

12 JUL 2000

Hollow Fiber Membranes and Methods for their Production

The present invention relates to hollow fibers and methods for their production and, more particularly, gas separation membranes made from fibers comprising fluoro-polyimides and copolyimides.

There is a need, in the field of gas treatment, for systems to separate mixtures of gases into their component gases. For example, natural gas (CH_4) may be contaminated with carbon dioxide and it is desirable for the carbon dioxide to be removed. One means of separating the gas is by using a membrane and membrane gas separation systems tend to be simpler and involve lower operational costs than other separation systems.

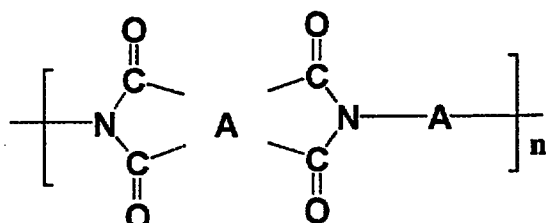
The problem with existing gas separation membrane systems is that they have low efficiency. Returning to the previous example of the separation of CO_2/CH_4 mixtures, methane may be lost during processing to remove carbon dioxide using a membrane since typically membrane separation systems have low selectivities.

One solution to the relatively low selectivities of existing gas separation membrane systems is the provision of an additional membrane stage with a compressor between the two membrane stages. However the need for a compressor tends to result in such systems being mechanically unreliable. Furthermore, the additional size and weight of the compressor makes such systems undesirable for offshore applications.

Accordingly, in order to develop more suitable gas separation membrane systems, membrane materials with superior permeability and selectivity and advanced fabrication technologies to yield hollow fibers with an ultra-thin dense selective layer have been the primary focuses for most membrane

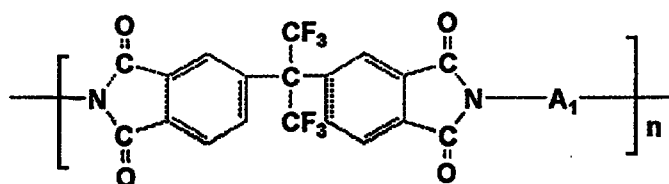
inventions in the last two decades. Significant progresses have been made in membrane materials (1-4), dope preparation (5-9), and fabrication technology (5-9).

In terms of material development, membranes prepared from aromatic polyimides of common chemical structure:



Where A is any organic aromatic group, have received special attention for gas separation due to some of them possessing surprisingly high gas selectivities for particular gas pairs, such as O_2/N_2 , and CO_2/CH_4 (1-4, 7, 10-17). Aromatic polyimides also have many other desirable properties, such as spinnability, thermal and chemical stability, and mechanical strength. These properties are essential to yield a membrane module with stable and predicable long-term performance.

In the polyimide family, some of the fluorinated polyimides of common structure:



containing 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), having the formula:

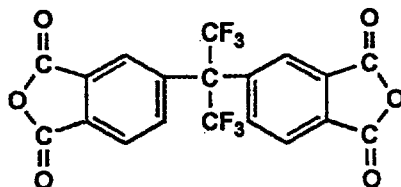
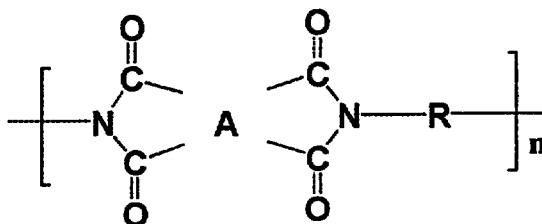


exhibit remarkable performance in both gas permeability and selectivity as compared with non-fluoropolyimides (3-4, 7, 10-17) of common structure:



Where A is made up of any organic Aromatic group/s and R is made up of organic Aromatic Group/s. Also A and R may not be the same.

Fabrication of asymmetric hollow fiber membranes with an ultra-thin dense selective layer is not a trivial task. An asymmetric membrane generally consists of a thin, selectivity skin layer, supported by a porous substructure. For an asymmetric membrane useful for gas separation, its skin layer must be

almost defect free (surface defect is less than 10^{-6}) to ensure that permeation is exclusively controlled by a solution/diffusion mechanism (8). In order to achieve the maximum permselectivity, its skin layer should be as thin as possible to maximize the membrane productivity. Since the dense skin layer is formed by a phase inversion process which occurs by bringing an initially thermodynamically stable polymer solution to an unstable state during the coagulation step, it is very difficult simultaneously to prepare a defect-free integral asymmetric hollow fiber membrane with an ultra-thin skin layer (i.e. having a thickness less than 1000Å). In the case of fluoro-polyimide hollow fiber membranes, Chung *et al.* (7, 19-20) applies a phase inversion technology to develop a defect-free Fluoro-polyimide containing Durene moiety asymmetric fiber with a skin layer of around 2000-3000 Å.

In order to produce hollow fibers without defects, it is possible to deposit another material to seal defective membrane skins when preparing gas separation membranes.

The separation performance of as-spun hollow fiber membranes (i.e. the performance without any coating) is controlled by the fiber spinning process. Although extensive works have been published and patented to yield high performance membranes in terms of spinning conditions, such as quench conditions and dope formulation (10-22), only in recent years has it been recognized that the rheological conditions established in the spinneret during hollow fiber spinning also play an important role on membrane performance (23-24). The effects of shear induced orientation and chain packing have been observed in the separation performance of ultrafiltration (UF) (25) and gas separation hollow fibers (18, 23-24). For example, Aptel *et al.* (26) and Qin and Chung (25) found that increasing dope flow rate would increase the shear stress and, in turn, reduce the permeability of hollow fibers for UF membranes.

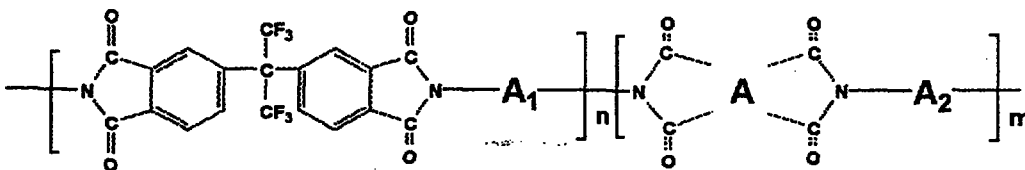
East *et al.* (27) studied dry-jet wet-spun polysulfone hollow fibers and reported that the selectivity increased with increasing dope extrusion rate while the gas permeation rate reduced, Chung *et al.* (25) also studied the effect of shear stress within the spinneret on wet-spun polyethersulfone membranes for gas separation, and reached similar conclusions as Aptel and East *et al.*

While the above described developments in fiber production have resulted in improvements in the selectivities of fibers, the selectivities of existing membranes are still relatively low. For example, commercial membrane systems for the removal of CO₂ from CO₂/CH₄ have selectivity in the region of only 15 to 25.

Accordingly, there is a need to provide fibers having a higher selectivity for use in gas separation membranes. There is also a need to provide fibers having an increased permeance to certain gases. Additionally, there is a need for fibers having specific selectivities and permeances for certain gases. In particular, fibers having a CO₂ permeance of around 40 GPU and a CO₂ selectivity of 50 or fibers having a CO₂ permeance between 75 and 100 GPU and a CO₂ selectivity between 25 and 50 are desired. The present invention seeks to address one or more of these needs.

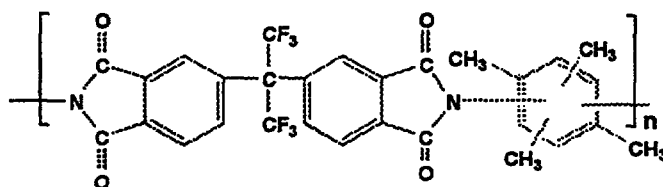
According to one aspect of the present invention there is provided a method of producing a fluoro-polyimide or copolyimide fiber comprising the steps of:

- a) providing a fluoro-polyimide or copolyimide dope;
- b) spinning the fluoro-polyimide or copolyimide dope to produce a fluoro-polyimide or copolyimide fiber; and
- c) coating the fiber with polyvinylpyrrolidone.



wherein A_1 and A_2 comprise any organic aromatic group.

Preferably, the polymer chain of the fluoro-polyimide or copolyimide comprises at least the chemical structure of [6F-Durene] polyimide, having the formula:



Advantageously, the step of providing a [6F-Durene] polyimide dope comprises the steps of: providing a polyamic acid (PAA) solution and imidizing the polyamic acid solution to Polyimide.

Conveniently, the polyamic acid solution is synthesized using a solution polycondensation reaction of 6FDA and 2,3,5,6-tetramethyl-1,4-phenylene Diamine.

Preferably, the solution polycondensation reaction is between 50 mole % 6FDA and 50 mole % 2,3,5,6-tetramethyl-1,4-phenylene Diamine.

Advantageously, the reaction mixture is stirred for at least twenty hours at between 15 and 25°C to yield a polyamic acid solution.

Conveniently, the imidizing step comprises adding Propionic-anhydride and Beta-picoline to the polyamic acid solution.

Preferably, the Propionic anhydride Acetic Anhydride or Butyric anhydride and Beta-picoline are reacted for between seventeen and nineteen hours in the polyamic acid solution.

Advantageously, the fluoro-polyimide dope is spun in a spinneret.

Conveniently, water is provided as an external coagulant during spinning.

Preferably, a solution of polyamic acid and 1-methyl-2-pyrrolidinone is used as a bore fluid during spinning.

Advantageously, the polyamic acid and 1-methyl-2-pyrrolidinone solution is in proportions of 42.7: 57.3 wt % polyamic acid: 1-methyl-2-pyrrolidinone.

Conveniently, the fluoro polyimide or copolyimide dope is spun at a shear rate between 200 and 2000 s^{-1} .

Preferably, the fluoro polyimide or copolyimide dope is spun at a shear rate between 400 and 1400 s^{-1} .

Advantageously, the step of coating the fiber with polyvinylpyrrolidone comprises dipping the fiber in a solution of 0.05 to 1.0 wt% polyvinylpyrrolidone in methanol for less than two minutes and drying the fiber.

Conveniently, the solution of polyvinylpyrrolidone is a solution of 0.1 to 0.2 wt% polyvinylpyrrolidone.

Preferably, the solution of polyvinylpyrrolidone is a solution of 0.15 wt% polyvinylpyrrolidone.

According to another aspect of the present invention, there is provided a method of preparing a polyimide or copolyimide hollow fiber comprising the steps of:

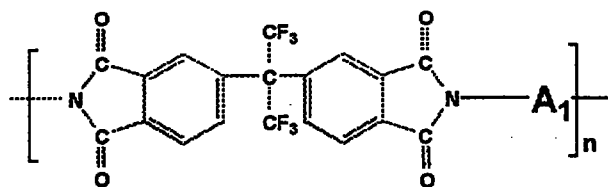
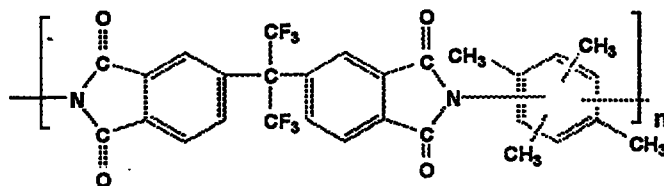
- a) preparing a polyimide or copolyimide dope; and
- b) spinning the polyimide or copolyimide dope at a shear rate of between 200 and 1400 s^{-1} .

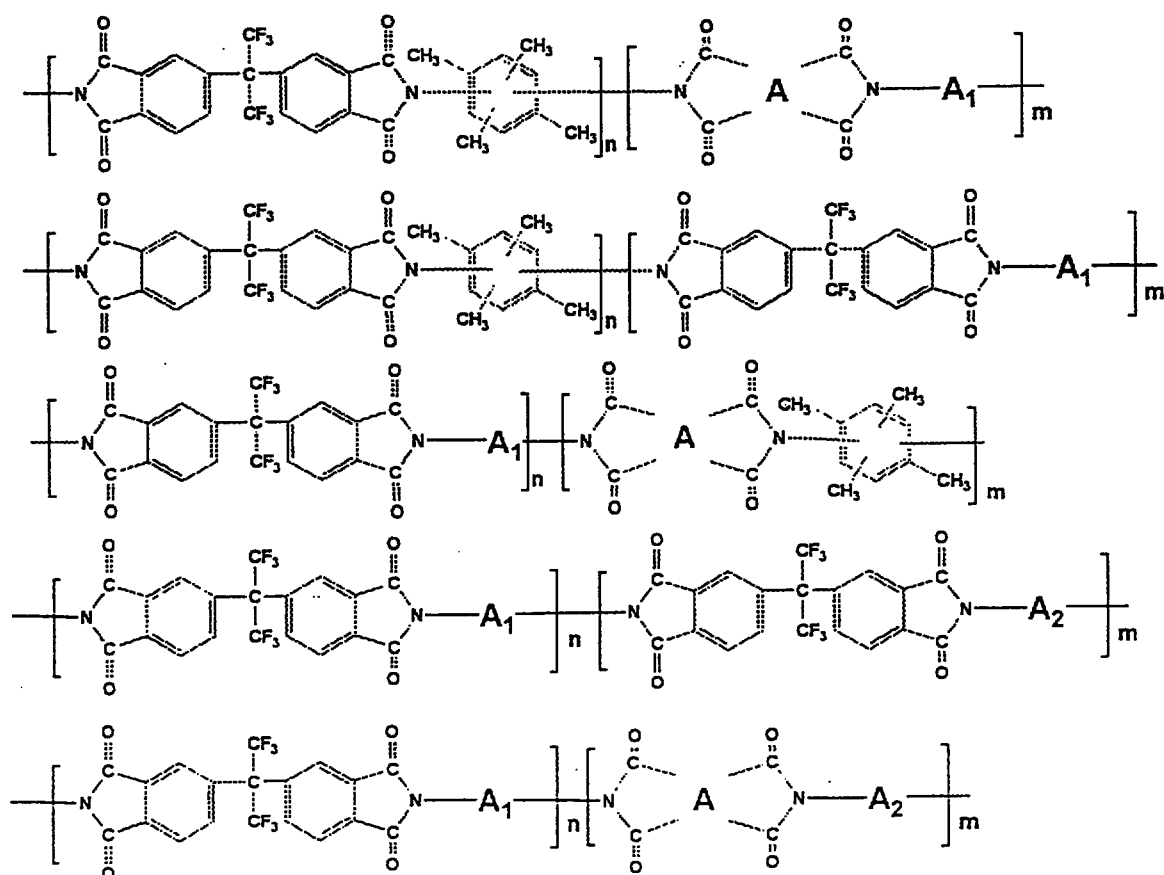
Conveniently, the method further comprises the step of:

- c) incorporating the hollow fiber into a gas separation membrane.

Preferably, the polyimide or copolyimide is a fluorinated polyimide or copolyimide.

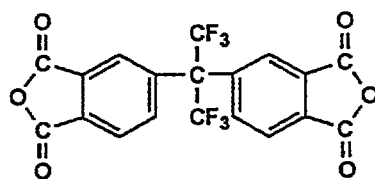
Advantageously, the fluorinated polyimide comprises a polyimide or copolyimide having one of the following formulae:



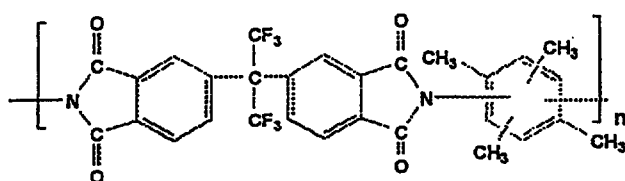


wherein A_1 and A_2 comprise any organic aromatic group.

Conveniently, the fluorinated polyimide comprises 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), having the formula:



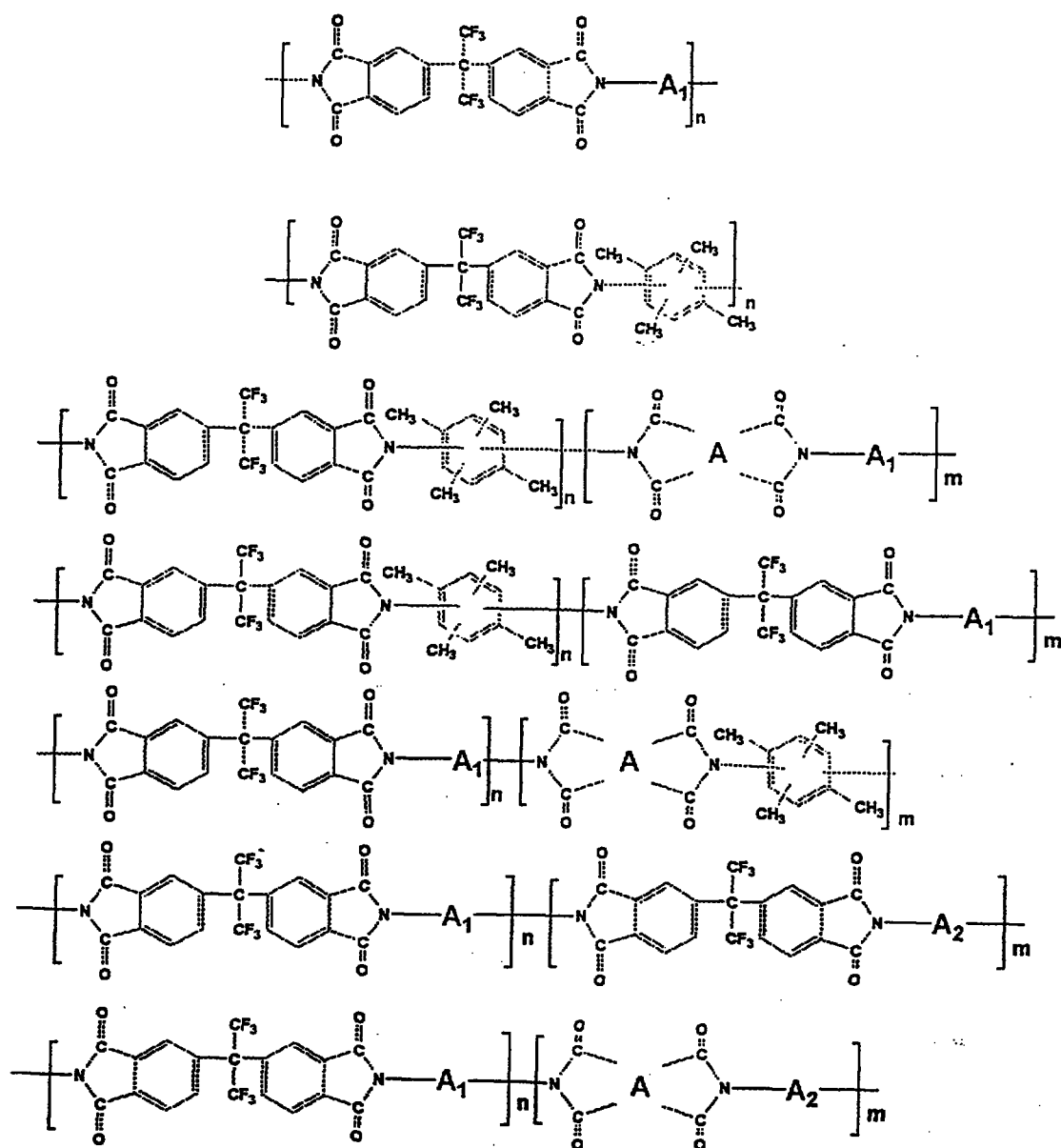
Preferably, the fluorinated polyimide is [6F-Durene], having the formula:



According to a further aspect of the present invention there is provided a fiber prepared according to the above methods or by a method equivalent thereto.

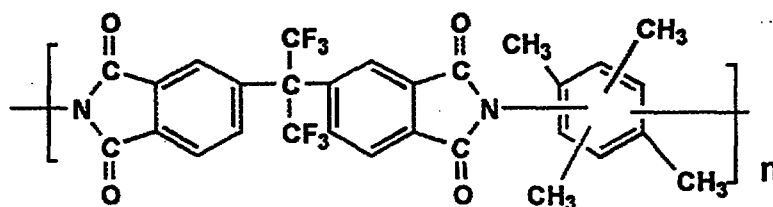
According to another aspect of the present invention there is provided a fiber comprising a fluoro polyimide or copolyimide, having a coating comprising polyvinylpyrrolidone.

Conveniently, the fluoro-polyimide or copolyimide comprises a copolyimide having one of the following formulae:



wherein A_1 and A_2 comprise any organic aromatic group.

Preferably, the polymer chain of the fluoro-polyimide or copolyimide comprises at least the chemical structure of [6F-Durene] having the formula:



Advantageously, the fiber has been spun at a shear rate between 200 and 2000 s^{-1} .

Conveniently, the fiber has been spun at a shear rate of between 400 and 1400 s^{-1} .

According to yet another aspect of the invention there is provided a fiber as described above prepared according to any of the methods described above.

According to a further aspect of the present invention there is provided a gas separation membrane comprising a fiber.

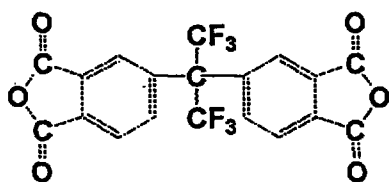
According to yet a further aspect of the present invention there is provided a method of separating a mixture of constituents the method comprising the step of passing the mixture through a membrane as described above.

Conveniently, the mixture comprises non-polar gases.

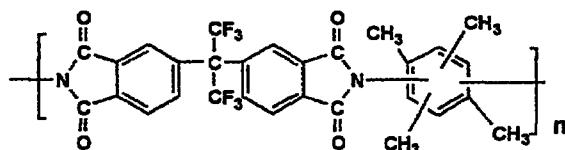
Alternatively, the mixture comprises polar gases.

Preferably, the mixture comprises CO_2 and CH_4 .

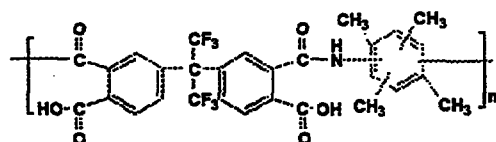
Throughout this specification, 6FDA is an abbreviation for 2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride, having the chemical structure:



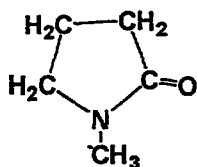
[6F-Durene] is the polyimide having the formula:



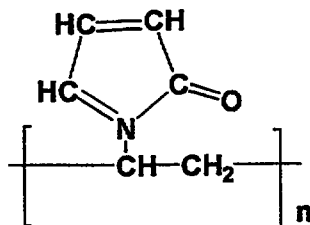
PAA is an abbreviation for polyamic acid, having the chemical structure:



NMP is an abbreviation for 1-methyl-2-pyrrolidinone.



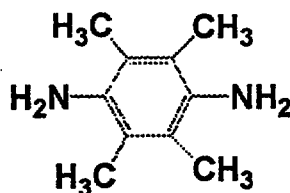
PVP is an abbreviation for polyvinylpyrrolidone having a common chemical structure:



Furthermore, in the present specification "comprise" means "includes or consists of" and "comprising" means "including or consisting of".

The present invention relates generally to the provision of fluorinated polyimide or copolyimide fibers for use in membranes for gas separation. Fluorinated polyimide or copolyimide is employed as a membrane material in this invention because of its superior gas separation, thermal and mechanical properties (19-20).

According to particular embodiments of the present Application, certain variations to the broad statements of invention above may be made. In particular, [6F-Durene] is the preferred polyimide. Furthermore, in the preparation of [6F-Durene] fibers, the polyamic acid solution may be synthesised in a different manner from that described above. In particular, the proportion of 6FDA and 3,6-durene diamine in the polycondensation reaction may be different. Proportions of 30 to 70 mole % 6FDA and 70 to 30 mole % 2,3,5,6 Tetramethyl-1,4-Phenylene diamine (or 1,4 Diamino Durene), having the chemical structure:



(i.e. Durene diamine) may, for example, be used instead. Furthermore, the duration for which the reaction mixture should be stirred may be varied between 10 and 30 hours and combinations and variations of the above conditions may be made.

In other embodiments of the present invention, the imidizing of the polyamic acid solution may be achieved using any appropriate reactants. Furthermore, the duration of the imidizing step may be varied. For example, in embodiments where Propionic anhydride and Beta picoline are reacted, this may be for between 15 and 25 hours or even for other lengths of time.

A wet-spun or dry-jet wet-spun hollow fiber technique is used in order to spin the [6F-Durene] polyimide or copolyimide fibers. It is preferred that a wet-spun technique is used. When the [6F-Durene] polyimide or copolyimide dope is spun into [6F-Durene] polyimide or copolyimide hollow fiber, a range of spinning conditions may be used. However, for optimal properties of the [6F-Durene] polyimide or copolyimide fiber, there are certain preferred spinning conditions. In particular, the [6F-Durene] polyimide or copolyimide fiber should be spun at a shear rate between 200 and 2000 s^{-1} , more preferably between 400 and 1400 s^{-1} . In order to achieve such shear rates, the spinning conditions must be altered accordingly. Preferably, the spinneret die length to flow gap channel ratio is greater than 7, ratios in the range of 11.5 to 12 being typical and a ratio of 11.7 being optimal. In a preferred embodiment of the invention, the spinneret bore fluid is a solution of 42.7/57.3 wt% Propionic acid/1-methyl-2-pyrrolidinone. However, in other embodiments of the present invention, this ratio may be, for example, between 40 to 60 wt% Propionic acid to 60 to 40 wt% 1-methyl-2-pyrrolidinone. Again, variations in the

combinations of the above conditions may be used in certain embodiments of the invention.

Once the fibres are formed, it is preferable that they are stored in water for twenty-four hours but may be stored in this way for longer periods such as forty-eight and ninety-six hours. Following storage in water, the fibres can be dried in air at a temperate between 10°C and 50°C, preferably for eight hours. Alternatively, instead of air drying, the fibers may be immersed in a low-boiling non-solvent, preferably methanol. It is most preferred that the methanol is fresh, and immersion is for at least two hours but in some embodiments of the invention this immersion can be extended for four or eight hours or even longer.

The fibers that are prepared may have a skin layer of between 1000 and 3000Å.

The various conditions for spinning the [6F-Durene] polyimide or copolyimide dope into [6F-Durene] polyimide hollow fiber may be combined in a variety of ways in accordance with certain embodiments of the present invention.

The separation properties of the fluorinated polyimide or copolyimide fibers may be altered and, indeed, improved by coating the fibers. The preferred coating for the fluorinated polyimide or copolyimide fibers is polyvinylpyrrolidone (PVP). The coating of [6F-Durene] fibers with PVP results in a particularly significant and unexpected synergism in that the selectivities of such fibers are greatly increased. In order to coat [6F-Durene] fibers with PVP, the fibers are dipped in a solution of PVP. The solution is preferably 0.15 wt % PVP in methanol but may be of between, for example, 0.05 wt% and 1.00wt% PVP. Furthermore solvents other than methanol may be used. The coating may preferably be for less than five minutes, most preferably

less than two minutes. The PVP coated [6F-Durene] fibers are fully dried after the coating in order to achieve their optimum performance.

Variations and combinations of the conditions for preparing and coating the fibers as described above may be effected in order to achieve various embodiments of the present invention.

It is to be appreciated that, while in preferred embodiments of the present invention, the fluoro-polyimide or copolyimide hollow fibers are prepared according to the above methods, in other embodiments, the fibers may be prepared using alternative methods. Furthermore, in other embodiments of the invention, fibers made from different materials. In other embodiments, different fibers may be prepared by spinning a suitable dope at shear rates between 200 and 2000 s^{-1} .

According to some embodiments of the present invention, fibers having the following performance are prepared: $\alpha(\text{O}_2/\text{N}_2) > 4.6$; $P(\text{O}_2) > 40 \text{ GPU}$; $\alpha(\text{CO}_2/\text{CH}_4) > 50$; $P(\text{CO}_2) > 200 \text{ GPU}$; $\alpha(\text{H}_2/\text{N}_2) > 30$; and $P(\text{H}_2) > 300 \text{ GPU}$.

Following the preparation of a fiber, as described above, the fiber may be incorporated into a gas separation membrane. The gas separation membrane may then be used to separate mixtures of gases by passing the mixture through the membrane. For example a mixture of CO_2 and CH_4 may be passed through the membrane in order to remove CO_2 from the mixture.

In order that the invention may be more readily understood and so that further features thereof may be appreciated, examples of the invention will now be described, by way of example, with reference to the accompanying figures in which:

Figure 1 is a scheme showing an approach to synthesis of Fluoro-polyimides and Copolyimides with and without Durene moieties;

Figure 2 is a Synthesis Scheme of [6F-Durene] Polyimide; and

Figure 3 is a schematic diagram of the hollow fiber spinning process according to one part of the present invention.

Example 1

Preparation and Testing of Fluoro-polyimide containing Durene moiety fibers

A hexafluoro-isopropylidene-group-containing polyimide dope was prepared in two steps. First, a polyamic acid was synthesized as shown in Figure 2, using a solution polycondensation reaction of 50 mole percent 2,2'-bis (3,4'-dicarboxyphenyl) hexafluoropropane diandrydride (6FDA) and 50 mole percent 2,3,5,6-tetramethyl-1,4-phynelene Diamine (Durene diamine). The reaction mixture was stirred for at least 20 hours at room temperature to yield a viscous polyamic acid solution in NMP solvent. Then, the mixture was imidized by adding specific amounts of Propionic anhydride and Beta picoline to the solution and reacted for another 17 to 19 hours. Since most Propionic anhydride was converted to Propionic acid during imidization because water was a by-product, it was possible to obtain an in-situ dope of imidized [6F-Durene] polyimide in a NMP / Beta picoline / Propionic acid/anhydride solvent mixture directly from polymerization. The as-prepared spinning dope consisted of 14.94 weight percent [6F-Durene] polyimide in a (70.24/21.5/7.51/0.75) NMP/beta picoline/propionic acid/anhydride solvent mixture. The Inherent Viscosity [η_{inh}] measured at 0.5 gm/dl in NMP. The weight average molecular weight (Mw) and number average molecular weight (Mn) of the dope were determined by Gel permeation Chromatography (GPC) using Polystyrene as

internal standard and are 143,000 and 90,000 respectively. This dope showed highly shearing thinning characteristics.

The Fluoro-polyimide containing Durene moiety hollow fibers were spun by wet spinning technology illustrated in Figure 3. [6F-Durene] polyimide [1], comprising a supply of [6F-Durene] polyimide dope [2] was provided under pressure of nitrogen [3] to a spinneret [4]. A 42.7/57.3 wt % Propionic acid/1-Methyl-2-pyrrolidinone (NMP) solution [5] was also provided via an ISCO pump [6] to the spinneret [4] as bore fluid. The bore fluid was chosen in order to yield asymmetric hollow fibers with a dense outer layer and a porous inner substructure. Water (not shown) was utilized as an external coagulant. The spinneret had a die length (L) to flow channel gap (ΔD) ratio of 11.7 to ensure that a steady shear was reached within the spinneret before precipitation. Table 1 summarizes the other spinneret dimensions and hollow fiber spinning conditions.

Table 1. 6F-durene polyimide hollow fibers spinning conditions

Spinning Conditions	
Spinning Solution	[6F-Durene] polyimide in a (70.24/21.5/7.51/0.75) NMP: /Beta picoline/ Propionic anhydride solvent mixture
Polymer Concentration	14.94 wt%
Dope rheological properties	Power law index: 0.5732
	Power law constant: 4195 (Pa-s ⁿ)
Dope Temperature, °C	25°C
L/(OD-ID)	11.7
Spinneret dimensions	0.35/0.526/0.826mm
Bore Fluid Composition	Propionic acid/NMP 42.7/57.3 wt%

Bore Fluid Flow Rate, cc/min	Varied
Dope Pressure, psig	43.3, 80.0, 60.0, 100.0,
Dope Flow Rate, g/min	Varied
Bore Fluid Flow Rate/Dope Flow Rate Ratio	0.71
Air-gap Distance, cm	0 (wet spinning)
Take-up speed, cm/min	Varied
External Coagulant	Tap water
Coagulant Temperature, °C	25°C
Drying Procedure	1 day in water at 25°C

The shear rates and shear stresses experienced at the external wall of the annular flow in the spinneret were then estimated using appropriate equations, which have been derived elsewhere (29-30).

After the hollow fibers [7] were formed, they were removed from the spinneret 4 and were stored in a water bath [8] for at least 1 day. The fibers 7 were then washed with water [9] and were immersed into fresh methanol 20 for at least 2 hours to allow sufficient solvent exchange and air-dried overnight at room temperature (20°C). Hollow fibers thus treated were used for further tests and study.

In order to test gas permeation of those fibers, four fibers around 10cm in length were assembled into bundles to make test modules, the procedure for which has been described elsewhere (7-8, 28). Pure gas pressure-normalized permeance as reported herein was obtained for hollow fiber membrane samples at a pressure difference of 40 psi (276×10^3 Pa) at 25°C. Volumetric gas flow rates were determined using soap bubble flow meters. The permeance was calculated using the following equation:

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{\Delta P A} = \frac{Q_i}{\Delta P n \pi D l}$$

where

$\left(\frac{P}{l}\right)_i$ = Permeance of a membrane to gas i (GPU = 1×10^{-6} cm³ (STP) / cm²-sec-cm Hg)

Q = Volumetric flow rate of gas i at standard temperature and pressure (cm³ (STP)/sec)

ΔP = Trans-membrane pressure difference (cm-Hg)

A = Membrane surface area (cm²)

n = Number of fibers tested

D = Outer diameter of the hollow fibers (cm)

l = Effective length of the hollow fibers (cm)

The ideal selectivity of an asymmetric membrane, $\alpha_{A,B}$, is defined as the pure gas pressure-normalized permeation rate ratio of gas A to gas B as follows:

$$\alpha_{A,B} = \frac{\left(\frac{P}{l}\right)_A}{\left(\frac{P}{l}\right)_B}$$

From the above equations, it is evident that the permeance of a membrane depends on the thickness of the effective separation layer while the selectivity is independent of the dense layer thickness.

Table 2 summarizes the gas separation performance of uncoated asymmetric [6F-Durene] polyimide hollow fibers as a function of shear rate at room temperature (20°C). For all uncoated fibers, their selectivities indicate that gases transport through the membranes by means of a combination of Knudsen and solution diffusions. For non-polar gas pairs, selectivity increases and then decreases with increasing shear rate. The up and down, Λ , pattern is clearly inconsistent with some theories that selectivity increase is mainly due to tightened chain packaging are reduced, surface porosity induced by shear rate, while the selectivity decrease is mainly due to relatively porous skin structures induced by low viscosity. At low shear rates, the permeances of H₂, O₂, N₂, and CH₄ decrease with increasing shear rate. Increasing the shear rate above 1391 s⁻¹, results in the permeance also increasing because of increasing skin porosity. However, the permeance of CO₂ has the most peculiar profile as it increases with an increase in shear rate even at shear rates above 1391 s⁻¹.

Table 2. The gas separation performance of uncoated [6F-Durene] polyimide hollow fibers.

Shear Rate	(P/L) _i , GPU*					α_{ij}		
s ⁻¹	H ₂	O ₂	N ₂	CH ₄	CO ₂	O ₂ /N ₂	CO ₂ /CH ₄	H ₂ /N ₂
249	1853	430	359	443	910	1.20	2.08	5.20
457	1602	359	225	256	1080	1.62	4.47	7.26
581	1603	344	185	198	1210	1.88	6.36	8.85
1391	5969	1512	1388	1764	2671	1.09	1.53	4.31

*GPU=1x10⁻⁶ cm³ (SPT)cm² -s-cmHg

Example 2:

Polyvinylpyrrolidone coated [6F-Durene] polyimide hollow fibers

The uncoated [6F-Durene] polyimide fibers of example 1 were dip-coated in a coating solution of 0.15 wt % PVP (Polyvinylpyrrolidone) in methanol for 2 minutes. The fibers were air-dried at room temperature (20°C) fully before gas separation performance tests.

Table 3 summarizes the results and shows that there is a V (down and up) pattern for permeance vs. shear rate relationship, while a Λ (up and down) pattern for selectivity vs. shear rate relationship. However, the selectivity and permeance reaches very impress values at 581 s⁻¹ as follows:

$\alpha(\text{O}_2/\text{N}_2) = 4.7$, $P(\text{O}_2) = 45$ GPU; $\alpha(\text{CO}_2/\text{CH}_4) = 54$, $P(\text{CO}_2) = 216$ GPU; $\alpha(\text{H}_2/\text{N}_2) = 32.5$, $P(\text{H}_2) = 312$ GPU.

Table 3: Permeation Properties of 6F-Durene Hollow Fibers with PVP Coating

Shear Rate s ⁻¹	(P/L) _i , GPU*					α_{ij}		
	H ₂	O ₂	N ₂	CH ₄	CO ₂	O ₂ /N ₂	CO ₂ /CH ₄	H ₂ /N ₂
249	172	29	7.0	2.7	141	4.06	52.0	24.5
457	232	34	7.3	3.0	165	4.60	54.9	31.8
581	312	45	9.7	4.1	216	4.7	53.7	32.5
1391	391	53	12.4	8.0	271	4.44	37.5	32.7

*GPU=1x10⁻⁶ cm³ (SPT)cm² -s-cmHg

Example 3:

Examples 3 and 4 are provided by way of comparison with the present invention exemplified in Examples 1 and 2.

Silicone rubber coated [6F-Durene] hollow fibers

The uncoated [6F-Durene] polyimide fiber fibers of example 1 were dip-coated in a coating solution of 3 wt% polydimethylsiloxane (Sylgard-184) in 97% hexane for 2 minutes. The fibers were air-dried at room temperature for at least 2 days so that the silicone rubber coating was fully cured before gas separation performance tests.

Table 4. Gas separation performance of silicone rubber coated [6F-Durene] polyimide hollow fibers.

Shear Rate	(P/L) _i , GPU*						α_{ij}	
s ⁻¹	H ₂	O ₂	N ₂	CH ₄	CO ₂	O ₂ /N ₂	CO ₂ /CH ₄	H ₂ /N ₂
249	251	66	33	34	282	2.00	8.27	7.61
457	229	63	20	19	367	3.12	19.25	11.38
581	242	64	20	19	373	3.20	19.69	12.00
1391	435	115	57	66	519	2.15	8.70	7.99

*GPU=1x10⁻⁶ cm³ (SPT)/cm² -s-cmHg

Table 4 shows gas selectivity and permeance vs. shear rate. Similar trends occur as for PVP coated [6F-Durene] polyimide hollow fibers. For non-polar gas pairs, selectivity increases and then decreases with increasing shear rate. The up and down, Λ , pattern with increasing shear rate is clearly inconsistent with theories that the selectivity increase is mainly due to tightened chain packaging are reduced, surface porosity induced by shear rate, while the selectivity decrease is mainly due to relatively porous skin structures induced by low viscosity.

However, the silicone rubber coated [6F-Durene] polyimide hollow fibers have much lower selectivities for various gas pairs than the those of polyvinylpyrrolidone (PVP) coated [6F-Durene] polyimide hollow fibers.

Example 4:

Poly(4-vinylpyridine) (4-PVP) coated [6F-Durene] polyimide hollow fibers

The uncoated [6F-Durene] polyimide fibers of example 1 were dip-coated in a coating solution of 0.15 wt% 4-PVP in methanol for 3 minutes. The fibers were air-dried at room temperature fully before tests.

Table 5. Gas separation performance of 4-PVP coated [6F-Durene] polyimide hollow fibers. (Shear rate = 581 s^{-1})

(P/L) _i , GPU*						α_{ij}	
H ₂	O ₂	N ₂	CH ₄	CO ₂	O ₂ /N ₂	CO ₂ /CH ₄	H ₂ /N ₂
340	46.1	15.1	9.0	261	3.05	28.8	22.5

*GPU = $1 \times 10^{-6} \text{ cm}^3 \text{ (SPT)/cm}^2 \cdot \text{s} \cdot \text{cmHg}$

Table 5 shows gas selectivity and permeance. Similar results occur to relatively porous skin structures induced by low viscosity. However, the poly(4-vinylpyridine) (4-PVP) coated [6F-Durene] polyimide fibers have much lower selectivities for various gas pairs than the those of polyvinylpyrrolidone (PVP) coated [6F-Durene] polyimide hollow fibers.

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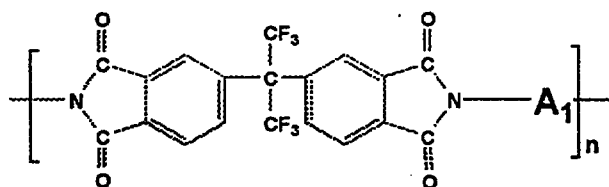
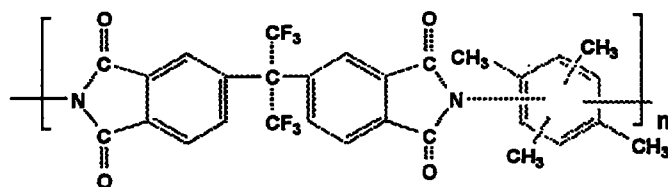
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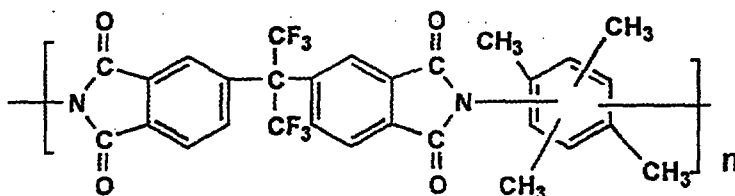
CLAIMS

1. A method of producing a fluoro-polyimide or copolyimide fiber comprising the steps of:
 - a) providing a fluoro-polyimide or copolyimide dope;
 - b) spinning the fluoro-polyimide or copolyimide dope to produce a fluoro-polyimide or copolyimide fiber; and
 - c) coating the fiber with polyvinylpyrrolidone.

2. A method according to Claim 1 wherein the fluoro-polyimide or copolyimide comprises a polyimide or copolyimide having one of the following formulae:

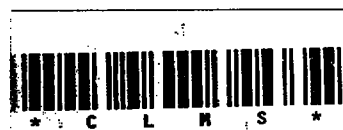


3. A method according to Claim 2 wherein the polymer chain of the fluoropolyimide or copolyimide comprises at least the chemical structure of [6F-Durene] polyimide, having the formula:



4. A method according to Claim 3 wherein the step of providing a [6F-Durene] polyimide dope comprises the steps of: providing a polyamic acid (PAA) solution and imidizing the polyamic acid solution to Polyimide.
5. A method according to Claim 4, wherein the polyamic acid solution is synthesized using a solution polycondensation reaction of 6FDA and 2,3,5,6-tetramethyl-1,4-phenylene Diamine.
6. A method according to Claim 5 wherein the solution polycondensation reaction is between 50 mole% 6FDA and 50 mole% 2,3,5,6-tetramethyl-1,4-phenylene Diamine.
7. A method according to Claim 5 or 6 wherein the reaction mixture is stirred for at least twenty hours at between 15 and 25°C to yield a polyamic acid solution.
8. A method according to any one Claims 4 to 7 wherein the imidizing step comprises adding Propionic-anhydride, Acetic anhydride or Butyric anhydride and Beta-picoline to the polyamic acid solution.
9. A method according to Claim 8, wherein the Propionic anhydride and Beta-picoline are reacted for between seventeen and nineteen hours in the polyamic acid solution.
10. A method according to any one of the preceding claims wherein the fluoro-polyimide dope is spun in a spinneret.
11. A method according to Claim 10 wherein water is provided as an external coagulant during spinning.





12. A method according to Claim 10 or 11 wherein a solution of polyamic acid and 1-methyl-2-pyrrolidinone is used as a bore fluid during spinning.
13. A method according to Claim 12 wherein the polyamic acid and 1-methyl-2-pyrrolidinone solution is in proportions of 42.7: 57.3 wt % polyamic acid: 1-methyl-2-pyrrolidinone.
14. A method according to any one of the preceding claims wherein the fluoro polyimide or copolyimide dope is spun at a shear rate between 200 and 2000 s^{-1} .
15. A method according to Claim 14 wherein the fluoro polyimide or copolyimide dope is spun at a shear rate between 400 and 1400 s^{-1} .
16. A method according to any one of the preceding claims wherein the step of coating the fiber with polyvinylpyrrolidone comprises dipping the fiber in a solution of 0.05 to 1.0 wt% polyvinylpyrrolidone in methanol for less than two minutes and drying the fiber.
17. A method according to Claim 16 wherein the solution of polyvinylpyrrolidone is a solution of 0.1 to 0.2 wt% polyvinylpyrrolidone.
18. A method according to Claim 17 wherein the solution of polyvinylpyrrolidone is a solution of 0.15 wt% polyvinylpyrrolidone.
19. A method of preparing a polyimide or copolyimide hollow fiber comprising the steps of:
 - a) preparing a polyimide or copolyimide dope; and

b) spinning the polyimide or copolyimide dope at a shear rate of between 200 and 1400 s^{-1} .

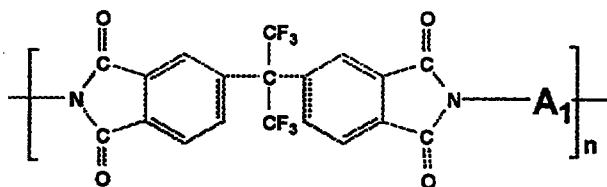
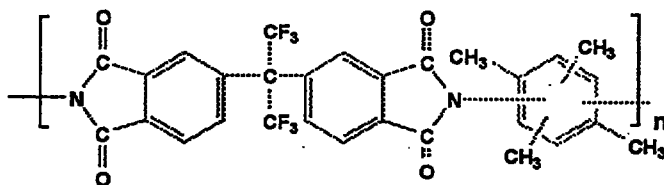


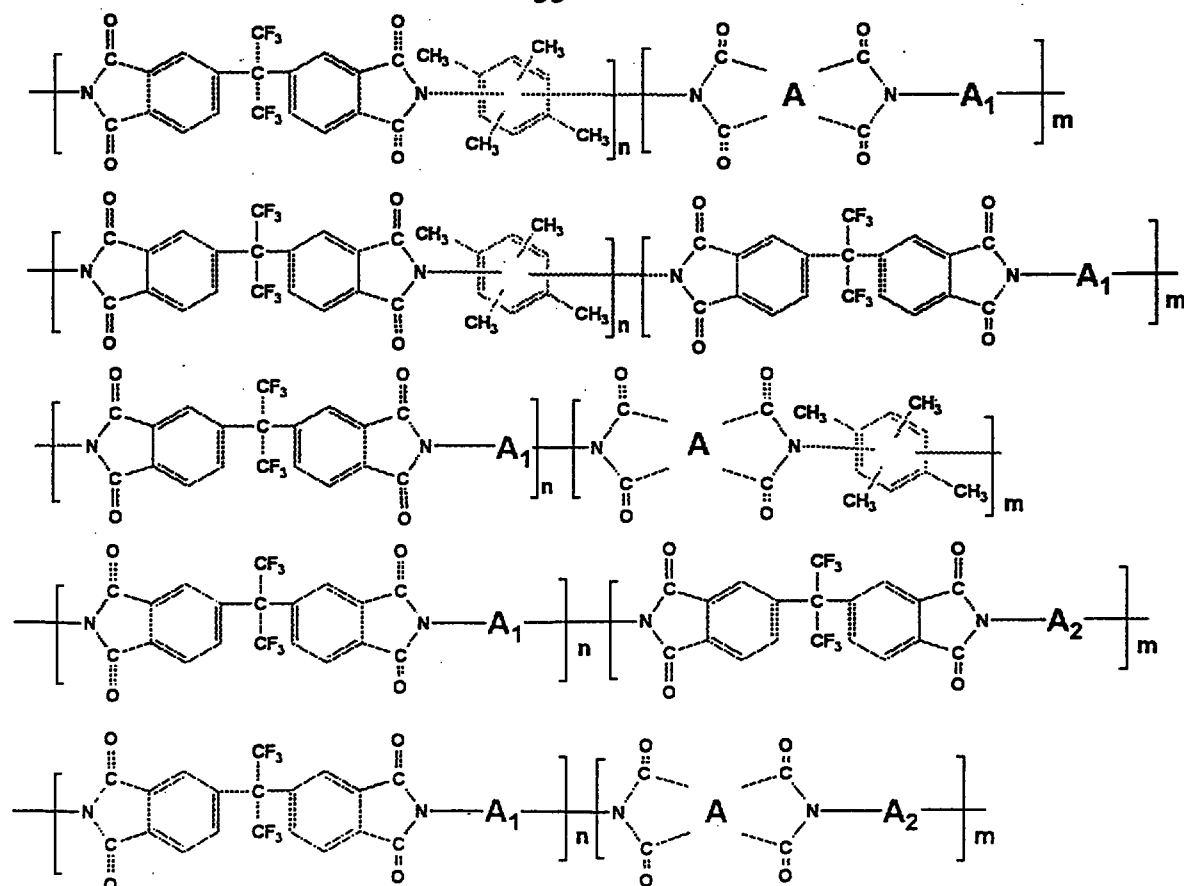
20. A method of preparing a polyimide or copolyimide hollow fiber according to Claim 19 further comprising the step of:

c) incorporating the hollow fiber into a gas separation membrane.

21. A method of preparing a polyimide or copolyimide hollow fiber according to Claim 19 or 20 wherein the polyimide or copolyimide is a fluorinated polyimide or copolyimide.

22. A method of preparing a polyimide or copolyimide hollow fiber according to Claim 21 wherein the fluorinated polyimide comprises a polyimide or copolyimide having one of the following formulae:

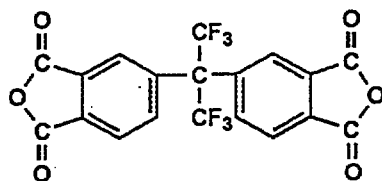




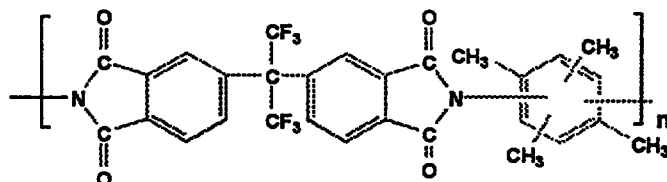
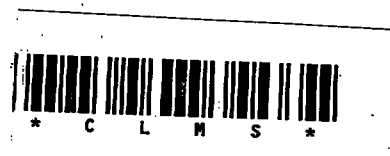
wherein A₁ and A₂ comprise any organic aromatic group.



23. A method of preparing a polyimide or copolyimide hollow fiber according to Claim 33 wherein the fluorinated polyimide comprises 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), having the formula:



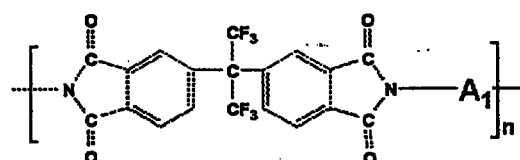
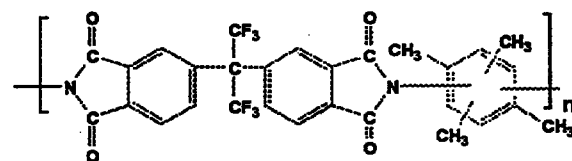
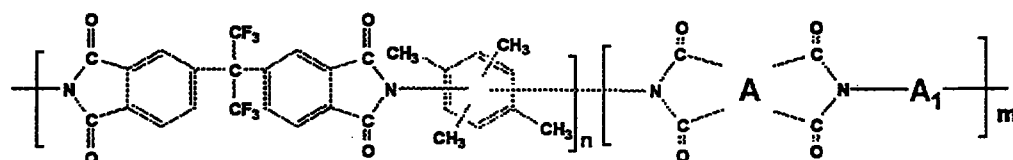
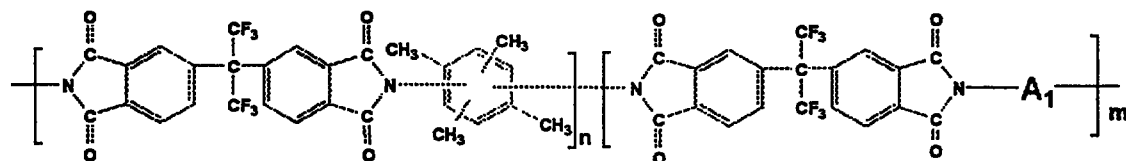
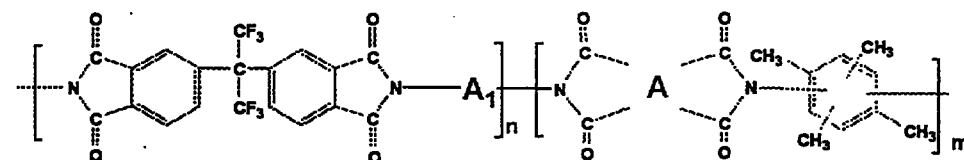
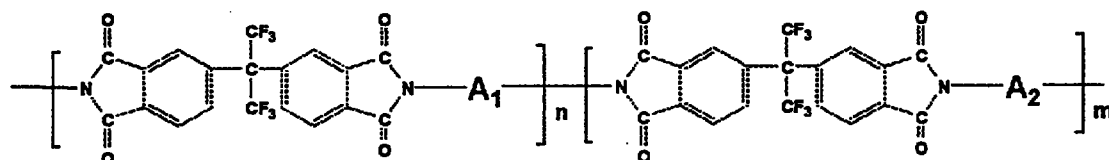
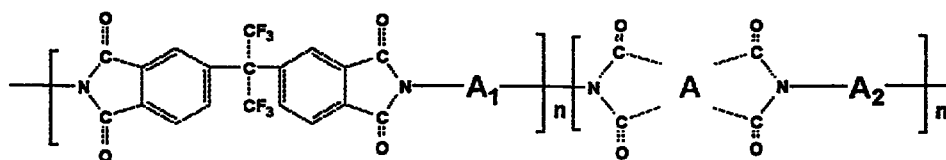
24. A method of preparing a polyimide or copolyimide hollow fiber according to Claim 22 wherein the fluorinated polyimide is [6F-Durene], having the formula:



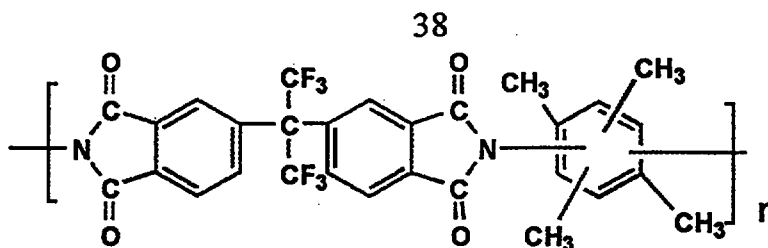
25. A fiber prepared according to the method of any one of the preceding claims, or by a method equivalent thereto.

26. A fiber comprising a fluoro polyimide or copolyimide, having a coating comprising polyvinylpyrrolidone.

27. A fiber according to Claim 26 wherein the fluoro-polyimide or copolyimide comprises a copolyimide having one of the following formulae:



28. A fiber according to Claim 27 wherein the polymer chain of the fluoropolyimide or copolyimide comprises at least the chemical structure of [6F-Durene] having the formula:



29. A fiber according to any one of Claims 26 to 28 wherein the fiber has been spun at a shear rate between 200 and 2000 s⁻¹.
30. A fiber according to Claim 29 wherein the fiber has been spun at a shear rate of between 400 and 1400 s⁻¹.
31. A fiber according to any one of Claims 26 to 30 prepared according to the method of any one of Claims 1 to 18.
32. A gas separation membrane comprising a fiber according to any one of Claims 25 to 31.
33. A method of separating a mixture of constituents, the method comprising the step of passing the mixture through a membrane according to Claim 32.
34. A method of separating a mixture of constituents according to Claim 33 wherein the mixture comprises non-polar gases.
35. A method of separating a mixture of constituents according to Claim 33 wherein the mixture comprises polar gases.
36. A method of separating a mixture of constituents according to Claim 35 wherein the mixture comprises CO₂ and CH₄.