Feb. 26, 1963 O. L. SHEALY 3,078,544

CRIMPABLE SYNTHETIC FILAMENTS AND PROCESS OF MANUFACTURING SAME

Filed May 19, 1960 2 Sheets-Sheet 1

FIG. 1

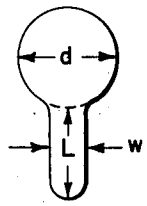


FIG. 2

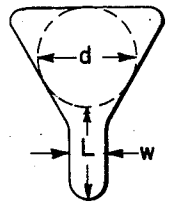


FIG. 3

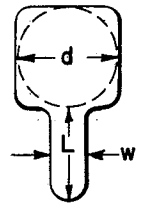


FIG. 4

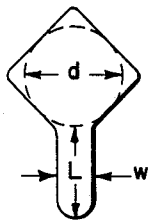


FIG. 5

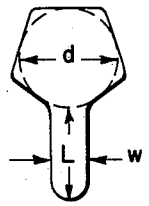


FIG. 6

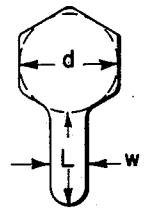


FIG. 7

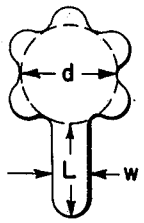


FIG. 8

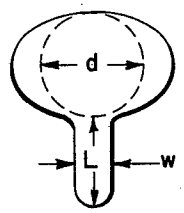


FIG. 9

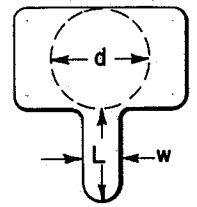
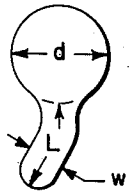


FIG. 10



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FIG. 11

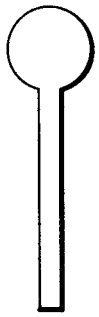


FIG. 12

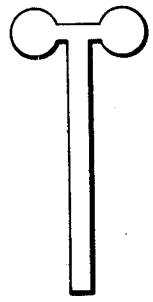


FIG. 13

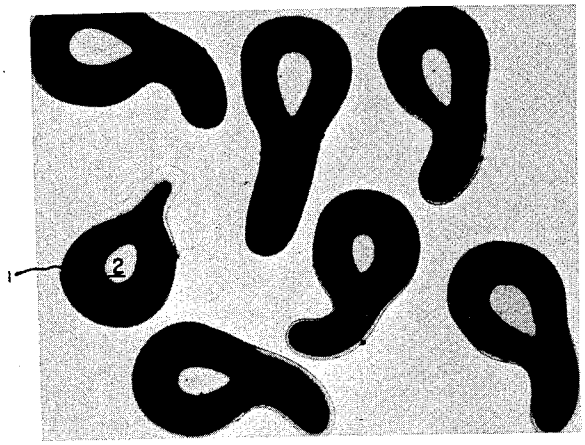
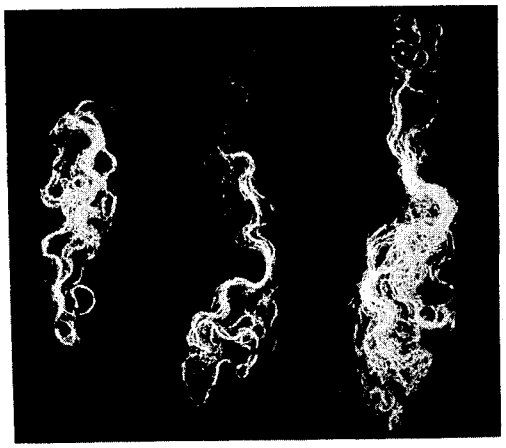


FIG. 14



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United States Patent Office 3,078,544 Patented Feb. 26, 1963

3,078,544

CRIMPABLE SYNTHETIC FILAMENTS AND PROCESS OF MANUFACTURING SAME

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Filed May 19, 1960, Ser. No. 30,332
9 Claims. (Cl. 28—82)

This invention relates to a novel and useful synthetic polymeric filament or yarn and to a process for its production. More particularly it is concerned with a crimped filament or yarn, formed from a synthetic polymer, having a "keyhole" cross section as defined in detail hereinafter.

It is an object of the present invention to provide a novel and useful crimped filament or yarn formed from a synthetic polymer, the said filament or yarn having a "keyhole" shaped cross section.

Another object is to provide a novel and useful process for crimping a filament or yarn formed from a synthetic polymer.

These and other objects will become apparent in the course of the following specification and claims.

The present invention provides a heat relaxable crimpable filament or yarn of "keyhole" cross section, formed from a synthetic polymer, having a differential of concentration of graft-copolymeric component across its cross-sectional area of such nature that a relatively larger graft copolymeric component is present along its outer surface than is present at its innermost core, which may be completely free of any grafted component. The process for forming the above defined structure involves spinning a yarn or filament of keyhole cross section from a synthetic polymer by wet, dry or extrusion methods known to the art, thereafter penetrating (as by soaking) the structure with a polymerizable vinyl compound and finally initiating polymerization of the said polymerizable vinyl compound. Heat relaxation of the structure so formed, as by a boil-off, results in crimping.

By a "filament or yarn" is meant any funicular body such as staple, continuous filament fiber of single or multiple strands, which may be twisted or untwisted, spun yarn, floc and the like. The process may be applied before or after the funicular body is processed into a textile.

By "a filament or yarn of 'keyhole' cross section" is meant a filament or yarn, the cross-sectional outline of which consists of a substantially symmetrical main body having a finger-like protrusion extending therefrom, the relative proportions of the main body and protrusion being such that the length "L" of the protrusion is at least equal to the effective diameter "*d*" of the main body (i.e. the diameter of the largest circle that may be inscribed within the said main body) and the said diameter "*d*" being at least twice the width "*w*" of the said protrusion. Typical key-hole shapes are illustrated in FIGURES 1 to 9 inclusive.

By "innermost core" is meant that section of the "main body" as defined above furthest from the outer surface of the said body.

The invention will be more readily understood by reference to the drawings.

As pointed out above, FIGURES 1–9 inclusive are typical keyhole-shaped structures useful in preparing the relaxable, crimpable filament of the present invention.

FIGURE 10 illustrates the type of crimp obtained upon heat relaxation of the keyhole cross section filament as represented by FIGURE 1.

FIGURES 11 and 12 are typical spinneret orifice designs suitable for the production of filaments or yarns

of "keyhole" cross section, that of FIGURE 11 being applicable for the production of structures as represented by FIGURES 1 and 10, whereas the design of FIGURE 12 is suitable for making the filament of cross section shown in FIGURE 8.

FIGURE 13 is a photomicrograph of the cross section of a filament of the present invention after crimping, identified more fully hereinafter in Example 1, magnified about 500×, **1** being the graft copolymeric component and **2** the ungrafted core.

FIGURE 14 is a photograph showing a longitudinal view of the staple of Example 1 as identified therein, after crimping.

Referring in particular to FIGURES 1–10, the letter "*d*" represents the effective diameter of the main body in each illustration, and the letter "L" represents the length of the protrusion. The width of the protrusion is designated "*w*."

The following examples are cited to illustrate the invention. They are not intended to limit it in any manner.

Example I

Polyhexamethylene adipamide is melt spun at a speed of 276 y.p.m. through a 13-hole spinneret, the holes having the shape illustrated in FIGURE 11 and being arranged in a circular pattern with the heads of each of the keyhole shapes pointing in the same direction. In the particular embodiment the dimension "*d*" is 20 mils, "L" is 40 mils and "*w*" is 4 mils. A grid temperature of 288° C. is employed. A room temperature air quench blowing across the face of the spinneret toward the heads of the keyhole orifices at a rate of 140 c.f.m. is employed. The resulting 180 total denier yarn is cut to 3-inch staple. The filaments of the yarn have a *w/d/L* ratio of 1.0/2.7/2.0. 5 grams of this sample is dipped in a 40% solution of acrylic acid in water at 24° C. After wringing free of excess solution the sample is irradiated with high energy electrons to a dose of 12.5 watt-sec./cm.^{2} (i.e./mrad.), using a Van de Graaff accelerator. The radiation is begun about two minutes after the dipping operation. The staple is rinsed with cold water, washed three times for 5 minutes each in water of 80° C. and dried at 100° C. for 1 hour. A weight gain due to grafting of 18.1% is observed. The product has 5.3 crimps per inch. A comparative control of the same staple processed as described, including the 80° C. boil-off, but omitting soaking and irradiation, shows 1.8 crimps per inch.

The above experiment is repeated except that a 20% solution of acrylic acid is applied for a period of one minute, a photomicrograph at a magnification of about 500 times of a typical cross section of the yarn so produced after crimping is shown in FIGURE 13. The dark outer ring indicates an area wherein grafting has occurred whereas the nuclei-like, light innermost core is an area free from substantial graft copolymerization. This represents a penetration of graft component of about 0.5 *w*. FIGURE 14 is a photomicrograph of the crimped yarn. A similar result is obtained when soaking is increased for five minutes although the filament cross section is more nearly completely composed of graft copolymer, the ungrated innermost core being represented by a smaller light core in a photomicrograph similar to that of FIGURE 13. This corresponds to a penetration of graft component of about 0.7 *w*. When the soaking time is increased to 30 minutes, thereby creating a uniformly graft polymerized cross section, the amount of crimp obtained is about the same as that of the unmodified control.

Example II

A 500-yard skein of a 40 total denier 13-filament key-

hole cross section yarn of polyhexamethylene adipamide, having a *w/d/L* ratio of 1.0/2.4/4.0, is soaked for 15 hours in 100 ml. aqueous solution containing 20% by weight of sodium styrene sulfonate. The excess solution is removed by decantation. The skein is irradiated with 1 mrad. high energy electron under a Van de Graaff accelerator in order to effect grafting of the sodium styrene sulfonate onto the polyhexamethylene adipamide. The skein is then boiled-relaxed in 400 ml. of 0.5% sodium carbonate solution for 30 minutes. During this boil-off, crimp is developed in the yarn. The yarn is then rinsed in water and dried-relaxed at 25° C. for 3 days. The weight gain due to grafting is 6.2%. The resulting yarn has about 9 crimps per inch. A comparative control of the same yarn processed as described, including the boil-off, but omitting the soaking and irradiation, shows 2 crimps per inch.

Example III

A 500-yard skein of a 40 total denier 13-filament keyhole cross section yarn of polyhexamethylene adipamide, having a *w/d/L* ratio of 1.0/2.4/4.0, is soaked for 1 hour in 100 ml. aqueous solution containing 20% by weight of styrene sulfonic acid. The excess solution is removed by decantation. The skein is irradiated with 1 mrad. high energy electron using a Van de Graaff accelerator in order to effect grafting of the sulfonic acid onto the polyhexamethylene adipamide. A weight gain of 28% is observed. The skein is then boiled 30 minutes in 4% sodium carbonate solution in water. During this boil-off, crimp is developed in the yarn. The skein is dried-relaxed at 25° C. for 26 hours. The resulting yarn has 8 crimps per inch.

Example IV

A 2,000-yard skein of a 40 total denier, 13-filament keyhole cross section yarn of polyhexamethylene adipamide, having a *w/d/L* ratio of 1.0/2.7/3.5, is irradiated with 1 mrad. of high energy electrons under a Van de Graaff accelerator at −80° C. The skein is stored at −80° C. for 15 minutes and then soaked for 3 minutes at 50° C. in an aqueous solution containing 20% by weight of acrylic acid. The skein is immersed in one liter of distilled water at 25° C. for about 12 hours, then rinsed five times with one liter each time of distilled water at 70° C. The skein is dried in air. The weight gain due to grafting is 4.75%. The product shows 10 crimps per inch.

While the invention has been illustrated in detail by specific examples to filaments and yarns of poly(hexamethylene adipamide) it will be obvious that it is applicable as well to all such structures formed from a synthetic polymer. Thus polymers suitable for use in this invention may be found among all types of polymeric, fiber-forming materials, such as fiber-forming polyamides, polyureas, polyurethanes, polysulfonamides, polyesters (such as polyethylene terephthalate), and polyvinyls (such as polyacrylonitrile and copolymers thereof, polyethylene, and polypropylene). Condensation polymers such as polyesters, polyamides, or polyester amides as described in United States Patents 2,071,250; 2,071,253; 2,130,523; 2,130,948; 2,190,770; 2,465,319, as well as polyurethanes as in United States Patent 2,731,446 and polyureas are satisfactory. Addition type polymers such as polyhydrocarbons, polyethers and those made from ethylenically unsaturated monomers such as acrylonitrile, vinyl chloride, vinylidene chloride, vinyl acetate and their copolymers with each other and other copolymerizable monomers may be used.

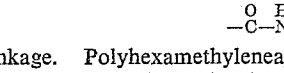
Filaments and yarns of polyamides are preferred. Suitable polyamides are those synthetic linear polyamides which are prepared from polymerizable monoamino monocarboxylic acids or their amide-forming derivatives, or from suitable diamine and suitable dicarboxylic acids or from amide-forming derivatives of these compounds. The —R— group of the intercarbonamide linkages



may be hydrogen, halogen, monovalent organic radical, alkylene or the like. Typical of such polyamides are those formed from an aliphatic diamine and an aliphatic di-acid containing the repeating unit:

—X—Z—Y—Z—

wherein —X— and —Y— represent divalent aliphatic or cycloaliphatic groups and —Z— represents the



linkage. Polyhexamethyleneadipamide and caproamide (i.e., "66" and "6" nylons) are typical. Other suitable polyamides are those having the repeating structure:

—A—Z—X—Z—

wherein —A— is a divalent aromatic radical and —X— and —Z— are as previously defined. Polyhexamethylene terephthalamide is illustrative of such polymers. Additionally polyamides having repeating units such as:

—A—Z—B—Z—

and

—X—Z—B—Z—

wherein —B— is divalent alkaryl (such as xylylene) may be used. Another class of suitable polyamides containing other than aromatic intracarbonamide repeating units are those prepared from piperazine, such as those from piperazine and adipic acid, piperazine and terephthalic acid, and the like. Copolyamides, condensation copolymers wherein the amide linkage is the predominant linkage and polyamide mixtures are also useful. As pointed out previously, such polyamides, to form the structures of the present invention, are of a high molecular weight, i.e. they are fiber-forming. Preparation of high molecular weight polyamides is illustrated in United States Patents 2,071,250; 2,071,253 and 2,130,948. Particularly suitable polyamides include polyhexamethylene adipamide, poly(epsilon-aminocaproic) acid, poly (p-xylylene azalamide), poly (m-xylylene adipamide).

The preferred polyesters to be used in this invention are obtained from polyethylene terephthalate wherein at least about 75% of the recurring structural units of the polyester are ethylene terephthalate structural units. These should be fiber-forming and have a relative viscosity of at least about 12. Such polymers may be represented in a more general way by the formula

$$HO—G—(OOC—D—COO—G)_y—OH$$

where —G— and —D— are divalent organic radicals corresponding, respectively, to the radicals in the initial glycol, $G(OH)_2$, and to the initial dicarboxylic acid, $D(COOH)_2$, and y is a large number sufficient that the polymer is of fiber-forming molecular weight; at least about 75% of the —D— radicals being terephthalate radicals. Preferably at least about 75% of the —G— radicals are ethylene radicals. The terephthalate radical may be the sole dicarboxylate constituent of the recurring structural units, or up to about 25% of the recurring structural units may contain other dicarboxylic radicals, such as the adipate, sebacate, isophthalate, 5-(sodium sulfo)-isophthalate, bibenzoate, hexahydroterephthalate, diphenoxyethane-4,4′-dicarboxylate, or p,p′-sulfonylbibenzoate radicals, derived from the corresponding dicarboxylic acids or ester-forming derivatives thereof. Similarly, ethylene glycol may be the sole glycol constituent of the polyester, or up to about 25 mol percent of another glycol may be used, such as tetramethylene glycol, hexamethylene glycol, decamethylene glycol, 2,2-dimethylpropane-

diol, trans-p-hexahydroxylylene glycol, diethylene glycol, bis-p-(beta-hydroxyethoxy)benzene, bis-1,4-(beta-hydroxyethoxy)-2,5-dichlorobenzene, or bis-[p-(beta-hydroxyethoxy)phenyl]difluoromethane.

Polymers containing 85% or more combined acrylonitrile are especially useful due to their resistance to chemical reagents, ultra-violet light degradation and outstanding physical properties. Numerous monomers including ethylenically unsaturated sulfonic acids as the methallyl sulfonic acids and others as disclosed in United States Patents 2,527,300 and 2,601,256 can be copolymerized with acrylonitrile as disclosed in Jacobson United States 2,436,926 and in Arnold United States 2,456,360 to produce copolymers useful herein.

The "polymerizable vinyl compounds" include N-vinyl pyrrolidone, 2-vinyl pyridine, 4-vinyl pyridine, N-vinyl N-methyl formamide, acrylamide, allyl alcohol, vinyl acetate, vinyl sulfonamide, and the following acids and their sales (e.g., Na, K, NH_4, Ca): acrylic acid, methacrylic acid, maleic acid, crotonic acid, dichloro maleic acid, furoic acid, vinyl phosphonic acid, vinyl sulfonic acid, styrene sulfonic acid, 2-methyl propene-1,3-disulfonic acid.

Funicular structures such as filaments and yarns are formed from synthetic polymers as described above by conventional means. A typical melt extrusion process to produce such structures is described in French Patent 1,096,943, dated June 28, 1955. For highest crimpability the structures have a d/w ratio between about 3.0 and about 4.0 when a high level of crimp is desired, but a ratio of about 2.0 or even somewhat lower will result in some crimp. The ratio L/d is preferably between about 1.25 and about 1.50 when a high level of crimp is desired, but a ratio of about 1.0 or even somewhat less will result in some crimp. Heat relaxation is preferably accomplished by the immersion of the fabric or fiber in water or an aqueous solution at elevated temperature, i.e. about 45° C. The period to effect the crimping will vary with the degree of composition differential, the temperature employed and the like. Immersion in water or an aqueous solution heated to a temperature above the second order transition temperature of the polymer is recommended. Immersion in boiling water or a boiling aqueous solution generally results in the desired self-crimping in less than 30 minutes. This preferred mode of immersion is referred to in the trade as "boil-off."

As discussed above, the "penetration" of the polymerizable vinyl into the filamentary substrate prior to grafting is "partial." By "partial penetration" is meant a penetration to an essentially uniform depth from the outer surface of the substrate inward, wherein the penetration does not extend uniformly to the center of the head. Preferably the depth of penetration may have any value between just a very thin skin of about 0.01 w and a value of about 0.7 w. The preferred penetration is in the range between 0.4 w and 0.6 w. Best results are obtained when the penetration is approximately 0.50 w. Control of the depth of penetration is essential for obtaining the desired high level of crimp. For any particular yarn (i.e. any particular combination of keyhole dimensions, linear polymer and vinyl monomer) the level of crimp is determined by the depth of penetration. The depth of penetration itself in turn depends on such variables as density, crystallinity of the linear polymer, concentration, and temperature of the solution of the vinyl monomer, nature of the solvent, soaking time, mode of removal of excess solution, time of delay between soaking and irradiation, etc.

Some vinyl monomers which penetrate one particular polymer so fast as to be impractical for use on a low denier yarn of this polymer, when irradiation follows soaking, may be suitable for a higher denier yarn of that same polymer, following that same sequence, or for a low denier yarn of another polymer which it penetrates more slowly. For example, acrylic acid, methacrylic acid, and N-vinyl pyrrolidone are suitable for partially penetrating polyethylene terephthalate or poly (p-xylene azelamide) since their penetration in these polymers is relatively slow and easily controlled. On the other hand, when combining these vinyl compounds with polyhexamethylene adipamide, it is more convenient to employ high denier yarn in order to control the very fast penetration of the acrylic acid to the required depth.

Another means of adjusting the process to the rate of penetrating of a certain vinyl compound plus polymer combination is the sequence of the operations. Considerable variation in the sequence of operations is possible. For a vinyl compound plus polymer combination with relatively low rate of penetration, a preferred sequence is spinning, drawing, soaking and decanting. For a vinyl compound plus polymer combination with relatively high rate of penetration a preferred sequence is spinning, drawing, irradiating, soaking, decanting, and/or centrifuging and immersing (Example IV). This sequence requires a longer penetration time which facilitates the control of the penetration depth. Other sequences are possible, such as spinning, soaking, drawing, irradiating, and immersing.

Grafting of the polymerizable vinyl compound to the synthetic linear polymer may be initiated by ionizing irradiation, by chemical initiators or by heat. Initiation by ionizing radiation is preferred. Both high energy particle radiation and ionizing electromagnetic radiation may be employed. By "high energy particle radiation" is meant an emission of high energy electrons or nuclear particles such as protons, neutrons, alpha particles, deuterons, and the like. The charged particle may be accelerated to high speeds by means of a suitable voltage gradient, using such devices as a resonant cavity accelerator, a Van de Graaff generator, a betatron, a synchroton, a cyclotron or the like. Neutron radiation may be produced by bombardment of selected light metal (e.g., beryllium) targets with high energy positive particles. In addition, suitable particle radiation may be obtained from an atomic pile or some radioactive isotopes or some other material or artificial radioactive material. By "ionizing electromagnetic radiation" is meant radiation produced when a metal target (e.g., tungsten) is bombarded by electrons possessing appropriate energy. Such energy is imparted to electrons by accelerating potentials in excess of 0.1 million electron volts (mev.), with 0.5 mev. and over preferred. Such radiation, conventionally termed X-ray, will have a short wave length limit of about 0.1 Angstrom units (in the case of 1 mev.) and a spectral distribution of energy at longer wave lengths determined by the target material and the applied voltage. X-rays of wave lengths longer than 1 or 2 Angstrom units are attenuated in air thereby placing a practical long wave length limit on the radiation. In addition to X-rays produced as indicated above, suitable ionizing electromagnetic radiation for carrying out the process of the invention may be obtained from a nuclear reactor ("pile") or from natural or artificial radioactive material, for example, cobalt 60. In all of these latter cases, the radiation is conventionally termed gamma rays.

Grafts containing acid groups may be advantageously boiled off in an aqueous solution containing alkali metal. For these grafts an aqueous sodium carbonate solution in the concentration range 0.4 to 2.0% is particularly suitable.

It is believed that the self-crimping nature of the yarn is effected by the large difference in shrinkage between the partially penetrated and grafted head section and the more completely penetrated and grafted fin tail section of the keyhole, during the boil-off. A sodium carbonate solution is particularly suitable for grafts containing acid groups, presumably because the difference in shrinkage for the salts of the graft copolymers is greater than the corresponding acids.

The novel yarns of this invention show improved bulk,

cover, and resistance to pilling. The crimped yarns are useful for staple end uses, such as carpets, sweaters, worsted suiting, and for flat woven end uses, and knitted goods.

Some crimp results when an unsoaked, ungrafted keyhole cross section yarn is boiled off, but the level of crimp obtained is very low. On the other hand, the process of this invention results in high levels of crimp. So also while binary, laminated fibers or films which crimp or curl due to difference in shrinkage of the two components may be prepared by combining polymers which have different moisture regains at the same relative humidity, e.g. by co-extrusion of 6-nylon polymer and polymer prepared from p-xylene diamine and azelaic acid, such structures are inferior to those of the present invention in that they do not crimp to the same degree and the crimp changes with the humidity level.

Many equivalent modifications will be apparent to those skilled in the art from a reading of the above without a departure from the inventive concept.

What is claimed is:

1. A heat relaxable, crimpable fiber, the cross-sectional outline of which consists of a substantially symmetrical main body having a finger-like protrusion extending therefrom, the relative proportions of the main body and protrusion being such that the length of the protrusion is at least equal to the diameter of the largest circle that may be inscribed within the said main body and the said diameter being at least twice the width of the said protrusion, the said fiber being formed from a synthetic polymeric substrate, having a differential of concentration of graft-copolymeric component across its cross-sectional area of such nature that a relatively larger graft copolymeric component is present throughout the entire area of its outer surface than is present at its inner-most core.

2. The structure of claim 1 wherein the innermost core is completely free of graft copolymeric component.

3. The structure of claim 1 wherein the graft copolymeric component penetrates the substrate to an extent at least equal to about 0.01 of the width of the said protrusion.

4. The structure of claim 1 wherein the graft copolymeric component penetrates the substrate to an extent of from about 0.4 to about 0.7 of the width of the said protrusion.

5. A process for forming a heat-relaxable, crimpable fiber which comprises penetrating a polymeric fiber, the cross-sectional outline of which consists of a substantially symmetrical main body having a finger-like protrusion extending therefrom, the relative proportions of the main body and protrusion being such that the length of the protrusion is at least equal to the diameter of the largest circle that may be inscribed within the said main body and the said diameter being at least twice the width of the said protrusion, with a polymerizable vinyl compound to provide a differential in concentration of the said polymerizable vinyl compound over the cross-sectional area of the said substrate and thereafter initiating polymerization of the said vinyl compound.

6. The process of claim 5 wherein the polymerization initiation is acomplished by exposure to high energy particle radiation.

7. The process of claim 5 wherein the product obtained is thereafter heated in a relaxed state.

8. The process of claim 7 wherein the temperature of heating is at least the second order transition temperature of the polymeric substrate.

9. A crimped fiber, the cross-sectional outline of which consists of a substantially symmetrical main body having a finger-like protrusion extending therefrom, the relative proportions of the main body and protrusion being such that the length of the protrusion is at least equal to the diameter of the largest circle that may be inscribed within the said main body and the said diameter being at least twice the width of the said protrusion, the said fiber being formed from a synthetic polymeric substrate, having a differential of concentration of graft-copolymeric component across its cross-sectional area of such nature that a relatively larger graft copolymeric component is present throughout the entire area of its outer surface than is present at its innermost core.

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2,238,694	Graves	Apr. 15, 1941
2,287,099	Hardy et al.	June 23, 1942
2,439,815	Sisson	Apr. 20, 1948