoxazoles.

By including a vinyl-substituted heterocyclic tertiary amine (or other basic, monoethylenically unsaturated monomer), specifically a vinylpyridine, in the polymerizable mixture, copolymers are obtainable from which can be made filamentary materials having improved receptivity toward acid dyes as compared with a similarly made product that contains no such basic monomer as an integral part of the polymer molecule.

In lieu of, or in addition to, a basic monomer as the different monoethylenically unsaturated substance which is added to the polymerizable mixture, one can use other such substances to impart specific improvements in properties to the copolymer; e.g., vinyl acetate where better color and/or color stability under heat, or better spinning characteristics, may be desired; or acrylamide when it is desired that fibers made from the copolymer have improved union dyeability with wool (more particularly in those cases where a vinylpyridine also is used in producing the copolymer); or, for instance, acrylic acid, methacrylic acid, dimethylaminopropylacrylamide, methacrylamide, hydroxyethyl methacrylate, methacrylonitrile, dimethylaminoethyl acrylate, etc., when it is desired to impart still other distinctive and desirable properties, or combination of properties, to the copolymer.

The acrylonitrile copolymers of this invention can be produced in various average molecular weights, depending, for instance, upon the particular polymerization conditions employed, but ordinarily are within the range of about 25,000 or 30,000 to about 200,000 or higher, e.g., from about 50,000 to about 100,000, as calculated from viscosity measurements using the Staudinger equation (reference: U.S. Patent No. 2,404,713).

Acrylonitrile copolymers of this invention that have an average molecular weight of between about 60,000 and

90,000 and which have been made from a polymerizable mixture containing from about 75% to about 95% by weight of acrylonitrile (based on the weight of total monomers of the kind used in this invention), and which also contain from 1 to 15 mole percent (based on the total amount of copolymerizable ingredients which are present in the aforesaid mixture) of a compound embraced by Formula I, are especially suitable for use in making oriented fibers by wet- or dry-spinning methods. The oriented fibers thereby obtained have the improved properties discussed earlier in this specification.

The acrylonitrile polymers produced by this invention are useful in numerous applications in the plastics and coating arts, but are particularly suitable for use in the formation of filamentary materials having improved properties over that provided by homopolymeric acrylonitrile or most of the other previously known polymers of acrylonitrile. They are soluble in a wide variety of solvents, e.g., tetramethyl oxamide, N-formyl pyrrolidine, metaphenylene diamine, dimethyl sulfone, tetramethylene sulfoxide, dimethyl formamide, N,N,N',N'-tetramethyl succinamide, N,N-dimethylacetamide, N,N-dimethylmethoxyacetamide, succinonitrile, N-formylmorpholine, aqueous nitromethane, concentrated aqueous solutions of water-soluble salts which yield highly hydrated ions in an aqueous solution, for instance, calcium and sodium thiocyanates, zinc chloride, and others. As hereinbefore mentioned, they can be fabricated into filaments by the known wet-spinning and dry-spinning techniques. The resulting filaments (or other shaped articles that can be made, for instance films, sheets, tapes, tubes, rods, and other articles) have, in general, good moisture-regain properties, from fair to good resistance to the accumulation of static charges of electricity (that is, good antistatic properties), and improved dye receptivity (as compared with homopolymeric acrylonitrile) toward a wide variety of dyes, and particularly toward acid dyes when, for example, a vinylpyridine is an integral part of the polymer molecule. Furthermore, the sticking temperature is, in general, sufficiently high to meet the requirements of the trade.

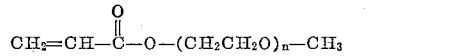
The aforementioned properties (as well as others), in combination with the outstanding physical and chemical characteristics imparted thereto by the high content of acrylonitrile combined in the polymer molecule, render the acrylonitrile polymers obtained by practicing the present invention suitable for fields of utility for which the previously known polymers of acrylonitrile had only limited, if any, usefulness. The practical and economic significance of this fact will be readily appreciated by those who are experienced in this art.

In order that those skilled in the art may better understand how the present invention can be carried into effect, the following examples are given by way of illustration and not by way of limitation. All parts and percentages are by weight.

Example 1

This example illustrates the preparation of an acrylic ester of a methoxy polyethylene glycol, more particularly an acrylic ester represented by the general formula

(VII)



where n has an average value of about 7.

		Moles
"Methoxy Polyethylene Glycol 350"	70 g.	0.20
Acrylyl chloride	22.7 g.	0.25
Triethyl amine (redistilled)	30.4 g.	0.30
Acetonitrile	100 ml.	

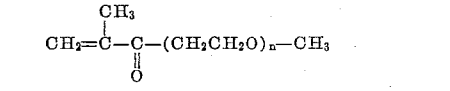
All of the above ingredients with the exception of the acrylyl chloride are placed in a 3-necked reaction vessel provided with a stirrer, thermometer, addition funnel and a reflux condenser surmounted with a drying tube. The acrylyl chloride is added slowly over a period of 8 minutes. About 1/7 of the total amount is added in 2 minutes, causing the temperature of the reaction mass to rise from 28° C. to 41° C. The remainder of the acrylyl chloride is added within the next 6 minutes, causing a further increase in the temperature to 51° C. An ice bath is used to keep the temperature between 50° C. and 55° C. The ice bath is now removed. After stirring rapidly for 35 minutes after the addition of all of the acrylyl chloride, the speed of stirring is decreased and the mass is stirred for 30 minutes more. Stirring is now stopped and the reaction mass is allowed to stand undisturbed for about 16 hours.

At the end of this period the reaction mass is stirred for 30 minutes at 5°–10° C. with finely divided decolorizing carbon. The resulting slurry is filtered through a bed of diatomaceous earth held in a Büchner funnel, yielding an amber-colored filtrate. The cake is washed with two 25-ml. portions of acetonitrile. The combined filtrate and washings are then vacuum-distilled to remove the acetonitrile and to isolate the acrylic ester of the methoxy polyethylene glycol, which is obtained in a yield corresponding to 92.8% of the theoretical (or 96.5% of the theoretical if a small amount retained in the filter cake is included). Analysis shows that the ester has a Saponification No. of 323, and an unsaturation determination by mercaptan titration indicates a purity of about 94%.

Example 2

The methacrylic ester of a methoxy polyethylene glycol, more particularly the ester represented by the general formula

(VIII)



where n has an average value of about 7, is prepared in essentially the same manner described under Example 1 with reference to the production of the corresponding acrylic ester with the exception that 0.25 mole of methacrylyl chloride is used instead of 0.25 mole of acrylyl chloride.

The acrylic and methacrylic esters of other alkoxy polyethylene glycols embraced by Formula IV (or V) are prepared by similarly reacting acrylyl or methacrylyl chloride with the desired alkoxy polyethylene glycol within the scope of said Formula IV.

Other methods of preparing the alkoxy polyethylene glycol acrylates and methacrylates used in practicing the present invention obviously can be employed, as desired or as conditions may require.

Example 3

A three-necked reaction vessel is provided with an electrically-driven stirrer, a reflux condenser, a dropping funnel, a thermometer and three ports for introducing nitrogen (if desired) and catalyst. The temperature is controlled by the rate of monomer addition as well as by an electric mantle. Deionized water (643 g.) and 5 ml. of 0.1 N H_2SO_4 are added to the reaction vessel, and the water is heated to boiling. After refluxing for about 5 minutes the contents of the vessel is allowed to cool to 80° C. At about this temperature a mixture of 345.8 g. of acryonitrile (about 96.8% CH_2=CHCN, remainder water) and 37.2 g. of the acrylic ester of methoxy polyethylene glycol of Example 1 is slowly added to the vessel at a constant rate so that all of the mixture is added over a 2-hour period. This is conveniently accomplished by adding the mixed monomers at approximately 3 ml. per minute. A redox-catalyst system is added to the vessel at a constant rate in two separate streams. This catalyst system is comprised of 2.79 g. of potassium persulfate dissolved in 120 ml. of deionized water and 1.395 g. of potassium meta-bisulfite dissolved in a separate portion of 120 ml. of deionized water. The potassium persulfate and potassium metabisulfite solutions are separate-

ly added to the reaction vessel at the rate of 1 ml. per minute. Copolymerization starts after about 5 minutes as evidenced by the development of opalescence, and particles of copolymer begin to appear in about 10 minutes. After the addition of the mixture of monomers has been completed the temperature of the heating mantle is increased and the reaction mass is refluxed for 45 minutes. At the end of this period the reflux temperature is about 91° C.

During the later stage of the polymerization reaction small portions of water are added to reduce thickening. Specifically, 50 ml. of water is added at the end of 1 hour, another 50 ml. 12 minutes later, a third portion of 50 ml. of water at the end of another 8 minutes, and a final portion of 50 ml. of water after the reaction has proceeded for another 15 minutes.

At the end of the reaction period (2¾ hours) the reaction mass is cooled, the copolymer is isolated by filtration through a Büchner funnel, and then washed with several portions of deionized water. The wet cake of copolymer, which contains about 60% by weight of water, is dried for about 16 hours at 70° C. Nitrogen analysis shows 23.42% N, from which it is calculated that the copolymer contains about 89.5% acrylonitrile. The average molecular weight of this copolymer is about 75,000.

Example 4

Example 3 is repeated, using 344.6 g. of 96.8% acrylonitrile and 38.4 g. of the methacrylic ester of methoxy polyethylene glycol of Example 2 instead of 345.8 g. of 96.8% acrylonitrile and 37.2 g. of the acrylic ester of methoxy polyethylene glycol as in Example 3. A good yield of copolymer of the starting comonomers is obtained.

Example 5

This example illustrates the preparation of a ternary polymer of acrylonitrile, 2-methyl-5-vinylpyridine and an acrylic ester of methoxy polyethylene glycol (produced as described under Example 1).

The copolymerization is effected continuously, using apparatus which includes a reaction vessel that is provided with an overflow tube located at the top of the reaction vessel. Agitation is effected primarily by recirculating the contents of the reaction vessel continuously through a high-speed centrifugal pump. Additional agitation in the reaction vessel is effected by means of a motor-driven propeller. The temperature is regulated by means of a heat-exchanger located in the circulating system. The system is purged with nitrogen, and the solutions of monomeric material and of catalyst, hereafter described, are fed into the reaction vessel using variable-speed pumps.

The reactor is charged with a previously prepared aqueous slurry (e.g., a 30% aqueous slurry) of, for example, the same ternary polymer to be produced (obtained from a prior run). After "steady state" conditions have been reached, the following solutions are then fed in at such a rate that the stated quantities are delivered each hour.

	Parts
Feed 1:	
Ammonium persulfate	24.1
Sulfuric acid	8.3
Demineralized water	1230.0
Feed 2:	
2-methyl-5-vinylpyridine	19.5
Acrylic ester of methoxy polyethylene glycol (produced as descride under Example 1)	78.0
Acrylonitrile	875.0
Feed 3:	
Sodium meta-bisulfite	2.89
Demineralized water	1250.00

The temperature of the slurry is maintained at 40° C., and the copolymerization reaction is stopped at the end of 6½ hours. The slurry resulting from the last 1½ hours of operation is combined with the final slurry in the reaction vessel.

The ternary polymer is isolated from the slurry by centrifuging, washed in the centrifuge with 40,000 parts of demineralized water, and dried in an oven at 70° C. for about 16 hours. A dry, white, dimethylformamide-soluble ternary polymer is obtained. Chemical analysis indicates that it contains about 8.4% of units of the acrylic ester, about 2.1% of units of 2-methyl-5-vinylpyridine, and the remainder acrylonitrile units.

Example 6

This example illustrates the preparation of a ternary polymer containing in the polymer molecule an average of, by weight, about 2.5% of methyl acrylate units, about 7.5% of units of the methacrylic ester of methoxy polyethylene glycol (produced as described under Example 2), and the remainder acrylonitrile units.

The same apparatus and general procedure are employed as in Example 5. The reactor is charged with an aqueous slurry composed of 420 parts of homopolymeric acrylonitrile and 1,180 parts of demineralized water having dissolved therein 2.67 parts of sulfuric acid. The system is purged with nitrogen as in Example 5. After reaching steady state conditions, the following solutions are then fed in at such a rate that the stated quantities are delivered each hour:

	Parts
Feed 1:	
Acrylonitrile	194.4
Methyl acrylate	5.4
Methacrylic ester of methoxy polyethylene glycol (produced as described under Example 2)	16.2
Tert.-dodecyl mercaptan	0.3
Feed 2:	
Sodium chlorate	0.85
Sodium sulfite	2.98
Demineralized water	390.00
Feed 3:	
Sulfuric acid	1.4
Demineralized water	390.0

The temperature of the slurry is maintained at 45° C., and the copolymerization reaction is stopped at the end of 5 hours. The ternary polymer is isolated from the reactor slurry by collection on a Büchner funnel, washed with demineralized water, and dried in an oven at 70° C. for about 16 hours. A dry, white, dimethylformamide-soluble ternary polymer is obtained. Its chemical constitution is given in the first paragraph of this example.

Example 7

	Parts
Acrylonitrile	44.00
2-methyl-5-vinylpyridine	2.65
N-(3-dimethylaminopropyl)acrylamide	1.06
Acrylic ester of methoxy polyethylene glycol (produced as described under Example 1)	5.30
Water	1000.00
6 N H_2SO_4	6.00
Ammonium persulfate in 50 parts water	1.71
Sodium meta-bisulfite in 50 parts water	0.36

A reaction vessel, equipped with a stirrer, reflux condenser, thermometer and gas-inlet tube, is placed in a water bath maintained at a temperature of 28°–35.5° C. A solution of all of the above ingredients, with the exception of the acrylonitrile, acrylic ester of methoxy polyethylene glycol, ammonium persulfate and sodium meta-bisulfite, is added to the reaction vessel. A rapid stream of pre-purified nitrogen is passed over the surface of the solution for 30 minutes. The nitrogen flow is then reduced to one bubble per second. The remaining ingredients are added, the solution becoming cloudy after stirring for a short period at a temperature of about

28° C. The reaction is allowed to proceed at about 35° C., while continuing the stirring, for a total of about 6 hours. The resulting quaternary polymer is collected on a Büchner funnel, washed with 2000 parts of deionized water, and dried in an oven at 70° C. for about 16 hours. The yield of dry, white polymer of acrylonitrile, 2-methyl - 5 - vinylpyridine, N-(3-dimethylaminopropyl)-acrylamide and acrylic ester of methoxy polyethylene glycol amounts to about 48 parts.

Example 8

A reaction vessel, equipped with stirrer, reflux condenser, thermometer, and a graduated addition funnel is placed in a constant-temperature bath which is maintained at 35° C. To the vessel is added 1180 parts of distilled water, 1.5 parts of hydrochloric acid (100% HCl), 4 parts of 2-methyl-5-vinylpyridine (commercial grade), 4 parts of vinyl acetate, 12 parts of the methacrylic ester of methoxy polyethylene glycol (produced as described under Example 2), and 140 parts of acrylonitrile. A rapid stream of pre-purified nitrogen is passed over the surface of the solution for 30 minutes. The nitrogen flow is then reduced to about one bubble per second.

A reduction-oxidation catalyst system ("redox" system) consisting of 0.66 part of sodium chlorate and 2.36 parts of sodium sulfite diluted to 150 ml. in water is added portionwise according to the following schedule.

Time (minutes):	Catalyst solution (ml.)
0	60.0
25	22.5
50	22.5
75	15.0
100	15.0
125	7.5
150	7.5

The monomers in the mixture begin to conjointly polymerize within a short time after the first addition of catalyst solution, and the polymerization is somewhat exothermic for the first 2 hours. After all of the catalyst solution has been added, the polymerization is continued at 35° C. for an additional 2 hours.

The resulting polymer is collected on a Büchner funnel, washed with 3000 parts of distilled water and dried in an oven for about 16 hours. A very good yield of a dry, white, quaternary polymer of acrylonitrile, vinyl acetate, 2-methyl-5-vinylpyridine and the methacrylic ester of methoxy polyethylene glycol is obtained.

Example 9

	Parts
N-vinyl-2-oxazolidone	6.0
Acrylic ester of methoxy polyethylene glycol (produced as described under Example 1)	4.0
Acrylonitrile	40.0
α,α'-Azodiisobutyronitrile	0.5

are mixed together and charged to a heavy-walled glass tube, which thereafter is sealed under vacuum. Copolymerization is effected by heating the sealed tube in a 60° C. water bath for 40 hours. The resulting copolymer is fiber-formate, and can be made into both mono- and multifilaments by known wet-spinning and dry-spinning techniques. N-vinyl-2-oxazolidone is prepared as described in, for instance, the application of Erhart K. Drechsel, Serial No. 430,740, filed May 18, 1954, which has matured into Patent No. 2,818,362, dated December 31, 1957.

Example 10

	Parts
N-vinyl-2-pyrrolidone	4.0
Methacrylic ester of methoxy polyethylene glycol (produced as described under Example 2)	4.0
Acrylonitrile	42.0
α,α'-Azodiisobutyronitrile	0.5

The same procedure is followed as described under Example 9. A fiber-formable copolymer is obtained which seems to have somewhat better spinning characteristics than the product of Example 9.

Example 11

Twenty (20) parts of the copolymer of Example 4 is slurried by rapid stirring at room temperature in 80 parts of dimethylformamide. While protected by a blanket of carbon dioxide the temperature of the mixture is raised to 80° C. with slow stirring until all of the copolymer has dissolved to form a clear, viscous solution.

After deaeration and filtration the warm solution is extruded downwardly through a spinnerette having 40 holes, each 70 microns in diameter, into a spinning cell, the inner wall of which is maintained at a temperature of approximately 425° C. by means of a fluid heating medium which circulates around the outer wall of the cell. A current of preheated gas at 125° C. is introduced at the bottom of the cell and passes upwardly countercurrent to the filaments which pass downwardly from the spinnerette. By this means the major proportion of the dimethylformamide is evaporated from the filaments by the time the filaments have reached the bottom of the cell.

From the bottom of the cell the group of filaments or thread is led through water to remove the last of the dimethylformamide solvent, after which it is continuously dried by passing it over a pair of heated drying rolls. The dry multifilament thread is then thermoplastically stretched by conducting it through a slot which is maintained at 400° C. and thence to stretch rolls. Stretch is applied to the thread by having the surface speed of the rolls on the delivery end of the heated slot about 8 times that of the surface speed of the rolls which feed the thread to the slot. The filaments are oriented along the fiber axis by this stretching operation.

The thermoplastically stretched thread is more lustrous than that of the unstretched thread. To remove residual strains or shrinkage, the thread is conducted through a second, heated slot at 400° C. and thence to a pair of rolls, the surface speed of which is adjusted to permit about 15% shrinkage of the thread in the slot. After this thermoplastic treatment the thread is collected on a ring-twister bobbin.

The finished thread is resistant to the accumulation of static charges of electricity and has good moisture-regain properties, whereas a thread similarly prepared from homopolymeric acrylonitrile rapidly accumulates static charges of electricity and has poor moisture-regain characteristics. These differences in properties of the respective threads are reflected in fabrics made therefrom, and in the properties of wearing apparel made from the fabrics. The higher-moisture-regain properties (e.g., of the order of 5% to 8% by weight of the fiber at 65% relative humidity) result, in general, in greater comfort to the wearer of wearing apparel (especially that which comes in contact with the skin) made from fabrics comprised of these threads.

Example 12

In this example the copolymer of Example 3 is used in making a filamentary material by wet-spinning technique. The copolymer is dissolved in a 47% aqueous solution of sodium thiocyanate to make a spinning solution containing about 10.1% by weight of the copolymer. After filtration and deaeration the copolymer solution is preheated and then extruded through a spinnerette having 2330 holes of 90 microns diameter into a coagulating bath of 10% aqueous sodium thiocyanate solution at −2° C. Spinning is done at 80 meters per minute (final speed). The gelled tow is given a so-called "solvent" stretch (that is, a stretch without washing) of about 300% immediately after leaving the coagulating bath, after which it is washed, and then stretched 330%

in water at about 99.5° C. The resulting tow is continuously dried under controlled and correlated conditions of temperature and humidity sufficient to cause all of the water to be evolved from the gelled tow and collapse of its structure.

After leaving the drying unit, the tow is fed to subsequent processing operations. For example, the dried material may be crimped and further processed to yield a product which is sold as tow; or, after crimping, it may be cut to staple lengths and further processed to yield staple fibers which are baled and sold as such.

The dried filamentary material in tow or staple form is glossy, and the filaments have a high tensile strength and good elongation characteristics. The filamentary material is further characterized by its high moisture-regain characteristics and good antistatic properties as compared with filamentary material similarly made from homopolymeric acrylonitrile and other known copolymers of acrylonitrile. These latter properties are reflected in fabrics made from the filaments and in wearing apparel made from the fabrics.

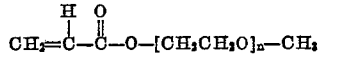
In a similar manner to that described under Examples 11 and 12, oriented filamentary materials are made from the copolymers of Examples 5 to 10, inclusive. Where the copolymer has a basic monomer incorporated therein, as in the copolymers of Examples 5, 7 and 8, further improvements in dye-receptivity, especially towards acid dyes, are obtained.

It will be understood, of course, by those skilled in the art that my invention is not limited to the specific ingredients named in the above illustrative examples nor to the particular proportions and methods of copolymerization mentioned therein. Thus, other modifying comonomers (numerous examples of which have been given hereinbefore) can be used in lieu of, or in addition to, those named in the specific examples. Also, instead of, or in addition to, the specific acrylic (or methacrylic) ester of the alkoxy polyethylene glycol employed in making the copolymers of Examples 1–10, one can use any other such ester of the kind embraced by Formula I. Likewise, other polymerization techniques and filament-forming methods can be employed as has been indicated in the portion of this specification prior to the examples.

This application is a continuation of my copending application Serial Number 610,646, filed September 18, 1956.

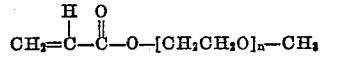
I claim:

1. A product comprising a fiber-formable copolymer obtained by polymerization of a mixture of copolymerizable ingredients including (1) from 75 to 99 mole percent of acrylonitrile and (2) from 1 to 15 mole percent of a compound represented by the formula



wherein *n* represents a positive integer having an average value of about 7, said copolymer having an average molcular weight within the range of from about 25,000 to about 200,000.

2. The method of preparing a fiber-formable copolymer which comprises polymerizing in an aqueous medium, with the aid of a polymerization catalyst, a mixture of copolymerizable ingredients including (1) from 75 to 99 mole percent of acrylonitrile and (2) from 1 to 15 mole percent of a compound represented by the general formula



wherein *n* represents a positive integer having an average value of about 7, the polymerization reaction being carried out at a temperature ranging from 20° C. up to a temperature which is below the decomposition temperature of the monomeric materials of (1) and (2), and being continued until there is produced a fiber-formable copolymer having an average molecular weight within the range of from about 25,000 to about 200,000.

References Cited in the file of this patent

UNITED STATES PATENTS

2,129,694	Izard	Sept. 13, 1938
2,436,926	Jacobson	Mar. 2, 1948
2,676,953	Ham	Apr. 27, 1954
2,815,369	Holt	Dec. 3, 1957

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,035,031 May 15, 1962

Robert D. Evans

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

Column 2, line 49, for "acrylontrile" read -- acrylonitrile --; column 9, line 43, for "recirculating" read -- circulating --; line 67, for "descride" read -- described --; column 11, line 61, for "fiber-formate" read -- fiber-formable --; column 12, line 55, for "higher-moisture-regain" read -- higher moisture-regain --.

Signed and sealed this 28th day of August 1962.

(SEAL)
Attest:

ESTON G. JOHNSON
Attesting Officer

DAVID L. LADD
Commissioner of Patents