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CHEMICALLY CRIMPED NYLON FIBERS

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2 Claims. (Cl. 260-78)

This invention relates to crimped nylon fibers and more particularly to chemically-crimped nylon fibers.

The present invention is a division of application Serial No. 154,371, "Chemically Crimped Nylon Fibers and Procedure for Obtaining Same," filed November 22, 1961, in the name of Stephen D. Bruck.

Filaments made from various synthetic linear polyamides (generically known as nylon) have come into widespread commercial use for the fiber basis of numerous textile materials. Such filamentary polyamides (nylon) form a unitary chemically related class to which the practice of the instant invention is particularly adapted, regardless whether the specific polyamide has been formed by condensation of a diamine with a dicarboxylic acid, e.g., hexamethylenediamine and adipic acid (nylon-66), by self-condensation of a lactam, e.g., E-caprolactam (nylon-6), or of an amino carboxylic acid, e.g., 11 amino undecanoic acid (nylon-11), or from interpolymers of these and other similar materials. Ordinarily, the nylons employed for the practice of the instant invention are those obtained from reactants such as above-described which yield linear polyamides having hydrogen bearing amide ($-\text{NH}-$) groups.

Importantly, the nylon filaments employed for the practice of the present invention are partly crystalline in structure, and preferably have been already stretch-oriented to the desired degree. The cross-linking treatment herein contemplated will, to a large extent, interfere with subsequent efforts to stretch orient the filament.

A principal object of the instant invention is to provide a novel cross-linked, crimped nylon filament.

A further object of the instant invention is to provide a chemical procedure for permanently crimping a nylon filament.

Briefly stated, the procedure of the instant invention involves first, asymmetric introduction of cross-links at the amide radicals in the polyamide molecules which make up the nylon filament to the total extent of from 1-50% of the amide hydrogen ($-\text{NH}-$). The linking radical must be longer than a simple methylene bridge and correspond at least to an ethylene chain in length. Importantly, the degree of cross-linking attained is asymmetric, i.e., not uniform across the cross-sectional area of the fiber. In effect a greater degree of cross-linking is attained on or near the peripheral surface of the filament than at the centermost regions thereof. Also the crystallinities in the fiber are not severely cross-linked. Secondly, the cross-linked fiber is then swelled sufficiently to achieve a volumetric change of from 2-20 times the volume of the initial unswelled filament. This swelling action will cause the fiber or filament to crimp to an extent consistent with the swelling agent employed, the character of the fiber and the degree of cross-linking effected. Lastly, the swelling agent is removed and the filament dried. In its dry state the nylon filament so treated retains the crimp as a permanent characteristic.

The chemical nature of the cross-link and the manipulative procedures employed to effect the differential cross-linking are subject to wide variations and there is no intent to restrict the instant invention to the specific cross-linking agents and procedures specifically set forth herein-after by way of examples and preferred embodiments.

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Similarly, the three steps above-described, namely asymmetric partial cross-linking, solvent swelling, and removal of the swelling agents need not be practiced as three separate and discrete steps. Expressly contemplated is a procedure wherein the final step of the cross-linking sequence is effected in the presence of solvents which will at the same time swell the filament being cross-linked.

An essential aspect of the instant invention is employment of the chemically crimping procedure upon an already formed nylon crystalline filament. Once the filament has been prepared according to conventional practice, e.g., melt spun, stretch oriented to the desired degree, heat set, etc., with or without delustrants, e.g., titanium dioxide, it is suitable for practice of the instant invention. A filamentary nylon well adapted for practice of the instant invention is an undyed tow or skein of high tenacity nylon filament.

Indeed, the degree of crystallinity present in the nylon filament has such bearing upon the crimp attainable by a specific cross-linking and solvent swelling sequence that adjustment of the preimparted degree of crystallinity present in the nylon filament is an important parameter in the final qualities of the crimped cross-linked nylon filament which results from practice of the instant invention. For effective practice of the instant invention the filaments should have in excess of about 30% crystallites (vol. percent) therein. Other parameters are controls on the process itself and the chemical nature of the nylon filament. In passing it is noteworthy that the instant crimping procedure need not materially decrease the strength or stability of the nylon filament.

The degree of crimping possible with practice of the instant invention can vary from the merest twist to formation of helical coils, and the term crimp as used herein is intended to include also within its purview such physical effects as might be described by terms like: twist, bend, coil, etc.

Allusion has already been made as to how the various polyamide resins which as a class may be termed nylon can be cross-linked through the amide radical $-\text{NH}-$. Ordinarily the amide hydrogen is itself replaced by a group of cross-linking radicals, but any already present substitute (i.e., $-\text{NR}-$) could be either converted into a cross-linking radical or replaced by one. However, the presence of substituents on the amide nitrogen other than hydrogen must be consistent, for practice of this invention with the physical limitation that the particular resin must somehow be formed into textile quality filaments, i.e., partly crystalline, often stretch oriented nylon filaments. Such filaments constitute the starting material for practice of the instant invention. Thus within quality limitation for nylon filaments process parameters can be suitably adjusted to compensate for composition variations such as for example the relative number of amide groups freely available for cross-linking purposes per unit molecular weight in the polyamide.

Some mention has already been made of the importance of effecting the desired cross-linking in an asymmetrical manner. To begin with it has been found that the crystallites remain virtually unaffected by the cross-linking reactions. Essentially therefore, the cross-linking reactions occur virtually entirely in the amorphous matrix in which the crystallites are embedded. Even in the amorphous polymer a substantial degree of asymmetry exists. The cross-linking reactions are deliberately not carried out to completion. As has been indicated only from 2-50% of the total number of the available amide groups in the filament are reacted. Since the cross-linking reaction is carried out on a macroscopic solid article, to wit, a filament, incomplete cross-linking necessarily results in a higher degree of substitution at or near the periphery of the filament than at the innermost portions thereof.

ected in the alkylene sulfide cross-linked fibers by a sensitive technique, specially devised for this purpose.

The swelled disulfide cross-linked nylon-6 fibers exhibited three-dimensional wavy crimping of uneven distribution and dimensions, both in the wet and dry states, similar to wool. This crimping was especially pronounced in those fibers which have been treated in the presence of methyl alcohol and cross-linked by either rapid air oxidation or by dilute solutions of H_2O_2 for 30 minutes. Much reduced, but still noticeable crimping was also exhibited by those samples which had been cross-linked in the presence of water instead of methyl alcohol. The more pronounced crimp of helical coiling was produced by either series of fibers when they were treated with m-cresol (a solvent which destroyed the remaining crystallites).

The alkylene sulfide cross-linked nylon-6 homofilaments exhibited self-crimping of uneven distribution and dimensions in both dry and water wet states similar to those of the disulfide cross-linked fibers. However, these macroscopic crimp deformations differed in at least three respects from those of the disulfide cross-linked samples: (1) the crimp frequency was much higher and the crimp amplitude smaller, (2) an extreme crimping, i.e., some helical coiling occurred even when the fiber was in the unswollen state, and (3) the extent of crimping was not gradually decreased by air-oxidation of unreacted sulfhydryl groups.

Without being bound thereto it is believed that the crimping effect can be explained by the asymmetric inhomogeneity of the cross-linking. Allusion has already been made as to how the crystallites are not, by and large, methoxylated and as a result do not become cross-linked to the extent which the amorphous portions of the fiber are cross-linked. Mention has been made that the cross-linking of the amorphous portions is not complete and how almost of necessity, the degree of cross-linking varies throughout the amorphous resin in the fiber cross-section, being greatest nearest the outside surfaces and being proportionately least at the innermost regions of the filament. However, some cross-linking should occur even at the innermost portions of the filament. In the instance of cross-linking through disulfide cross-links, the final oxidation to the cross-linking disulfide was brought about either by rapid air oxidation or by a brief treatment with dilute solutions of hydrogen peroxide. It is reasonable to believe that this treatment will oxidize the sulfhydryl groups located near to the surface of the fiber to a greater extent than those situated toward the center. Furthermore, onset of oxidation will be accelerated at points along the fiber axis which are more easily penetrated. Inasmuch as the cross-linking reactions are not really carried to actual completion there results a substantial asymmetry of the various cross-linking density across the fiber cross-section. Even though the fiber is cross-linked throughout it has an outer portion with a higher degree of cross-linking, an inside portion with fewer cross-links, and in addition scattered throughout the fiber volume essentially uncross-linked crystallites.

In consequence of this asymmetry, solvating the fiber filament by contact with a solvent capable of swelling the filament as a whole to at least twice its original volume will cause differential swelling at microscopic sized portions of the filament. The least cross-linked amorphous portion will swell more than the more cross-linked portions; in good solvents the crystallites themselves will be solvated. In total, internal stresses arise which cause the swelled fiber to crimp. The degree of crimping which results can be related to the solvating effect of the solvent.

The crimp so attained is permanent, remaining when the solvent is removed and the filament dried.

The foregoing explanation is consistent with the experimental tests wherein the cross-linked fiber was treated with a poor solvent, i.e., water, capable of swelling only the amorphous, least cross-linked portions of the fiber,

but not the crystallites. Little or no deformation occurs. Apparently the internal forces which tend to deform and crimp the fiber are opposed by the crystallites in the fiber. The relatively small differential swelling in water is insufficient to overcome the dimensionally stabilizing effect of the crystallites which remain dominant, particularly in the instances where the particular fiber employed during the test was approximately 50% crystalline. The small degree of crimping which, however, did occur shows what substantial internal forces are involved.

On the other hand, when a very good solvent (specifically m-cresol) was employed, complete destruction of the crystallites was effected and as a result of solvation the fiber deformed to the extent of helical coils.

For actual practice of the instant invention, it is contemplated that other swelling agents besides m-cresol or water would be employed judiciously in order to achieve a desired level of crimping with the least effect on the crystallinity of the fiber. Suitable swelling agents are the 1-4 carbon alcohols, their acetates, benzylalcohol, etc.

Still further tests tend to corroborate the above proposed explanation of why the instant procedure effects crimping. These tests also indicate the cross-linking of the fibers throughout, not only near the surface, is significant. Tests were made in which cross-linking was deliberately restricted to near the surface areas; the resulting fibers when treated with swelling agents (m-cresol) capable of dissolving the uncross-linked structure, produced merely a hole in the middle of the fiber. In these fibers no crimping was observed, apparently because virtually no differential swelling occurred.

Similarly, the existence and importance of differential swelling was demonstrated in the case of the disulfide cross-linked fiber by a test on the already cross-linked fibers, wherein the final oxidation was extended by more prolonged oxidation with dilute hydrogen peroxide, whereby the filaments exhibited a greatly diminished crimping tendency. The result, most likely, is due to the more uniform distribution of the cross-links throughout the filament achieved by virtue of better penetration of the oxidizing agent.

Still additional corroboration appeared in the experimental work directed to the introduction of alkylene sulfide cross-links. Some disulfide cross-links apparently were formed due to partial air oxidation of the mercaptide groups during the handling of the filaments. These cross-links appear to exercise a localized restraining effect upon the amorphous structure since some crimping resulted during the mild swelling which occurred during the washing and handling of the mercaptide fiber. Also since the subsequent cross-linking step actually involves simultaneously (1) swelling of the fiber in a mixture of benzyl alcohol and ethyl alcohol and (2) additional cross-linking through formation of the alkylene sulfide groups, a continuing swelling and internal plasticization of the fiber occurs with partial disruption of the crystallites gradually taking place during penetration of the alkylene dihalide reagent throughout the fiber. Initially as the crystallites are disrupted some of this resistance is removed; the crimping becomes more pronounced. Introduction of further alkylene sulfide cross-links when the fiber is in the thusly deformed state creates a tendency to reinforce the deformation and accentuate the extent of crimping. If later complete destruction of the crystallites is permitted (as occurs by swelling in m-cresol) the fiber crimps further, helically coiling; apparently then all counterforce to deformation has been removed.

Still further corroboration is available in the X-ray data. An oriented highly crystalline fiber filament crimped by both the alkylene sulfide and the disulfide cross-link exhibited virtually the same degree of crystallinity, but a lesser degree of orientation than the untreated filament. This result is consistent with the existence of differential swelling when the fiber is solvated and

is attributable to relative displacement of the crystallites, decreasing thereby the orientation.

In passing, it is noteworthy that the disulfide product can largely be converted to an alkylene sulfide cross-link ($-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\rightarrow-\text{CH}_2-\text{S}-\text{CH}_2-$) by heating the disulfide material to nearly the softening point of the filament. As a point of preference the alkylene sulfide cross-link is considered superior since the end product is more stable. Also subsequent treatment to block free sulfhydryl groups, as for example with silver nitrate, is not necessary.

For further understanding of the instant invention reference is now made to the following examples.

EXAMPLE I.—N-METHOXYMETHYLATION

Step A

A small skein of semi-dull 70/32 denier nylon-6 fiber, weighing approximately 0.1-0.2 gram was scoured for 30 minutes in water containing 1-2% Na_3PO_4 , washed in distilled water and dried.

A solution was prepared containing 500 grams of paraformaldehyde and 500 grams (625 ml.) methyl alcohol by heating the solution to 60° C. and adding 3-4 pellets of KOH. The solution was stirred at this temperature until all paraformaldehyde dissolved (approx. 15 minutes) and then it was allowed to cool to room temperature. The pH of the solution was then adjusted to 0.6-0.7 with anhydrous oxalic acid (approximately 40 grams). The skein was soaked in this solution for 12 hours at room temperature after which it was removed from the bath and heated at 120° C. in a closed oven for one minute, rinsed in methyl alcohol, water, and dried. Methoxy analysis: 3.4%.

EXAMPLE II.—INTRODUCTION OF SULFHYDRIL GROUP AND OXIDATION TO DISULFIDE CROSS-LINKS

Steps B, C, and D

Run No. 1.—The N-methoxymethylated nylon-6 fiber was soaked in a solution containing 38.0 grams thiourea (0.5 mole), 700 ml. distilled water and 35 ml. conc. HCl (0.42 mole) at room temperature for 12 hours. After this period 28.0 grams (0.5 mole) of KOH was added in 100 ml. distilled water and the fiber was permitted to soak at room temperature for 12 hours with concurrent air-oxidation from a porous-disc bubbler. Next, the fiber was removed from the solution, thoroughly washed with distilled water and dried. $S=2.1\%$.

Run No. 2.—Same as above, except that fiber was soaked for one hour in the thiourea, H_2O , and HCl mixture and for one hour in KOH. $S=1.0\%$.

Run No. 3.—The N-methoxymethylated nylon-6 fiber was soaked in a solution containing 38.0 grams thiourea (0.5 mole) and 700 ml. distilled water for 12 hours at room temperature. Next, 25 ml. of conc. HCl (0.42 mole) was added and the fiber soaked for one hour at room temperature. After this period 28.0 grams (0.5 mole) of KOH was added in 100 ml. distilled water and the fiber was permitted to soak at room temperature for one hour with concurrent air-oxidation from a porous-disc bubbler. The fiber was then washed with distilled water and dried. $S=1.3\%$.

Run No. 4.—The N-methoxymethylated nylon-6 fiber was soaked in a solution containing 38.0 grams thiourea (0.5 mole) and 700 ml. distilled water for 2 hours at 60° C. The solution was cooled to room temperature and then 28.0 grams (0.5 mole) of KOH was added in 100 ml. distilled water, the fiber was soaked in this solution for one hour at room temperature with concurrent air-oxidation from a porous-disc bubbler. The fiber was then washed with distilled water and dried. $S=1.0\%$.

The following table shows the analytical data on the

products of Runs 1-4 including solvating effect of water, the dry condition and the effect of subsequent solvation with m-cresol.

ANALYTICAL DATA ON STRUCTURALLY MODIFIED NYLON-6 FIBERS (WATER USED AS REACTION MEDIUM)¹

Run	Total, ² Percent	Amide Substitution, Percent	qm ³	Comments	
				Dry or Wet (Water)	m-Cresol
10 1-----	2.1	7.4	11.7	Very few crimps...	Helix.
2-----	1.0	3.6	14.4do.....	Do.
3-----	1.3	4.8	6.9do.....	Do.
4-----	1.0	3.6	8.5do.....	Do.

¹ N-methoxymethylated nylon-6; 3.4% methoxy groups.

² Total sulfur includes both sulfhydryl groups and disulfide cross-linkages.

³ Measured photomicrographically after 24 hrs. air-oxidation, $qm = V/V_0$, where V = volume of network at swelling equilibrium, in m-cresol and V_0 = volume of network before swelling.

Run No. 5.—Same as Run No. 1, except that methyl alcohol was used instead of water as the reaction medium. $S=2.9\%$.

Run No. 6.—Same as Run No. 2, except that methyl alcohol was used instead of water as the reaction medium. $S=3.5\%$.

Run No. 7.—Same as Run No. 3, except that methyl alcohol was used instead of water as the reaction medium. $S=2.7\%$.

The following table shows the analytical data on the products of runs 5-7 and also the solvating effects of methanol reaction medium in the dry and water wet condition, and the effect of subsequent solvation with m-cresol:

ANALYTICAL DATA ON STRUCTURALLY MODIFIED NYLON-6 FIBERS (METHYL ALCOHOL USED AS REACTION MEDIUM)¹

Run No.	Total S ²	Amide Substitution	qm ³	Comments	
				Dry or Wet	m-Cresol
40 5-----	2.9	10.3	6.7	Highly crimped.	Helix.
6-----	3.5	12.4	3.4do.....	Do.
7-----	2.7	9.5	4.3do.....	Do.

¹ N-methoxymethylated nylon-6; 3.4% methoxy groups.

² Total sulfur includes both sulfhydryl groups and disulfide cross-linkages.

³ Measured photomicrographically after 24 hrs. air-oxidation, $qm = V/V_0$, where V = volume of network at equilibrium swelling, V_0 = volume of network before swelling.

EXAMPLE III.—OXIDATION OF SULFHYDRIL GROUPS TO DISULFIDE LINKAGES WITH H_2O_2

To determine the effect of further oxidation the skeins from runs 1 to 7, respectively, were soaked at room temperature in a solution consisting of 250 ml. distilled water, 2 pellets of KOH and 10 ml. of 3% H_2O_2 for 30 minutes to 4 hours, depending on the particular experiment. The following table shows to what an extent the cross-linking is increased as measured by the decrease in swelling when solvated by m-cresol.

EQUILIBRIUM VOLUME SWELLING RATIOS¹ OF SAMPLES OXIDIZED BY AIR AND HYDROGEN PEROXIDE

Sample No. (Run)	Air, 24 hr., qm	H_2O_2 , 30 min., qm	H_2O_2 , 4 hr., qm
65 5-----	6.7	5.9	5.5
6-----	4.3	3.9	3.5
7-----	4.3	4.1	3.9

¹ Measured photomicrographically, $qm = V/V_0$, where V = volume of network at equilibrium swelling, V_0 = volume of network before swelling.

EXAMPLE IV

In this example all work was carried out with 7.8 Tex (60 denier) 32 filament round cross-section nylon-6 homo-

Step 1.—N-methoxymethylation

This reaction was carried out according to the procedure of Example 1.

Step 2.—Preparation of the mercaptides (F), Exp. No. 1, Table IV

A small skein (0.1–0.2 gram) of the N-methoxymethylated nylon-6 fiber was soaked for 12 hours at room temperature in a solution containing 37.5 grams (0.5 mole) of thioacetamide and 700 ml. of methyl alcohol. Next, 35 ml. of conc. HCl (0.42 mole) was added and the fiber soaked for one hour at room temperature. After this period 60.0 grams (1.06 moles) of KOH was added to 200 ml. of methyl alcohol and the fiber was permitted to soak at room temperature for one hour. The fiber was then washed thoroughly twice with methyl alcohol, twice with distilled water, and again twice with methyl alcohol.

Step 3.—Introduction of Type A alkylene sulfide cross-linkages, Exp. No. 1, Table IV

(a) The fiber from (2) was soaked for 5 hours at room temperature in a solution of 150 ml. of ethyl alcohol, 150 ml. of benzyl alcohol, and 29 ml. (0.36 mole) of ethylene diiodide. After this period the sample was thoroughly washed twice with ethyl alcohol, twice with distilled water, and twice with methyl alcohol and allowed to dry at room temperature. $S=3.7\%$.

(b) The procedure was the same as in (a), except that soaking time was 24 hours instead of 5 hours, (Exp. No. 2, Table IV). $S=3.6\%$.

Step 3A.—Introduction of Type B alkylene sulfide cross-linkages, Exp. No. 3 and 4, Table IV

The fiber from (2) was soaked for 24 hours at room temperature in a solution of 90 ml. of ethyl alcohol, 90 ml. of benzyl alcohol, and 90 ml. (1.04 moles) of 1,2-dibromoethane. After this period the sample was thoroughly washed twice with ethyl alcohol, twice with distilled water, and twice with methyl alcohol, and allowed to dry at room temperature. $S=2.0\%$.

Step 3B.—Introduction of disulfide cross-links (E), Exp. No. 5, Table IV

This reaction was carried out according to the procedure of Example 2. $S=2.7\%$.

ANALYTICAL DATA ON CROSS-LINKED NYLON-6 FIBERS

Exp.	Total S	Predominant cross-link Type ¹	Swelling Ratio, q_m^2	Macroscopic Deformation	
				Dry or Wet	m-Cresol
1.....	3.7	A.....	8.0	Very highly crimped; some helices.	Helices.
2.....	3.6	A.....	5.1	do.....	Do.
3.....	2.9	B.....	6.2	do.....	Do.
4.....	2.9	B.....	6.8	do.....	Do.
5.....	2.7	O.....	5.8	Crimped.....	Do.

¹ Type A = N—CH₂—S—CH₂—S—CH₂—N.
Type B = N—CH₂—S—(CH₂)₂—S—CH₂—N.
Type O = N—CH₂—S—S—CH₂—N.

² $q_m = V/V_0$, where V = volume of network at equilibrium swelling, V_0 = volume of network before swelling. Swelling agent: m-Cresol.

EXAMPLE V

Skeins of 3-denier filament of nylon-11 and 66 were asymmetrically partially cross-linked according to the procedure set forth in Example IV to produce both Type A alkylene sulfide and Type B alkylene sulfide cross-linking. The resulting swelling ratios were not measured exactly, but for nylon-66 appeared about the same as for nylon-6, and about 50% greater for nylon-11. The degree of crimping was considerably less for the nylon-66 as for nylon-6, and even less for nylon-11.

While the examples have shown the practice of the invention in terms of disulfide and alkylene sulfide cross-linking bonds, it should be understood that other cross-linking chains might be employed with or without completely different cross-linking procedures. Thus, for example, irradiation of the filament with high voltage electron beams might be employed in suitable cross-linking procedures to form a cross-link of at least the length of an ethylene chain. Many different embodiments of this invention may be made without departing from the spirit and scope thereof, as defined in the appended claims.

What is claimed is:

1. A crimped polycarbonamide fiber made by:

- reacting an oriented polycarbonamide fiber having at least 20% by volume crystallites therein with the hemiacetal of formaldehyde and methanol,
- thereafter reacting said fiber with a member of the group consisting of thiourea and thioacetamide in the presence of methanol and a mineral acid,
- thereafter reacting said fiber with a solution of an alkali metal hydroxide and methanol, and simultaneously bubbling air through said solution, and
- washing and drying said fiber.

2. A crimped polycarbonamide fiber made by:

- reacting an oriented polycarbonamide fiber having at least 20% by volume crystallites therein with the hemiacetal of formaldehyde and methanol,
- thereafter reacting said fiber with a member of the group consisting of thiourea and thioacetamide in the presence of methanol and a mineral acid,
- thereafter reacting said fiber with an alkali metal hydroxide in the presence of methanol,
- thereafter reacting said fiber with an alkylene dihalide in the presence of ethanol and benzyl alcohol, and
- washing and drying said fiber.

References Cited by the Examiner

UNITED STATES PATENTS

2,157,117	5/1939	Miles	260—78
2,249,756	7/1941	Finzel	260—78
2,430,859	11/1947	Cairns	260—78
2,598,407	5/1952	Marvel	260—78
3,203,934	8/1965	Wellens	260—78

OTHER REFERENCES

Mark et al.: Physical Chemistry of High Polymeric Systems, Interscience, New York, 160, pp. 357 to 359, 363.

Tobolsky: Properties and Structure of Polymers, John Wiley & Sons, Inc., New York, 1960, p. 198.

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