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**Patentanmeldung Nr.**

**Patent application No.**

**Demande de brevet n°**

13166233.0 / EP13166233

The organization code and number of your priority application, to be used for filing abroad under the Paris Convention, is EP13166233.

Der Präsident des Europäischen Patentamts;  
Im Auftrag  
For the President of the European Patent Office  
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BLOCK COPOLYMERS

In Anspruch genommene Priorität(en) / Priority(Priorities) claimed / Priorité(s) revendiquée(s)  
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## Block Copolymers

## Description

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The present invention relates to novel block copolymers comprising polyarylene ether blocks and polyalkylene oxide blocks, wherein said block copolymer comprises at least two different polyalkylene oxide blocks that are endcapped with different alkyl groups.

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The present invention further relates processes for the manufacture of such block copolymers and their use as membrane material.

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Polyether sulfones and polysulfones belong to the group of high-performance thermoplastics (E.M. Koch, H.-M. Walter, *Kunststoffe* 80 (1990) 1146; E. Döring, *Kunststoffe* 80 (1990), 1149). Owing to their good biocompatibility, polyether sulfones and polysulfones are also used as material for the production of dialysis membranes (S. Savariar, G.S. Underwood, E.M. Dickinson, P.J. Schielke, A.S. Hay, *Desalination* 144 (2002) 15).

20

The preparation of the polyether sulfones and polysulfones is usually effected by polycondensation of suitable monomer building blocks in dipolar aprotic solvents at elevated temperature (R.N. Johnson et al., *J. Polym. Sci. A-1* 5 (1967) 2375, J.E. McGrath et al., *Polymer* 25 (1984) 1827).

25

The preparation of polyarylene ether sulfones from suitable aromatic bis(alkyl)sulfones and aromatic bisphenols or salts thereof in the presence of at least one alkali metal or ammonium carbonate or bicarbonate in an aprotic solvent is described, for example, in US 4,870,153, EP 113 112, EP-A 297 363 and EP-A 135 130.

30

One disadvantage of pure polyarylene ethers is their low hydrophilicity. To enhance the hydrophilicity of polyarylene ethers, polyethersulfone (PESU) – polyethyleneoxide (PEO) block copolymers have been prepared.

35

The synthesis of polyarylene ether-polyalkylene oxide copolymers described in *Macromolecules* 29 (23) p. 7619 (1996) requires long reaction times.

40

EP 739 925, US 5,700,902 and US 5,700,903 also describe polyarylene ether and polyalkylene oxide copolymers.

40

US 5,700,902 discloses block copolymers with hydrophobic blocks and hydrophilic blocks, wherein hydrophilic blocks can be PEO blocks that are endcapped on one side with an alkyl group.

US 5,798,437, US 5,834,583, WO 97/22406 disclose processes for the manufacture of hydrophilic copolymers.

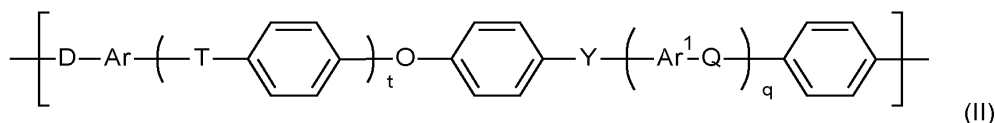
5 US 5,911,880 discloses membranes made of polyether sulfone comprising an amphiphilic additive.

It was an object of the present invention to provide block copolymers that have a high glass transition temperature and that do not show the problems of copolymers known from the art.

10 This problem has been solved by block copolymers comprising polyarylene ether blocks and polyalkylene oxide blocks, wherein said block copolymer comprises at least two different polyalkylene oxide blocks that are endcapped with different endcapping groups.

15 The term "block copolymer" shall not mean an individual polymer molecule but the entirety of all polymeric components in a polymer.

20 Suitable polyarylene ether blocks of copolymers according to the invention are known as such to those skilled in the art and can be formed from polyarylene ether units of the general formula II



with the following definitions:

25

t, q: each independently 0, 1, 2 or 3,

Q, T, Y: each independently a chemical bond or group selected from -O-, -S-, -SO<sub>2</sub>-, S=O, C=O, -N=N-, -CR<sup>a</sup>R<sup>b</sup>- where R<sup>a</sup> and R<sup>b</sup> are each independently a hydrogen atom or a C<sub>1</sub>-C<sub>12</sub>-alkyl, C<sub>1</sub>-C<sub>12</sub>-alkoxy or C<sub>6</sub>-C<sub>18</sub>-aryl group, where at least one of Q, T and Y is not -O-, and at

30 least one of Q, T and Y is -SO<sub>2</sub>-, and

Ar, Ar<sup>1</sup>: each independently an arylene group having from 6 to 18 carbon atoms,

D: a chemical bond or -O-.

35 In particular, D is an oxygen atom -O- when bound to another arylene ether unit. D is a chemical bond when bound to a polyalkyleneoxide block.

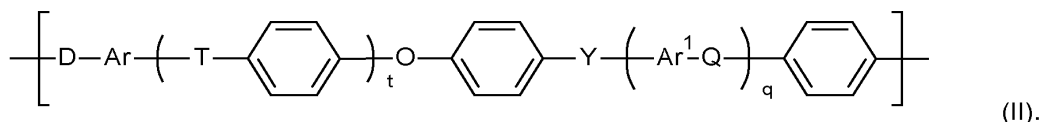
The polyarylene ethers are typically prepared by polycondensation of suitable starting compounds in dipolar aprotic solvents at elevated temperature (see, for example, R.N. Johnson et al., J. Polym. Sci. A-1 5 (1967) 2375, J.E. McGrath et al., Polymer 25 (1984) 1827). Possible

syntheses of the OH-terminated polyarylene ethers are also described in WO 2010/057822 on p. 2 In. 27 to p.14, In. 35 as well as p. 16, In 8 to 18, In 29.

Suitable polyarylene ether blocks can be provided by reacting at least one starting compound of the structure X-Ar-Y (M1) with at least one starting compound of the structure HO-Ar<sup>1</sup>-OH (M2) in the presence of a solvent (L) and of a base (B), where

- Y is a halogen atom,
- X is selected from halogen atoms and OH, preferably from halogen atoms, especially F, Cl or Br, and
- Ar and Ar<sup>1</sup> are each independently an arylene group having 6 to 18 carbon atoms.

In one embodiment, a polyarylene ether which is formed from units of the general formula II with the definitions as above is provided in the presence of a solvent (L):



If Q, T or Y, with the abovementioned prerequisites, is a chemical bond, this is understood to mean that the group adjacent to the left and the group adjacent to the right are bonded directly to one another via a chemical bond.

Preferably, Q, T and Y in formula (I), however, are independently selected from -O- and -SO<sub>2</sub>-, with the proviso that at least one of the group consisting of Q, T and Y is -SO<sub>2</sub>-.

When Q, T or Y are -CR<sup>a</sup>R<sup>b</sup>-, R<sup>a</sup> and R<sup>b</sup> are each independently a hydrogen atom or a C<sub>1</sub>-C<sub>12</sub>-alkyl, C<sub>1</sub>-C<sub>12</sub>-alkoxy or C<sub>6</sub>-C<sub>18</sub>-aryl group.

Preferred C<sub>1</sub>-C<sub>12</sub>-alkyl groups comprise linear and branched, saturated alkyl groups having from 1 to 12 carbon atoms. Particularly preferred C<sub>1</sub>-C<sub>12</sub>-alkyl groups are: C<sub>1</sub>-C<sub>6</sub>-alkyl radicals such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, 2- or 3-methylpentyl and longer-chain radicals such as unbranched heptyl, octyl, nonyl, decyl, undecyl, lauryl, and the singularly or multiply branched analogs thereof.

Useful alkyl radicals in the aforementioned usable C<sub>1</sub>-C<sub>12</sub>-alkoxy groups include the alkyl groups having from 1 to 12 carbon atoms defined above. Cycloalkyl radicals usable with preference comprise especially C<sub>3</sub>-C<sub>12</sub>-cycloalkyl radicals, for example cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclopropylmethyl, cyclopropylethyl, cyclopropylpropyl, cyclobutylmethyl, cyclobutylethyl, cyclopentylethyl, -propyl, -butyl, -pentyl, -hexyl, cyclohexylmethyl, -dimethyl, -trimethyl.

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