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(54) Title: RAPID THERMAL CONVERSION OF A POLYAMIC ACID FIBER TO A POLYIMIDE FIBER

(57) Abstract: The invention provides a process comprising heating a
polyamic acid fiber to a temperature in the range of a first temperature
and a second temperature for a period of time in the range of 5 seconds
to 5 minutes to form a polyimide fiber, wherein the first temperature is
the imidization temperature of the polyamic acid and the second tem-
perature is the decomposition temperature of the polyimide.
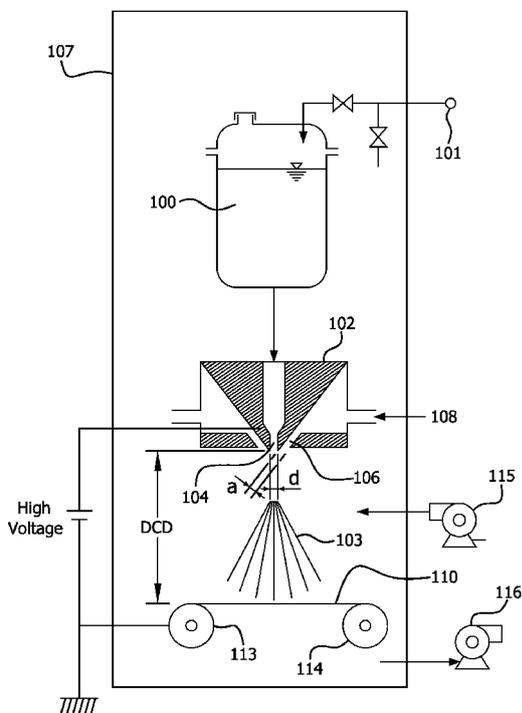
FIG. 1

TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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<u>TITLE</u>

RAPID THERMAL CONVERSION OF A

<u>POLYAMIC ACID FIBER TO A POLYIMIDE FIBER</u>

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This application claims foreign priority under, and the benefit of, U.S. Application SN 12/899,770, filed October 7, 2010, which is by this reference incorporated in its entirety as a part hereof for all purposes.

10

<u>RELATED APPLICATIONS</u>

This application is related in subject matter to copending U.S. Provisional Patent Application Nos. 61/286618, 61/286628, and 61/286623 filed on December 15, 2009.

15

<u>FIELD OF THE INVENTION</u>

The present invention is directed to a process of rapid thermal conversion of a polyamic acid fiber, nanofiber, or nanoweb to a polyimide fiber, nanofiber, and nanoweb respectively.

20

BACKGROUND OF THE INVENTION

Polyimides (PIs) are an important class of high performance polymers and are used in a wide range of applications e.g., microelectronics, aviation industry,

5   separation membranes, separators for batteries. PIs are traditionally synthesized in a two step process. First, a polyamic acid is prepared by low-temperature polycondensation of a tetracarboxylic acid dianhydride with an organic diamine in an aprotic polar solvent. The polyamic acid so prepared is then converted to polyimide thermally, chemically, or using a combination of both. According to

10   mechanism behind the conversion of polyamic acid to polyimide, as discussed by Bryant, R. G., Polyimides, *Encyclopedia of Polymer Science and Technology*, 2006, the rate of imidization is faster in the early stages of conversion due to lower Tg of the polymer and higher availability of solvent to assist in the ring closure. However, with increased conversion, the rate of imidization decreases as the Tg

15   of the polymer increases and availability of solvent decreases. This two step rate effect was observed in fibers (high surface area) and cast films, with thicker films having a higher initial imidization rate. Furthermore, dry polyamic acid powders with the highest surface to volume ratio imidized the slowest. Thermal conversion of polyamic acid to polyimide disclosed in the literature are long,

20   taking anywhere from 20 minutes to hours.

Huang et al., *European Polymer Journal* **42** (2006) 1099–1104, disclose preparation of BPDA–PDA polyimide films and electrospun nanofiber sheets by imidizing electrospun BPDA–PDA polyamic acid by thermal annealing in vacuum

25   at temperature in the range of 100 °C to 450 °C for a total time of over 3 hours.

Zhang et al., *The 2006 International Conference on MEMS, NANO and Smart Systems* disclose a series of sequential thermal treatments at 80°C to 300°C, to convert PMDA-ODA PAA electrospun fibers into polyimide, requiring a total time of 4 hours and 30 minutes.

5

Jirsak et al., *Journal of Nanomaterials*, doi:10.1155/2010/842831 disclose thermally imidizing thin layer of electrospun fibers of ODPA-ODA polyamic acid by following a series of thermal annealing steps at a temperature range of 60 °C to 300 °C for a total time of 6 hours.

10

Long imidization times for the conversion of PAA to PI results in an overall increase in the cost of manufacturing, which in turn can affect the profit margin. Hence, there is a need for new methods of making a polyimide fiber from a polyamic acid fiber using a shorter time for the thermal conversion of polyamic

15   acid to polyimide.

SUMMARY OF THE INVENTION

In an aspect, this invention provides a process comprising heating a polyamic acid fiber to a temperature in the range of a first temperature and a
20   second temperature for a period of time in the range of 5 seconds to 5 minutes to form a polyimide fiber, wherein the first temperature is the imidization temperature of the polyamic acid and the second temperature is the decomposition temperature of the polyimide.

25

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of an exemplary electroblowing apparatus.

Figure 2 is a schematic illustration of a portion of an exemplary infra-red

5   oven.

DESCRIPTION OF THE INVENTION

In accordance with the present invention, there is provided a process comprising heating a polyamic acid (PAA) fiber to a temperature in the range of a

10   first temperature and a second temperature for a period of time in the range of 5 seconds to 5 minutes to form a polyimide fiber, wherein the first temperature is the imidization temperature of the polyamic acid and the second temperature is the decomposition temperature of the polyimide.

15   As used herein, the term "fiber" refers to fibers having a number average diameter less than 10 microns, even less than 3 microns, and even less than 1500 nm. Furthermore, the term "nanofibers" as used herein refers to fibers having a number average diameter less than 1000 nm, even less than 800 nm, even between 50 nm and 500 nm, and even between 100 and 400 nm. In the case of

20   non-round cross-sectional nanofibers, the term "diameter" as used herein refers to the greatest cross-sectional dimension.

Polyamic acid **I** can be converted to polyimide **II** thermally, chemically, or using a combination of both, as shown below in the reaction scheme (1).

25   Depending upon the nature of the R group, the polyimide **II** can be partially

aromatic or fully aromatic. The invention as disclosed herein of converting PAA **I**

fibers to PI **II** fibers focuses on thermal conversion only. However, the thermal

conversion of PAA I to PI II as disclosed herein, can be combined with chemical

conversion to further decrease the conversion time or optimize the process.

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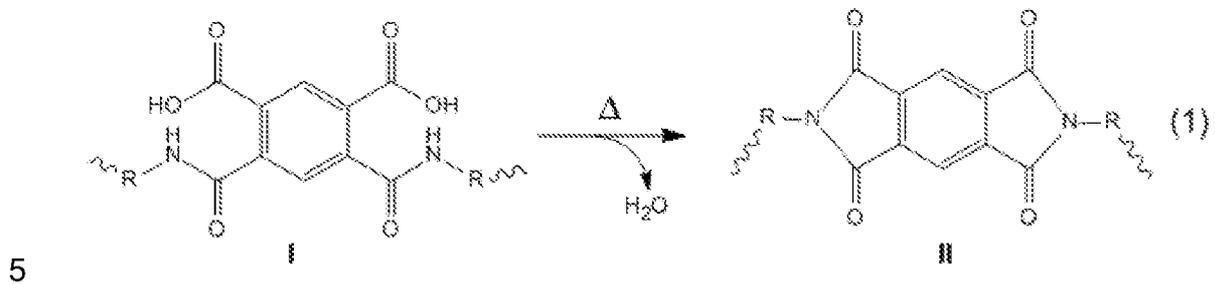
A polyamic acid fiber can be fabricated by any suitable process. In one

method suitable for the invention, a polyamic acid fiber is obtained by

electroblowing a solution of polyamic acid, as described in detail, *infra*. In

another method, a polyamic acid fiber is obtained by electrospinning a solution of

10   polyamic acid. Electrospinning is well known in the art and Huang et al., *Adv.*

Mat. DOI: 10.1002/adma.200501806 disclose electrospinning a polyamic acid

solution to form a mat of polyamic acid nanofibers. However, other fiber making

techniques such as melt blowing can be used. In one embodiment, the polyamic

acid fiber comprises a polyamic acid nanofiber. In another embodiment, the

15   polyamic acid nanofiber is in the form of a polyamic acid nanoweb. In one

embodiment, the nanoweb comprises a plurality of polyamic acid nanofibers.

The term "nanoweb" as employed herein represents a subset of

"nonwoven" articles wherein the fibers are designated "nanofibers" that are

20   characterized by number average cross-sectional diameters of less than 1000 nm.

For the purposes of the present invention, the ISO 9092 definition of the term

"nonwoven" article shall be used: "A manufactured sheet, web or batt of

directionally or randomly orientated fibers, bonded by friction, and/or cohesion

and/or adhesion, excluding paper and products which are woven, knitted, tufted,

stitch-bonded incorporating binding yarns or filaments, or felted by wet-milling,

whether or not additionally needled. The fibers can be of natural or

5   manufactured origin. They can be staple or continuous filaments or be formed in

situ." The nanowebs employed herein define a planar structure that is relatively

flat, flexible, and porous, and is formed by the lay-down of one or more

continuous filaments.

10   Polyamic acid **I** used in electroblowing and electrospinning described

supra can be obtained by reacting a tetracarboxylic acid dianhydride **III** with an

organic diamine **IV** in an aprotic polar solvent at low to moderate temperatures,

as shown in the reaction scheme (2):
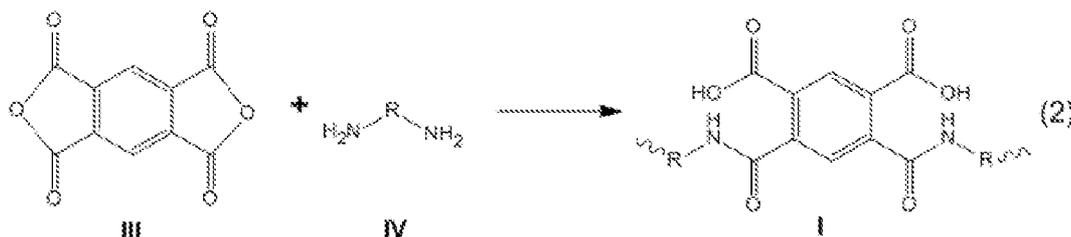
15   The mole ratio of tetracarboxylic acid dianhydride **III** and an organic

diamine **IV** in the reaction (2) is between 0.2 to 6, or 0.5 to 2.0 or 0.9 to 1.0.
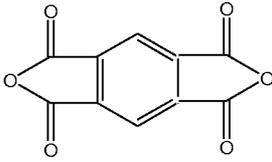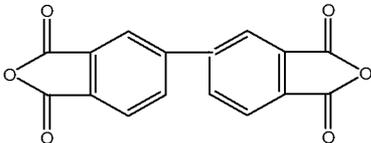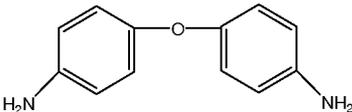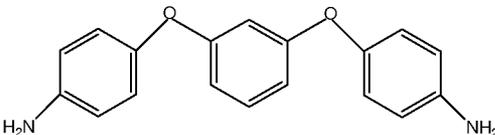
Any suitable tetracarboxylic acid dianhydride **III** can be used in the

reaction scheme (2), including, but not limited to, pyromellitic dianhydride

20   (PMDA); biphenyltetracarboxylic dianhydride (BPDA); 3,3',4,4'-benzophenone

tetracarboxylic dianhydride (BTDA); 2,3,6,7-naphthalene tetracarboxylic

dianhydride; 3,3',4,4'-tetracarboxybiphenyl dianhydride; 1,2,5,6-

tetracarboxynaphthalene dianhydride; 2,2',3,3'-tetracarboxybiphenyl

dianhydride; 2,2-bis(3,4-dicarboxyphenyl) propane dianhydride; bis(3,4-

dicarboxyphenyl) sulfone dianhydride; bis(3,4-dicarboxyphenyl) ether

dianhydride; naphthalene-1,2,4,5-tetracarboxylic dianhydride; naphthalene-

5   1,4,5,8-tetracarboxylic dianhydride; pyrazine-2,3,5,6-tetracarboxylic

dianhydride; 2,2-bis(2,3-dicarboxyphenyl) propane dianhydride; 1,1-bis(2,3-

dicarboxyphenyl) ethane dianhydride; 1,11-bis(3,4-dicarboxyphenyl) ethane

dianhydride; bis(2,3-dicarboxyphenyl) methane dianhydride; bis(3,4-

dicarboxyphenyl) methane dianhydride; benzene-1,2,3,4-tetracarboxylic

10   dianhydride; 3,4,3',4'-tetracarboxybenzophenone dianhydride; Perylene-

3,4,9,10-tetracarboxylic dianhydride; Bis-(3,4-dicarboxyphenyl) ether

tetracarboxylic dianhydride; and mixtures thereof.

Suitable organic diamines **IV** include, but are not limited to, oxydianiline

15   (ODA), 1,3-bis(4-aminophenoxy)benzene (RODA), and 1,4 Phenylenediamine

(PDA); m-Phenylenediamine; p-Phenylenediamine; 4,4'-Diaminodiphenyl

propane; 4,4'-Diaminodiphenyl methane Benzidine; 4,4'-Diaminodiphenyl

sulfide; 4,4'-Diaminodiphenyl sulfone; 4,4'-Diaminodiphenyl ether; 1,5-

Diaminonaphthalene; 3,3'-Dimethyl benzidine; 3,3'-Dimethoxy benzidine; Bis-

20   (para-beta-amino-t-butylphenyl)ether; 1-Isopropyl-2,4-m-phenylenediamine; m-

Xylylenediamine; p-Xylylenediamine; Di(paraminocyclohexyl) methane;

Hexamenthylenediamine; Heptamethylenediamine; Octamethylenediamine;

Decamethylenediamine; Nonamethylenediamine; 4,4-

Dimethylheptamethylenedia-2,11-Diaminododecane; 1,2-Bis(3-

25   aminopropoxyethane); 2,2-Dimethylpropylenediamine; 3-

Methoxyhexamethylenediamine; 2,5-Dimethyl hexamethylenediamine; 3-

Methylheptamethylenediamine; Piperazine; 1,4-Diamino cyclohexane; 1,12-

Diamino octadecane; 2,5-Diamino-1,3,4-thiadiazole; 2,6-Diaminoanthraquinone;

9,9'-Bis(4-aminophenyl fluorene); p,p'-4,4 Bis(aminophenoxy); 5.5'-Diamino-2,2'-
bipyridylsulfide; 2,4-Diaminoisopropyl benzene; and mixtures thereof.

For the purposes of the present invention, Table 1 shows the

5   abbreviations and designations of some of the commonly used dianhydrides **III**
and diamines **IV**, consistent with the practice in the polyimide art:

Table 1		
Abbreviation	Chemical Name	Chemical Structure
PMDA	Pyromellitic Dianhydride	 PMDA
BPDA	Biphenyltetracarboxylic Dianhydride	 BPDA
ODA	Oxydianiline	 ODA
RODA	1,3-bis(4-aminophenoxy)benzene	 RODA

PDA	1,4 Phenylenediamine	
TDI	2,4 – toluene diisocyanate and 2,6 toluene diisocyanate	
MDI	Methylene diphenyl 4,4'-diisocyanate	
BTDA	3,3',4,4'-benzophenone tetracarboxylic dianhydride	
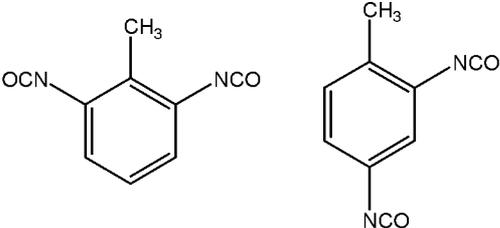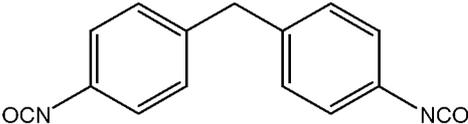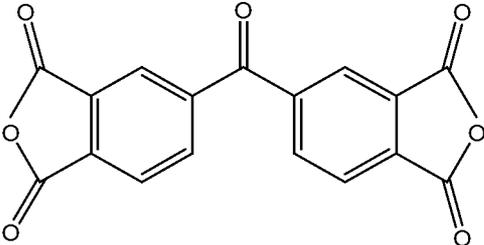
Any suitable aprotic polar solvent can be used in the synthesis of polyamic acid **I**, in the reaction scheme (2). A suitable organic solvent acts as a solvent for the polyamic acid and at least one of the reactants. A suitable solvent is inert to the reactants (the dianhydrides **III** or the diamines **IV**). In one embodiment, the solvent is a solvent for polyamic acid and both the dianhydride and the diamine. The normally liquid organic solvents of the N,N-dialkylcarboxylamide class are useful as solvents in the process of this invention. Exemplary solvents include, but are not limited to, N,N-dimethylformamide and N,N-dimethylacetamide

(DMAC), N,N-diethylformamide (DMF), N,N-diethylacetamide, N,N-dimethylmethoxyacetamide, N-methyl-2-pyrrolidone, N-methylcaprolactam, and the like. Other solvents which can be used in the present invention are: dimethylsulfoxide, tetramethyl urea, pyridine, dimethylsulfone,

5   hexamethylphosphoramide, tetramethylene sulfone, formamide, N-methylformamide, butyrolactone, and N-acetyl2-pyrrolidone. The solvents can be used alone, in combinations of solvents, or in combination with poor solvents such as benzene, benzonitrile, dioxane, xylene, toluene, and cyclohexane.

10   The molecular weight of the polyamic acid **I** obtained from the reaction scheme (2) is dependent upon several factors, such as, purity of the monomers, extent of moisture exclusion, choice of solvent, and maintenance of low to moderate temperatures. Reaction (2) can be performed at temperatures up to 175°C, but preferably at temperatures below 75°C. The temperature limitation

15   results from three possible reactions which would limit molecular weight: (a) partial conversion to polyimide, releasing water which would hydrolyze the polyamic acid **I**; (b) extensive conversion to polyimide **II** above 100°C, which, in addition to hydrolysis, could result in premature precipitation of low-molecular weight polymer out of the reaction medium; and (c) possible transamidation with

20   the solvents.

       The process hereof comprises heating the polyamic acid fiber so obtained, to a temperature in the range of a first temperature and a second temperature for a period of time in the range of 5 seconds to 5 minutes to form a polyimide fiber

25   or from 5 seconds to 4 minutes or from 5 seconds to 3 minutes, or from 5 seconds to 30 seconds. The first temperature is the imidization temperature of the polyamic acid. For the purposes of the present invention, the imidization temperature for a given polyamic acid fiber is the temperature below 500 ºC at which in thermogravimetric (TGA) analysis performed at a heating rate of 50

ºC/min, the % weight loss/ºC decreases to below 1.0, preferably below 0.5 with a precision of ± 0.005% in weight % and ± 0.05 ºC. The second temperature is the decomposition temperature of the polyimide fiber formed from the given polyamic acid fiber. Furthermore, for the purposes of the present invention, the
5   decomposition temperature of the polyimide fiber is the temperature above the imidization temperature at which in thermogravimetric (TGA), the % weight loss/ºC increases to above 1.0, preferably above 0.5 with a precision of ± 0.005% in weight % and ± 0.05 ºC.

10   In one method suitable for the practice of invention, a polyamic acid fiber is pre-heated at a temperature in the range of room temperature and the imidization temperature before the step of heating the polyamic acid fiber at a temperature in the range of the imidization temperature and the decomposition temperature. This additional step of pre-heating below the imidization
15   temperature allows slow removal of the residual solvent present in the polyamic acid fiber and prevents the possibility of flash fire due to sudden removal and high concentration of solvent vapor if heated at or above the imidization temperature.

20   The step of thermal conversion of the polyamic acid fiber to the polyimide fiber can be performed using any suitable technique, such as, heating in a convection oven, vacuum oven, infra-red oven in air or in inert atmosphere such as argon or nitrogen. A suitable oven can be set at a single temperature or can have multiple temperature zones, with each zone set at a different temperature.
25   In an embodiment, the heating can be done step wise as done in a batch process. In another embodiment, the heating can be done in a continuous process, where the sample can experience a temperature gradient. In certain embodiments, the

polyamic acid fiber is heated at a rate in the range of 60 ºC/minute to 250 ºC/second, or from 250 ºC/minute to 250 ºC/second.

5   In one embodiment, the polyamic acid fiber is heated in a multi-zone infra-red oven with each zone set to a different temperature. In an alternative embodiment, all the zones are set to the same temperature. In another embodiment the infrared oven further comprises an infra-red heater above and below a conveyor belt. In a further embodiment of the infrared oven suitable for use in the invention, each temperature zone is set to a temperature in the range

10   of room temperature and a fourth temperature, the fourth temperature being 150 ºC above the second temperature. Figure 2 schematically illustrates a portion of an exemplary 6 zone infra-red oven, described in detail *infra*. It should be noted that the temperature of each zone is determined by the particular polyamic acid, time of exposure, fiber diameter, emitter to emitter distance,

15   residual solvent content, purge air temperature and flow, fiber web basis weight (basis weight is the weight of the material in grams per square meter). For example, conventional annealing range is 400-500 °C for PMDA/ODA, but is around 200 °C for BPDA/RODA; BPDA/RODA will decompose if heated to 400 °C. Also, one can shorten the exposure time, but increase the temperature of the

20   infra-red oven and vice versa. In one embodiment, the fiber web is carried through the oven on a conveyor belt and goes though each zone for a total time in the range of 5 seconds to 5 minutes, set by the speed of the conveyor belt. In another embodiment, the fiber web is not supported by a conveyor belt.

25   The process of heating a polyamic acid fiber at a temperature in the range of the first temperature and the second temperature results in a degree of imidization (DOI) defined *infra*, of at least 0.51, preferably a DOI of at least 0.54, most preferably a DOI of at least 0.57. Under most circumstances, analytical methods show that complete imidization is rarely achieved, even after long

imidization times. For practical purposes, complete imidization is achieved when the slope of the percentage imidization versus time curve approaches zero over some selected time interval to be determined according to the needs of the practitioner hereof.

5

In one embodiment, the polyamic acid fiber comprises a polyamic acid nanofiber. In another embodiment, the polyamic acid nanofiber is in the form of a polyamic acid nanoweb. In a method suitable for the practice of the invention, a polyamic acid nanoweb is calendered before the step of heating the polyamic acid

10 at a temperature in the range of the first temperature to the second temperature for the conversion of the polyamic acid to the polyimide.

Polyimides are typically referred to by the names of the condensation reactants that form the monomer unit. That practice will be followed herein.

15 Thus, the polyimide formed from the monomer units: pyromellitic dianhydride (PMDA) and oxy-dianiline (ODA) and represented by the structure below is designated PMDA/ODA.
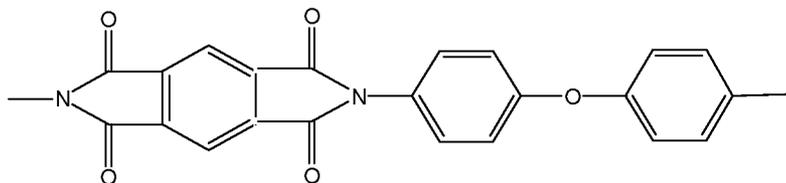
In one embodiment, the polyimide nanoweb consists essentially of

20 polyimide nanofibers formed from the monomer units: pyromellitic dianhydride (PMDA) and oxy-dianiline (ODA), using the method described *supra.*

In another embodiment, the polyimide fiber of this invention comprises more than 80 weight% of one or more fully aromatic polyimides, more than 90 weight% of one or more fully aromatic polyimides, more than 95 weight% of one or more fully aromatic polyimides, more than 99 weight% of one or more fully aromatic polyimides, more than 99.9 weight% of one or more fully aromatic polyimides, or 100 weight% of one or more fully aromatic polyimides. As used herein, the term "fully aromatic polyimide" refers specifically to polyimides in which the ratio of the imide C-N infrared absorbance at 1375 cm^{-1} to the p-substituted C-H infrared absorbance at 1500 cm^{-1} is greater than 0.51 and wherein at least 95% of the linkages between adjacent phenyl rings in the polymer backbone are effected either by a covalent bond or an ether linkage. Up to 25%, preferably up to 20%, most preferably up to 10%, of the linkages can be effected by aliphatic carbon, sulfide, sulfone, phosphide, or phosphone functionalities or a combination thereof. Up to 5% of the aromatic rings making up the polymer backbone can have ring substituents of aliphatic carbon, sulfide, sulfone, phosphide, or phosphone. Preferably the fully aromatic polyimide suitable for use in the present contains no aliphatic carbon, sulfide, sulfone, phosphide, or phosphone.

<u>EXAMPLES</u>

<u>TEST METHODS</u>

<u>DETERMINATION OF DEGREE OF IMIDIZATION (DOI)</u>

The infrared spectrum of a given sample was measured, and the ratio of
the imide C-N absorbance at 1375 cm^{-1} to the p-substituted C-H absorbance at
1500 cm^{-1} was calculated. This ratio was taken as the degree of imidization
(DOI). It has been found that a PMDA/ODA polyamic acid nanoweb that has been
subject to imidization conditions for a time well in excess of that thought to be
necessary to achieve maximum imidization exhibits a DOI of 0.57. By
comparison, a PMDA/ODA film sample had a DOI of 0.65. The difference can be
attributable to sample effects, such as orientation in the nanofibers in the
nanoweb that is not present in the film.

For the purposes of the present invention, a fully imidized nanoweb is one
in which the 1375/1500 cm^{-1} peak ratio (DOI) is greater than 0.51.

The polyimide nanowebs hereof were analyzed by ATR-IR using a
DuraSampl*IR* (ASI Applied Systems) accessory on a Nicolet Magna 560 FTIR
(ThermoFisher Scientific). Spectra were collected from 4000-600 cm^{-1} and were
corrected for the ATR effect (depth of penetration versus frequency).

<u>CRYSTALLINITY INDEX METHOD</u>

The parameter "crystallinity index" as employed herein refers to a relative
crystallinity parameter determined from Wide-Angle X-ray Diffraction (WAXD).
X-ray diffraction data were collected with a PANalytical X'Pert MPD equipped
with a Parabolic X-ray Mirror and Parallel Plate Collimator using Copper
radiation. Samples for transmission geometry were prepared by stacking the
thin films to a total thickness of approximately 0.7 mm. Data was collected over a

range of two-theta of 3 to 45 degrees with a step size of 0.1 degree. Count time per data point was 10 seconds minimum with the sample rotating about the transmission axis at a rate of 0.1 revolutions per second.

The WAXD scan so generated consisted of three contributions: 1) a
5   background signal; 2) scattering from ordered but amorphous regions; and 3) scattering from crystalline regions. A polynomial background was fitted to the baseline of the diffraction data. The background function was chosen to be a third order polynomial in the two-theta diffraction angle variable. The background subtracted data was then least squares fitted with a series of Gaussian peaks
10   which represented either ordered amorphous or crystalline components. Guided by experience with numerous samples of the same composition but widely differing in crystallinity, it was decided which peaks represented the crystalline regions. The ratio of the integral under the crystalline peaks so selected, to the integral under the overall scan curve with the background subtracted was the
15   crystallinity index.

Peaks shown in Table 2 were obtained for PMDA-ODA polyimides.

Since the determination of which peaks are sufficiently sharp that they ought to be considered part of the crystalline phase is somewhat arbitrary, the absolute crystalline content of the sample is still unknown. However, the
20   crystallinity index determined in this way allows us to compare the relative crystallinity of two polymers of the same polymer type.

Table 2

WAXD (Two-theta degrees)
11.496
15.059
16.828
22.309

VISCOSITY DETERMINATION

Solution viscosity was determined using a Brookfield Engineering HADV-II+ Programmable Viscometer equipped with an RV/HA/HB-5 or – 6 spindle, and calibrated using NIST traceable silicone fluids. The spindle was immersed into the polymer solution at room temperature until the liquid level reached the indent on the spindle. The motor was turned on with the RPMs set to produce 10-20% nominal torque. For solutions of 40-70 poise, it was found that 10-20 rpm was appropriate with the RV/HA/HB-5 spindle and 20 rpm was appropriate for RV/HA/HB-6 spindle.

FIBER SIZE DETERMINATION

Fiber diameter was determined using the following method.

1. One or more SEM (Scanning Electron Microscope) images were taken of the nanoweb surface at a magnification that included 20~60 measurable fibers.

2. Three positions on each image were selected which appeared by visual inspection to represent the average appearance of the nanoweb.

3. Image analysis software was used to measure the fiber diameter of 60 to 180 fibers and calculate the mean from the selected areas.

POLYMER PREPARATION

POLY(AMIC ACID) SOLUTION 1 (PAA-1)

34.10 kg of PMDA (DuPont Mitsubishi Gas Ltd.) was combined in a 100 Gallon stirred stainless steel reactor with 32.19 kg of 4,4 ODA (Wakayama Seika)

and 1.30 kg of phthalic anhydride (Aldrich Chemical) in 234.33 kg of DMF

(DuPont). They were mixed and reacted while stirring at room temperature for

30 hours to form polyamic acid by first adding the ODA to the DMF, then adding

the PMDA and finally adding the phthalic anhydride. The resulting polyamic acid

5   had a room temperature solution viscosity of 68 poise.

Similar procedure was used to form two other polyamic acid solutions:

PAA-2 and PAA3. Table 3 summarizes the reactants used, molar ratios thereof,

weight % solids, and viscosity for each polyamic acid solution

Table 3						
Sample #	Monomers (mole ratio)			Polyamic acid solution		
	PMDA	ODA	Phthalic Anhydride	Solvent	Polymer weight %	Viscosity (Poise)
PAA-1	0.97	1.0	0.06	DMF	22.4	68
PAA-2	0.98	1.0	0.04	DMF	23.7	72
PAA-3	0.97	1.0	0.06	DMF	23.5	67

10

NANOWEB PREPARATION

APPARATUS

Electroblowing was introduced to overcome the productivity problem in

15   electrospinning thin fibers. In electroblowing, a turbulent air flow is directed to

the fibers as they are spun thereby forming a "cloud" of polymer fibers that is

blown down onto the target surface as well as being electrostatically attracted.

The combination of blowing and electrostatic forces greatly increases the

productivity of the system. Electroblowing is described in detail in U.S. Published

20   Patent Application No. 20050067732.

Nanowebs were prepared from the polyamic acid solutions prepared
supra by electroblowing. Figure 1 depicts one embodiment of suitable
electroblowing apparatus. The polymer solution was manually loaded using a

5   syringe, not shown, into a 250 ml Hoke cylinder, **100**. A pressurized nitrogen
supply, **101**, was used to deliver the solution to a 10 cm wide spinneret, **102**,
having 3 nozzles each with a diameter of 0.38 mm and length 3.8 mm, arranged 1
cm apart, centered in the spinneret. Heated, compressed air, **108**, was fed to the
spinneret and was ejected through slots, **106**. The fibers, **103**, were both blown

10   by the air and attracted by a DC voltage electric potential to a metallic plate
collector, **110** which maintains the ground connection to a battery operated
windup, **113**. A roll of scrim material, **114** was mounted on the end of the plate
collector. In an alternative configuration, the metallic plate collector, **110**, the
battery operated windup, **113**, and the scrim material, **114** were removed and

15   replaced with a rotating drum collector (not shown) **connected to a ground.**
Heated, pressurized air, **115,** was also blown into a Plexiglas® enclosure, **107**,
containing the entire spinning apparatus. An exhaust blower, **116**, was used to
maintain atmospheric pressure inside the enclosure and to remove all
evaporated solvent.

20

NANOWEB PREPARATION

NANOWEB #3 (NW – 1)

       60 cc of PAA – 1 was manually charged to the apparatus depicted in Figure
1. The distance from the nozzle, **104**, to the metallic plate collector, **110**, was

25   35.6 cm and the potential difference applied was between the nozzle and the belt
was 110 kV. Solution discharge pressure was 57 psig, and process gas flow was
15 cfm at a temperature of 23 °C. The auxiliary air supply, **115**, was heated to 55

°C and blown into the fiber spinning chamber, **107,** at a flow rate of 10 cubic feet per minute. The nanoweb structure was collected on a rotating drum collector.

NANOWEBS #2-6 (NW 2-5)

5   PAA-2 – PAA-6 were employed in the preparation of nanowebs using the equipment and procedures employed in preparing NW-1. Specific conditions employed in preparing NW-1 to NW-6 are summarized in Table 18.

The nanowebs were then calendered at room temperature between a hard steel roll and a cotton covered roll at the pressures shown in Table 4 (pounds per

10   linear inch) on a BF Perkins calender.

Table 4								
Sample #	Polymer solution	Solution temp., ºC	Solution feed pressure, psi	Process gas temp., ºC	Process gas flow, cfm	Auxiliary air temp., ºC	Auxiliary air flow, cfm	Calender pressure, pli
NW-1	PAA-1	26	57	23	15	55	10	1245
NW-2	PAA-1	27	75	24	17	75	10	1245
NW-3	PAA-2	25	90	22	18	110	10	1245
NW-4	PAA-3	30	130	24	18	130	10	830
NW-5	PAA-3	30	130	24	18	130	10	830

POLYIMIDE NANOWEB PREPARATION

15   The calendered polyamic acid nanowebs (NW-1 to NW-5) were then heated by passing them through a Glenro Radplane® infrared oven with heating panels arranged such that identical panels were placed above and below the

nanoweb, with an emitter to emitter distance of 9 inches. Figure 2 shows a schematic illustration of a portion of an infra-red oven, **200**. The oven enclosure, **222** contained four heating panels, **223**, each divided into three separate temperature zones. Zones facing each other in the panels, **223**, were controlled

5   so that the temperature above and below the nanoweb, **221** was the same, thereby resulting in a total of 6 temperature zones in the oven, **200**. The total heated length within the oven, **200**, was 48 inches. The oven, **200**, also had optional support media, **225**, for the nanoweb, **221**, as shown in the Figure 2. The nanowebs NW-1 and NW-2, were supported in the oven by a woven

10   fiberglass fabric, **225**, which travelled with the nanowebs as a scrim or support material. The nanowebs NW-3, NM-4, and NW-5 were unsupported. The infrared oven, **200**, also had an exhaust system to prevent solvent vapors from entering the laboratory. Room temperature air was pulled through entrance and exit openings of the oven, **200**, and vented through plenums, **224**. Temperatures

15   of the emitters in each temperature zone and the total residence time of the nanowebs through the oven, **200**, are summarized in Table 5. Temperature of the nanoweb was not measured.

Table 5							
Imidization and Annealing Conditions							
Example	Polyamic acid nanowebs	Zone 1 Temp., ºC	Zone 2 Temp., ºC	Zone 3 Temp., ºC	Zone 4 Temp., ºC	Zone 5 Temp., ºC	Zone 6 Temp., ºC	Residence time, seconds
PI-NW-1	NW-1	400	500	550	606	650	650	6
PI-NW-2	NW-2	400	400	450	500	550	550	16
PI-NW-3	NW-3	400	500	550	606	650	650	16
PI-NW-4	NW-4	400	500	550	606	650	650	35
PI-NW-5	NW-5	400	500	550	606	650	650	16

20

Following heating, samples were cut from the nanowebs and analyzed for the degree of imidization and crystallinity per the test methods described above. Multiple samples were taken from PI-NW 1.1, 1.2, and 3.1 to determine if there was any variation in the degree of imidization and crystallinity. This was particularly of concern on those examples processed with the use of the fiberglass support web. In these cases, in addition to taking multiple samples, the analyses were conducted with the samples facing either up or down within the instruments. Those noted as "top" were samples analyzed using the surface which had faced away from the fiberglass support during processing, while those noted as "bottom" were those analyzed using the surface that contacted the support in the oven. Basis weight is the weight of the nanoweb in grams per square meter. Mean fiber diameter was determined by examining a scanning electron microscope image and estimating the diameter of 100 fibers using image analysis software. Results are summarized in Table 6 as shown below:

Table 6						
Example	Imidization/Annealing time, seconds	Sample	DOI, IR peak ratio	Crystallinity index	Basis weight, g/m^2	Mean fiber diameter, nm
PI-NW-1	6	A top	0.58	0.35	Not measured	665
		B top	0.57	0.43		
		C top	0.58	0.39		
		A bottom	0.59	0.43		
		B bottom	0.53	0.33		
		C bottom	0.59	0.40		
PI-NW-2	16	A top	0.60	0.29	12.2	910
		B top	0.60	0.31		
		C top	0.61	0.32		
		A bottom	0.61	0.24		
		B bottom	0.59	0.28		
		C bottom	0.59	0.32		
PI-NW-3	16	A	0.59	0.31	10.3	876
PI-NW-4	35	A	0.59	0.44	12.8	1077
		B	0.59	0.29		
PI-NW-5	6	A	0.57	0.38	14.4	1077

Although the nanoweb temperature can not be measured directly during the rapid heating method described above, it is reasonable to expect that it is below the temperature of the infrared emitters due to convective losses and incomplete infrared absorption.

Table 6 shows that PI-NW-5 (1077 nm diameter) with a DOI of 0.57 can be imidized to similar extent as PI-NW-1 (660 nm diameter) with a DOI in the range of 0.53-0.59 when imidized for the same amount of time of 6 seconds. Furthermore, sub micron and micron sized fibers can be imidized at very short times, on the order of seconds. For example, PI-NW-5 was fully imidized at very short time of 6 seconds, even though with a mean fiber diameter of 1077 nm, PI-NW-5 had a distribution of fiber sizes with a small number of fibers as large as 2-3 microns and as small as 100 nm.

COMPARATIVE EXAMPLES AA AND BB USING LONGER HEATING TIMES:

A polyamic acid solution of PMDA, ODA, and phthalic anhydride in DMF
was formed using 0.98 moles of PMDA, 1 mole of ODA, and 0.04 moles of phthalic

5   anhydride. The polyamic acid solution with 22 weight % solids was spun into
nanowebs using the apparatus of Figure 1 per the conditions shown below in
Table 21:

Table 7							
Sample #	Solution temp., ºC	Solution feed pressure, psi	Process gas temp., ºC	Process gas flow, cfm	Auxiliary air temp., ºC	Auxiliary air flow, cfm	Calender pressure, pli
NW-AA	24	90	25	17	102	14	1250
NW-BB	23	50	25	17	80	14	1500

10

Nanowebs NW-AA and NW-BB were cut into hand sheets and calendered.
Hand sheets were placed into a convection oven set to the temperatures for the
times shown in Table 7. Samples were removed from the convection oven in
between the various temperatures as the oven was allowed to heat up to the set

15   temperature. The degree of imidization was then measured as described above.

Table 7		
Sample	Thermal imidization procedure	DOI, Ratio of peaks
NW-AA-a	200 ºC for 2 minutes; 350 ºC for 4 minutes	0.55
NW-AA-b	200 ºC for 2 minutes; 350 ºC for 4 minutes; 400 ºC for 2 minutes	0.57
NW-AA-c	200 ºC for 2 minutes; 350 ºC for 2 minutes; 450 ºC for 2 minutes	0.57
NW-AA-d	200 ºC for 2 minutes; 500 ºC for 2 minutes; 450 ºC for 2 minutes;	0.57
NW-BB-a	Ramp to 175 ºC, hold 30 minutes; ramp to 475 ºC, hold 30 minutes (total time: 79 minutes)	0.56
NW-BB-b	475 ºC for 30 minutes	0.62
NW-BB-c	Ramp to 175 ºC, hold 30 minutes; ramp to 350 ºC, hold 30 minutes	0.55
NW-BB-d	350 ºC 30 minutes	0.55

These comparative examples show that there is some variability in the degree of imidization at long heating times and also for various heating schemes. Comparison of examples NW-BB-a and NW-BB-b illustrate that even though both samples were held at 475 ºC for 30 minutes, the sample, NW-BB-a, which was ramped to that temperature prior to holding was measured to have a lower degree of imidization than the sample, NW-BB-b, placed into the convection oven at 475 ºC directly without a temperature ramp. Using these results we can state that for practical purposes, any infrared analysis of a polyimide nanoweb wherein the ratio of the peaks at $1375/1500$ cm^{-1} is above 0.51, which is 90 % of 0.57, can be considered to be fully imidized.

<u>CLAIMS</u>

We claim:

    1.   A process comprising:

          heating a polyamic acid fiber to a temperature in the range of a first temperature and a second temperature for a period of time in the range of 5 seconds to 5 minutes to form a polyimide fiber,

          wherein the first temperature is the imidization temperature of the polyamic acid and the second temperature is the decomposition temperature of the polyimide.

    2.   The process of Claim 1, further comprising pre-heating the polyamic acid fiber at a temperature in the range of a room temperature and the first temperature before the step of heating the polyamic acid fiber at a temperature in the range of a first temperature and a second temperature.

    3.   The process of Claim 1, wherein the step of heating the polyamic acid fiber to a temperature comprises heating the polyamic acid fiber at a rate in the range of 60 ºC/minute to 250 ºC/second.

    4.   The process of Claim 1, wherein the step of heating the polyamic acid fiber comprises heating the polyamic acid fiber in an infra-red oven.

    5.   The process of Claim 1, wherein the polyamic acid fiber comprises a fully aromatic polyamic acid fiber.

    6.   The process of Claim 5, wherein the fully aromatic polyamic acid fiber comprises PMDA/ODA.

7.   The process of Claim 1, wherein the polyimide fiber comprises PMDA/ODA.

8.   The process of Claim 1, wherein the polyamic acid fiber comprises a plurality of polyamic acid nanofibers.

9.   The process of Claim 8, wherein the plurality of polyamic acid nanofibers are in the form of a polyamic acid nanoweb.

10.   The process of Claim 9, further comprising calendering the polyamic acid nanoweb before the step of heating the polyamic acid fiber to a temperature.

11.   The process of Claim 1, wherein the polyamic acid fiber has a number average fiber diameter of 10 microns or less.

12.   The process of Claim 1, wherein the polyamic acid fiber has a number average fiber diameter of 1500 nm or less.

13.   The process of Claim 1, wherein the polyamic acid fiber has a number average fiber diameter in the range of 100 nm to 1000 nm.
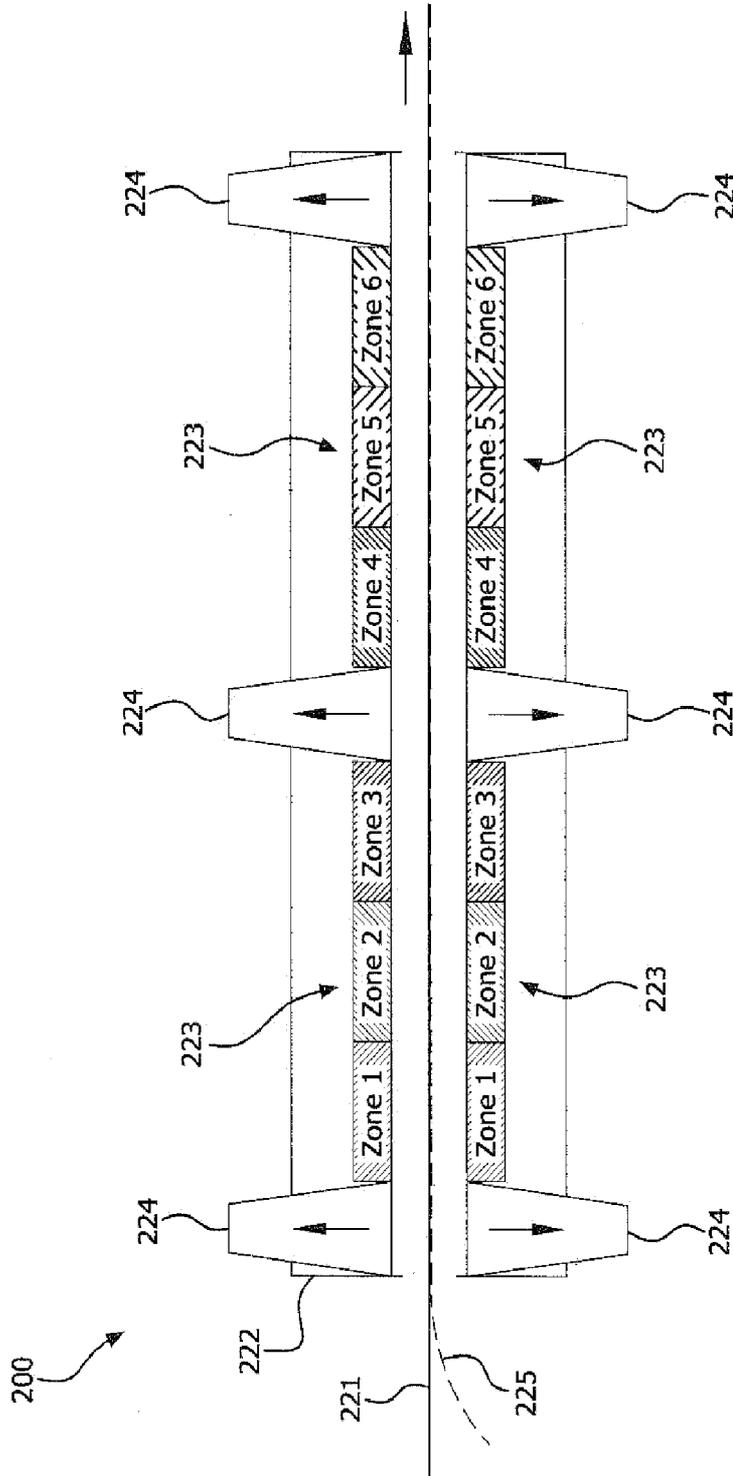
FIG. 1

FIG. 2