ABSTRACT OF THE DISCLOSURE

Vinyl-bis(trifluoromethyl) carbinoil and vinyllethynyl-bis(trifluoromethyl) carbinoil are disclosed and are useful in fiber-forming copolymers with acrylonitrile. Such fibers exhibit improved soiling resistance and hot-wet recovery properties.

This invention relates to novel copolymers of acrylonitrile. More specifically, this invention relates to acrylonitrile copolymers from which fibers and fabrics having a high degree of wash recovery from soiling and having increased resistance to wrinkling under hot-wet conditions are prepared. This invention further relates to a novel vinyl monomer which is copolymerized with acrylonitrile to form one of the novel copolymers.

Methods and processes directed to improving the soiling resistance of fabrics containing polyacrylonitrile have heretofore made extensive use of coatings and finishes in order to achieve this effect. Thus, according to British patent specification No. 919,896, carpet fabrics and the like containing a major portion of acrylic polymer fibers formed from polymers containing at least 80% by weight acrylonitrile units are stated to be more resistant to soiling after they have been treated with an aqueous solution prepared from ammonium bromide, urea derivatives, and an aldehyde. U.S. Patent No. 3,159,502 teaches the use of cationic surface active agents, derived from pyrrolidines and imidazolines, on polyacrylonitrile fibers and fabrics in order to obtain anti-soiling effects. In U.S. Patent No. 3,013,901 the soiling resistance of commercial knitted fabrics is improved when a copolymer prepared from a polymer formed of a major portion of acrylonitrile is shown to be improved when the fabric is treated with fibrous boehmite (alumina monohydrate).

It is apparent that the successful applications of these anti-soiling finishing compositions on a polyacrylonitrile-based fiber or fabric are highly dependent upon the nature of the specific receiving surface. It is also apparent that, however successfully the coating initially improves the fabric’s resistance to soiling, any loss of the applied coating through abrasion, washing, dry cleaning, or the like will permit increased soiling of the fabric and necessitate reaplication of a finish at added expense. Since the permanent retention of the maximum soiling resistance imparted to a fabric or fiber by an externally applied finish is not usually possible, improved methods for imparting and maintaining fabric anti-soillability are constantly being sought.

It is recognized in the prior art that yarns prepared from acrylonitrile homopolymers have poor affinity for dyes. However, in U.S. Patent No. 2,837,501 copolymers and terpolymers comprising acrylonitrile, other vinyl monomers (e.g., methyl acrylate), and/or sulfuryl ethylenes (e.g., potassium vinylbenzene sulfonate), are shown to exhibit excellent dyeability. It is observed that an increase in the sulfuryl ethylene content of these polymers is generally accompanied by a decrease in the value of the hot-wet modulus of fibers prepared from them. The hot-wet modulus is an indication of how fibers will act in the dye bath under conditions of tension which are normally used in the dyeing of fabrics. A very low hot-wet modulus indicates that the fiber will stretch out of shape and will also wrinkle during dyeing operations and is, therefore, an undesirable property. A proper balance among the components of these dyeable acrylonitrile-based polymers becomes necessary in order to provide a useful balance between dyeability and physical properties, such as hot-wet modulus.

The prior art has shown that in fiber-forming polymers, the fiber-forming stage is reached when the polymer has an inherent viscosity, $\eta_{inh}$ of about 0.5. "Inherent viscosity" is defined by the formula

\[
\eta_{inh} = \frac{10 \log \eta_p}{C}
\]

in which $\eta_p$ (relative viscosity) is the viscosity of a dilute solution of the polymer divided by the viscosity of the solvent measured under the same conditions. The concentration, $C$, of polymer is expressed in grams of polymer per 100 ml. of solution. For the polymers considered herein, the viscosity is measured at 30°C. in a capillary viscometer, the solvent is N,N-dimethylformamide, and $C=0.5$ g./100 ml. solution unless otherwise specified.

It is an object of the present invention to provide new acrylonitrile copolymers. Another object is to provide acrylonitrile copolymers from which filaments and fabrics with high hot-wet modulus values are prepared. It is still further object of the present invention to provide acrylonitrile copolymers from which fabrics having a high degree of wash recovery from soiling are prepared. These other objects and others will become apparent from the description that follows.

The objects of this invention are accomplished by preparing fiber-forming copolymers consisting essentially of the copolymerizates of acrylonitrile (AN) and a vinyl monomer selected from the group consisting of vinyl-bis(trifluoromethyl)carbinoil (I) and vinyllethynyl-bis(trifluoromethyl)carbinoil (II), recurring units of said vinyl monomer constituting from about 0.8% to about 10% by weight of said copolymer, said copolymer having an inherent viscosity of at least 0.5.

The vinyl monomer (I) is formed in good yields by the reaction of vinyl magnesium chloride, as a freshly prepared solution in tetrahydrofuran, with hexafluoroacetone. The vinyl monomer (II) is formed by the reaction of vinyllethynyl magnesium bromide with hexafluoroacetone.

Copolymerization of acrylonitrile (AN) and vinyl-bis(trifluoromethyl)carbinoil (I) is preferably performed by bulk or emulsion methods. Bulk polymerization is highly exothermic and sealed tube bulk polymerizations are best performed when the total volume of the monomers occupies only about 30% of the tube's capacity. Bulk copolymerizations under the above conditions may be run initially at room temperature for about 2 hours and are completed by a subsequent heating at 55°C. to 60°C. for 1 to 2 hours. Exact temperatures and heating periods are dependent on the free radical initiator employed. The conditions just cited are predicated on the use of azobisisobutyronitrile. Aqueous emulsion polymerization is also effective, due to the good heat control obtained through the heat-absorbing property of the water.

The copolymers of this invention prepared from acrylonitrile (AN) and vinyllethynyl-bis(trifluoromethyl)carbinoil (II) are advantageously synthesized by suspension polymerization procedures. According to one procedure, the monomers, boiled distilled water, and a polymerization initiator (e.g., a combination of potassium persulfate and sodium bisulfite) are mixed in a polymer tube. The tube is constricted, the contents degassed, and the tube
Polymerization takes place in from 1 to 2 hours at room temperature, but is generally permitted to run overnight prior to separating the polymer. Good yields of (AN)/(II) copolymers which contain up to 10% by weight of (II) and which have inherent viscosities of 1.6 or greater are obtained by these methods. The relative proportions of the monomers, and of the water, which are useful in this method of copolymerization may be varied within wide limits to produce copolymers of the composition ranges previously stated. Usually, the acrylonitrile is, together with the water, present in large excess (by volume). For example, high viscosity copolymers of (AN)/(II) have been obtained when the percent by volume of (AN)/(II)/water in the reaction vessel is varied within the ranges of 32.6-49/0.33-2.49/46.4%, respectively. The initiators may be present in the amount from about 0.3% to about 0.7%, based upon the weight of monomers. Other useful initiators include other aqueous redox systems and conventional organic initiators such as benzoyl peroxide and azobisisobutyronitrile for bulk or solution copolymerization. In addition, a small quantity of a chain transfer agent, such as lauryl mercaptan, may be present.

The process is a vinyl addition polymerization yielding an essentially linear polymer. It can be represented for the vinyl monomer (I) as:

\[
\begin{align*}
&\text{H} \quad \text{F} \quad \text{O} \quad \text{P} \\
\text{X} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{OH} \quad \text{Y} \\
&\text{H} \quad \text{F} \quad \text{C} \quad \text{O} \quad \text{F} \\
&\text{H} \quad \text{F} \quad \text{F} \quad \text{C} \quad \text{N} \quad \text{Y}
\end{align*}
\]

where the ratio X/Y represents the relative number of moles of each unit which is present in the copolymer. The weight percent of (I) units in the copolymer is between 0.8% and 10.0%. The units are randomly arranged in the linear polymer chain.

The polymerization process with vinyl monomer (II) is a similar vinyl addition and a similar random arrangement in the linear polymer chain produced occurs.

The copolymers of this invention characteristically are high molecular weight materials which can be readily processed into filamentary shape by conventional dry spinning techniques.

Copolymers prepared from acrylonitrile and vinylbis-(trifluoromethyl)carbinol (I) are advantageously dry spun from N,N-dimethylacetamide solutions containing about 5% lithium chloride and 12 to 30% polymeric material, preferably 15 to 25% of the latter. Other solvents useful for spinning fibers from these copolymers include N,N-dimethylformamide, N-methylpyrrolidone, and dimethyl sulfoxide.

Copolymers of acrylonitrile and vinylmethylnylethylvinylbis-(trifluoromethyl)carbinol (II) are advantageously dry spun into fibers from N,N-dimethylformamide solutions containing from 12 to 30% by weight solids, preferably from 15 to 25% solids. Other solvents useful for spinning fibers from these copolymers include N,N-dimethylacetamide, N-methylpyrrolidone and dimethyl sulfoxide.

Analogous copolymers, prepared from acrylonitrile and other carbinols related to vinyl monomers (I) and (II), were also investigated but were not fully characterized as textiles. These other carbinols included vinylmethylnylethylvinylbis-(chlorodifluoromethyl)carbinol (B.P. 75° C./14 mm.), p-vinyl-phenyl-bis(trifluoromethyl) carbinol (B.P. 69° C., 46 mm.), and vinyl-bis-(chlorodifluoromethyl)carbinol.

The following examples are illustrative of the practice of the preferred embodiment. The following terms and abbreviations are used in the examples: Fiber properties of tenacity, elongation, and initial modulus are coded as T/E/Mi, and reported in their conventional units of g./den., percent, and g./den., respectively. The terms work recovery and tear recovery are coded as WR and TR, and are reported in percent. These terms are used as defined in R. G. Beaman and F. B. Cramer, J. Polymer Sci., vol. 21, 228 (1956). The subscripts on WR and TR refer to the percent elongation (e.g., 3%, 5%).

The following example illustrate the preparation of the vinyl monomer (I), vinyl-bis(trifluoromethyl)carbinol.

**Example 1**

Into a 3 l., 4-necked flask equipped with stirrer, addition funnel, condenser, and thermometer are placed 75 g. of magnesium and 2 ml. of 1,2-dibromoethane. To this is added slowly, with stirring, a solution of 265 g. of vinyl chloride in 1 l. of dried tetrahydrofuran (distilled from lithium aluminum hydride). A reaction begins almost immediately and the temperature rises to a maximum of 36.5° C. The temperature of the reaction mixture returns to room temperature after being stirred overnight. The solution is straw to brown in color, has a density of 0.986 g./ml., and by titration is 2.46 molar in vinyl magnesium chloride. The clear solution is decanted, while in a dry box, from the unreacted magnesium.

Into a 2 l. flask equipped with a gas inlet tube, stirrer, and a solid carbon dioxide cooled condenser connected to a bubbler containing cyclohexane, are added 610 ml. (1.50 moles) of the above-described Grignard reagent. Stirring is begun and 207 g. (1.25 moles) of gaseous hexafluoroacetone is slowly added through the inlet tube, while maintaining the temperature below 30° C. by intermittent cooling of the flask in an external ice bath. After the hexafluoroacetone is added, the reaction mixture is stirred for an additional 1.5 hours. A total of 130 ml. of concentrated hydrochloric acid (1.56 moles), followed by 425 ml. of ether, are then added to the reaction mixture. A copious white precipitate forms and is subsequently collected on a filter. The precipitate is washed thoroughly portionwise with 1 l. of ether and with 40 ml. xylene. The filtrate and washing is added through the ether, after which the bulk of the ether is removed by a simple distillation. A total of 460 g. of salt remains on the filter. The brown liquid remaining after removal of the ether is fractionated in a spinning band column. The product distils as the tetrahydrofuran adduct at 100-101° C., 1.26 g./ml. at 25° C., 1.342. The tetrahydrofuran is removed by mixing 20 ml. fractions of the adduct with 10 ml. portions of concentrated sulfuric acid in semi-micro equipment and rapidly distilling off the product, keeping the heating bath temperature below 120° C. The resulting distillates are combined and fractionated through a spinning band column to produce vinyl-bis-(trifluoromethyl)carbinol, B.P. 72° C., 1.421 g./ml. at 25° C., 1.310. Vapor phase chromatography indicates that the product is 98.99±% pure. The infrared spectrum of the product is in accord with the stated structure.

The following example illustrates the preparation of a copolymer from vinyl-bis(trifluoromethyl)carbinol (I) and acrylonitrile (AN) by bulk polymerization.

**Example 2**

A mixture of 0.12 g. azobis(isobutyronitrile), a polymerization catalyst sold under the trademark "Vazo," 0.05 ml. of lauryl mercaptan, 15 ml. of acrylonitrile, and 0.6 ml. of vinyl-bis(trifluoromethyl)carbinol is placed in a 55 ml. polymer tube. The mixture is degassed two times by alternately freezing and thawing in vacuo and the contents are finally sealed in vacuo. Polymerization is ef-
ected by a reaction period of 16 hours at room temperature and two hours at 60° C. The solid white polymer produced in two such experiments had a weight of 19.5 g. (76% yield). The combined polymers are broken up in a homogenizer with methanol, collected, and washed with methanol.

In Table 1, below, are summarized results of other copolymerizations of vinyl-bis(trifluoromethyl)carbinol (I) and acrylonitrile (AN) performed by emulsion, bulk, and solution (in dimethyl sulfoxide) copolymerization procedures listed as Examples 3 to 6. Emulsion copolymerizations were carried out at about 30° C. and utilized 3 ml. of the monomer solution and 3 ml. of water containing 0.005 g. of potassium persulfate, 0.005 g. of sodium bisulfite, and 0.03% sodium lauryl alcohol sulfate, a dry surface active agent, sold under the trade- mark, “Duponol” ME.

### Table 1—Copolymerizations of Acrylonitrile (AN) and Vinyl-Bis (Trifluoromethyl) Carbinol (I)

<table>
<thead>
<tr>
<th>Example</th>
<th>Feed composition, wt. percent</th>
<th>Yield</th>
<th>n ln</th>
<th>Copolymer composition, wt. percent of (I)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AN(I)</td>
<td></td>
<td></td>
<td>B 1 E 1</td>
</tr>
<tr>
<td>3</td>
<td>50/50</td>
<td>41</td>
<td>40</td>
<td>2.3 3.5 1.9</td>
</tr>
<tr>
<td>4</td>
<td>87/13</td>
<td>74</td>
<td>79</td>
<td>2.6 3.3 1.9</td>
</tr>
<tr>
<td>5</td>
<td>95/5</td>
<td>98</td>
<td>96</td>
<td>4.9 3.3 1.9</td>
</tr>
<tr>
<td>6</td>
<td>95/5</td>
<td>98</td>
<td>101</td>
<td>5.1 4.8 1.6</td>
</tr>
</tbody>
</table>

B = Bulk, E = Emulsion, S = Solution.

These results show the greater weight percent incorporation of (I) in the copolymer when bulk or emulsion polymerization methods are used.

The following example illustrates spinning of a fiber from the copolymer of Example 2.

### Example 7

This copolymer, 16.76 g., is dissolved in 85 ml. of N,N-dimethylformamide containing 5% lithium chloride to give a 17.0% by weight solution. This solution is dry spun at 85° C. and the fiber, after extraction in water, is drawn 5X in 20 lb. steam and relaxed 15% at 160° C.; n ln = 2.3; F = 0.48% (percentage of fluoride) corresponding to 0.82 weight percent of units formed of vinyl-bis(trifluoromethyl)carbinol in the copolymer fiber. Summarized below in Table 2 are tensile properties exhibited by the copolymer fibers of this example. Included for comparison is the comparable data shown by control fibers prepared from polycrylonitrile. The control fibers are dry spun from a N,N-dimethylformamide solution containing 23% solids, and drawn 5X in 20 lb. steam, and are relaxed 10% at 160° C.; n ln = 2.0.

### Table 2

<table>
<thead>
<tr>
<th>Control</th>
<th>Copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/R/M</td>
<td>4.2/38/80</td>
</tr>
<tr>
<td>T/R/Al</td>
<td>1.7/38/7</td>
</tr>
<tr>
<td>TR/Al</td>
<td>51.40.41</td>
</tr>
<tr>
<td>WR/Al</td>
<td>26.20.19</td>
</tr>
</tbody>
</table>

The initial modulus Mf of the control and the copolymer of the present invention are comparable at room temperature. However, under hot wet conditions, the initial modulus of the copolymer of the present invention is clearly higher than that of the control. This data also shows the significant fact that this improvement occurs without substantially affecting the other properties. Neither TR nor WR is adversely affected.


The following example shows the preparation of a copolymer from vinyl-ethynyl-bis(trifluoromethyl)carbinol (II) and acrylonitrile (AN) corresponding to 1.1% by weight of vinyl-ethynyl-bis(trifluoromethyl)carbinol units in the copolymer.

### Example 8

Into a 100 ml. standard taper flask are placed 15 ml. of acrylonitrile, 0.6 ml. of vinyl-ethynyl-bis(trifluoromethyl)carbinol, 0.9 ml. of water solution of lauryl mercaptan in cyclohexane, and 30 ml. of an aqueous solution containing 0.08 g. of potassium persulfate and 0.08 g. of sodium bisulfite. The mixture, a two-phase system, is degassed 3 times by alternately freezing and thawing the evacuated system. The flask is then sealed in vacuo and the contents stirred magnetically overnight at room temperature. The white mass of polymer is collected, washed with water 3 times and then with methanol, and dried; yield 97%, n ln = 2.11. The products from four such polymerizations (yields 90-98%) are mixed to give a uniform product, n ln = 2.17, F = 0.57%.

40 grams of the combined copolymer products of the previous example are dissolved in 200 ml. of N,N-dimethylformamide to form a spinning solution containing 17.5% solids. The solution is dry spun at 100° C. through a 5 hole protrusion type spinneret with holes 10 mils in diameter. The fibers are dried by passing through a nitrogen column heated to 180-195° C. The yarn is wound up at 115-150 yds. per minute. The as-extracted fibers are extracted in water, are drawn 3X in 20 lb. steam, and are relaxed 15% at 175° C.; n ln = 2.0. The following tensile properties are exhibited:

T/E/Mi: 1.7/43/44; T/E/Mi (90° wet): 0.5/101/16; WR 2.5/8.5; WR 2.5/8.5; WR 2.5/8.5.

A commercially available fiber containing a major portion of polycrylonitrile, tested as a control, exhibited the following hot-wet tensile properties: T/E/Mi (90° wet): 1.2/110/12.

The filaments formed in Example 9 and fabrics made therefrom unexpectedly exhibit a high degree of wash recovery from soiling. These filaments and fabrics have a high "soiling resistance." The term "soiling resistance" is defined herein as the apparent resistance of a textile material to visible soil. This characteristic is determined by measuring the light reflected by the textile material before and after soiling and washing.

The following example shows the results obtained utilizing the fabric containing filaments of Example 9.

### Example 10

Each test fabric sample was of plain weave construction and each consisted of a warp of polypropylene monofilament on which filaments of a control polycrylonitrile, i.e., homopolymer, and of the filaments of Example 9, respectively, were woven as fillings. Anti-soiling properties were determined by the testing procedures described in U.S. Patent No. 2,959,202, employing the dry soil mixture.
described therein. The fabric samples were soiled, then washed.

The improved wash recovery from soiling is shown in Table 3.

Table 3

<table>
<thead>
<tr>
<th>Textile fabric source</th>
<th>Percent original reflectance retained after soiling and washing, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 9 filaments</td>
<td>83</td>
</tr>
<tr>
<td>Control</td>
<td>88</td>
</tr>
</tbody>
</table>

EXAMPLE 11

In an extension of the soiling test of the previous example, the test fabric prepared from the Example 9 filaments was soiled a second time, then washed again, as above. This second soiling test was modified to the extent that a commercially available and previously unsoiled sample of a fabric prepared from a terpolymer comprising acrylonitrile, sodium styrene sulfonate, and methyl acrylate was used as a control (coded below as “Control 2”). The results of this test, tabulated in Table 4, indicate an enhanced recovery from soiling for filaments prepared according to the present invention.

<table>
<thead>
<tr>
<th>Textile fabric source</th>
<th>Percent original reflectance retained after soiling</th>
<th>Percent original reflectance retained after soiling and washing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control B</td>
<td>84</td>
<td>81</td>
</tr>
<tr>
<td>Rx. 9 filaments 5</td>
<td>84</td>
<td>81</td>
</tr>
</tbody>
</table>

The novel copolymers of this invention are useful for the preparation of textile fibers, both monofilaments and yarns. They can be used alone, blended or co-spun with other polymers by procedures well known in the art. They can contain conventional additives, such as stabilizers, antioxidants, delusterants, pigments, dyes, antistatic agents, and the like.

The high hot-wet modulus values of the copolymer of the novel vinyl monomer, vinyl-bis(trifluoromethyl)carbinol (1), and acrylonitrile, makes the copolymer especially useful due to its increased resistance to wrinkling and stretching out of shape under the hot-wet conditions present in dyeing. It is significant that such improvement exists without detrimental effect on the important fiber properties.

The high degree of wash recovery from soiling, exhibited by the copolymers of vinyl-ethyl-bis(trifluoromethyl)carbinol (I) and acrylonitrile is especially useful because coating or finishing materials, as shown in the prior art, are not required.

It is to be understood that the foregoing description is by way of example only and that various modifications and changes in the details may be made without departing from the spirit of the invention and the scope of the following claims.

What is claimed is:

1. A fiber-forming copolymer consisting essentially of the copolymerizates of acrylonitrile and a vinyl monomer selected from the group consisting of vinyl-bis(trifluoromethyl)carbinol and vinyl-ethyl-bis(trifluoromethyl) carbinol, recurring units formed of said vinyl monomer constituting from about 0.8% to about 10% by weight of said copolymer, said copolymer having an inherent viscosity of at least 0.5, as measured at 30°C, in N,N-dimethylformamide at a concentration of 0.5% by weight.

2. The copolymer of claim 1 wherein the said vinyl monomer is vinyl-bis(trifluoromethyl)carbinol.

3. The copolymer of claim 1 wherein said vinyl monomer is vinyl-ethyl-bis(trifluoromethyl)carbinol.

4. A fiber of the copolymer as defined by claim 1.

5. A fiber of the copolymer as defined by claim 2.

6. A fiber of the copolymer as defined by claim 3.

7. A vinyl monomer having the formula

\[
\begin{align*}
&F \\
&\text{H} \quad \text{H} \quad \text{F} \quad - \quad \text{O} \\
&\text{C} \quad \text{C} \quad - \quad \text{O} \\
&\text{H} \quad \text{F} \quad - \quad \text{O} \\
&\text{F}
\end{align*}
\]

References Cited

UNITED STATES PATENTS

2,490,753 12/1949 Hill et al. 260—85.5 X

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H. WONG, Jr., Assistant Examiner.