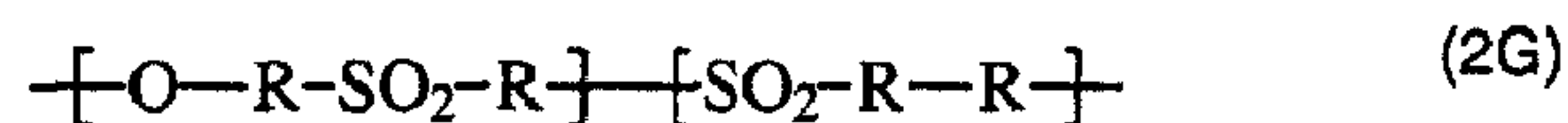
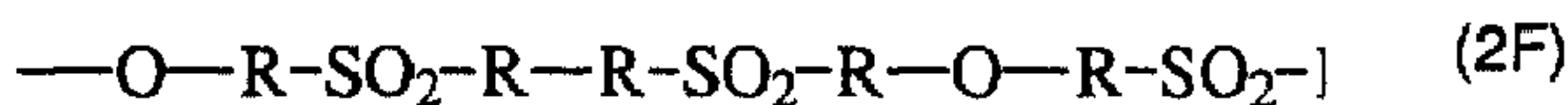
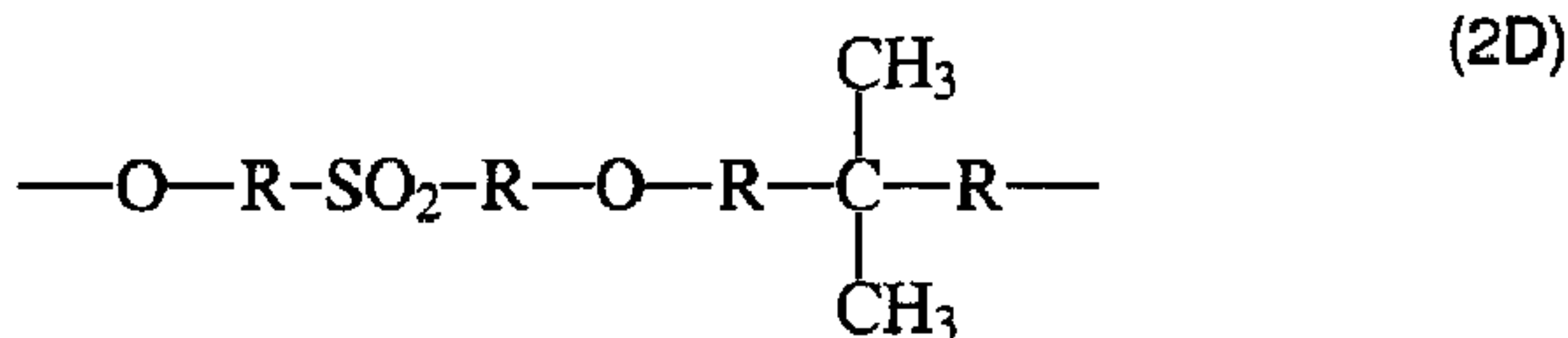
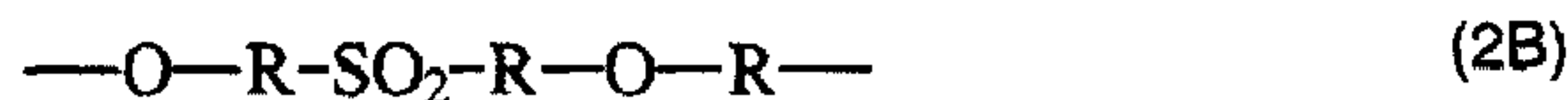
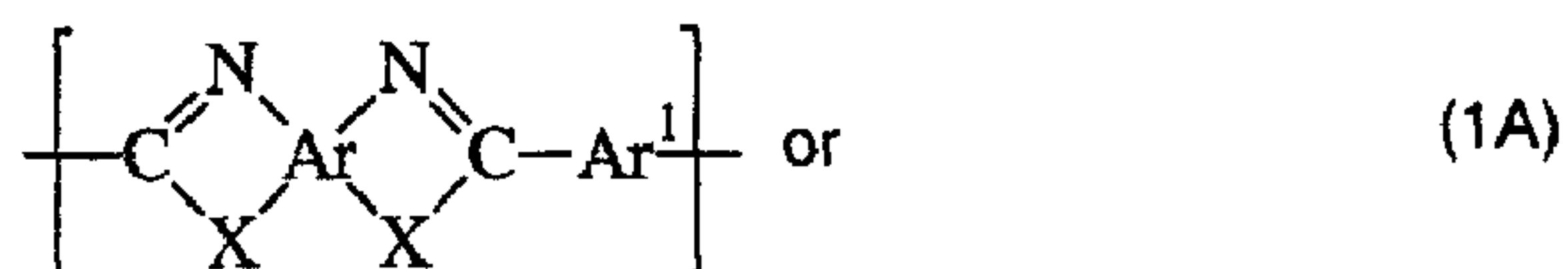




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(54) Titre : NOUVELLES MEMBRANES PRESENTANT DE MEILLEURES PROPRIETES MECANIKUES, DESTINEES A UN USAGE DANS DES PILES A COMBUSTIBLE
 (54) Title: NOVEL MEMBRANES HAVING IMPROVED MECHANICAL PROPERTIES, FOR USE IN FUEL CELLS



(57) Abrégé/Abstract:

The invention relates to an acid-doped, single-layer or multilayer polymer membrane comprising at least one layer A of a polymer blend comprising a) from 0.1 to 99.9% by weight of one or more polymers comprising recurring azole units of the formula 1 A

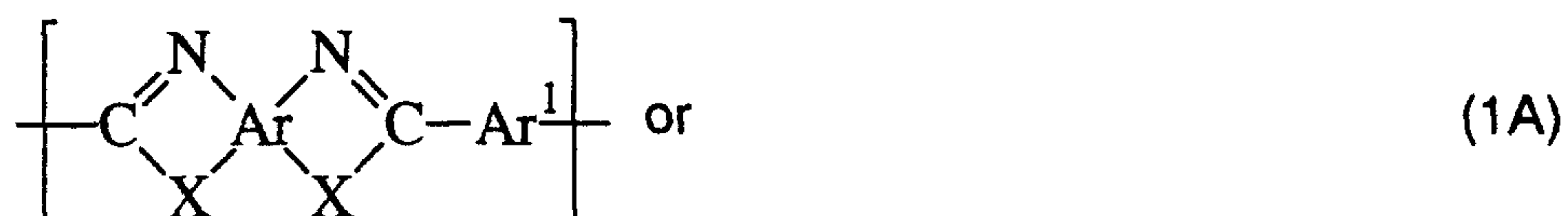
(57) **Abrégé(suite)/Abstract(continued):**

and/or 1 B: (see formula 1A) (see formula 1B) where the radicals Ar, Ar¹ and Ar² are tetravalent, divalent or trivalent aromatic or heteroaromatic groups and the radicals X, which are identical within a repeating unit, are each an oxygen atom, a sulfur atom or an amino group bearing a hydrogen atom, a group having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical, in admixture with b) from 99.9 to 0.1 % by weight of a polysulfone comprising recurring units of the formula 2A, 2B, 2C, 2D, 2E, 2F and/or 2G and having no sulfonic acid groups: (see formula 2A) (see formula 2B) (see formula 2C) (see formula 2D) (see formula 2E) (see formula 2F) (see formula 2G), where the radicals R are identical or different and are each, independently of one another, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 4,4'-biphenyl, a divalent radical of a heteroaromatic, a divalent radical of a C₁₀-aromatic and/or a divalent radical of a C₁₄-aromatic. Furthermore, a process for producing the doped polymer membrane, its use in fuel cells, in electrolysis, in capacitors, in battery systems and in electrochromic applications and also membrane electrode units comprising at least one polymer membrane according to the invention are described.

Abstract

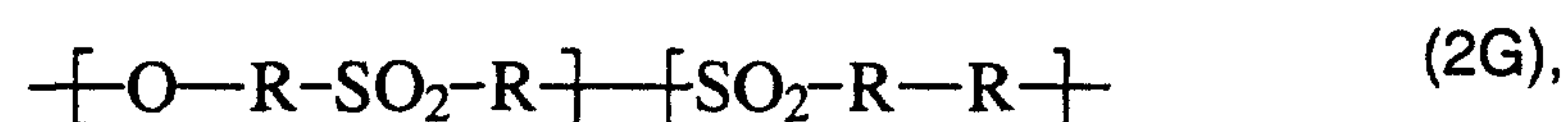
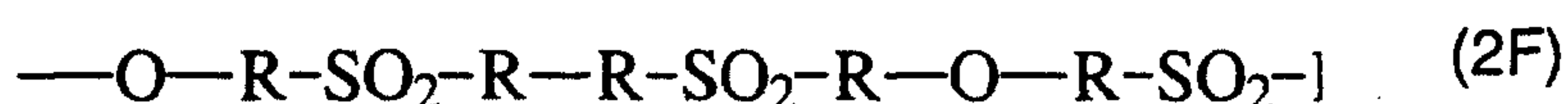
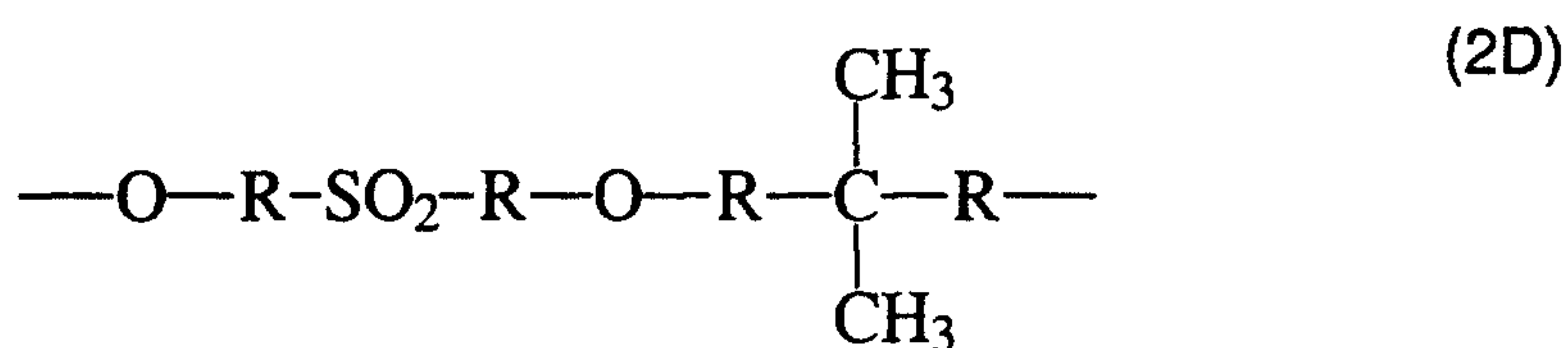
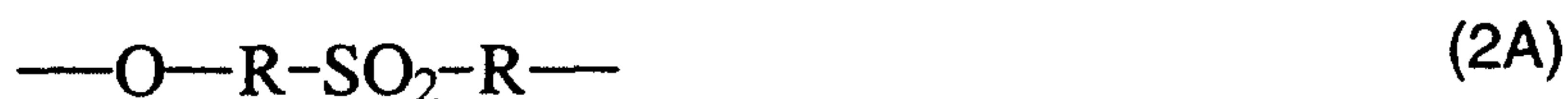
5 The invention relates to an acid-doped, single-layer or multilayer polymer membrane comprising at least one layer A of a polymer blend comprising

a) from 0.1 to 99.9% by weight of one or more polymers comprising recurring azole units of the formula 1A and/or 1B:



10 where the radicals Ar, Ar¹ and Ar² are tetravalent, divalent or trivalent aromatic or heteroaromatic groups and the radicals X, which are identical within a repeating unit, are each an oxygen atom, a sulfur atom or an amino group bearing a hydrogen atom, a group having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical, in admixture with

15 b) from 99.9 to 0.1% by weight of a polysulfone comprising recurring units of the formula 2A, 2B, 2C, 2D, 2E, 2F and/or 2G and having no sulfonic acid groups:



where the radicals R are identical or different and are each, independently of one another, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 4,4'-biphenyl, a divalent radical of a heteroaromatic, a divalent radical of a C₁₀-aromatic and/or a divalent
5 radical of a C₁₄-aromatic.

Furthermore, a process for producing the doped polymer membrane, its use in fuel cells, in electrolysis, in capacitors, in battery systems and in electrochromic applications and also membrane electrode units comprising at least one polymer
10 membrane according to the invention are described.

Description

Novel membranes having improved mechanical properties, for use in fuel cells

Acid-doped, single-layer or multilayer polymer membrane having layers comprising
5 polymer blends comprising polymers having recurring azole units, process for producing
such polymer membranes and their use.

The present invention concerns the field of polymer membranes. In particular, the
invention relates to an acid-doped polymer membrane. In addition, the invention relates
10 to a process for preparing the doped polymer membrane and to its use.

The polymer membrane which has been doped according to the invention can be used
in a variety of ways. Owing to its excellent mechanical properties, it is of particular
importance as a polymer membrane in fuel cells.

15 Polyazole membranes for use in fuel cells are already known. The basic membranes
are doped with concentrated phosphoric acid or sulfuric acid and serve as proton
conductors in polyelectrolyte membrane fuel cells (PEM fuel cells). Such membranes
allow the membrane electrode unit (MEE) to be operated at from 100°C to 200°C and in
20 this way significantly increase the tolerance of the catalyst to the carbon monoxide
formed as by-product in reforming, so that gas preparation or gas purification is
significantly simplified.

Disadvantages of these membranes are their mechanical instability with a low E
modulus, a low tear strength and a low upper flow limit and also their relatively high
25 permeability to hydrogen and oxygen.

Kerres, J. et al. (Kerres, Jochen; Ullrich, Andreas; Meier, Frank; Häring, Thomas
*„Synthesis and characterization of novel-acid-base polymer blends for application in
membrane fuel cells”* Solid State Ionics 125, 243 to 249, 1999) provide membranes of
sulfonated polyether ether ketone sPEEK[®] Victrex or polyether sulfone sPSU[®] Udel and
30 PSU[®] Udel which has been diaminated in the ortho position relative to the sulfone
bridge, poly(4-vinylpyridine), poly(benzimidazole) PBI[®] Celazole or poly(ethylenimine)
PEI. These membranes display good proton conductivity at an ion exchange capacity
IEC of 1 (IEC = meq of SO₃H/g of dry membrane) and a good thermal stability.

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However, they have the disadvantage that the conductivity of the membranes breaks down under atmospheric pressure above 100°C due to the loss of water. For this reason, these membranes cannot be used in fuel cells
5 above 100°C under atmospheric pressure.

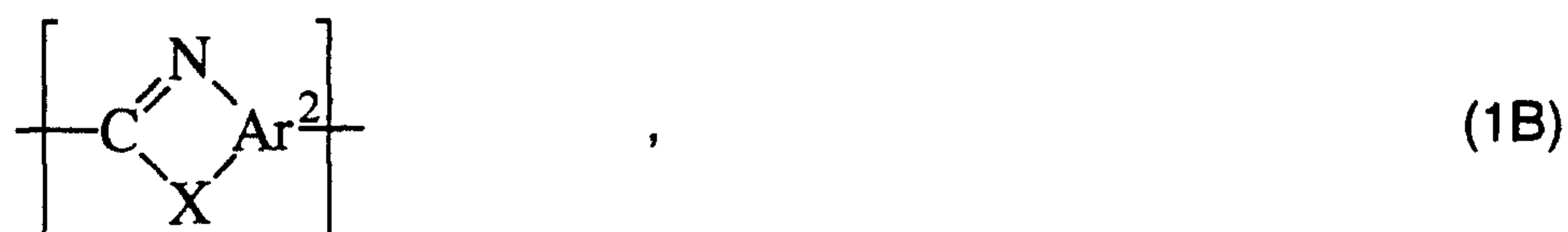
The present invention provides a doped polymer membrane having improved properties. The polymer membrane of the invention displays good proton conductivities and a low permeability to hydrogen and oxygen.

10 Further, there is provided a doped polymer membrane which can be used in fuel cells. In particular, the doped polymer membrane is suitable for use in fuel cells above 100°C under atmospheric pressure.

The invention also provides a process for
15 producing the doped polymer membrane, which process can be carried out in a simple way, inexpensively and on an industrial scale.

Provision of an acid-doped, single-layer or multilayer polymer membrane comprising at least one layer A
20 of a polymer blend comprising

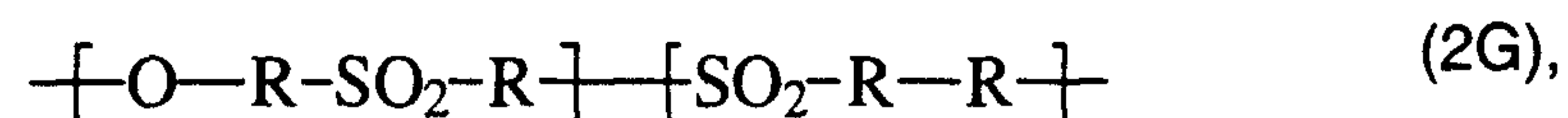
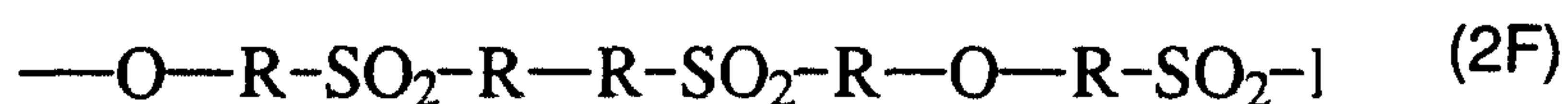
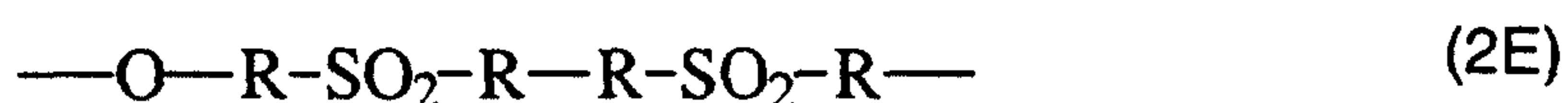
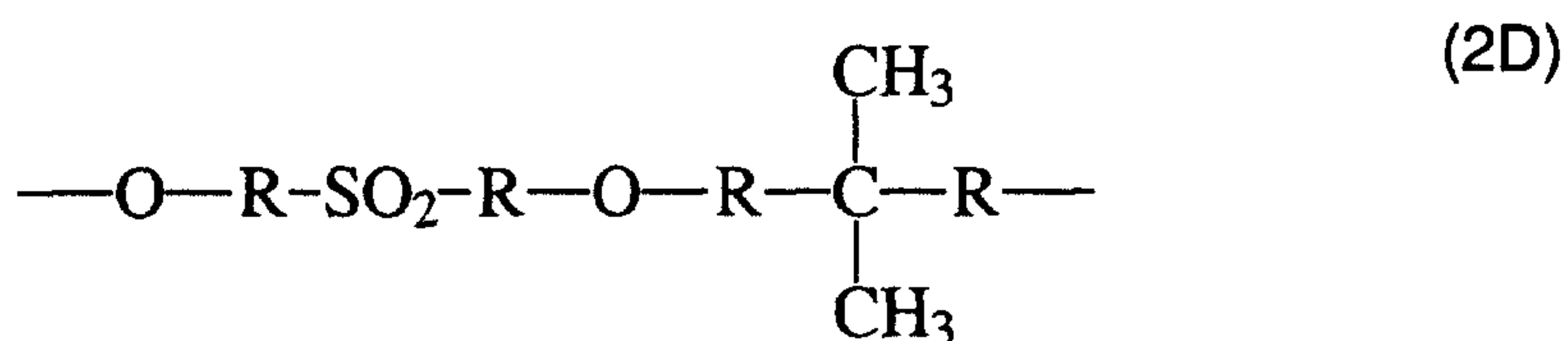
a) from 0.1 to 99.9% by weight of one or more polymers comprising recurring azole units of the formula 1A and/or 1B:



where the radicals Ar, Ar¹ and Ar² are tetravalent, divalent or trivalent aromatic or heteroaromatic groups and the radicals X, which are identical within a repeating unit, are each an oxygen atom, a sulfur atom or an amino group bearing a hydrogen atom, a group having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical, in admixture with

5

b) from 99.9 to 0.1% by weight of a polysulfone comprising recurring units of the formula 2A, 2B, 2C, 2D, 2E, 2F and/or 2G and having no sulfonic acid groups:



where the radicals R are identical or different and are each, independently of one another, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 4,4'-biphenyl, a divalent radical of a heteroaromatic, a divalent radical of a C₁₀-aromatic and/or a divalent radical of a C₁₄-aromatic,

10

makes it possible, in a manner which could not readily have been foreseen, to obtain a doped polymer membrane having improved mechanical properties, in particular an increased E modulus and improved fracture strength.

5 At the same time, the doped polymer membranes of the invention display a series of further advantages. These include, inter alia:

⇒ The doped polymer membranes display good proton conductivities.

10 ⇒ The doped polymer membranes have only a low permeability to hydrogen and oxygen.

⇒ Even extremely thin, doped polymer membranes having a total thickness in the range from 10 to 100 μm have sufficiently good material properties at 100°C, in particular a very high mechanical stability and a low permeability to hydrogen and oxygen.

15 ⇒ The property profile of the doped polymer membrane can be improved further by means of a multilayer structure.

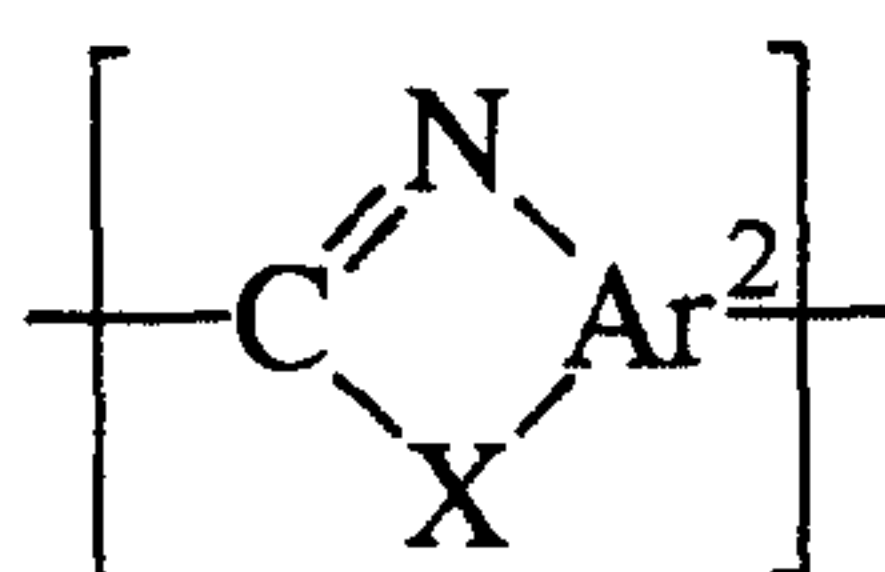
⇒ The doped polymer membrane is suitable for use in fuel cells above 100°C, in particular under atmospheric pressure.

20 ⇒ Partial replacement of the comparatively expensive polyazole by comparatively cheap polysulfone provides a doped polymer membrane which is cheaper to produce.

⇒ The doped polymer membrane can be produced in a simple way and on an industrial scale.

25 According to the present invention, the polymer membrane comprises at least one layer A of a polymer blend which comprises from 0.1 to 99.9% by weight of one or more polymers comprising recurring azole units of the formula 1A and/or 1B:





(1B).

The radicals Ar, Ar¹ and Ar² are tetravalent, divalent or trivalent aromatic or heteroaromatic groups which may each have one or more rings. Preferred groups are derived from benzene, naphthalene, biphenyl, diphenyl ether, diphenylmethane, diphenyldimethylmethane, bisphenone, diphenyl sulfone, quinoline, pyridine, anthracene and phenanthrene, which may also be substituted. Ar¹ can have any substitution pattern; in the case of phenylene, Ar¹ can be, for example, ortho-, meta- or para-phenylene. Particularly preferred groups are derived from benzene and biphenyl which may also be substituted.

The radicals X are each an oxygen atom (benzoxazole unit), a sulfur atom (benzothiazole unit) or an amino group (benzimidazole unit) bearing a hydrogen atom, a group having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical. Preferred alkyl groups are short-chain alkyl groups having from 1 to 4 carbon atoms, e.g. methyl, ethyl, n- or i-propyl and t-butyl groups. Preferred aromatic groups are phenyl or naphthyl groups. The alkyl groups and the aromatic groups may be substituted. Preferred substituents are halogen atoms such as fluorine, amino groups or short-chain alkyl groups such as methyl or ethyl groups.

If polyazoles comprising recurring units of the formula (1A) are used for the purpose of the present invention, the radicals X should be identical within a recurring unit.

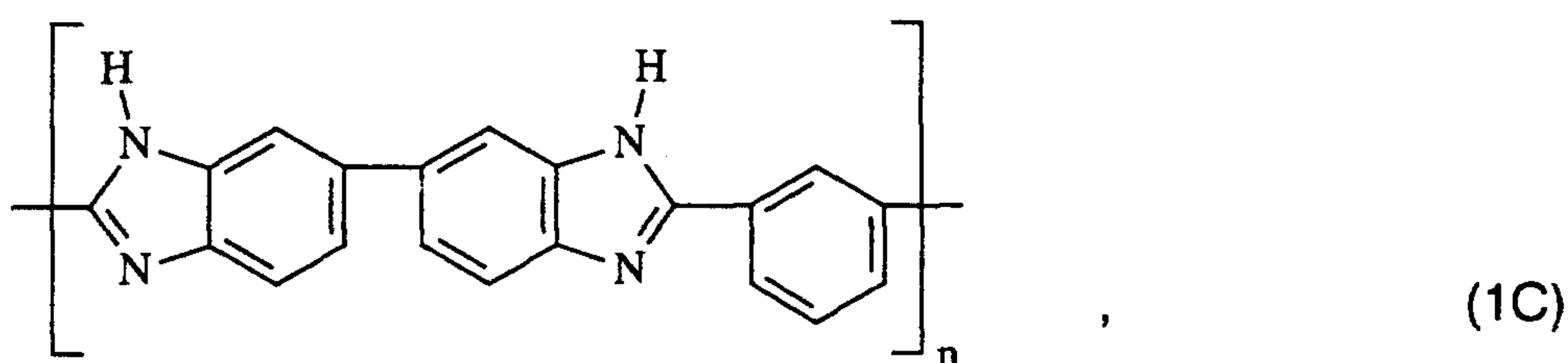
A polyazole used for the purposes of the invention can in principle comprise different recurring units which, for example, differ in their radical X. However, it preferably has only identical recurring units.

In a preferred embodiment of the present invention, the polymer comprising recurring azole units is a copolymer comprising at least two units of the formula (IA) and/or (IB) which differ from one another.

In a particularly preferred embodiment of the present invention, the polymer comprising recurring azole units is a polyazole consisting of only units of the formula (1A) and/or (1B).

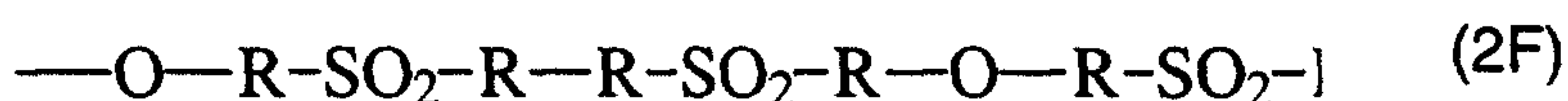
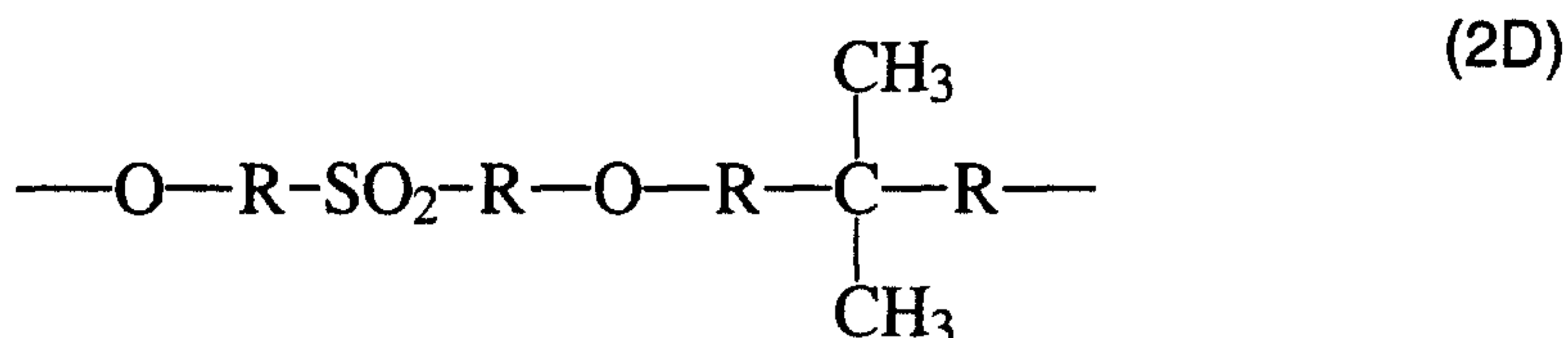
- 5 The number of recurring azole units in the polymer is preferably greater than or equal to 10. Particularly preferred polymers contain at least 100 recurring azole units.

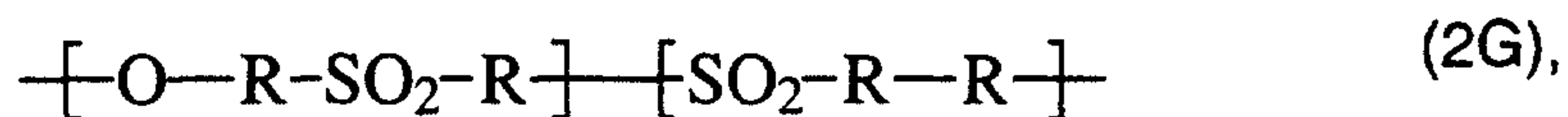
For the purposes of the present invention, preference is given to using polymers comprising recurring benzimidazole units. An example of an extremely advantageous polymer comprising recurring benzimidazole units is represented by the formula (1C):



where n is an integer greater than or equal to 10, preferably greater than or equal to 100.

According to the present invention, the polymer blend comprises from 99.9 to 0.1% by weight of a polysulfone which contains no sulfonic acid groups. The polysulfone comprises recurring units having linking sulfone groups corresponding to the formulae 2A, 2B, 2C, 2D, 2E, 2F and/or 2G:





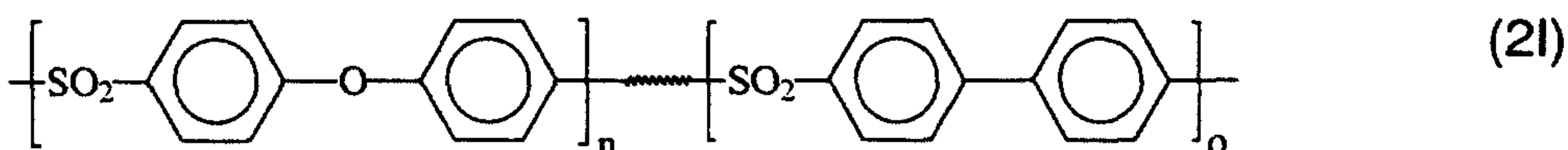
where the radicals R are identical or different and are each, independently of one another, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 4,4'-biphenyl, a divalent radical of a heteroaromatic, a divalent radical of a C₁₀-aromatic and/or a divalent radical of a C₁₄-aromatic. Examples of heteroaromatics are pyridine and quinoline. An example of a C₁₀-aromatic is naphthalene, and an example of a C₁₄-aromatic is phenanthrene.

Polysulfones which are preferred for the purposes of the present invention include homopolymers and copolymers, for example random copolymers such as [®]Victrex 720 P and [®]Astrel. Particularly preferred polysulfones are:

[®]Victrex 200 P

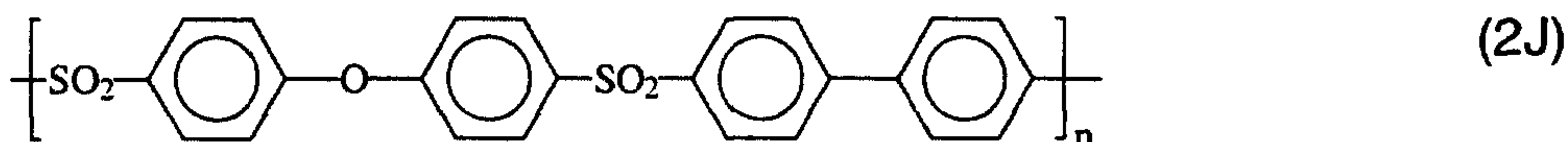


[®]Victrex 720 P

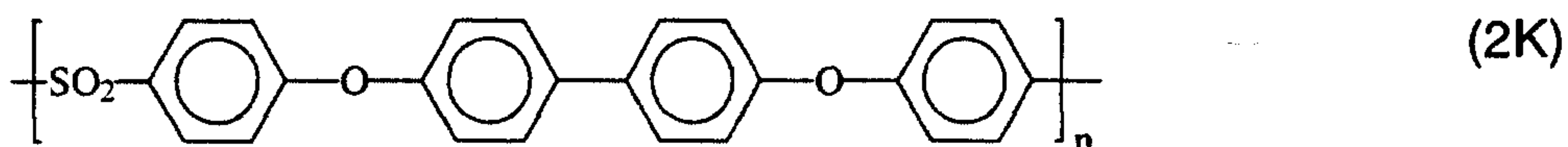


where $n > o$

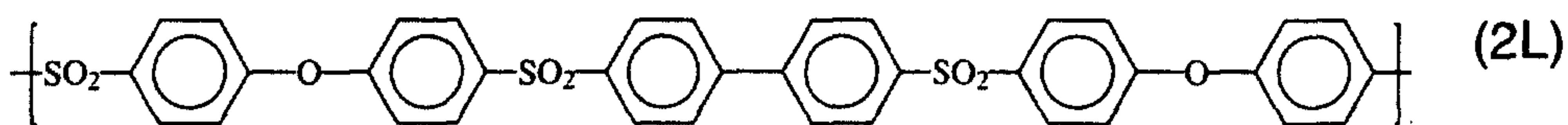
[®]Radel



[®]Radel R

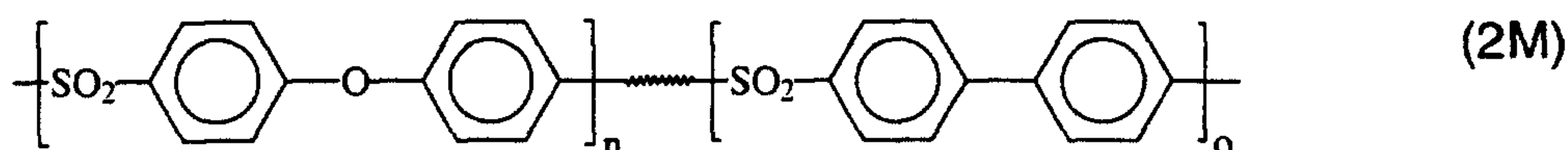


[®]Victrex HTA



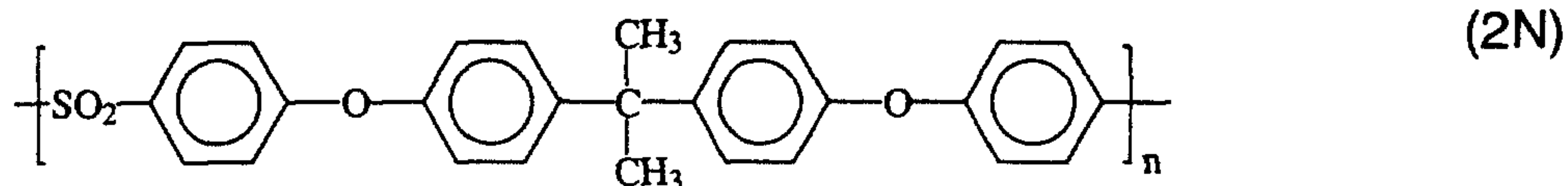
[®]Astrel

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where $n < o$

®Udel



A very particularly preferred polysulfone is ®Radel R.

The polysulfones which can be used according to the invention may, if desired, be substituted. However, they must contain neither protonated sulfonic acid groups



5 nor protonatable sulfonic acid salt groups



where M^+ is an inorganic or organic cation, because these can impair the mechanical properties of the doped polymer membrane.

10 In a preferred embodiment of the present invention, the polysulfones are unsubstituted.

In another preferred embodiment of the present invention, the number average molecular weight of the polysulfones is greater than 30 000 g/mol.

15 The polymer membranes of the invention are doped. For the purposes of the present invention, doped polymer membranes are polymer membranes which due to the presence of dopants display an increased proton conductivity compared to the undoped polymer membranes. Dopants for the polymer membranes of the invention are acids. In this context, acids include all known Lewis and Brønsted acids, preferably inorganic Lewis and Brønsted acids. Furthermore, the use of polyacids, in particular isopolyacids and heteropolyacids and of mixtures of various acids is also possible. For the purposes
20 of the present invention, heteropolyacids are inorganic polyacids having at least two different central atoms which are formed from weak, polybasic oxo acids of a metal

(preferably Cr, Mo, V, W) and of a nonmetal (preferably As, I, P, Se, Si, Te) as partial mixed anhydrides. They include, inter alia, 12-molybdophosphoric acid and 12-tungstophosphoric acid.

5 Particularly preferred dopants according to the invention are sulfuric acid and phosphoric acid. A very particularly preferred dopant is phosphoric acid (H_3PO_4).

The degree of doping can be used to influence the conductivity of the polymer membrane of the invention. The conductivity increases with increasing concentration of the dopant until a maximum value is reached. According to the invention, the degree of
10 doping is reported as mol of acid per mole of repeating unit of the polymer. For the purposes of the present invention, a degree of doping of from 3 to 15, in particular from 6 to 12, is preferred.

15 The property spectrum of the polymer membrane of the invention can be altered by varying its composition. In a preferred embodiment of the present invention, the polymer blend comprises

a) from 50 to 99% by weight of a polymer comprising recurring azole units of the formula 1A and/or 1B,

20 in admixture with

b) from 1 to 50% by weight of a polysulfone which has no sulfonic acid groups.

In a particularly preferred embodiment of the present invention, the polymer blend comprises

25 a) from 70 to 95% by weight of a polymer comprising recurring azole units of the formula 1A and/or 1B,

in admixture with

b) from 5 to 30% by weight of a polysulfone which has no sulfonic acid groups.

30 The doped polymer membrane has a single-layer or multilayer structure. A multilayer structure enables its material properties such as the E modulus, the tensile strength and the proton conductivity to be varied in a desired way. The polymer membrane of the invention preferably comprises at least two layers A and B which are each obtainable

from the polymer blend according to the invention and differ from one another in the content of polysulfone b). In addition, it is particularly advantageous for the thicknesses of the two layers A and B also to be different.

5 According to the invention, particular preference is given to a doped polymer membrane which comprises at least three layers A, B and C which are each obtainable from the polymer blend according to the invention, with the middle layer C differing from the two outer layers A and B in the content of polysulfone b). Variation of the layer thicknesses can likewise be advantageous. In a particularly preferred embodiment of the present
10 invention, the doped polymer membrane comprises three layers A, B and C. Here, the outer layers A and B are thinner than the middle layer C and have a higher content of polysulfone b) than the middle layer C. In a very particularly preferred embodiment of the present invention, the middle layer C contains no polysulfone.

15 The properties of the polymer membrane of the invention can be controlled to some extent by its total thickness. However, even extremely thin polymer membranes have very good mechanical properties and a low permeability to water and oxygen. They are therefore suitable for use in fuel cells at above 100°C, in particular for use in fuel cells at above 120°C, without the edge region of the membrane electrode unit having to be
20 reinforced. The total thickness of the doped polymer membrane of the invention is preferably in the range from 5 to 100 μm , advantageously from 10 to 90 μm , in particular from 20 to 80 μm .

The polymer membrane of the invention has improved material properties compared to
25 the previously known doped polymer membranes. In particular, it has very good mechanical properties and a low permeability to hydrogen and oxygen. In a particularly preferred embodiment of the present invention, its proton conductivity at room temperature is above 30 mS/cm and its E modulus after 10 minutes at 100°C is greater than 10 MPa.

30 Processes for preparing doped polymer membranes are known. In a preferred embodiment of the present invention, they are obtained by wetting a polymer blend according to the invention with concentrated acid, preferably highly concentrated

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phosphoric acid, for an appropriate time, preferably 0.5-96 hours, particularly preferably 1-72 hours, at temperatures in the range from room temperature to 100°C and atmospheric or superatmospheric pressure.

5 For the purposes of the present invention, "polymer blends" are physical mixtures of polymers. Processes for preparing polymer blends are known. They can be obtained, for example, from a solution containing the polymers to be blended by evaporation of the solvent. The evaporation of the solvent is preferably carried out in such a way that a self-supporting and preferably transparent film is obtained. For the purposes of the present invention, N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide, 10 N-methylpyrrolidone or mixtures of these solvents are preferably used.

Possible applications of the doped polymer membranes of the invention include, inter alia, the use in fuel cells, in electrolysis, in capacitors and in battery systems. Owing to 15 their property profile, the doped polymer membranes are preferably used in fuel cells.

The present invention also provides a membrane electrode unit which comprises at least one polymer membrane according to the invention. For further information on membrane electrode units, reference may be made to the technical literature, in particular the patents US 4,191,618, US 4,212,714 and US 4,333,805. 20

The invention is illustrated below by means of examples and comparative examples, without the invention being restricted to these examples.

1. Example

25 a) Preparation of a PBI-DMAc solution

®Celazole from Celanese is dissolved in N,N-dimethylacetamide (15% by weight of Celazole) at a temperature of 200 °C over a period of 2-4 hours.

b) Preparation of a polysulfone solution

30 Polysulfone ®Radel-R 5700 from Amoco (or polyether sulfone ®Ultrason E 6000 from BASF) is dissolved in N,N-dimethylacetamide or N-methylpyrrolidone (15% by weight). The polysulfone solution is filtered through a pressure filter at room temperature.

c) Preparation of the polymer mixture in solution

The PBI-DMAc solution and the polysulfone solution are mixed by means of a slow-running anchor stirrer at a temperature of 60-95°C. Lower temperatures or high rotational speeds of the stirrer lead, as a result of the Weissenberg effect which is displayed by the polybenzimidazole solution, to at least partial demixing of the solution. The mixed solution is degassed by application of a vacuum for a period of at least 15 minutes at a temperature of 80°C.

d) Production of the polymer membrane

The solution is applied in a thickness of about 250 μm by means of a doctor blade to a glass plate in a low-dust environment (laminar flow box) and dried at temperatures of up to 120°C in a convection drying oven provided with a dust filter. The dried polymer membrane is peeled off from the glass plate.

e) Doping of the polymer membrane

The membrane is wetted with 85% strength phosphoric acid for 72 hours at room temperature.

2. Comparative example

Victrex polyether ketone (PEK) is, as described in DE 19847782 A1 20000420, converted into the sulfonated product. The sulfonated product has a degree of sulfonation of 42%. The sulfonic acid polymer is converted into the sodium salt by stirring overnight in 5% strength aqueous sodium hydroxide at 50°C, filtered off, washed and dried.

The sulfonic acid polymer is dissolved in N,N-dimethylacetamide or N-methylpyrrolidone (15% by weight). The polysulfone solution is filtered through a pressure filter at room temperature.

The dissolution of the polymer is carried out in a manner analogous to 1.b). Conversion of the sodium salt into the free acid is carried out by treatment of the blend membrane with phosphoric acid. The preparation of the polymer mixture in solution, the production

of the polymer membrane and the doping of the membrane are carried out by methods analogous to those in the above example.

3. Determination of the phosphoric acid concentration

5 The doped membranes are stirred overnight in precisely 1 l of distilled water. They are then taken from the water and dried at 150°C and 20-50 mbar for 3 hours. The dried membranes are weighed. The acid content of the water is determined by titration with a standard solution of sodium hydroxide.

10 The number of acid molecules per repeating unit of the respective polymer is calculated from the dry mass of the membrane and the titration data. The results obtained are summarized in table 1.

Table 1: Degree of doping of the polymer membrane

Sample	Blending component [%]	H ₃ PO ₄ /repeating unit of the polymer
E 1	5% PES	9.26
E 2	10% PES	8.75
E 3	20% PES	8.44
E 4	5% PSU	9.29
E 5	10% PSU	8.92
E 6	20% PSU	7.75
CE 1	0%	9.35
CE 2	5% sPEK	9.85
CE 3	10% sPEK	9.51
CE 4	20% sPEK	8.76

15 E: Example; CE: Comparative example

4. Measurement of the conductivity

Measurements were carried out at room temperature by means of a 4-pole arrangement using platinum electrodes (wire, 0.25 mm diameter) and a Zahner IM 6 impedance spectrometer. The spectrum obtained is fitted using a simple model consisting of a

parallel circuit, a capacitor and a resistance. The dimensions of the sample were determined prior to doping. The results are shown in table 2.

Table 2: Conductivity measurements

Sample	Blending component	Fitting results			Membrane				Conductivity [S/cm]
		R [ohm]	Error [%]	C _{par} [pF]	Thickness [cm]	Error [%]	Width [cm]	Error [%]	
E 1	5% PES	2004	2.67	102.2	3.2E-03	1.0	3.5	3.0	0.0891
E 2	10% PES	2293	2.45	119.7	3.1E-03	1.0	3.5	3.0	0.0804
E 3	20% PES	2756	3.21	131.4	2.8E-03	1.0	3.5	3.0	0.074
E 4	5% PSU	2395	1.58	120.5	3.3E-03	1.0	3.5	3.0	0.072
E 5	10% PSU	2392	2.77	127.9	3.3E-03	1.0	3.5	3.0	0.072
E 6	20% PSU	2923	2.06	126.5	3.0E-03	1.0	3.5	3.0	0.065
CE 1	0	2091	2.72	115.9	2.9E-03	1.0	3.5	3.0	0.094
CE 2	05% sPEK	2485	1.29	122.8	2.9E-03	1.0	3.5	3.0	0.079
CE 3	10% sPEK	2797	0.72	123.0	2.7E-03	1.0	3.5	3.0	0.076
CE 4	20% sPEK	3191	2.64	129.1	3.2E-03	1.0	3.5	3.0	0.056

E: Example; CE: Comparative example

PSU (Radel R5700); PES (Ultrason E6000); PEK [M420 (Op.3/99) Na salt]

5. Measurement of the mechanical properties

5 The mechanical properties are determined in a uniaxially tensile test on a Zwick testing machine (100 N load cell). The geometry of the test specimen is determined in the undoped state. The specimen width in the undoped state is 15 mm, and the specimen length between the pneumatically operated chucks is 100 mm. The initial force is 0.1 N, and the test is carried out at a speed of 100 mm/min.

10 The samples are installed in the sample chamber preheated to 100°C, the sample chamber is closed and the measurement is started after precisely 10 minutes. Table 3 summarizes the results.

Table 3: Measurement of the mechanical properties

Sample	E modulus [MPa]	Fracture toughness [J/m ²]	Elongation at F _{max} [%]	R _{max} [N/mm ²]
E 1	8.67	37733	24.41	1.75
E 2	8.32	32590	27.80	1.67
E 3	8.04	47931	33.14	1.99
E 4	7.21	41715	27.25	1.60
E 5	9.81	22473	20.22	1.62
E 6	22.59	190428	55.90	4.66
E 1	7.71	23263	22.06	1.51
CE 2	8.27	47650	33.08	1.97
E 3	7.52	37561	27.87	1.93
CE 4	6.65	47483	38.68	1.72

E: Example; CE: Comparative example

15 F_{max}: Maximum force in the tensile stress/elongation curve

R_{max}: Ultimate tensile strength

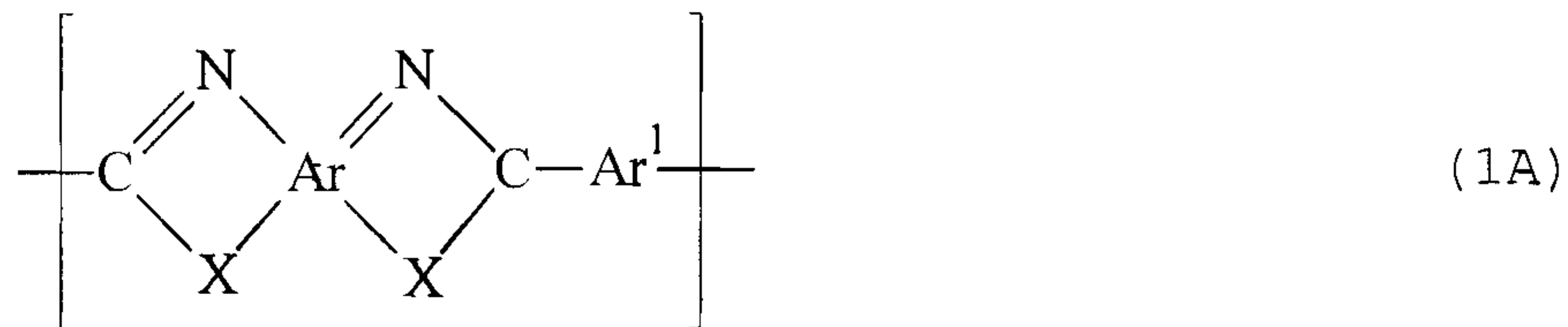
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CLAIMS:

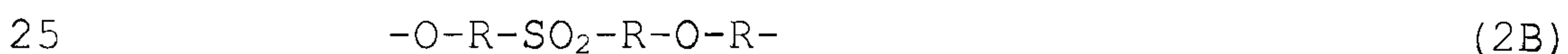
1. An acid-doped, single-layer or multilayer polymer membrane comprising at least one layer A of a polymer blend, comprising:

- 5 (a) from 0.1 to 99.9% by weight of one or more polymers comprising recurring azole units of the general formula (1A), (1B) or both:



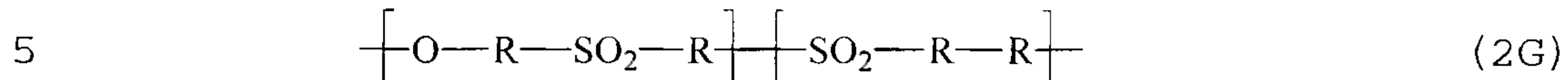
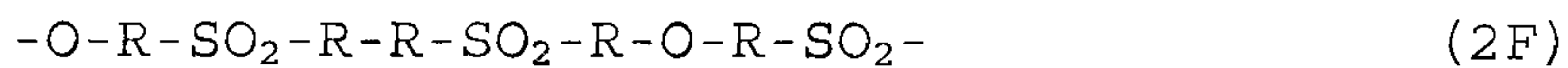
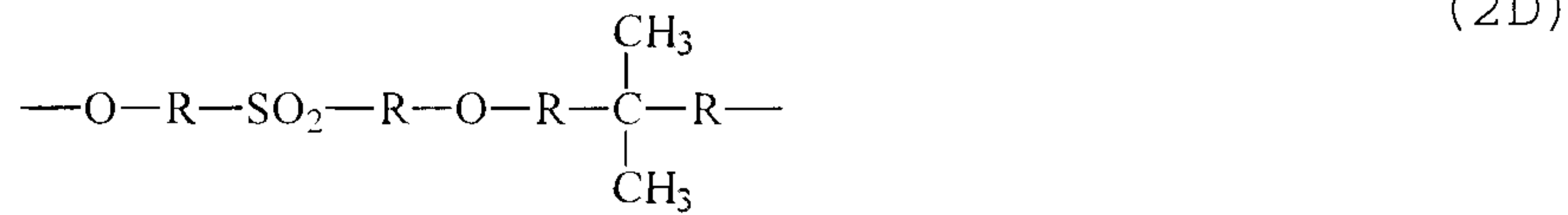
wherein the radicals Ar, Ar¹ and Ar² are tetravalent, 15 divalent or trivalent aromatic or heteroaromatic groups and the radicals X, which are identical within a repeating unit, are each an oxygen atom, a sulfur atom, an amino group bearing a hydrogen atom, a group having 1-20 carbon atoms or an aryl group, in admixture with

- 20 (b) from 99.9 to 0.1% by weight of a polysulfone comprising recurring units of the general formula (2A), (2B), (2C), (2D), (2E), (2F), (2G) or a combination thereof and having no sulfonic acid groups:



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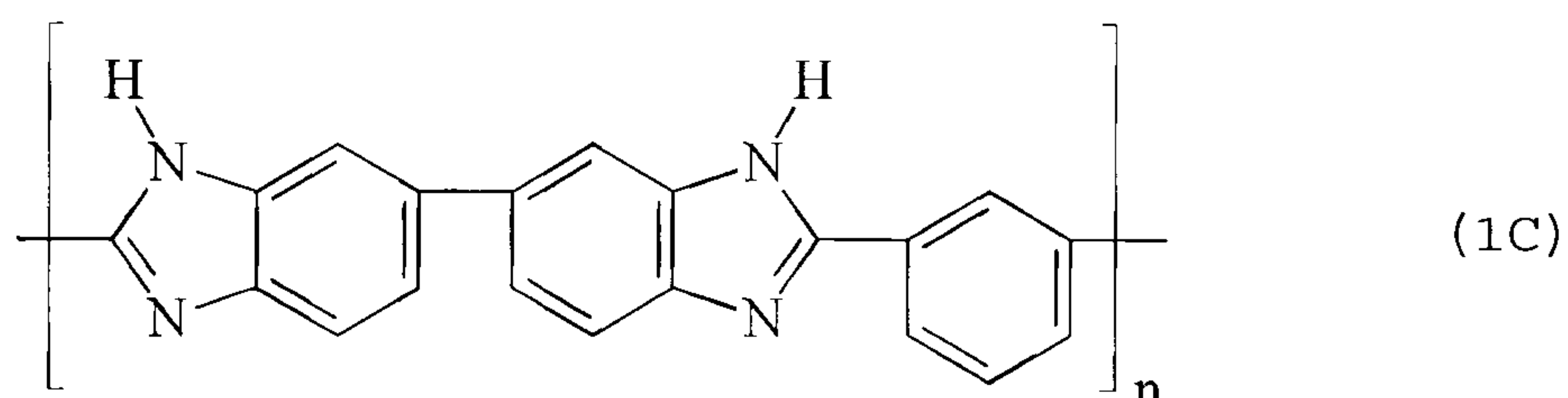
wherein the radicals R are identical or different and are each, independently of one another, 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 4,4'-biphenyl, a divalent radical of a heteroaromatic, a divalent radical of a C₁₀-aromatic or a divalent radical of a C₁₄-aromatic.

2. A doped polymer membrane as claimed in claim 1, wherein for X the group having 1 to 20 carbon atoms is a branched or unbranched alkyl or alkoxy group.

3. A doped polymer membrane as claimed in claim 1 or 2, wherein the number of recurring azole units in the polymer is greater than or equal to 10.

4. A doped polymer membrane as claimed in claim 3, wherein the number of repeating units in the polymer is greater than 100.

20 5. A doped polymer membrane as claimed in any one of claims 1 to 4, wherein the polymer (a) is a polymer comprising recurring benzimidazole units of the formula (1C):

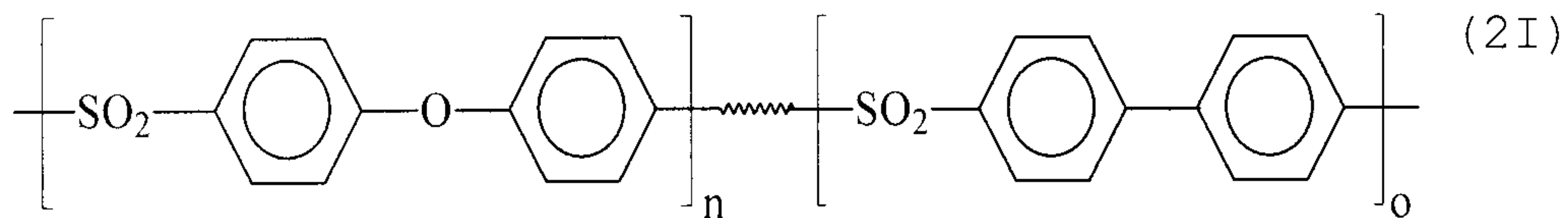
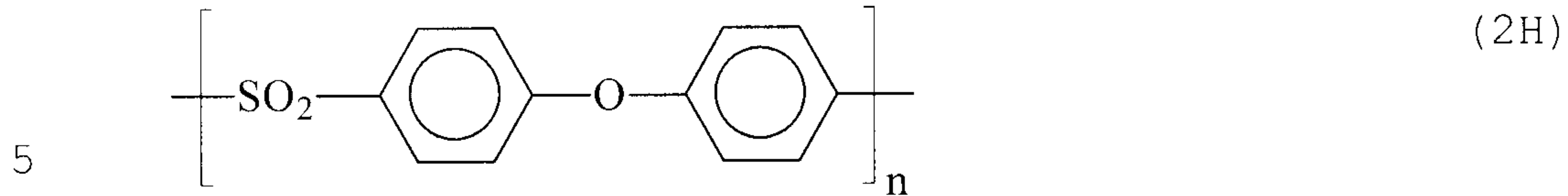


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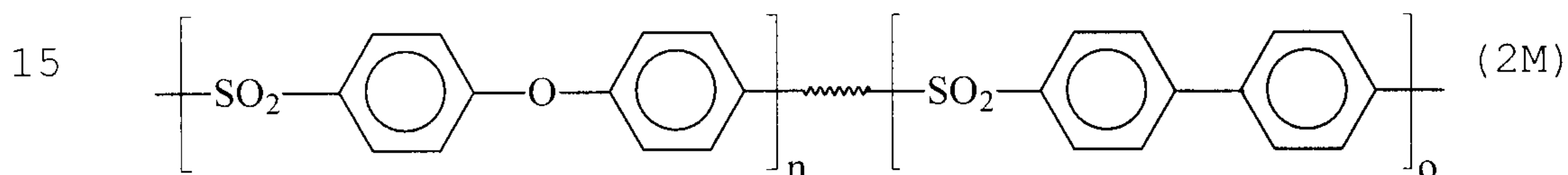
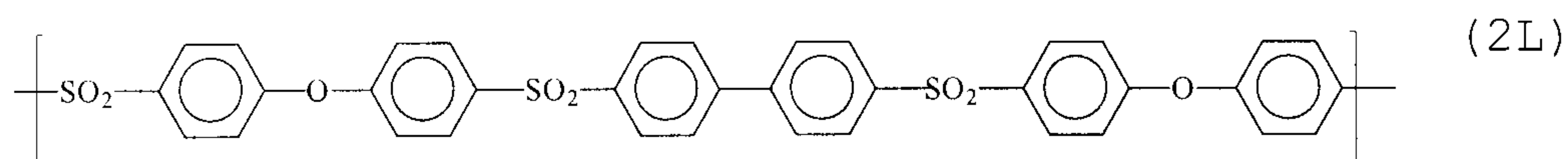
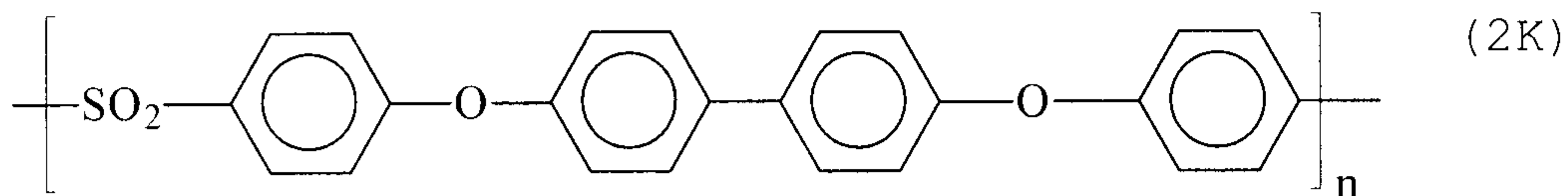
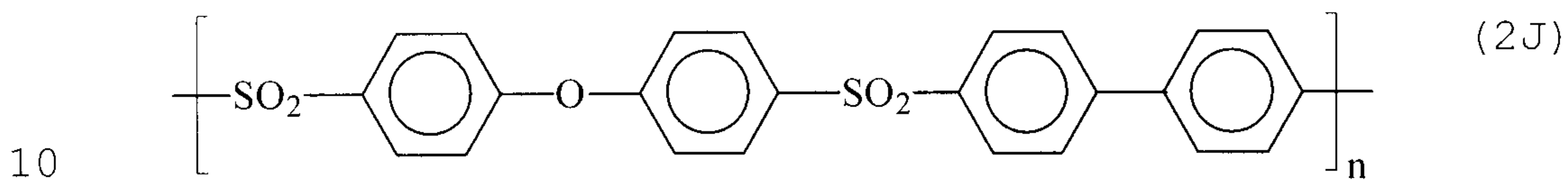
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where n is an integer greater than or equal to 10.

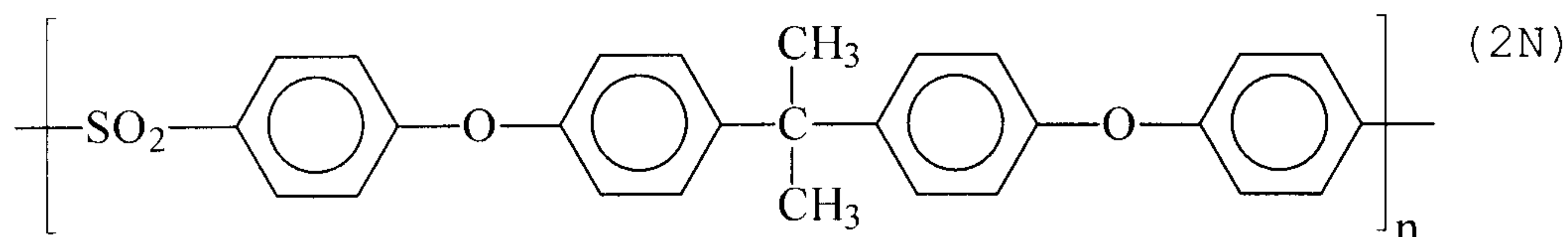
6. A doped polymer membrane as claimed in any one of claims 1 to 5, wherein the polysulfone is:



wherein $n > o$



wherein $n < o$



20

7. A doped polymer membrane as claimed in claim 6, wherein the polysulfone is (2K).

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8. A doped polymer membrane as claimed in any one of claims 1 to 7, which is doped with an inorganic Lewis or Brønsted acid.

9. A doped polymer membrane as claimed in claim 8,
5 wherein the acid is hydrochloric acid, sulfuric acid, phosphoric acid or a mixture thereof.

10. A doped polymer membrane as claimed in any one claims 1 to 9, wherein the polymer blend comprises:

from 50 to 99% by weight of (a) in admixture with,

10 from 1 to 50% by weight of (b).

11. A doped polymer membrane as claimed in any one of claims 1 to 10, which comprises at least two layers A and B which are each obtained from a polymer blend as defined in any one of claims 1 to 10, and differ from one another in
15 the content of polysulfone (b).

12. A doped polymer membrane as claimed in claim 11, wherein the layers A and B also differ in their thickness.

13. A doped polymer membrane as claimed in any one of claims 1 to 10, which comprises at least three layers A, B
20 and C, in the form ACB, which are each obtained from a polymer blend as defined in any one of claims 1 to 10, with the middle layer C differing from the two outer layers A and B in the content of polysulfone (b).

14. A doped polymer membrane as claimed in claim 13,
25 wherein the middle layer C contains no polysulfone (b).

15. A doped polymer membrane as claimed in any one of claims 1 to 14, which has a total thickness of from 5 to 100 μm .

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16. A doped polymer membrane as claimed in any one of claims 1 to 15, which has a proton conductivity at room temperature above 30 mS/cm and which has an E modulus after 10 minutes at 100°C greater than 10 MPa.
- 5 17. A process for producing a doped polymer membrane as claimed in any one of claims 1 to 16, which comprises wetting a polymer blend as defined in any one of claims 1 to 16 with a concentrated acid for an appropriate time at a temperature in the range from room temperature to 100°C and
10 at atmospheric or superatmospheric pressure.
18. Use of a doped polymer membrane as claimed in any one of claims 1 to 16, in a fuel cell, in electrolysis, in a capacitor or in a battery system.
19. The use as claimed in claim 18, in a fuel cell.
- 15 20. A membrane electrode unit comprising at least one polymer membrane as claimed in any one of claims 1 to 16.

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PATENT AGENTS

