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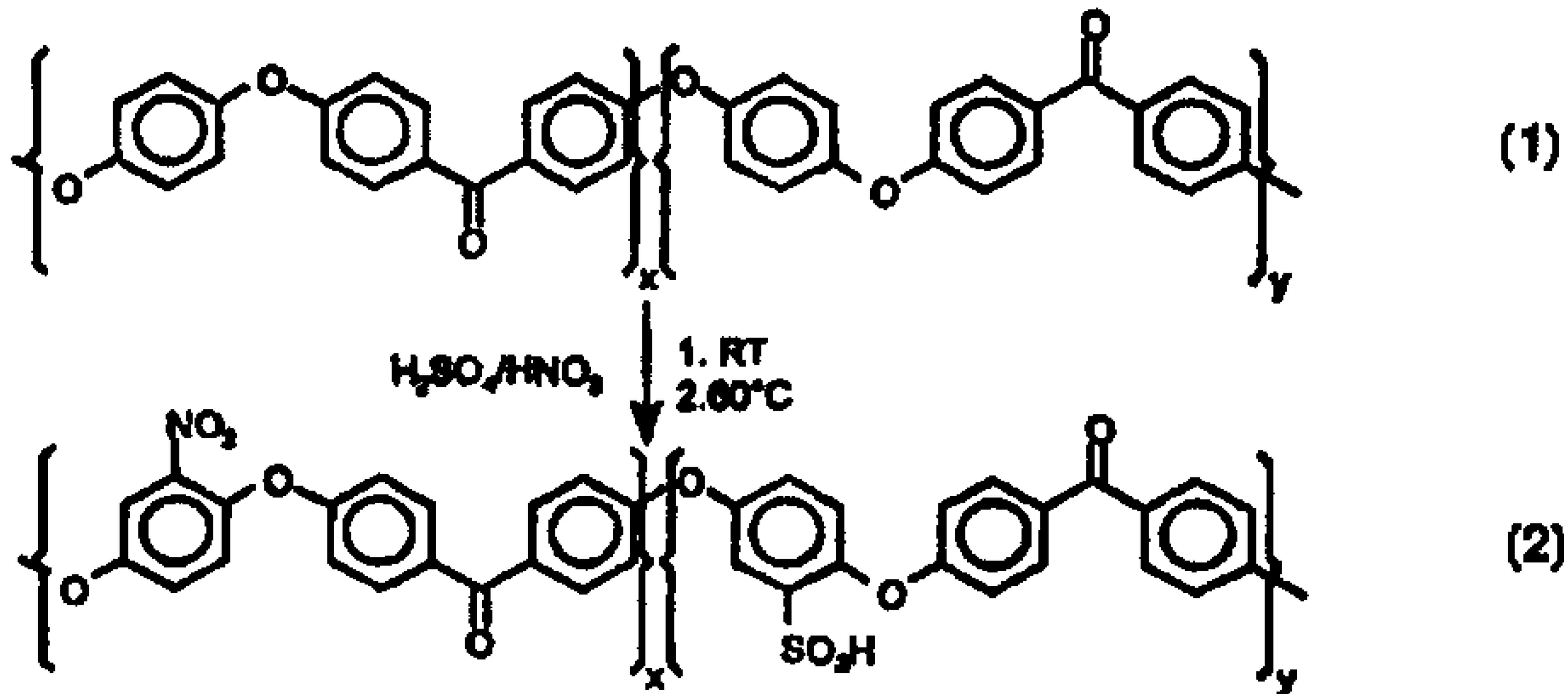
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(54) Titre : POLYMERIE MODIFIEE ET MEMBRANE POLYMERIE MODIFIEE

(54) Title: MODIFIED POLYMER AND MODIFIED POLYMER MEMBRANE



(57) Abrégé/Abstract:

The invention relates to a method for producing nitrated and optionally sulphonated and aminated and optionally sulphonated aryl main chain polymers, in addition to aryl main chain polymers thus modified. Aryl main chain polymers (e.g. (1)) are nitrated by dissolving them in expensive, toxic and environmentally damaging solvents. Aryl main chain polymers which are selectively and simultaneously nitrated and sulphonated were not previously known in literature. The inventive method makes it possible to produce low-cost nitrated (and optionally sulphonated (2)) or post-reduction aminated (and optionally sulphonated) aryl main chain polymers without any organic solvents. Nitration (and optionally additional sulphonation) of the aryl main chain polymers occurs by dissolving them in concentrated sulphuric acid and by adding desired amounts of nitric acid at different temperatures and with different agitating times. The reaction can be carried out (a) as a two-step process: nitration followed by isolation of the polymer, then optional sulphonation and (b) as a single-step process: simultaneous nitration and sulphonation (2). The nitrated (or additionally sulphonated) polymers can then be reduced to form aminated (or additionally sulphonated) polymer. The polymers can be reacted with other polymers to form polymer blends. The polymers and polymer blends can be used as ion conducting membranes in electro membrane processes.

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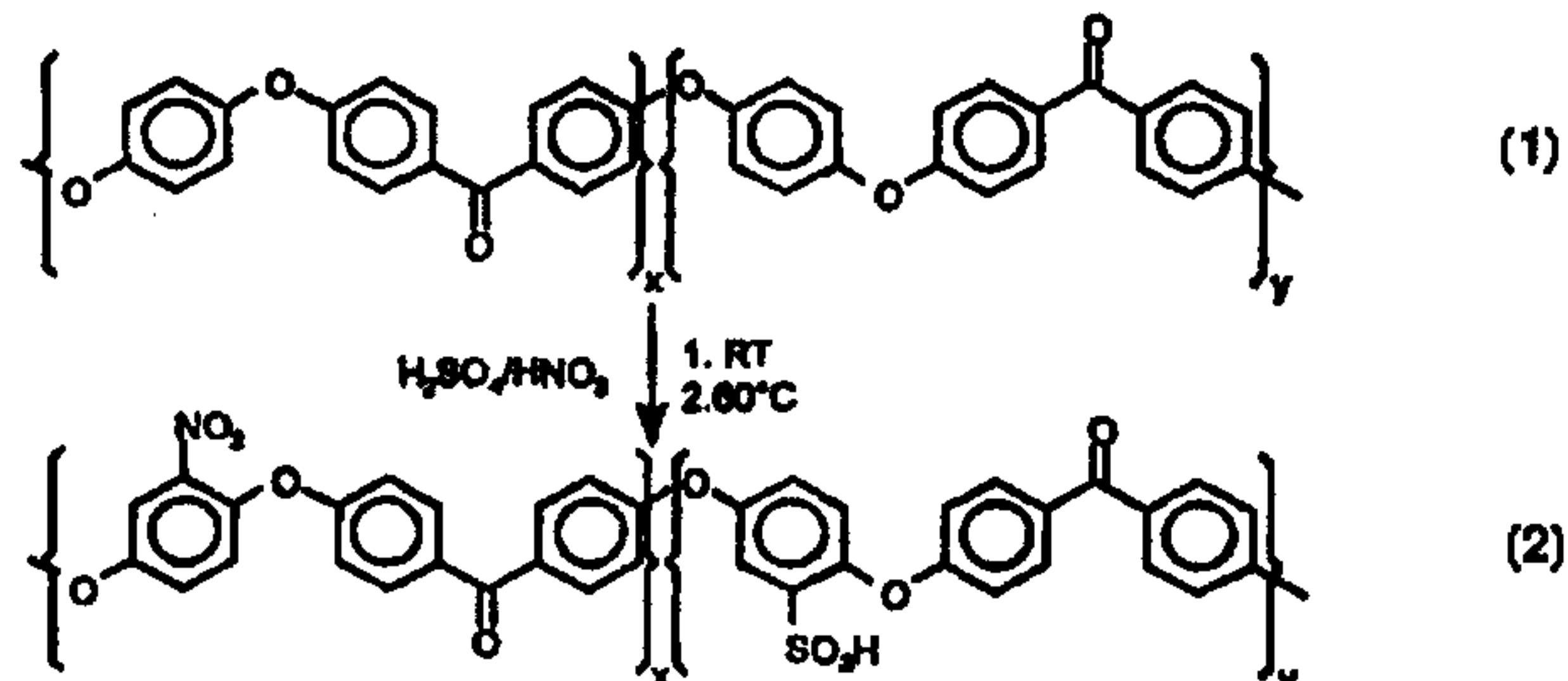
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(54) Title: MODIFIED POLYMER AND MODIFIED POLYMER MEMBRANE

(54) Bezeichnung: MODIFIZIERTES POLYMER UND MODIFIZIERTE POLYMERMEMBRAN

(57) Abstract

The invention relates to a method for producing nitrated and optionally sulphonated and aminated and optionally sulphonated aryl main chain polymers, in addition to aryl main chain polymers thus modified. Aryl main chain polymers (e.g. (1)) are nitrated by dissolving them in expensive, toxic and environmentally damaging solvents. Aryl main chain polymers which are selectively and simultaneously nitrated and sulphonated were not previously known in literature. The inventive method makes it possible to produce low-cost nitrated (and optionally sulphonated (2)) or post-reduction aminated (and optionally sulphonated) aryl main chain polymers without any organic solvents. Nitration (and optionally additional sulphonation) of the aryl main chain polymers occurs by dissolving them in concentrated sulphuric acid and by adding desired amounts of nitric acid at different temperatures and with different agitating times. The reaction can be carried out (a) as a two-step process: nitration followed by isolation of the polymer, then optional sulphonation and (b) as a single-step process: simultaneous nitration and sulphonation (2). The nitrated (or additionally sulphonated) polymers can then be reduced to form aminated (or additionally sulphonated) polymer. The polymers can be reacted with other polymers to form polymer blends. The polymers and polymer blends can be used as ion conducting membranes in electro membrane processes.



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Modified Polymer and Modified Polymer Membranes

1. Subject Matter of the Invention

The subject of the invention are novel, very economic processes for the preparation of:

- nitrated aryl polymers and optionally aminated aryl polymers prepared therefrom by a reduction of the nitro group;
- aryl polymers containing both nitro groups and sulfonic acid groups or both amino groups and sulfonic acid groups.

The subject of the invention are also novel, modified aryl polymers which can be produced very economically and aryl polymer membranes produced therefrom:

- a nitrated aryl polymer and an aminated aryl polymer which can be produced therefrom;
- a nitrated and sulfonated aryl polymer;
- an aminated and sulfonated aryl polymer;
- blend membranes made from the novel aryl polymers.

In addition, the subject of the invention is the application of the newly developed aryl polymers in membrane processes, in particular as polymeric electrolyte in electro membrane processes, e.g., in electrodialysis and in the PEM membrane fuel cell. Since the inventive membranes have high chemical and thermal stabilities, they are an economical alternative to the very expensive perfluorinated ionomeric membranes of the Nafion type which have mainly been used in PEM fuel cells up to the present.

2. The State of the Art

[1] describes the preparation of nitrated poly(etheretherketone) (PEEK-NO₂) by dissolving the PEEK in methanesulfonic acid and subsequently nitrating by adding concentrated nitric acid. A drawback of this process is the use of the relatively expensive methanesulfonic acid as the solvent.

[2] describes the preparation of amino-terminated poly(etheretherketone) oligomers by the nucleophilic displacement reaction of 4,4'-difluorobenzophenone by hydroquinone in the presence of a calculated excess of m-aminophenol. A drawback of said oligomers is a low amino group content, since only the terminal groups are modified by amino groups. There exist various patents for the preparation of sulfonated poly(etheretherketone) by dissolving the PEEK in concentrated sulfuric acid, with [3] being one example thereof. In [3], however, only sulfonated poly(etheretherketones) are claimed.

Naik et al. [4] describe the preparation and the properties of backbone-aminated poly(ether sulfone) (PES) and poly(etherether sulfone) (PEES), where the aminated polymer has been prepared by the nitration of the base polymer using nitrating acid (HNO₃/H₂SO₄) in nitrobenzene as the solvent and the subsequent reduction of the nitro group to the amino

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group. A drawback of this process is the toxicity of the nitrobenzene solvent.

There are numerous works regarding the nitration of aryl polymers, of which the works of Crivello [5] and Daly [6] may be mentioned here. The authors use ammonium nitrate and trifluoroacetic anhydride as nitrating agents. The drawback of this method is the high cost of trifluoroacetic anhydride and the liability to explosion of ammonium nitrate.

3. The Object Achieved by the Invention and the Improvement as Compared to the State of the Art

3.1 Preparation of a Nitrated Aryl Polymer

When trying to nitrate poly(etheretherketone) by dissolving PEEK in concentrated sulfuric acid and subsequently adding dropwise 70 % nitric acid (Fig. 1) it has surprisingly been found that the polymer has only been nitrated but not sulfonated. In this process only inexpensive bulk chemicals such as sulfuric acid and nitric acid are employed.

3.2 Preparation of a Sulfonated and Nitrated Aryl Polymer

It was surprisingly found that a sulfonated and nitrated aryl polymer, e.g., a sulfonated and nitrated PEEK, can be prepared very simply via any of two methods:

- Initially the polymer, e.g., PEEK, is dissolved in concentrated sulfuric acid at room temperature and concentrated nitric acid is added. Only nitration occurs. Subsequently, the polymer is isolated by precipitation in water, the acid is removed by washing, and the polymer is dried until its weight is constant. Thereafter, it is

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redissolved in concentrated sulfuric acid and heated to 60 °C with stirring. It is stirred at this temperature for a predetermined time. Subsequently, the polymer is precipitated in water, the acid is removed by washing, and the polymer is dried until its weight is constant.

- The polymer is dissolved in concentrated sulfuric acid. Thereafter, the desired amount of nitric acid is added dropwise. After a predetermined stirring time the reaction temperature is raised to 60 °C. Then the solution is stirred for a predetermined time. Thereafter, the polymer is worked up as stated above. The process is schematically illustrated in Fig. 2.

3.3 Amination of a Sulfonated and Nitrated Aryl Polymer

It has surprisingly been found that a sulfonated and nitrated PEEK can be reduced by a process [4] suitable for the reduction of nitrated to aminated polymers to yield an aminated and sulfonated PEEK. Said process is schematically illustrated in Fig. 3.

In additional steps the primary amino groups of the aminated and sulfonated polymer formed can be alkylated to quaternary ammonium groups by conventional alkylating agents with employing known methods.

4. Embodiments:

4.1 Preparation of Nitrated PEEK and PES

A three-neck glass flask equipped with a stirrer and a dropping funnel was charged with 96 % H₂SO₄. Subsequently, PEEK or PES was dissolved in the sulfuric acid with stirring at room temperature. Thereafter, 70 %

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HNO_3 was added dropwise to the reaction solution. The solution was stirred for 3 h. Thereafter, the polymer was precipitated in totally de-salted H_2O , and the acid was removed by washing. In each case an yield exceeding 90 % by weight was obtained. In table 1 some of the batches are listed.

Table 1: Nitration of PEEK and PES

Rct. no.	Polymer and amount [g]	Dissolving temperature [°C]	H_2SO_4 [ml]	HNO_3 [ml]	Reaction temperature [°C]	Degree of nitration [%]*
PEEK- NO_2 -1	PEEK 26.6	25	150	10	25	30
PEEK- NO_2 -2	PEEK 26.6	25	150	3	25	18.6
PES- NO_2 -1	PES 21.4	25	150	6	60	68.5

* % of polymer repeating units, determined by elementary analysis

4.2 Preparation of Nitrated and Sulfonated PEEK

In a three-neck stirring device 24 g of the nitrated PEEK obtained in reaction 4.1 (sample PEEK- NO_2 -2) is dissolved in 150 ml of 96 % sulfuric acid. After dissolution the reaction temperature is raised to 60 °C and the reaction mixture is stirred. Samples are taken from the reaction mixture in predetermined intervals; the samples are precipitated, freed from acid by washing, dried, and analyzed with regard to the degree of sulfonation by titration. The characteristics of the polymer samples taken after different reaction times are listed in table 2.

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Table 2: Sulfonation of Nitrated PEEK

Sample no.	Reaction time [min]	IEC [meq SO ₃ H/g]
PKNS-1	170	0.78
PKNS-2	240	0.82
PKNS-3	325	0.96
PKNS-4	360	1.45

4.3 Preparation of Sulfonated and Aminated PEEK

5 g nitrated and sulfonated PEEK (PKNS-4) is dissolved in 100 ml of DMF in a three-neck glass stirring device. Subsequently, 8 g of sodium dithionite is added to the reaction mixture. Thereafter, the temperature is increased to 150 °C and the reaction mixture is stirred at this temperature for 6 h. Then, the solution is filtrated, and after cooling the reaction mixture is precipitated in an HCl/methanol mixture (mixing ratio methanol:37 % hydrochloric acid = 8:2). The precipitated polymer is washed with totally desalinated water several times and dried.

The polymer has an ion-exchange capacity of 1.27 meq SO₃H/g of polymer.

4.4 Preparation of Membranes from Nitrated and Sulfonated PEEK and the Characterization Thereof

In order to prepare a cation-exchange membrane, 3 g of the polyetheretherketone modified according to the process of example 4.2 was dissolved in NMP. The prepared polymer solution was filtered off. The transparent solution was knife-coated on a glass plate. Thereafter, the glass plate with the film was placed into an oven and the solvent was

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evaporated off at 120 °C. The membrane was removed from the glass plate, and the characteristics thereof relevant for its use in the electro-membrane process (ion-exchange capacity IEC, surface resistance $R_a(H^+/Na^+)$, and permselectivity PS) were determined in experiments.

The results of the characterization are listed in table 3. It can be seen from table 3 that the characteristics of the newly developed membranes are comparable with those of commercial cation-exchange membranes [7].

Table 3: Preparation and Characterization of the Membrane

Sample no.	Substance	Solvent	IEC (meq/g)	d (μm)	$R_a(1/2 \text{ cm}^2)$ H^+/Na^+	PS (%)
MPKNS1	PKNS-1	NMP	0.78	28	0.979/6.12	98
MPKNS2	PKNS-2	NMP	0.82	17	0.426/3.05	98
MPKNS3	PKNS-3	NMP	0.96	26	0.180/1.01	97
MPKNS4	PKNS-4	NMP	1.45	35	0.093/0.53	98

Remarks:

d = membrane thickness

$R_a(1/2 \text{ cm}^2) H^+/Na^+$ = surface resistance of the membrane, measured in 0.5 H₂SO₄ and 0.5 NaCl by impedance spectroscopy

PS = permselectivity, measured in a 0.1 N/0.5 N NaCl solution

4.5 Application Test within a PEM Fuel Cell

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The MPKNS4 membrane of item 4.4 was installed in a PEM fuel cell provided by the Institut für Verfahrenstechnik of the University of Stuttgart. Commercial e-tek electrodes were cold-pressed onto the membrane. The pressure at the H₂ side was 2.1 bar, the O₂ pressure was 2.3 bar. The temperature of the cell was from 60 to 80 °C. The performance data of the PEM fuel cells were: a voltage of 700 mV at a current density of 120 mA/cm². The membrane turned out to be stable up to a temperature of 60 to 80 °C during a durability test over a period of 600 h.

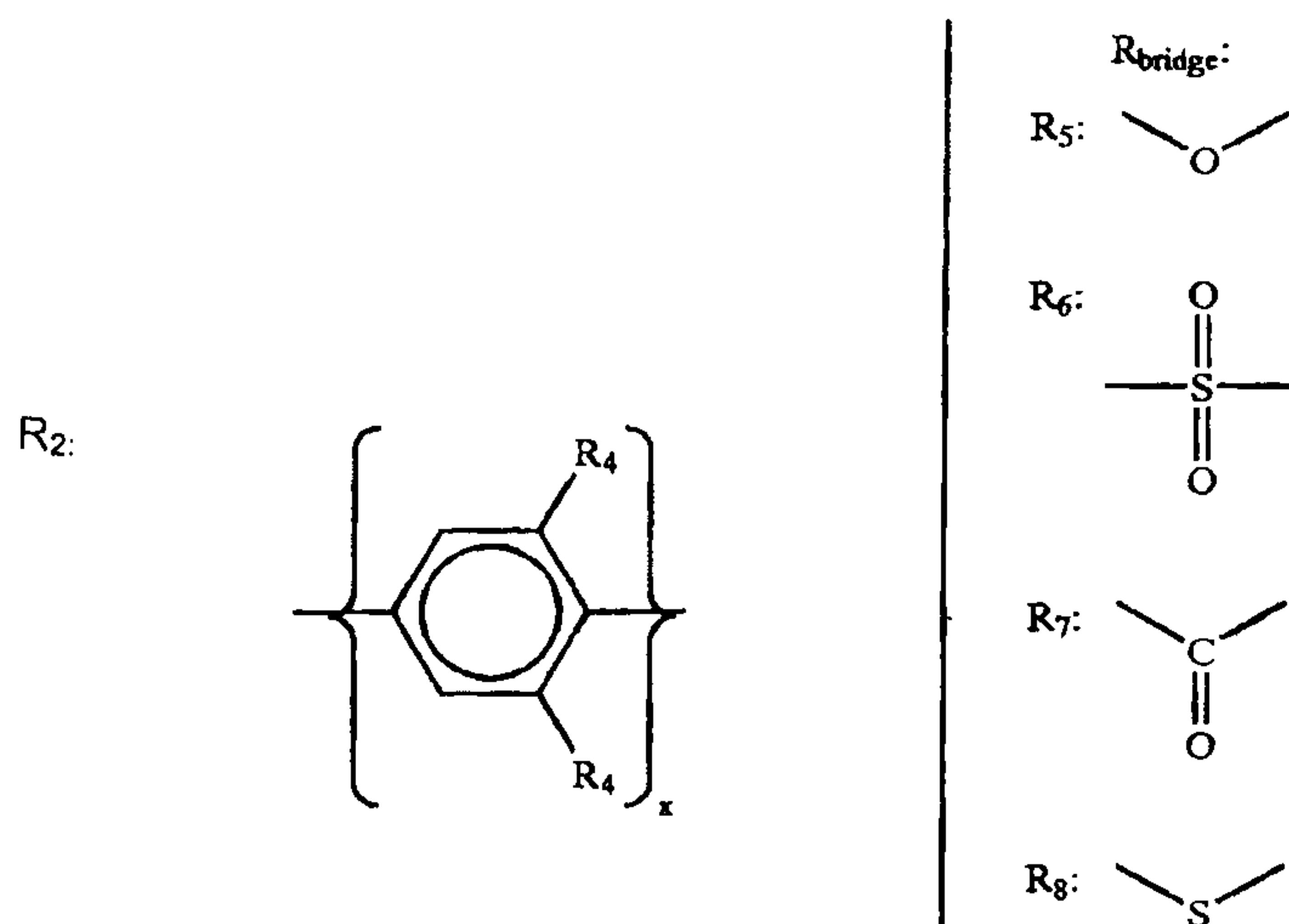
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- [1] R. J. Karcha, R. S. Porter, *J. Macromol. Sci.- Pure Appl. Chem.*, A32(5),957-967 (1995)
- [2] G. C. Corfield, G. W. Wheatley, D. G. Parker, *J. Polym. Sci.: Part A: Polymer Chem.*, 30, 845-849 (1992)
- [3] F. Helmer-Metzmann, et al., European Patent Application EP 0 574 791 A2 (1993)
- [4] H. A. Naik,I. W. Parsons, *Polymer*, 32, 140 (1991)
- [5] J. V. Crivello, *J. Org. Chem.*, 46, 3056 (1981)
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CLAIMS

1. A sulfonated and nitrated polymer having an aryl backbone comprising a plurality of aryl moieties having the formula R_2 , said aryl moieties being connected by bridging moieties selected from the group consisting of R_5 , R_6 , R_7 and R_8 ; wherein



Wherein R_4 is selected from the group consisting of H, methyl, and 4-phenoxybenzoyl, and wherein x is 1 or 2, said polymer having at least a portion of the aryl groups of the backbone substituted with $-SO_3H$ and at least a portion of the aryl group of the backbone substituted with $-NO_2$.

2. The polymers having aryl backbone chains according to claim 1, characterized in that said polymers are selected from:

- poly(etheretherketone) PEEK ($[R_5-R_2-R_5-R_2-R_7]_n$; $x = 1$, $R_4 = H$);
- poly(ethersulfone) PES ($[R_2-R_6-R_2-R_5]_n$; $R_2: x = 1$, $R_4 = H$);
- poly(etherethersulfone) ($[(R_2)_2-R_5-R_2-R_6-R_2]_n$; $R_2: x = 2$, $R_4 = H$);
- poly(phenylsulfone) ($[R_5-R_2-R_5-R_2-R_6]_n-[R_5-R_2-R_6-R_2]_m$; $R_2: x = 1$, $R_4 = H$, $n/m = 0.18$);
- poly(phenylene sulfide) PPS ($[R_2-R_8]_n$; $R_2: x = 1$, $R_4 = H$);
- poly(phenylene oxide) PPO ($[R_2-R_5]_n$; $R_4 = CH_3$) and;
- polyphenylene $[R_2]_n$, wherein one of the R_4 groups is H while the other R_4 group is 4-phenoxybenzoyl.

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3. The polymers having aryl backbone chains according to claim 1, characterized in that the polymer is PEEK or PES.

4. The polymers having aryl backbone chains according to either of claims 1 or 2, characterized in that the degree of nitration per polymer repeating unit is adjusted from $Y = 0.1$ to 2 and the degree of sulfonation per polymer repeating unit is adjusted from $Z = 0.1$ to 2.

5. The polymers having aryl backbone chains according to any one of claims 1 to 4, characterized in that the $\text{SO}_3\text{H}/\text{NO}_2$ ratio within the polymer is from 1% of SO_3H and 99% of NO_2 to 1% of NO_2 and 99% of SO_3H and the degree of modification of the polymer is adjusted from 0.1 SO_3H and NO_2 groups per polymer repeating unit to 2 SO_3H and NO_2 groups per repeating unit of the polymer.

6. A process for preparing polymers having aryl backbone chains according to any one of claims 1 to 5, characterized in that non-sulfonated and non-nitrated polymers having aryl backbone chains and the structural elements according to claim 1 are dissolved in 90 to 100% sulfuric acid, subsequently 70 to 100% nitric acid is added and the temperature is raised to 60°C .

7. A process for preparing polymers having aryl backbone chains according to any one of claims 1 to 5, characterized in that a nitrated polymer having an aryl backbone chain and the structural elements according to claim 1 is redissolved in sulfuric acid and sulfonated at a temperature within the range of 60 to 90°C .

8. A process for preparing nitrated and sulfonated polymers having aryl backbone chains according to any one of claims 1 to 5, characterized in that non-sulfonated and non-nitrated polymers having aryl backbone chains and the structural units according to claim 1 are dissolved in a one pot reaction in 90 to 100% sulfuric acid, the desired amount of 70 - 100% nitric acid is added and the temperature is adjusted such that the nitration and the sulfonation occur simultaneously or in immediately successive steps.

9. A process for preparing aminated and sulfonated polymers having aryl backbone

chains, characterized in that nitro groups of a polymer having an aryl backbone chain according to any one of claims 1 to 5 are reduced to primary amino groups by employing a process known as such.

10. The process for the preparation of aminated and sulfonated polymers having aryl backbone chains according to claim 9, characterized in that the nitro groups of the sulfonated and nitrated polymer having the structural units according to claim 1, which is dissolved in dipolar-aprotic solvents, is reduced with sodium dithionite or other sulfur salts having low valencies to primary amino groups.

11. The process according to claim 10 wherein said dipolar-aprotic solvents are NMP, DMAc, DMF, DMSO or sulfolane.

12. A process for preparing sulfonated polymers containing alkylated amine groups and having aryl backbone chains characterized in that the primary amino groups of the aminated and sulfonated polymers having aryl backbone chains prepared through the process of claim 9 are alkylated to secondary or tertiary amines or quaternary ammonium salts using haloalkanes by processes known as such.

13. A process to make sulfonated polymers containing alkylated amine groups and having aryl backbone chains characterized in that the primary amino groups of the aminated and sulfonated polymers having aryl backbone groups prepared through the process of claim 9 are quaternized by employing processes known as such.

14. A sulfonated and aminated polymer which is obtained according to any one of claims 9 to 13.

15. The polymers according to claim 14 characterized in that they contain sulfonate groups SO_3X ($\text{X} = \text{H}$, metal cation, ammonium ion NR_4 with $\text{R} = \text{H}$ and/or aryl and/or alkyl) and NH_2 groups on the polymer backbone chain, which are obtained by reducing the polymers of claim 14 with sodium dithionite or other sulfur salts having low valencies.

16. The polymers according to claim 14 containing sulfonate groups SO_3X ($\text{X} = \text{H}$, metal cation, ammonium ion NR_4 with $\text{R} = \text{H}$ and/or aryl and/or alkyl) and NH_2 groups on

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the polymer backbone chain, which are obtained by alkylating the primary amino groups of said polymers.

17. The polymers according to claim 14 containing sulfonate groups SO_3X ($\text{X} = \text{H}$, metal cation, ammonium ion NR_4 with $\text{R} = \text{H}$ and/or aryl and/or alkyl) and NH_2 groups on the polymer backbone chain, which can be obtained by alkylating the amino groups of the polymers during the quaternization step.

18. Polymer blends consisting of combinations of the polymers of claims 14 to 17 with additional polymers.

19. The polymer blends according to claim 18, characterized in that the additional polymers are selected from the group consisting of polyimides, polyether imides, polyamides, polyethersulfones, and polyphenylene oxides.

20. A process for preparing polymer membranes or polymer blend membranes, characterized in that the polymers according to any one of claims 14 to 17 or the polymer blends of any one of claims 18 to 19 are converted into dense or porous sheet membranes by conventional methods.

21. The process according to claim 20, characterized in that the polymers are converted into asymmetrical, porous capillary membranes or integral-asymmetrical, dense capillary membranes by employing processes known as such.

22. A process for the preparation of polymer or polymer blend membranes, characterized in that polymers according to any one of claims 14 to 19 are dissolved simultaneously or subsequently in a dipolaraprotic solvent selected from N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAc), N-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and sulfolane, subsequently the polymer solution is filtered, subsequently the polymer solution is degassed, subsequently the polymer solution is spread out as a thin film on a support, subsequently the solvent is removed by heating to 80 to 130°C and/or by applying reduced pressure or in a circulating air dryer, subsequently the polymer film is optionally removed from the support, subsequently the polymer film is aftertreated in a diluted mineral acid, and finally treated with deionized

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water at temperatures from room temperature to 95°C.

23. The process according to claim 22 wherein said diluted mineral acid has a concentration from 1 to 70% weight.
24. The process according to claim 22 wherein said support is a glass-plate, a metal plate, a fabric or a web.
25. The polymer or polymer blend membranes which can be obtained according to any one of claims 20 to 24.
26. Use of the polymer or polymer blend membranes according to claim 25 for the electrochemical generation of energy as a constituent part of membrane fuel cells working at temperatures from 0 to 180°C, in electrochemical cells, in secondary batteries, in electrolytic cells and in membrane separation methods.
27. The use according to claim 26 wherein said membrane separation methods are gas separation, pervaporation, perstraction, electrodialysis, inverse osmosis electrodialysis and diffusion dialysis.
28. The use according to claim 26 wherein said membrane fuel cells are H₂ fuel cells or direct methanol fuel cells.

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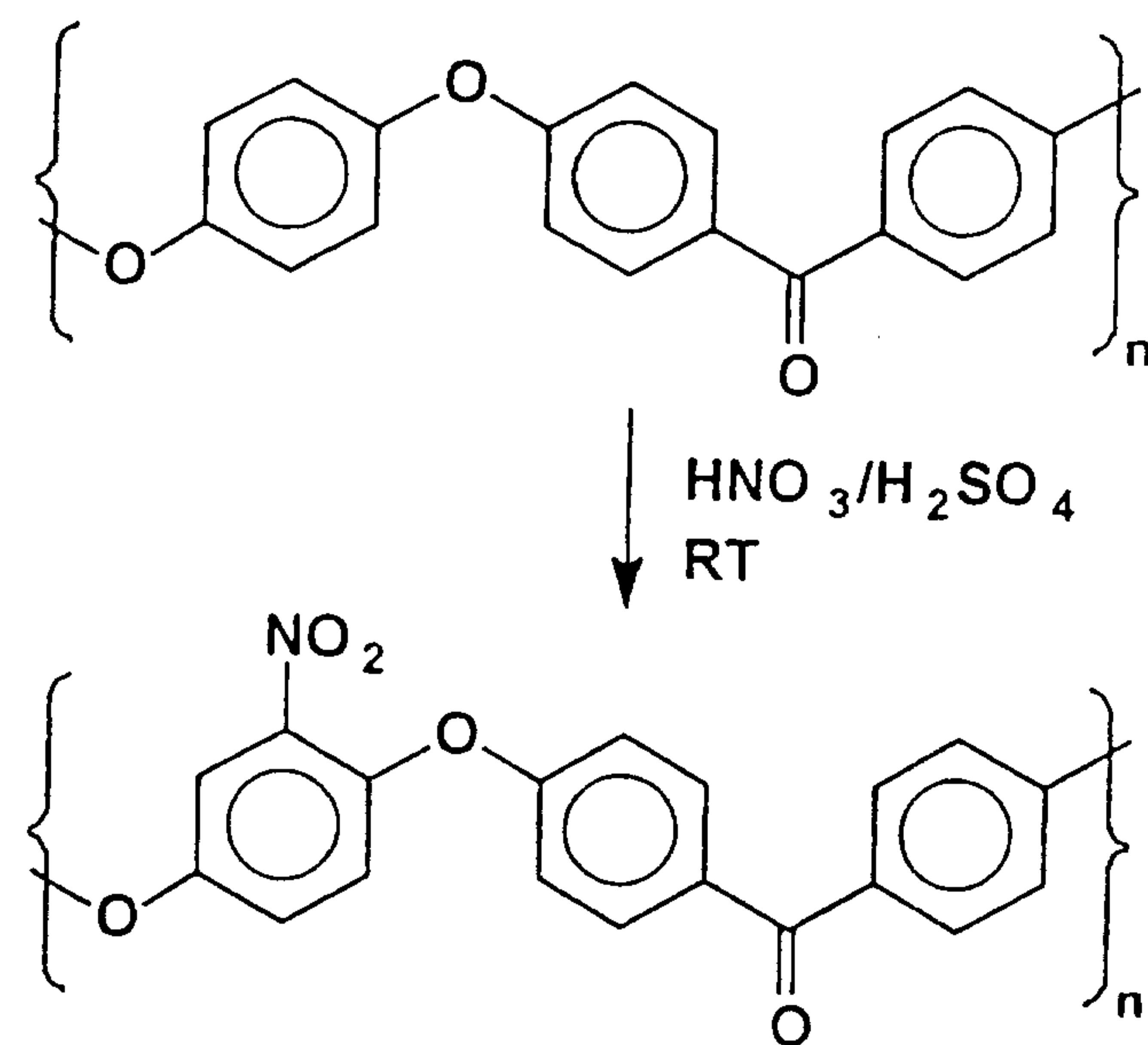


Fig. 1: Preparation of nitrated PEEK

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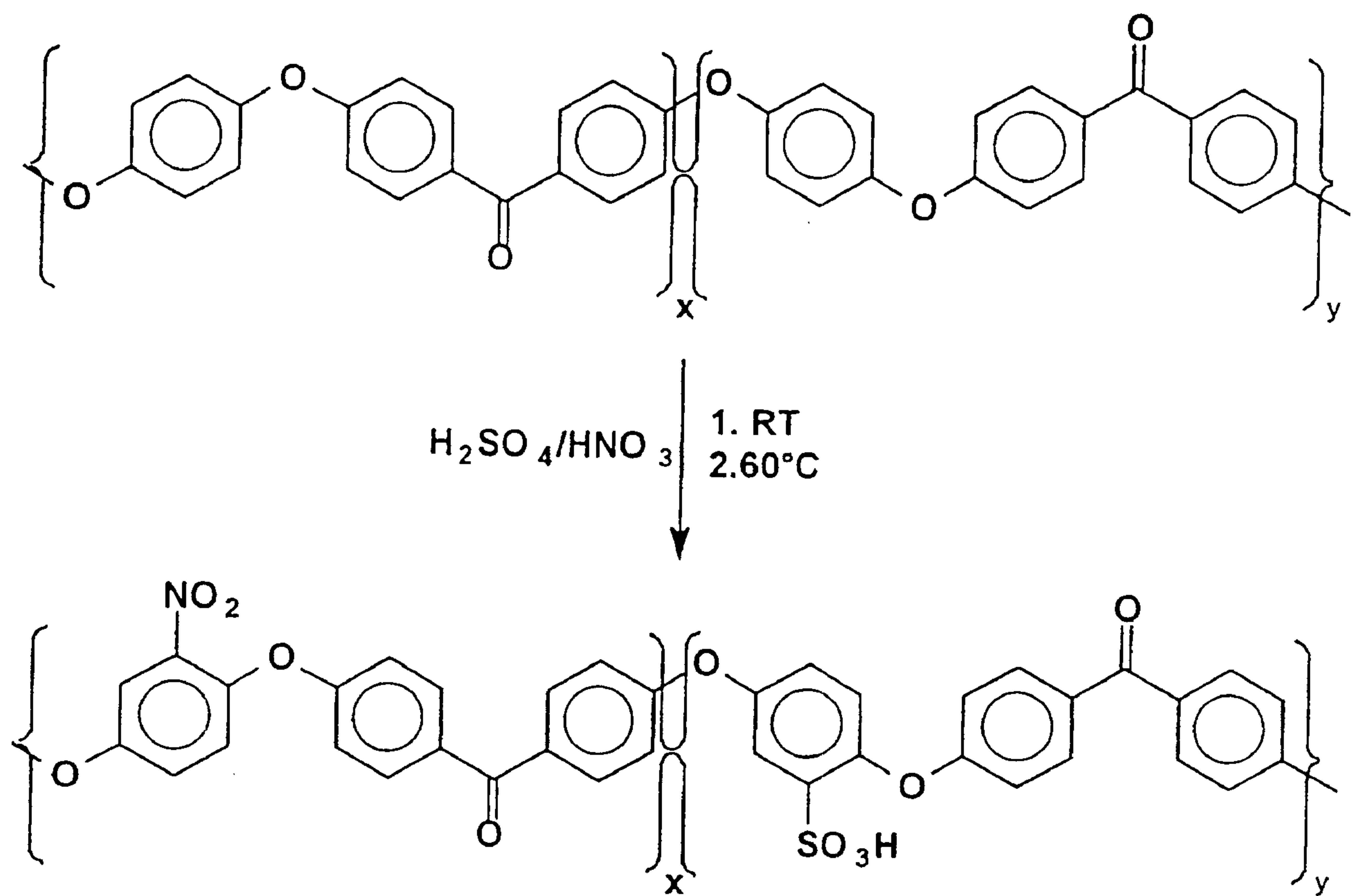


Fig. 2: Preparation of nitrated and sulfonated PEEK

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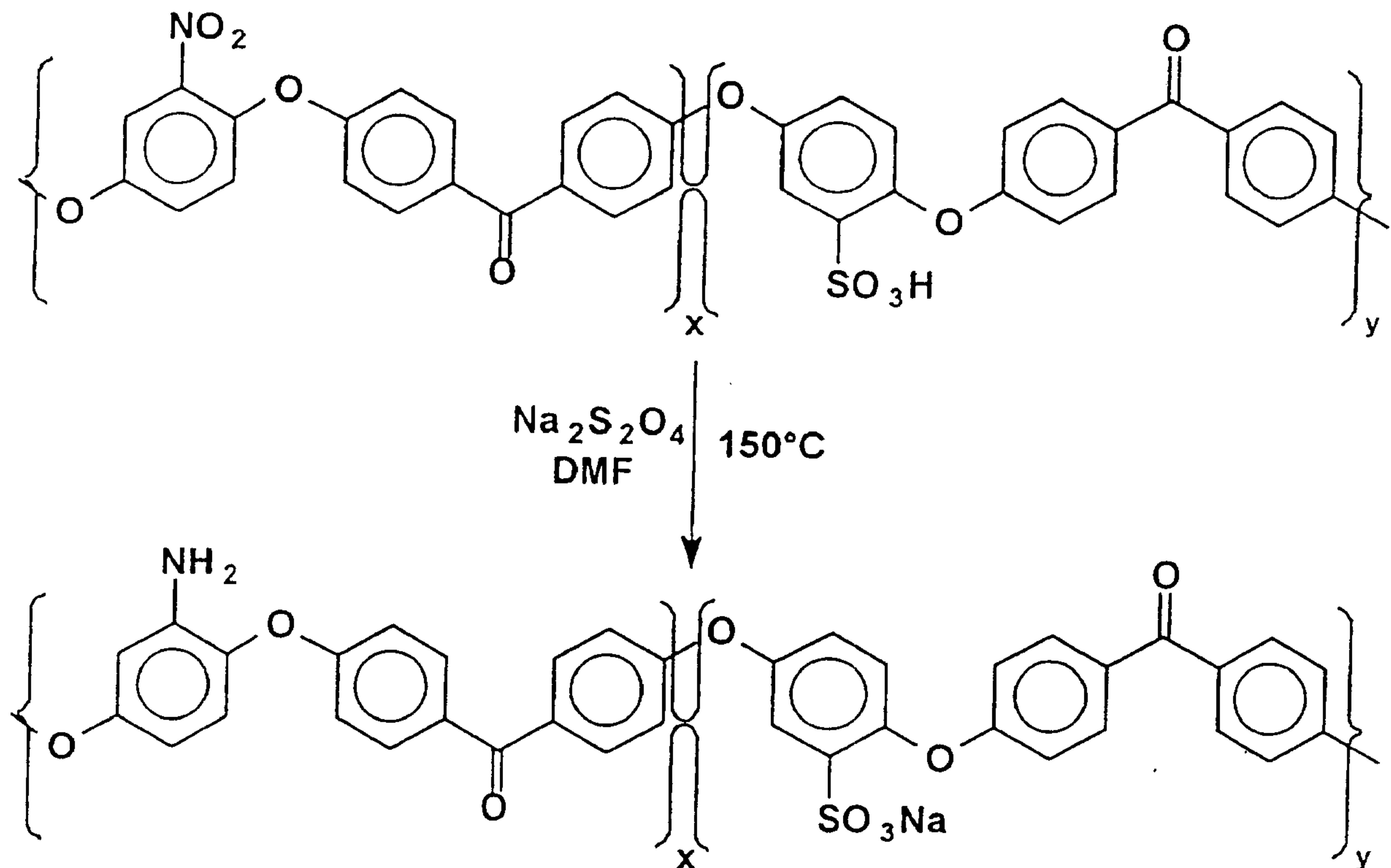


Fig. 3: Aminated and sulfonated PEEK from sulfonated and nitrated PEEK

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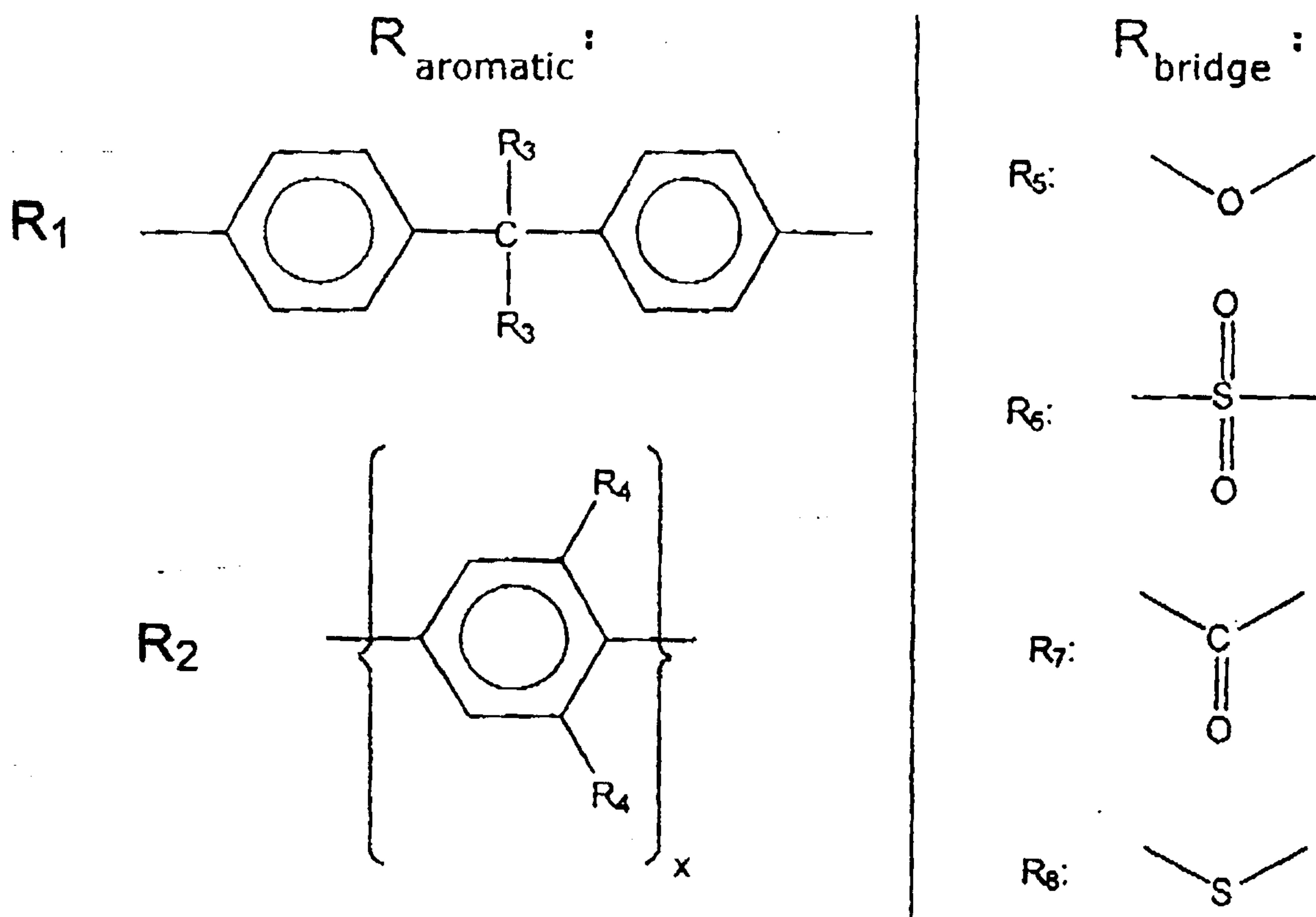
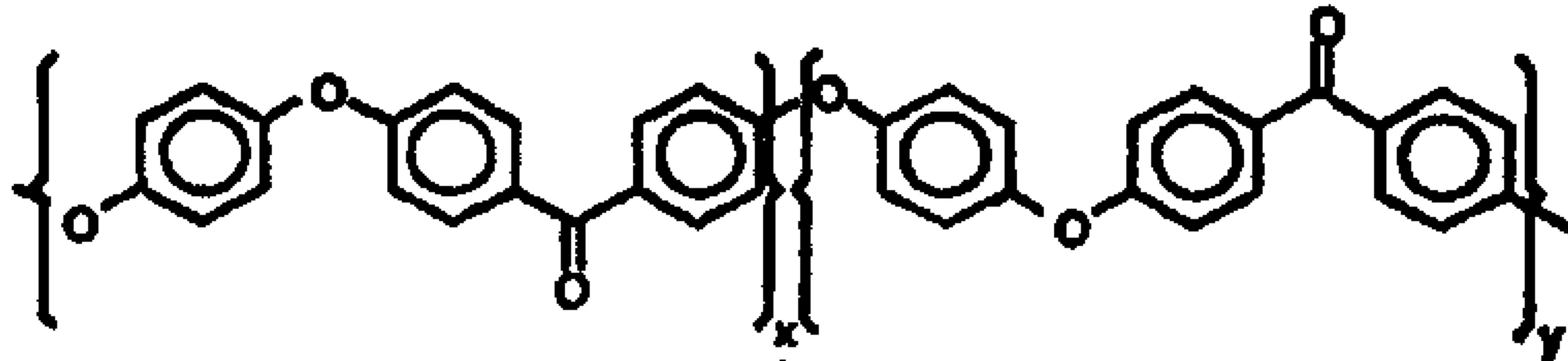
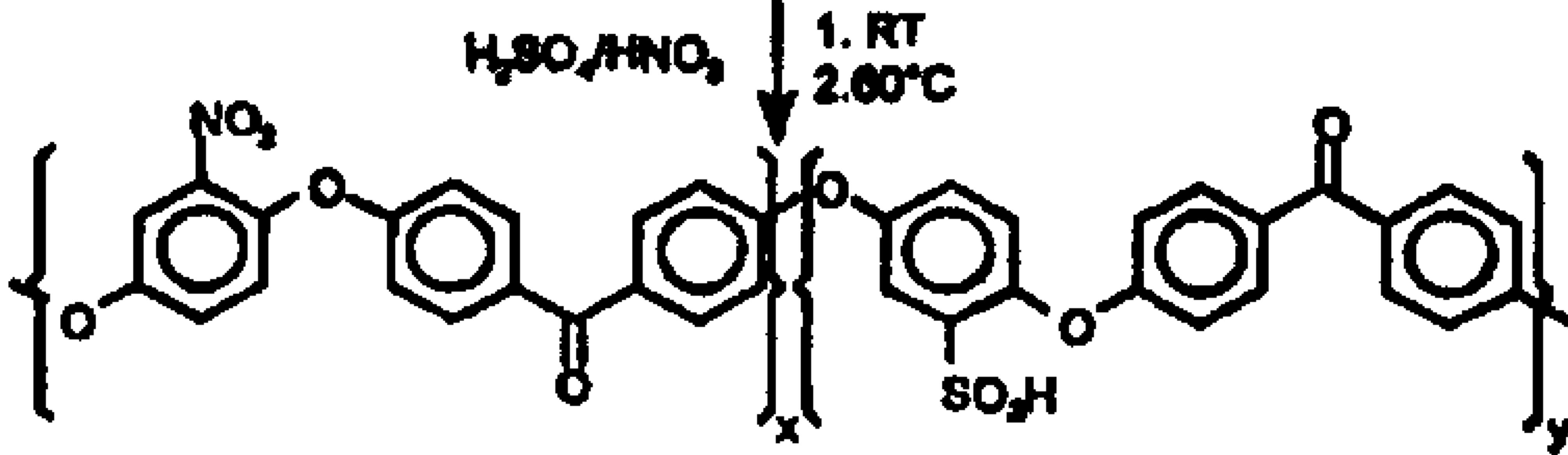


Fig. 4: Structural units of polymers having aryl backbone chains



(1)



(2)

$\text{H}_2\text{SO}_4, \text{HNO}_3$

1. RT
2. 00°C