

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 August 2008 (07.08.2008)

PCT

(10) International Publication Number
WO 2008/093971 A1

(51) International Patent Classification:
C08J 5/18 (2006.01)

440-716 (KR). KIM, Min Ju [KR/KR]; #386, Gasan-ri,
Gasan-myeon, Pocheon-si, Gyeonggi-do 487-811 (KR).

(21) International Application Number:
PCT/KR2008/000504

(74) Agents: JANG, Seongku et al.; 19th Fl., Trust Tower,
#275-7, Yangjae-dong, Seocho-ku, Seoul 137-130 (KR).

(22) International Filing Date: 28 January 2008 (28.01.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10-2007-0008810 29 January 2007 (29.01.2007) KR

(71) Applicant (for all designated States except US): SKC CO.,
LTD. [KR/KR]; #633, Jeongja-dong, Jangnan-gu, Suwon-si,
Gyeonggi-do 440-300 (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): LEE, Jung Gyu
[KR/KR]; Mugungwha Gyeongnam Apt. 306-903, Sin-
chon-dong, Dongan-gu, Anyang-si, Gyeonggi-do 431-738
(KR). WON, Dong Young [KR/KR]; #902-8, Dogok
1-dong, Gangnam-gu, Seoul 135-271 (KR). KIM, Do
Kyoung [KR/KR]; Jowon Joogong Apt. 209-1302,
Jowon-dong, Jangnan-gu, Suwon-si, Gyeonggi-do

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA,
CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE,
EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID,
IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR,
LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX,
MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO,
RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL,
NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG,
CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(54) Title: CROSSLINKED POLYIMIDE FILM AND PROCESS FOR PREPARATION THEREOF

(57) Abstract: The present invention is directed to a crosslinked polyimide film whose main repeating units is derived from a polyamic acid crosslinked with a sulphonic acid having two or more functional groups selected from -CO- and -O-, and a process for the preparation thereof. The crosslinked polyimide film according to the present invention is excellent in thermal dimensional stability and heat resistance, and has a low moisture absorbability and moisture expansion coefficient, and a high elastic modulus. Therefore, the crosslinked polyimide film of the present invention can be effectively used as an electronic material, for example for a flexible circuit board.



WO 2008/093971 A1

CROSSLINKED POLYIMIDE FILM AND PROCESS FOR PREPARATION THEREOF

FIELD OF THE INVENTION

The present invention relates to a crosslinked polyimide film useful as an electronic material and a process for the preparation thereof.

BACKGROUND OF THE INVENTION

10

Polyimide films have generally been widely employed in special applications such as covering a circuit or wiring of automobiles exposed to a high temperature/high humidity condition and covering aircraft wiring that must endure large temperature variations. Also, with ever increasing demand for scaling down of electronic devices, the wiring of a flexible wiring plates employed therein has undergone extensively miniaturization, and there has arisen a need for a polyimide film having good dimensional stability under high temperature, high tensile stress conditions encountered by much wirings.

20

In order to provide such a polyimide film having a high elastic modulus and a low thermal expansion coefficient, the use of a rigid and linear monomer, e.g., pyromellitic acid dianhydride or para-phenylene diamine, has been attempted. However, the polyimide film obtained therewith was not useful for the preparation of a flexible wiring plate due to its poor flexibility, a high moisture absorbability and a high moisture expansion coefficient.

30

Therefore, in order to provide a polyimide film having a low moisture absorbability and a low moisture expansion coefficient, in addition to a low thermal expansion coefficient and a high elastic modulus, the use of a monomer having a long chain and a decreased content of an imide moiety has been studied. For example, Japanese Patent Laid-open Publication Nos. 1999-54862 and 2001-72781 disclose a method for reducing the moisture absorbability and the moisture expansion coefficient of a polyimide by using para-phenylene bis(trimellitic acid monoester anhydride) as a long chain monomer. However, the resulting polyimide film exhibits poor dimensional stability and a poor adhesion strength to a metal.

Further, Japanese Patent Laid-open Publication No. 1997-328544 discloses a method for preparing a polyimide from pyromellitic acid dianhydride or 3,3',4,4'-benzophenonetetracarboxylic acid as an acid component, but the polyimide film thus obtained has a high moisture absorbability of 2.62 to 3.69 % and a high thermal

expansion coefficient of 16.8 to 29.8 ppm/°C.

Further, Japanese Patent Laid-open Publication No. 1997-235373 discloses a polyimide film prepared by using biphenyltetracarboxylic acid dianhydride, pyromellitic acid dianhydride, para-phenylenediamine and 4,4'-diaminodiphenylether, but the polyimide film has the problem of a high thermal expansion coefficient at a high temperature.

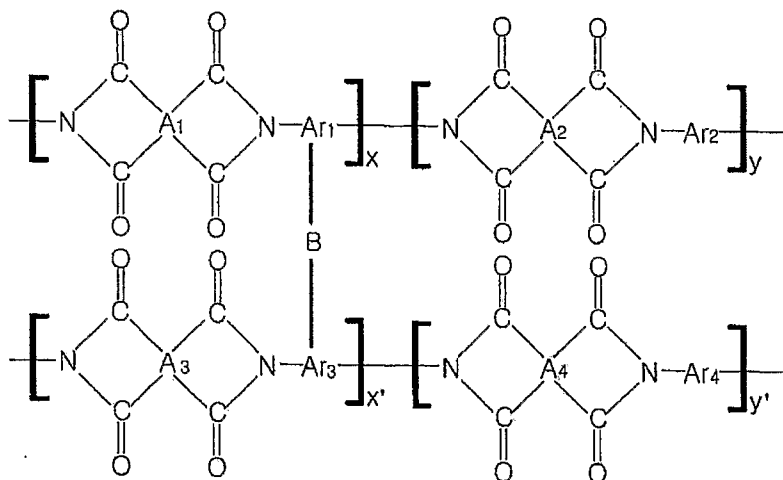
SUMMARY OF THE INVENTION

10 Accordingly, it is an object of the present invention to provide a polyimide film having improved dimensional stability, a low moisture absorbability, a low moisture expansion coefficient, and a high elastic modulus.

The above and other objects and features of the present invention will become apparent from the following description of the invention.

In accordance with one aspect of the present invention, there is provided a crosslinked polyimide film of Formula I, whose main repeating unit is derived from a crosslinked polyamic acid:

<Formula I>



20

wherein

A₁, A₂, A₃ and A₄ are each independently a moiety derived from an aromatic acid dianhydride,

Ar₁ and Ar₃ are each independently a moiety derived from an aromatic diamine having one or more functional groups selected from -CO- and -O-,

Ar₂ and Ar₄ are each independently a moiety derived from an aromatic diamine,

B is a moiety derived from a sulphonic acid derivative having two or more functional groups selected from -CO- and -O-,

x and x' are each independently an integer in the range of 2 to 20, and

y and y' are each independently an integer in the range of 2 to 30.

Further, in accordance with another aspect of the present invention, there is provided a process for the preparation of the crosslinked polyimide film of Formula I, comprising (a) copolymerizing an aromatic acid dianhydride with an aromatic diamine in the presence of an organic polar solvent to obtain a polyamic acid; (b) crosslinking the polyamic acid with a sulphonic acid derivative having two or more functional groups selected from -CO- and -O- as a crosslinker to obtain a crosslinked polyamic acid, and (c) applying the crosslinked polyamic acid on a substrate to obtain a film, and drying and heating to cure the film.

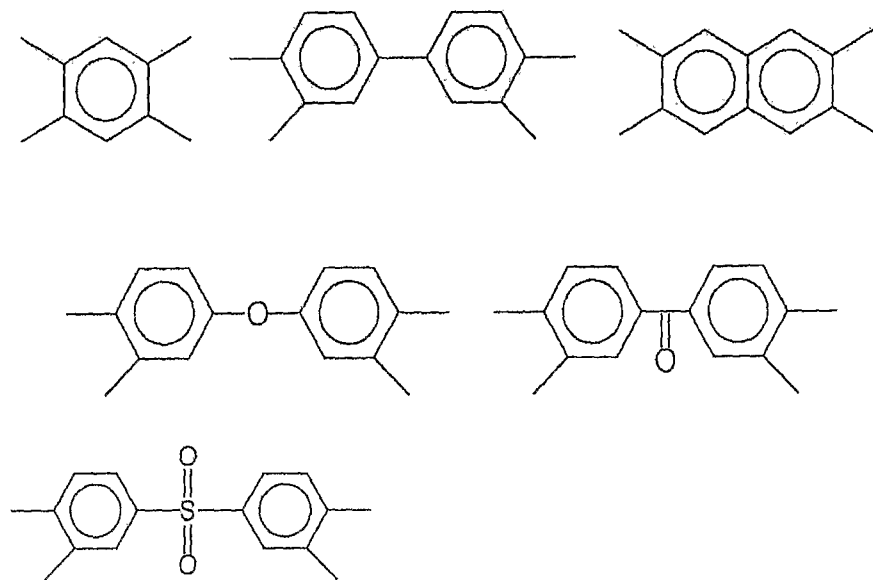
DETAILED DESCRIPTION OF THE INVENTION

A crosslinked polyimide film according to the present invention is obtained by crosslinking a polyamic acid with a crosslinker having a sulphonic acid group, and it has a low heat shrinkage at a high temperature, e.g., 300°C, a low thermal expansion coefficient, a low moisture absorbability, a low moisture expansion coefficient, and a high elastic modulus. Therefore, the polyimide film of the present invention can be effectively used as an electronic material, for example for a flexible circuit board, a base film of chip-on-films (COFs), a tape for tape automated bonding (TAB), a base film of a high density recording medium, and Digital Versatile Disc (PVD) 2-layer laminate.

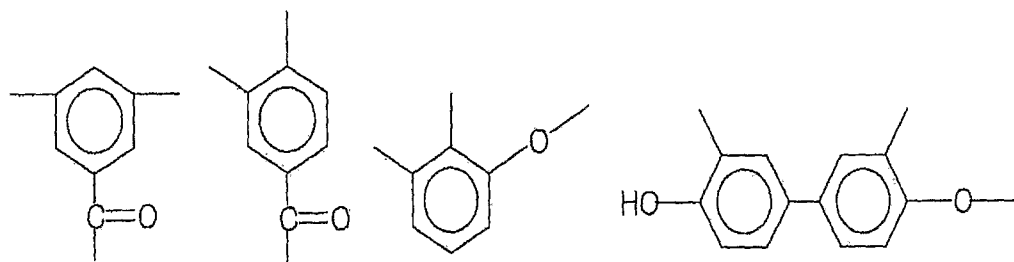
In the preparation of the polyimide film according to the present invention, the polyamic acid can be obtained by copolymerizing an aromatic acid dianhydride and an aromatic diamine.

The inventive polyimide film has a crosslinked structure, the main repeating units thereof being crosslinked using a sulphonic acid group. Preferably, the present invention provides a crosslinked polyimide film of Formula I, wherein A₁, A₂, A₃, A₄, Ar₁, Ar₂, Ar₃, and Ar₄ are each independently a moiety having one or more C₆₋₁₀ aromatic rings optionally substituted with hydroxyl, C₁₋₁₀ alkyl, C₁₋₁₀ alkoxy or halogen, with the proviso that when said moiety comprises two or more aromatic rings, one or more bonds selected from -S-, -O-, -NH-, -C₁₋₄ alkylene-, -CH(OH)-, -CO-, -SO₂- and -C(O)NH- intervene between the aromatic rings.

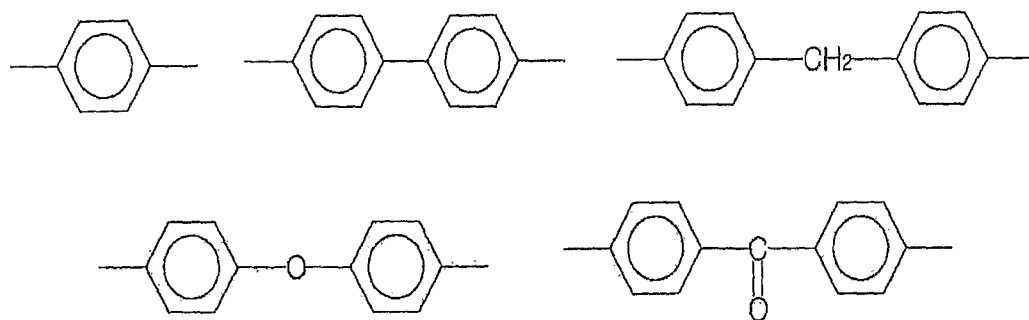
Examples of A₁, A₂, A₃ or A₄ are those represented by formulas below:

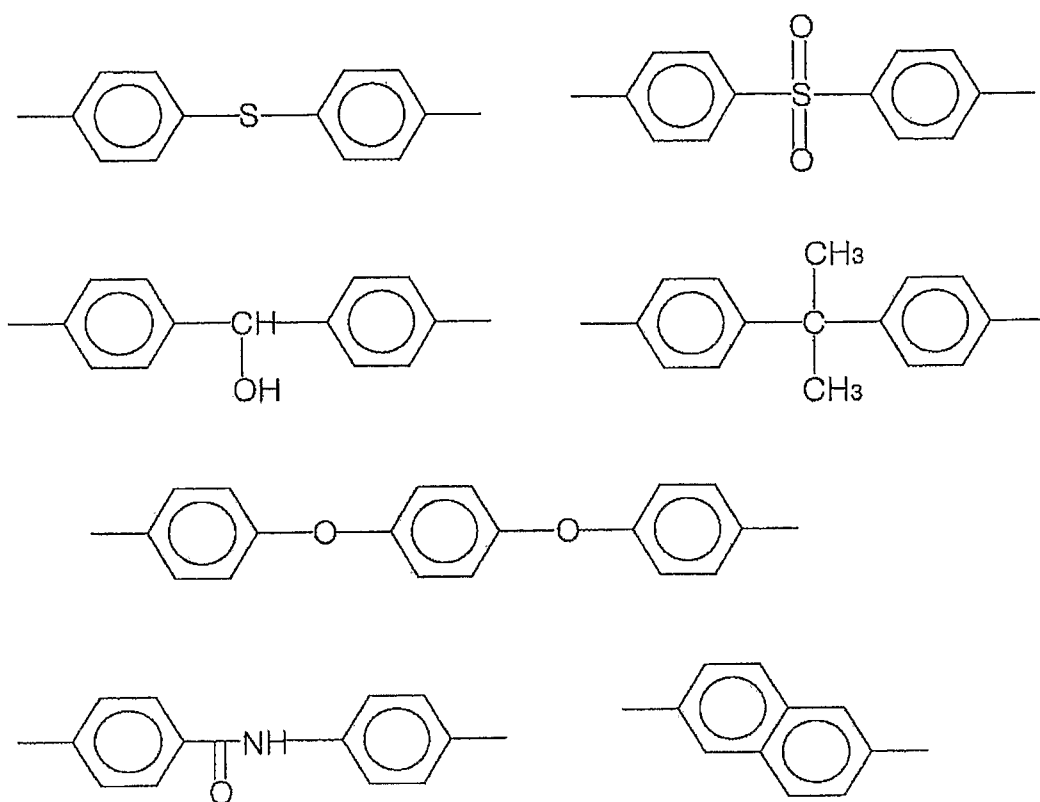


Examples of Ar_1 or Ar_3 are those represented by formulas below:

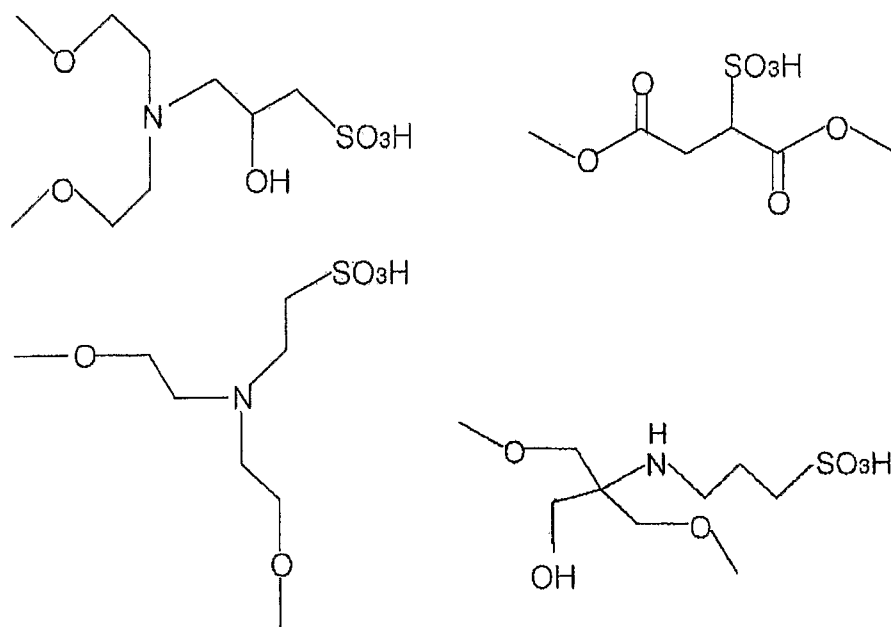


Further, examples of Ar_2 or Ar_4 are those represented by formulas below:





Also, examples of B include those represented by formulas below:



The content of B derived from a sulphonic acid derivative in the crosslinked polyimide film is in the range of 0.01 to 0.15 wt%, based on the total weight of the polymer.

The polyamic acid, a precursor of the polyimide of the present invention, may be prepared by the following processes:

(1) An aromatic acid dianhydride is allowed to react with a less than equivalent amount of an aromatic diamine in the presence of a polar organic solvent to obtain a prepolymer having acid anhydride groups at its both ends, and the prepolymer is further polymerized with a suitable amount of the aromatic diamine so that the total amount of the aromatic diamine used;

10 (2) An aromatic acid dianhydride is reacted with a higher than equivalent amount of an aromatic diamine in the presence of a polar organic solvent to obtain a prepolymer having amino groups at its both ends, and the prepolymer is further polymerized with a suitable amount of the aromatic acid dianhydride so that the total molar amounts of the aromatic acid dianhydride used becomes equivalent to the aromatic diamine;

(3) An aromatic diamine is dissolved in a polar organic solvent, and is then polymerized with a substantially equivalent amount of an aromatic acid dianhydride;

(4) An aromatic acid dianhydride is dissolved and/or dispersed in a polar organic solvent, and is then polymerized with a substantially equivalent amount of an aromatic diamine; or

(5) A mixture of substantially molar equivalent amounts of an aromatic acid dianhydride and an aromatic diamine is polymerized in a polar organic solvent.

20 The polar organic solvent that can be used in the synthesis of a polyamic acid includes an amide-based solvent, e.g., N,N-dimethylformamide, N-methyl-2-pyrrolidone, N,N-dimethylacetamide or a combination thereof.

The reaction of the aromatic diamine with the aromatic acid dianhydride for the preparation of the polyamic acid may be conducted at 0 to 60 °C, preferably 5 to 50 °C. However, when the polyamic acid prepolymer having acid anhydride end groups is used as an intermediate, as described above in process (1), the reaction is preferably conducted at a temperature below 30 °C, more preferably below 10 °C. Further, the reaction time is less than 10 hours, preferably less than 5 hours, and more preferably less than 3 hours.

30 Subsequently, a sulphonic acid derivative having two or more -CO- or -O- functional groups is added as a crosslinker to the polyamic acid solution obtained by one of above processes, to obtain a crosslinked polyamic acid. In this step, the crosslinker may be preferably used in an amount of 0.01 to 0.15 wt% based on the total amount of polyamic acid. The crosslinking reaction may be conducted at 0 to 60 °C, preferably at 10 to 50 °C, for 1 to 5 hours. A catalyst may be used for the crosslinking reaction. When ester bond-type crosslinking is desired, 1-[3-(dimethylamino)propyl]-3-ethyl carbodiimide hydrochloride (EDC) can be used as a catalyst, while when ether bond-type crosslinking is desired, NaH or PPh₃ may be used as the catalyst.

Examples of the crosslinker include N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES), N,N-bis(2-hydroxyethyl)-3-amino-2-hydroxypropanesulphonic acid, and a combination thereof.

Alternatively, a crosslinked polyamic acid may be obtained by subjecting an aromatic diamine having one or more -CO- or -O- groups to a reactor with a sulphonic acid derivative having two or more -CO- or -O- groups in a polar organic solvent, and then, by copolymerizing the resulting product with an aromatic acid dianhydride to obtain a crosslinked polyamic acid. If desired, the crosslinked polyamic acid thus obtained may be incorporated into another polyamic acid obtained separately.

10 The crosslinked polyamic acid resulting from the above mentioned processes may be kept in the form of a solution comprising 5 to 35wt%, preferably 10 to 30 wt%, more preferably 15 to 25 wt% of the polyamic acid. Further, the number average molecular weight (Mn) of the crosslinked polyamic acid is in the range of 10,000 to 1,000,000 and the viscosity of the crosslinked polyamic acid is in the range of 1,500 to 3,500 poises, which is measured with a Brookfield viscometer.

Then, the crosslinked polyamic acid thus obtained may be imidized into a crosslinked polyimide by a conventional method, e.g., a thermal or chemical curing method. According to the thermal curing method, imidization may be achieved by heat treatment in the absence of a dehydrating agent or an imidization catalyst. According to
20 the chemical curing method, a dehydrating agent, an imidization catalyst or both may be added to a solution of the crosslinked polyamic acid in an organic solvent.

In case of thermal curing, the polyamic acid solution may be applied on a substrate such as a support plate, heating drum, or endless belt and the applied layer may be dried preferably at a temperature of less than about 150 °C for about 10 to 60 minutes to obtain a self-supporting gel film. Subsequently, the gel film is fixed on a support plate and heated at 150 to 600 °C, preferably at 250 to 500 °C to completely imidize the residual polyamic acid into a polyimide film.

In case of chemically curing, the polyamic acid solution is mixed with a dehydrating agent and/or a imidization catalyst, and the resultant mixture is applied or
30 cast on a substrate such as a support plate, heating drum or endless belt, and heated at 50 to 200 °C, preferably at 70 to 150 °C, to induce partial curing and drying by activating the dehydrating agent and/or the imidization catalyst, to obtain a self-supporting gel film. Subsequently, the gel film is fixed on a support plate, and, heated at 200 to 600 °C for 3 to 30 minutes to completely imidize the residual polyamic acid into polyimide through dehydration and ring-closing reactions. If the heating temperature is higher than 600 °C or the heating time is longer than 30 minutes, film degradation may occur. Conversely, if the heating temperature is lower than 200 °C or the heating time is shorter than 3

minutes, the desired effect may not be achieved.

The dehydrating agent includes an aliphatic anhydride, an aromatic acid anhydride, an N,N'-dialkylcarbodiimide, a lower aliphatic halide, a halogenated lower aliphatic compound and a combination thereof, preferably an aliphatic acid anhydride. Examples of the aliphatic acid anhydride include acetic acid anhydride, propionic acid anhydride, butyric acid anhydride, or a combination thereof. The dehydrating agent may be used in an amount of 1 to 10 mole eq., preferably 1.5 to 8 molar eq., more preferably 2 to 5 molar eq. If the amount of the dehydrating agent is out of the above range, sufficient imidization may not be achieved or the imidized film has a poor releasing property from the substrate.

The imidization may be effectively conducted in the presence of both of the dehydrating agent and the imidization catalyst. Exemplary imidization catalyst is a tertiary amine, such as aliphatic tertiary amine, aromatic tertiary amine, and heterocyclic tertiary amine, and a heterocyclic tertiary amine is preferred. Examples of the heterocyclic tertiary amine include quinoline, isoquinoline, β -picoline, and pyridine. The imidization catalyst may be used in an amount of 0.1 to 2 molar eq., preferably 0.2 to 1.8 molar eq., more preferably 0.3 to 1.5 molar eq., based on the amount of the polyamic acid.

The polyimide film thus obtained typically has an average thickness of 7.5 to 125 μm .

The crosslinked polyimide film of the present invention has an elastic modulus of 500 to 800 kg/mm^2 , preferably 500 to 700 kg/mm^2 . If the elastic modulus of the polyimide film is less than 500 kg/mm^2 , the film may become loose when the film is heated to laminate IC or LIS on a flexible circuit board having metal wirings.

Further, the polyimide film of the present invention has an average thermal expansion coefficient in the mechanical direction (MD) and the transverse direction (TD) of 1 to 30 $\text{ppm}/^\circ\text{C}$, preferably 5 to 20 $\text{ppm}/^\circ\text{C}$ at 100 to 200 $^\circ\text{C}$. In the above mentioned range, even when an alkaline-etching of the polyimide film on the metal laminate is carried out at a high temperature, the disarrangement of an alkaline etching mask caused by thermal expansion and soaking of the etchant can be prevented. However, if the thermal expansion coefficient is higher than 30 $\text{ppm}/^\circ\text{C}$, the gap between the metal wirings may increase, lowering the adhesiveness.

The polyimide film of the present invention has an average heat shrinkage ratio in MD and TD of -0.1 to 1.0% at 300 $^\circ\text{C}$. In the above average heat shrinkage ratio range, even if the film is heated for mounting electronic parts such as IC or LSI on the small wirings, the shrinkage ratio of the film can be controlled into the desired range.

Further, the polyimide film of the present invention has a moisture absorbability

of less than 3.0%, preferably less than 2.0%, more preferably less than 1.8 %, most preferably less than 1.5%, and the moisture expansion coefficient is preferably 2 to 20 ppm/% RH. If the moisture expansion coefficient satisfies the above-mentioned ranges, adhesion problem can be prevented when electronic parts such as IC or LSI are mounted on a metal wiring on the polyimide film. However, if the moisture expansion coefficient is higher than 20 ppm/% RH, the component absorbed in the polyimide film can be discharged when the film is immersed in a soldering bath, and therefore, the film-shrinkage may happen, causing short-circuit of the metal wirings.

10 In connection with the improvement of the pattern density and reliability, the dimensional change in the course of heating to form the film, etching of a laminate with copper, cleaning, and drying, must be controlled and it is preferable that the polyimide film of the present invention has a low moisture expansion coefficient and a low thermal expansion coefficient.

As mentioned previously, the crosslinked polyimide film according to the present invention has an improved dimensional stability, a low thermal expansion ratio, a low moisture absorbability, a low moisture expansion coefficient, a high elastic modulus, and an excellent adhesiveness. Therefore, the polyimide film of the present invention can be beneficially used as an electronic material, for a flexible circuit board, a base film of COF, a tape for TAB, a base film of a high density recording medium, and PVD 2-layer
20 laminate.

The following Examples are intended to further illustrate the present invention without limiting its scope.

Examples

Example 1

30 A reactor equipped with a detachable stainless steel flask and two paddle blades positioned in the flask as a stirrer was used in combination with a cooler having cooling capability of 20.9 kJ/minute, to prepare a crosslinked polyamic acid. During the polymerization reaction, dehydrated nitrogen gas was passed through the polymerization reactor at 0.05L/minute to exclude moisture therefrom.

Dimethylformamide (DMF) was introduced into the flask, and equivalent amounts of pyromellitic acid (PMDA) and 4,4-diaminodiphenylether (ODA) were added thereto to obtain a solution containing 18.5wt% of the corresponding polyamic acid. N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) was dissolved in

dimethylformamide (DMF) in an amount that corresponds to 0.1wt% based on the polyamic acid which was slowly added to the 18.5wt% polyamic acid solution and the resulting mixture was subjected to a crosslinking reaction at 40 °C for 2 hours.

The crosslinked polyamic acid solution thus obtained was mixed with 5 molar eq. of acetic acid anhydride (AA) and 1 molar eq. of isoquinoline (IQ), based on the amount of the crosslinked polyamic acid, and the resulting mixture was uniformly coated on an aluminum plate, and dried stepwisely at 90 °C for 42 seconds, 110 °C for 2 minutes, and 130 °C for 3minutes 12 seconds.

10 Then, the polyamic acid film (gel film) thus obtained was released from the aluminum plate and was fixed on a supporting flame with a pin, followed by heating at 250 °C for 5 minutes and then at 450 °C for 5 minute, to induce the dehydration and ring-closing reaction, to obtain a crosslinked polyimide film with a thickness of 25 μ m.

Example 2

The procedure of Example 1 was repeated except that the amount of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) used was 0.05 wt% based on the weight of the polyamic acid, to obtain a crosslinked polyimide film.

20 Example 3

The procedure of Example 1 was repeated except that the amount of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) used was 0.03 wt% based on the weight of the polyamic acid, to obtain a crosslinked polyimide film.

Example 4

30 The procedure of Example 1 was repeated except that pyromellitic acid dianhydride (PMDA), 4,4-diaminodiphenylether (ODA), and para-phenylenediamine (PPD) were used at 4:3:1 molar ratio, to obtain a crosslinked polyimide film.

Example 5

The procedure of Example 4 was repeated except that the amount of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) used was 0.05wt% based on the weight of the polyamic acid, to obtain a crosslinked polyimide film.

Example 6

The procedure of Example 4 was repeated except that the amount of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) used was 0.03 wt% based on the weight of the polyamic acid, to obtain a crosslinked polyimide film.

Example 7

10 The procedure of Example 1 was repeated except that pyromellitic acid dianhydride (PMDA), biphenyl tetracarboxylic acid dianhydride (BPDA), 4,4-diaminodiphenylether (ODA) and para-phenylenediamine (PPD) were used at 3:1:3:1 molar ratio, to obtain a crosslinked polyimide film.

Example 8

The procedure of Example 7 was repeated except that the amount of 0.05 wt% of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) used was 0.05 wt% based on the weight of the polyamic acid, to obtain a crosslinked polyimide film.

20 **Example 9**

The procedure of Example 7 was repeated except that the amount of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) used was 0.03 wt% based on the weight of the polyamic acid used was 0.03wt%, to obtain a crosslinked polyimide film.

Example 10

30 The procedure of Example 1 was repeated except that pyromellitic acid dianhydride (PMDA), biphenyl tetracarboxylic acid dianhydride (BPDA), bisaminophenoxyphenylsulphone (BAPS) and para-phenylenediamine (PPD) were used at 3:1:3:1 molar ratio, to obtain a crosslinked polyimide film.

Example 11

The procedure of Example 10 was repeated except that the amount of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) used was 0.05 wt% based on the weight of the polyamic acid, to obtain a crosslinked polyimide film.

Example 12

The procedure of Example 10 was repeated except that the amount of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) powder used was 0.03 wt% based on the weight of the polyamic acid, to obtain a crosslinked polyimide film.

Comparative Example 1

- 10 The procedure of Example 1 was repeated except that N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) was not used, i.e., the crosslinking reaction was not conducted, to obtain a crosslinked polyimide film.

Comparative Example 2

The procedure of Example 1 was repeated except that the amount of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) used was 0.2 wt% based on the weight of the polyamic acid, to obtain a crosslinked polyimide film.

20 **Comparative Example 3**

The procedure of Example 4 was repeated except that N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) was not used, i.e., the crosslinking reaction was not conducted, to obtain a crosslinked polyimide film.

Comparative Example 4

- 30 The procedure of Example 4 was repeated except that the amount of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) powder used was 0.2 wt% based on the weight of the polyamic acid, to obtain a crosslinked polyimide film.

Comparative Example 5

The procedure of Example 7 was repeated except that N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) was not used, i.e., the crosslinking reaction was not conducted, to obtain a crosslinked polyimide film.

Comparative Example 6

The procedure of Example 7 was repeated except that the amount of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) used was 0.2 wt% based on the weight of the polyamic acid, to obtain a crosslinked polyimide film.

Comparative Example 7

10 The procedure of Example 10 was repeated except that N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) was not used, i.e., the crosslinking reaction was not conducted, to obtain a crosslinked polyimide film.

Comparative Example 8

The procedure of Example 10 was repeated except that the amount of N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES) used was 0.2 wt% based on the weight of the polyamic acid, to obtain a crosslinked polyimide film.

Experimental Example

20

The polyimide films prepared in Examples 1 to 12 and Comparative Examples 1 to 8 were evaluated for the following properties, and the results are summarized in Table 1 below.

(1) Thermal expansion coefficient (ppm/°C)

Equipment: TMA-2940 (TA Co., Ltd.)

Temperature profile: 20 to 400 °C

Heating rate: 10 °C/minute

30

Sample size: 5 x 20 mm

Loading: 3 g

(2) Moisture expansion coefficient defined by the following equation:

Moisture expansion coefficient (ppm/%RH) = $[(L1-L2) / L1] / (80-30) \times 10^6$

Film dimension (L1)

Standing temperature: 50 °C
 Relative humidity: 30 %RH
 Standing time: 24 hours

Film dimension (L2)
 Standing temperature: 50 °C
 Relative humidity: 80 %RH
 Standing time: 24 hours

10 Sample size: 5 mm x 20 mm
 Added loading: 3 g

(3) Moisture absorbability

A polyimide film sample was dried at 150°C for 30 minutes and weighed (W1). Then, after the film was immersed in a distilled water for 24 hours, the film surface was wiped to remove adsorbed water and the film was weighed again (W2). The moisture absorbability was calculated by the following equation:

20 Moisture absorbability(%) = $(W2-W1)/W1 \times 100$

(4) Tensile properties (tensile strength, tensile elongation, and elastic modulus): ASTM D882

(5) Heat shrinkage ratio

30 Sample size: 15 cm (TD: transverse direction, i.e., film width direction) x 25 cm
 (MD: mechanical direction, i.e., film length direction)
 Standing temperature: 20 °C
 Standing humidity: 60 %RH
 Standing time: 24 hours

The film sample was kept under the above-mentioned conditions, the lengths of the four edges of the film were measured (the lengths in TD: TD1, TD2, the lengths in MD: MD1, MD2). Next, the film was covered with an aluminum coil, and heated at 300°C for 2 hours. After heating, the film sample was kept under the condition of 20°C and 60%RH for 30minutes, followed by measuring the lengths of four edges of the film

again (the lengths in TD: TD1', TD2', the lengths in MD: MD1', MD2'). The heat shrinkage ratio was calculated by averaging the values obtained using the following equations:

Heat shrinkage ratio in TD (%)

$$= [(TD1-TD1')/TD1+(TD2-TD2')/TD2]/2 \times 100$$

Heat shrinkage ratio in MD (%)

$$= [(MD1-MD1')/MD1+(MD2-MD2')/MD2]/2 \times 100$$

Table 1

	Monomer (molar ratio)					Crossli nker (wt %)	Physical properties				
	PMDA	BPD A	ODA	PPD	BAP S		(a)	(b)	(c)	(d)	(e)
Examp. 1	4		4			0.10	16.8	620	0.6	1.2	14.6
Examp. 2	4		4			0.05	17.3	590	0.7	1.3	15.2
Examp. 3	4		4			0.03	18.7	520	0.7	1.3	15.8
Examp. 4	4		3	1		0.10	15.0	680	0.4	0.9	12.6
Examp. 5	4		3	1		0.05	15.8	610	0.6	1.1	13.0
Examp. 6	4		3	1		0.03	16.2	540	0.7	1.1	13.4
Examp. 7	3	1	3	1		0.10	13.2	680	0.3	2.2	12.9
Examp. 8	3	1	3	1		0.05	13.8	650	0.6	2.5	15.3
Examp. 9	3	1	3	1		0.03	14.0	640	0.6	2.7	17.8
Examp. 10	3	1		1	3	0.10	15.1	650	0.4	1.3	15.6
Examp. 11	3	1		1	3	0.05	14.7	660	0.6	1.8	18.6
Examp. 12	3	1		1	3	0.03	12.2	660	0.6	1.8	20.3
Comp. 1	4		4			-	35.7	310	1.8	4.3	32.5
Comp. 2	4		4			0.20	impossible to form film (break when cured)				
Comp. 3	4		3	1		-	16.5	390	0.8	3.8	28.7
Comp. 4	4		3	1		0.20	impossible to form film (break when cured)				
Comp. 5	3	1	3	1		-	14.7	540	1.2	5.2	39.4
Comp. 6	3	1	3	1		0.20	impossible to form film (break when cured)				
Comp. 7	3	1		1	3	-	10.3	680	2.4	3.6	33.7
Comp. 8	3	1		1	3	0.20	impossible to form film (break when cured)				
Exam.: Example											
Comp.: Comparative Example											
PMDA: pyromellitic acid dianhydride											
BPDA: biphenyl tetra carboxylic acid dianhydride											
ODA: 4,4-diamino diphenylether											
PPD: p-phenylene diamine											
BAPS: bisaminophenoxy phenyl sulfone											
(a): thermal expansion coefficient						(b): elastic modulus					
(c): heat shrinkage ratio						(d): moisture absorbability					
(e): moisture expansion coefficient											

As shown in Table 1, the crosslinked polyimide films of the Examples 1 to 12 had a thermal expansion coefficient at 100 to 200 °C of 5 to 20 ppm/°C, a heat shrinkage at 300 °C of -0.1 to 1.0 %, an elastic modulus of 500 to 700 kg/, a moisture absorbability of

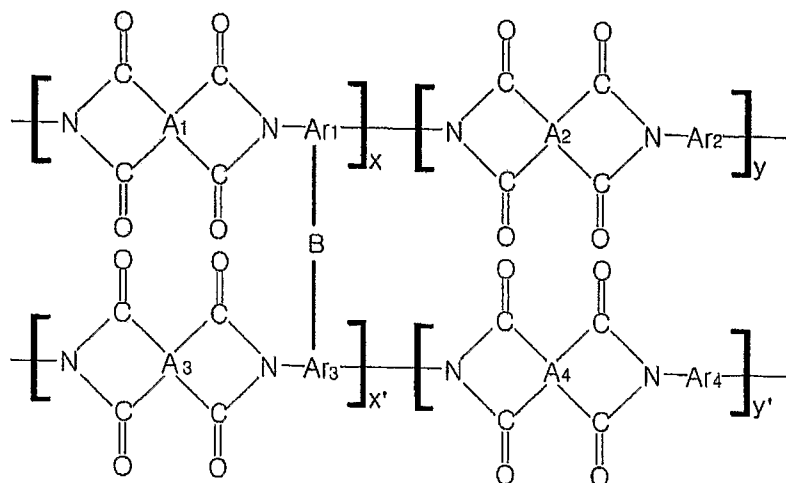
less than 3.0 %, and a moisture expansion coefficient of 2 to 20 ppm/% RH. Accordingly, the polyimide film of the present invention has physical properties superior to those of the films prepared in the Comparative examples 1 to 8.

Therefore, the crosslinked polyimide film of the present invention can be effectively used as the electronic materials, which can be applied to, e.g a flexible circuit board, without the problem of twisting or curving caused by the change in temperature or other process conditions.

WHAT IS CLAIMED IS

1. A crosslinked polyimide film of Formula I, whose main repeating unit is derived from a crosslinked polyamic acid:

Formula I



wherein

A₁, A₂, A₃ and A₄ are each independently a moiety derived from an aromatic acid dianhydride,

Ar₁ and Ar₃ are each independently a moiety derived from an aromatic diamine having one or more functional groups selected from -CO- and -O-,

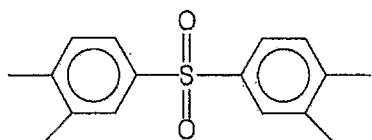
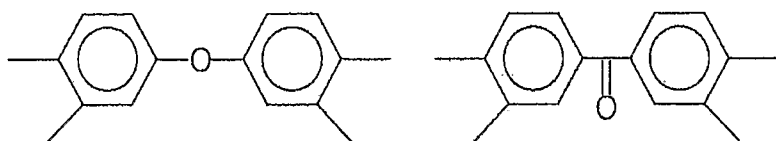
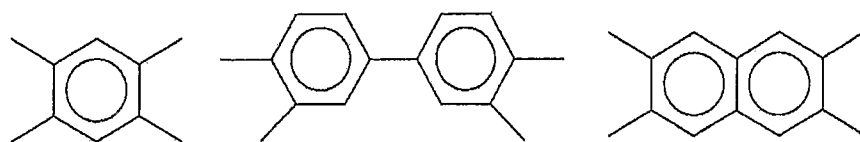
Ar₂ and Ar₄ are each independently a moiety derived from an aromatic diamine,

B is a moiety derived from a sulphonic acid derivative having two or more functional groups selected from -CO- and -O-,

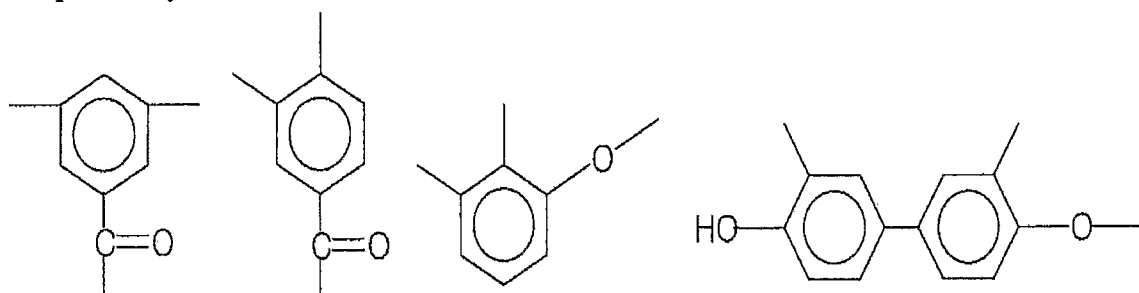
x and x' are each independently an integer in the range of 2 to 20, and

y and y' are each independently an integer in the range of 2 to 30.

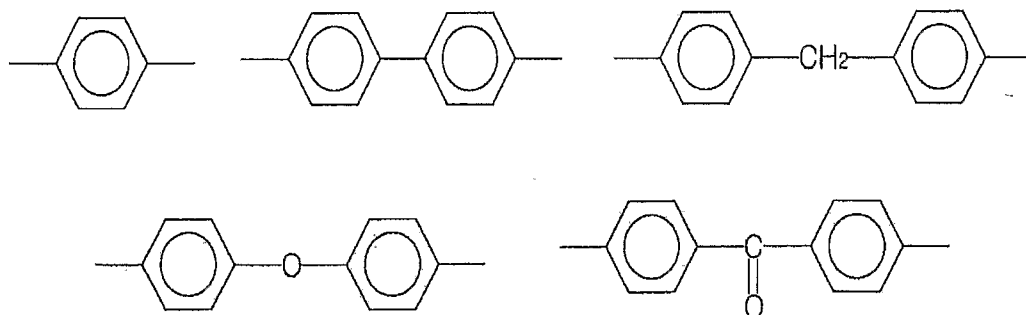
2. The crosslinked polyimide film of claim 1, wherein A₁, A₂, A₃, A₄, Ar₁, Ar₂, Ar₃ and Ar₄ are each independently a moiety having one or more C₆₋₁₀ aromatic rings optionally substituted with hydroxyl, C₁₋₁₀ alkyl, C₁₋₁₀ alkoxy or halogen, with the proviso that when said moiety comprises two or more aromatic rings, one or more bonds selected from -S-, -O-, -NH-, -C₁₋₄ alkylene-, -CH(OH)-, -CO-, -SO₂- and -C(O)NH- intervene between the aromatic rings.
3. The crosslinked polyimide film of claim 2, wherein A₁, A₂, A₃ and A₄ have each independently a structure selected from the structures shown below:

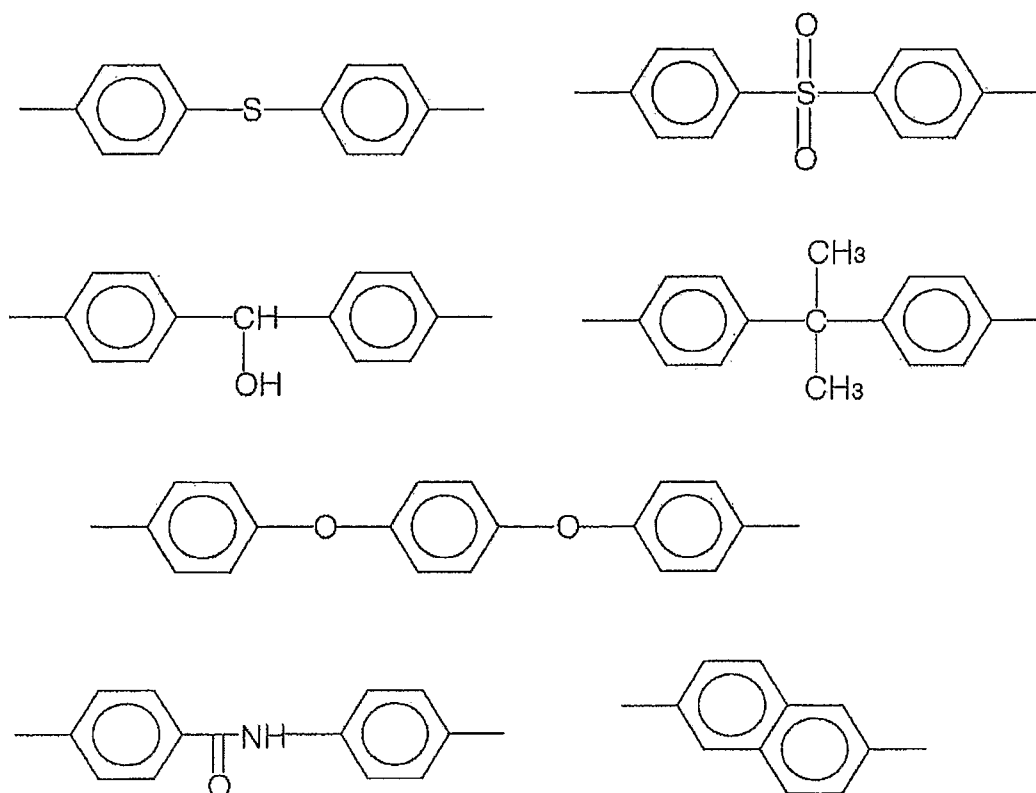


4. The crosslinked polyimide film of claim 2, wherein Ar_1 and Ar_3 have each independently a structure selected from the structures shown below:

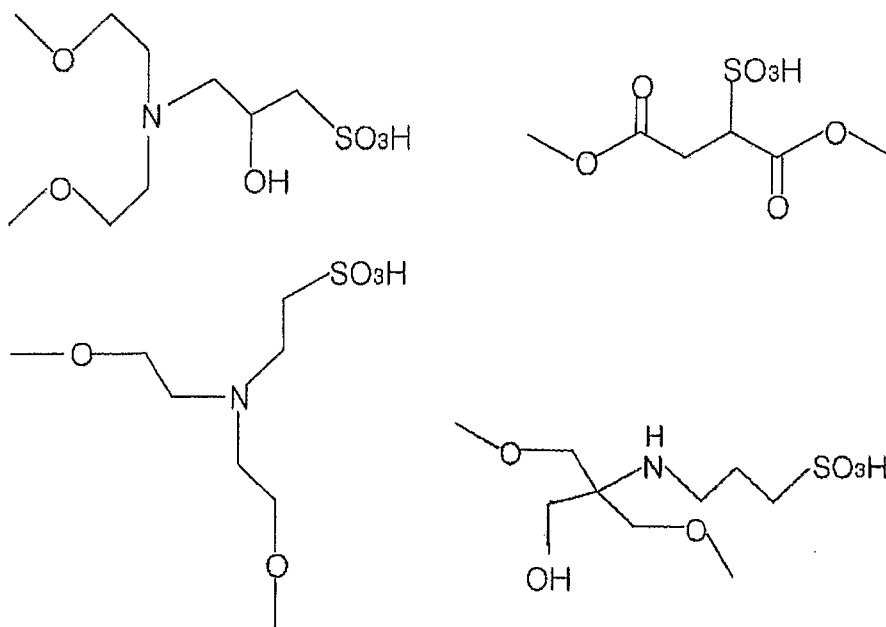


5. The crosslinked polyimide film of claim 2, wherein Ar_2 and Ar_4 have each independently a structure selected from the structures shown below:





6. The crosslinked polyimide film of claim 2, wherein B has a structure selected from the structures shown below:



7. The crosslinked polyimide film of claim 1, wherein the content of B is 0.01 to 0.15 wt%, based on the total amount of the crosslinked polyimide film.
8. The crosslinked polyimide film of claim 1, wherein the crosslinked polyamic acid is

obtained using a 5 to 35wt% polyamic acid solution.

9. The crosslinked polyimide film of claim 1, the crosslinked polyamic acid has number average molecular weight (M_n) of 10,000 to 1,000,000, and a viscosity of 1,500 to 3,500 poises measured with a Brookfield viscometer.
10. The crosslinked polyimide film of claim 1, wherein the average value of the thermal expansion coefficients in the mechanical direction (MD) and the transverse direction (TD) of the film at 100 to 200 °C is 5 to 20 ppm/°C, and the average value of the heat shrinkage ratios in the MD and the TD at 300 °C is -0.1 to 1.0%.
11. The crosslinked polyimide film of claim 1, wherein the film has an elastic modulus of 500 to 700 kg/mm².
12. The crosslinked polyimide film of claim 1, wherein the film has a moisture absorbability of not more than 3.0 %, and a moisture expansion coefficient of 2 to 20 ppm/%RH.
13. A process for the preparation of the crosslinked polyimide film of Formula I according to claim 1, comprising (a) copolymerizing an aromatic acid dianhydride with an aromatic diamine in the presence of an organic polar solvent to obtain a polyamic acid; (b) crosslinking the polyamic acid with a sulphonic acid derivative having two or more functional groups selected from -CO- and -O- as a crosslinker, to obtain a crosslinked polyamic acid, and (c) applying the crosslinked polyamic acid on a substrate to obtain a film, followed by drying and heating to cure the film.
14. The process of claim 13, wherein the crosslinker is added in an amount of 0.01 to 0.15 wt% based on the total amount of the polyamic acid.
15. The process of claim 13, wherein the crosslinking reaction is conducted at 0 to 60 °C for 1 to 5 hours.
16. The process of claim 13, wherein the crosslinker is selected from N,N-bis(2-hydroxyethyl)-2-aminoethanesulphonic acid (BES), N,N-bis(2-hydroxyethyl)-3-amino-2-hydroxypropanesulphonic acid, and a mixture thereof.
17. The process of claim 13, wherein the crosslinked polyamic acid is chemically cured in the presence of a dehydrating agent, an imidization catalyst or a combination thereof, or thermally cured.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2008/000504**A. CLASSIFICATION OF SUBJECT MATTER***C08J 5/18(2006.01)i*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8: C08G, C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS, STN(CA)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/018669 A1(HANYANG HAK WON CO., LTD.) 6 March 2003 See claims, summary of the invention , Formula 2 and Detailed description of the invention.	1-17
X	LEE, C.H. et al. ' Water Sorption, Proton Conduction and Methanol Permeation Properties of Sulfonated Polyimide Membranes Cross-Linked with N,N-Bis(2-hydroxyethyl)-2-aminoethanesulfonic acid(BES).' Macromolecules. 2006, Vol. 39, No. 2, pp. 755-764. See abstract, Experimental Section and Figure 3.	1-17
A	LEE, C.H. et al. 'Water-stable crosslinked sulfonated polyimide-silica nanocomposite containing interpenetrating polymer network.' Journal of Power Sources. 163(2006), pp. 339-348. See abstract and Experimental Section.	1-17
A	SYSEL, P. et al. 'Preparation and characterization of crosslinked polyimide-poly(dimethylsiloxane)s.' Polymer. 42(2001), pp. 10079-10085. See abstract and Experimental Section	1-17
A	PARK, H.B. et al. 'Effect of crosslinked chain length in sulfonated polyimide membranes on water sorption, proton conduction and methanol permeation properties.' Journal of Membrane Science. 285(2006), pp. 432-443. See abstract, Experimental Section and Figures 1-2.	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18 APRIL 2008 (18.04.2008)

Date of mailing of the international search report

18 APRIL 2008 (18.04.2008)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
Government Complex-Daejeon, 139 Seonsa-ro, Seo-
gu, Daejeon 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

SHIN Gwi Im

Telephone No. 82-42-481-8392



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2008/000504

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/015803A1(CELANESE VENTURES GMBH et al.) 19 February 2004 See abstract	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2008/000504

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
W02003018669A1	06.03.2003	CN1545531A	10.11.2004
		JP2005501152T2	13.01.2005
		KR1020030017320	03.03.2003
		US07157548	02.01.2007
		US20040236038A1	25.11.2004
		W003018669A1	06.03.2003
W02004015803A1	19.02.2004	AT314735E	15.01.2006
		CA2494530AA	19.02.2004
		CN1682400A	12.10.2005
		DE10235356A1	12.02.2004
		DE50302082C0	02.02.2006
		EP01527494A1	04.05.2005
		EP01527494B1	28.12.2005
		JP2005534785T2	17.11.2005
		KR1020050036964	20.04.2005
		US07332530	19.02.2008
		US20050244695A1	03.11.2005