

Polyurethane block copolymer based on poly siloxane tenside for membranes

Description

5 The instant invention relates to novel polyurethane block copolymers based on poly siloxane(tensides) with anchoring units, their use as anti bio-adhesion additives especially in membrane preparation, and polymer membranes, especially for microfiltration, ultrafiltration or gas separation or purification purposes, containing the novel copoly-
mers.

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The problem of biofouling is pronounced in semipermeable membranes used for separation purposes like microfiltration, ultrafiltration or reverse osmosis. Membranes may be classified according to their pore dimension in most of the application profiles. For example, in water filtration applications ultra filtration membranes (approximate pore
15 diameter: 100 – 1000 nm) are used for wastewater treatment retaining organic and bioorganic material. Much smaller diameters are required in desalination applications (reverse osmosis; approximate pore diameter 1 nm) for retaining ions. In these applications, the ambient medium is an aqueous phase, where potential blockage may occur by adhesion of micro-organisms and bio-film formation. In consequence, a membrane
20 with anti-adhesion properties is desired, which would reduce bio-film formation and thus require less cleaning cycles.

US-5102547 proposes various methods for the incorporation of of oligodynamic materials including silver powders and silver colloids into membranes. US-6652751 compares several bacteriostatic membranes obtained after contacting polymer solutions
25 containing a metal salt with a coagulation bath containing a reducing agent. Membranes containing certain modified polymers have also been proposed to improve fouling resistance; WO 09/098161 discloses certain alkoxyamine-functionalized polysulfones as additives for the purpose. WO 07/053163 recommends incorporation of certain graft-copolymers based on a polysiloxane backbone into polymeric materials such
30 as coatings to impart antifouling properties. Hydrophobic properties of polysiloxanes have already been exploited to impart "fouling release" properties to surfaces coated by these polymers or by certain copolymers containing polysiloxane blocks (see S. Krishnan, J. Mater. Chem. 2008, 18, 3405, and references cited therein).

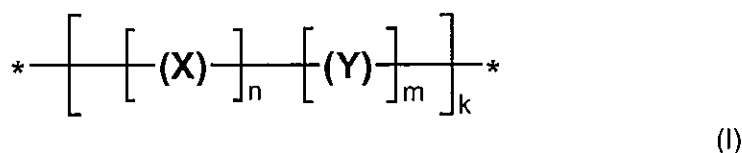
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Certain block-copolymers with urethane linkage have now been found, which show especially advantageous antifouling properties. Due to their good compatibility, the present block-copolymers may be fully incorporated into other matrix polymers, or rigidly anchored in these matrices and enriched at the surface. Thus, the present block-
40 copolymers may conveniently be used as an additive imparting antimicrobial and anti bioadhesion properties to polymeric articles and their surfaces, e.g. when incorporated into a membrane, especially a membrane for water filtration purposes. The present block-copolymers contain one or more polysiloxane blocks as diol component (B),

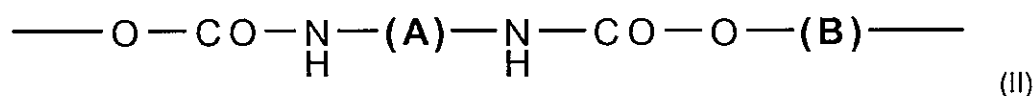
whose alkanol end groups are optionally extended by one or more ether moieties. Further conveniently contained are aromatic polysulfone blocks (C) as second diol component. Linkage between the diol blocks is effected by urethane linkers (A) derived from aromatic or aliphatic diisocyanates.

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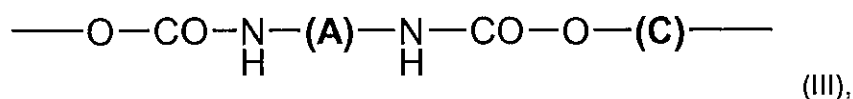
In a first general aspect, present invention thus pertains to oligo- and polyurethane molecules comprising said components (A), (B) and (C) of the formula



- 10 wherein k and n independently are numbers from 1 to 100,
m is from the range 1-50,
where
(X) is a block of formula



- 15 and (Y) is a block of the formula



- (A) is a residue of an aliphatic or aromatic diisocyanate linker,
(B) is a residue of a linear oligo- or polysiloxane containing alkanol end groups, and
20 optionally further containing one or more aliphatic ether moieties, and
(C) is an aromatic oligo- or polysulfone block.

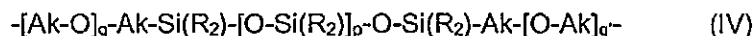
- The blocks (X) and (Y) in formula I may be in statistical order or, again, in blocks; the usual procedure (see present examples) yields blocks (X) and (Y) in statistical order.
25 The moieties (A), (B) and (C) may also comprise minor amounts of tri- or polyvalent residues, e.g. by including a minor quantity of a triisocyanate and/or tetraisocyanate into the preparation of the present oligo- or polyurethane. The resulting branched species share the advantageous properties of the present linear oligo- and polyurethanes, and are included by the present invention.

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- Preferred oligo- and polyurethane molecules of the invention contain at least one block (X) and at least one block (Y); preferred n and m ranging from 2 to 50, and preferred k ranging from 1 to 20. The molecular weight (Mn) is preferably from the range 1500 to 100000, more preferably from the range 4000 to 25000. Most preferred compounds
35 show a polydispersity ranging from 1.5 to 3.0.

Preferred (A) is a divalent residue selected from C₂-C₁₂alkylene and Ar.

Preferred (B) is a divalent residue of an oligo- or polysiloxane of the formula



- 5 wherein Ak stands for C₂-C₄alkylene, R stands for C₁-C₄alkyl, and each of p, q and q' independently is a number selected from the range 0-50. In more preferred moieties (B) of formula (IV), p ranges from 1 to 50, especially from 2 to 50.

Preferred (C) is a diphenyl sulfone monomer or linear oligomer or polymer block containing 1-50 moieties phenyl-SO₂-phenyl, and optionally further 1-50 further moieties Ar, which moieties are, in case of the oligomer or polymer, linked together by means selected from direct bonds and spacers Sp;

Ar is selected from -Ph-Ph- and -Ph-Sp-Ph-;

Ph is phenyl or phenyl substituted by C₁-C₄alkyl;

- 15 where the spacers Sp independently are -O- or C₁-C₃alkylene.

End groups in the oligomer or polymer (marked by asterisks * in formula I) mainly are mono-reacted constituents of the polyurethane (e.g. free OH from the diol component, or mono-reacted diisocyanate [-CO-NH-A-NCO], attached to (B) or (C) on the right side of formula I; or mono-reacted diol component HO-(B)- or HO-(C) attached on the left side of formula I). Chain termination may also be effected by including a certain amount (e.g. up to 20 mol-%) of monofunctional constituents, e.g. monoalcohols R'-(B)-OH or R'-(C)-OH where R' is alkyl (auch as C₁-C₄alkyl), Ar or especially H; R' (appropriately attached to (B) or (C)) thus forming one or both end group(s). In accordance, the present oligo- and polyurethanes are essentially free of typical silane end groups like Si(R'')₃, where R'' is any of H, alkyl, alkoxy.

The invention further pertains to a membrane, especially semipermeable membrane, comprising the above polymer composition. The membrane of the invention generally shows an at least 8-fold enrichment of silicon, especially an 8- to 25-fold enrichment of silicon, in the section 2-10 nm from the membrane surface over the membrane's average silicon content. The invention includes the use of this membrane as a filter membrane in a water treatment, water separation or gas separation process.

Further constituents of the membrane generally comprise (as component b) one or more further organic polymers selected from the group consisting of polyvinyl pyrrolidone, polyvinyl acetates, cellulose acetates, polyacrylonitriles, polyamides, polyolefines, polyesters, polysulfones, polyethersulfones, polycarbonates, polyether ketones, sulfonated polyether ketones, polyamide sulfones, polyvinylidene fluorides, polyvinylchlorides, polystyrenes and polytetrafluoroethylenes, copolymers thereof, and mixtures thereof; preferably selected from the group consisting of polysulfones, polyethersulfones, polyvinylidene fluorides, polyamides, cellulose acetate and mixtures thereof.

End groups in the sulfone-free oligo- or polyurethane mainly are mono-reacted constituents of the polyurethane (e.g. free OH from the diol component, or mono-reacted diisocyanate $[-CO-NH-A-NCO]$). In accordance, the present oligo- and polyurethanes are essentially free of typical silane end groups like $Si(R^n)_3$, where R^n is any of H, alkyl, alkoxy.

Preferred meanings for (A) and (B) are as defined for copolymers of formula I above; specifically, the molecular weight (M_n) of the polyurethane is preferably from the range 1500 to 100000;

(A) preferably is a divalent residue selected from C_2 - C_{12} alkylene and Ar;

(B) preferably is a divalent residue of an oligo- or polysiloxane of the formula



wherein Ak stands for C_2 - C_4 alkylene, R stands for C_1 - C_4 alkyl, and each of q and q' independently is a number selected from the range 0-50, and p ranges from 1 to 50, especially from 2 to 50;

Ar is $-Ph-Sp-Ph-$;

Ph is phenyl or phenyl substituted by C_1 - C_4 alkyl; and

Sp independently is selected from direct bond, $-O-$, C_1 - C_3 alkylene.

The water filtration membrane (semipermeable membrane) preferably consists essentially of a polymer composition comprising abovesaid oligo- or polyurethane in an amount of 0.1 to 25 % by weight of the total polymer composition, especially in a homogenous phase or within the same phase enriched at the surface. It may further

comprise one or more antimicrobial or bacteriostatic agents, especially silver in ionic and/or metallic form such as silver colloid, silver glass, silver zeolite, silver salts, elemental silver in form of powder, microparticle, nanoparticle or cluster, and often shows an at least 8-fold enrichment of silicon, especially an 8- to 25-fold enrichment of silicon, in the section 2-10 nm from the membrane surface over the membrane's average silicon content.

The process for preparing the semipermeable water treatment membrane of the invention generally comprises incorporation of the above oligo- or polyurethane, a further polymer as noted under component (b), and optionally further additives into the membrane material.

The following samples represent examples with mean analytical data for a variety of polyurethanes for use especially in water filtration membranes according to the invention (see examples below for abbreviations/identification of blocks or monomer components; ratios given are by mol):

Poly(polydimethylsiloxane-block-co-polyethylenoxid)urethane a polyurethane containing IM22 and HDI as linker characterized by:

Gel permeation chromatography for molecular mass (kDa): Mn 13±5; Mw 31±15; Mp 22±7; PD 2.4±0.5

¹H-NMR spectroscopy: (SiMe₂O)/(C₂H₄O): 0.71

Elementary analysis [%]: C: 44.7; H: 8.7; Si: 15.7

Poly(polydimethylsiloxane-block-co-polyether)urethane a polyurethane containing IM15-PEG 2000 (1:1) and HDI as linker characterized by:

Gel permeation chromatography for molecular mass (kDa): Mn 15±7; Mw 30±16; Mp 22±10; PD 2.0±0.6

¹H-NMR spectroscopy: (SiMe₂O)/(C₂H₄O): 0,27-1,07

Elementary analysis [%]: C: 40.06 – 47.2; H: 8.1 – 8.5; Si: 10.5-22.0

Poly(polydimethylsiloxane-block-co-polyethersulfonyl)urethane a polyurethane containing PSU1-IM15 (2:1) and HDI as linker characterized by:

Gel permeation chromatography for molecular mass (kDa): Mn 8±2; Mw 18±3; Mp 16±2; PD 2.2±0.3

¹H-NMR spectroscopy: (SiMe₂O)/(CMe₂): 0.58

Elementary analysis [%]: C: 56.8; H: 6.3; Si: 10.0

Poly(polydimethylsiloxane-block-co-polyethylenoxid-block-co-polyethersulfonyl)urethane containing PSU1-IM22 (2:1) and HDI as linker characterized by:

Gel permeation chromatography for molecular mass (kDa): Mn 5±2; Mw 14±4; Mp 14±5; PD 2.7±0.2

¹H-NMR spectroscopy: (SiMe₂O)/(CMe₂): 1.45

Elementary analysis [%]: C: 62.6; H: 6.2; Si: 10.6

5 Poly(polydimethylsiloxane-block-co-polyethylenoxid-block-polydimethylsiloxane)- urethane containing IM15-IM 22 (1:1) and HDI as linker characterized by:

Gel permeation chromatography for molecular mass (kDa): Mn 18±3; Mw 36±17; Mp 31±11; PD 1.9±0.6

¹H-NMR spectroscopy: (SiMe₂O)/(C₂H₄O): 0.91

Elementary analysis [%]: C: 40.2; H: 8.5; Si: 24.6

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Poly(polydimethylsiloxane-block-co-polyethylenoxid-block-polydimethylsiloxane)- urethane or containing IM11-IM22 (2:1) and HDI as linker characterized by:

Gel permeation chromatography for molecular mass (kDa): Mn 15±5; Mw 34±7; Mp 28±17; PD 2.3±0.4

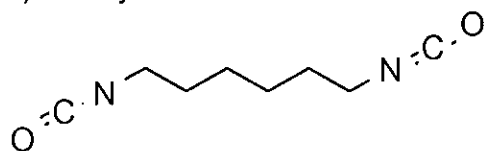
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The poly urethane reaction for the preparation of the present copolymers is analogous to the one commonly used to build up a broad variety of polymers such as soft and hard polyurethanes in multiple applications and use. Typically, the reaction is carried out in presence of aprotic none or less polar solvents and with the use of catalysts such as amines (imidazoles), tin organic compounds and others. Typical diols used are polyethlenglycols with varying molecular weight, poly-esterols or OH-terminated oligomers or even polymers. Thus, a great variety of copolymers are accessible regarding the use of technically available diisocyanates such as aliphatic diisocyanates (especially hexamethylenediisocyanate HDI), isophorone diisocyanate, aromatic methylenedi-phenyldiisocyanate (MDI) or 2,4-toluenediisocyanate (TDI). The variety of products is much more expandable, if mixtures of different diols are taken into account, resulting in fine-tuned polymeric structures with statistic linked diol blocks sequences. Therefore, the present urethane linked X_nY_m block copolymers are producible in a rational way with high variability to reach application requirements. As subject of the present invention, OH-terminated siliconbased surfactants are useful as diol components in combination with diisocyanates.

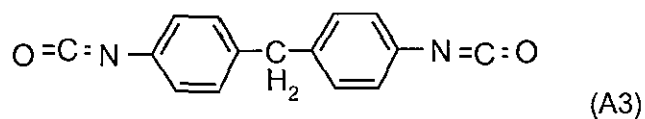
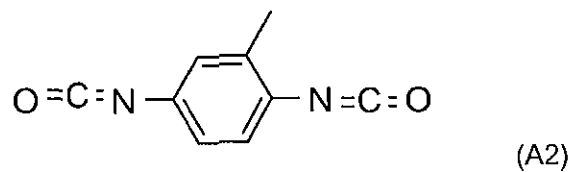
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Typical monomers for the preparation of the present polyurethanes are:

35 A) Diisocyanates

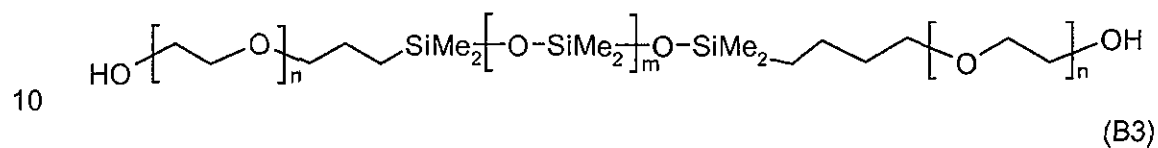
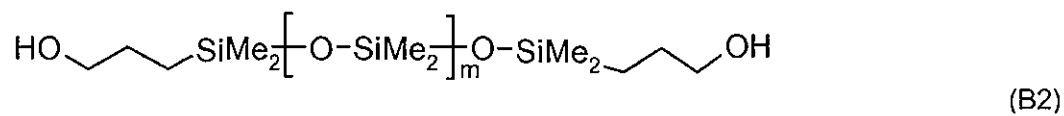


(A1)



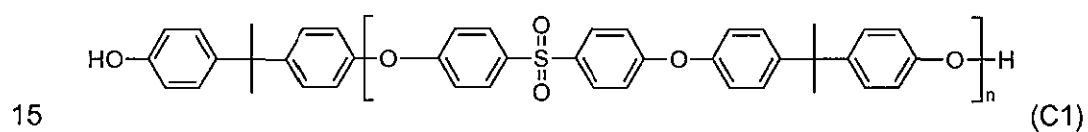
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B) Dioles

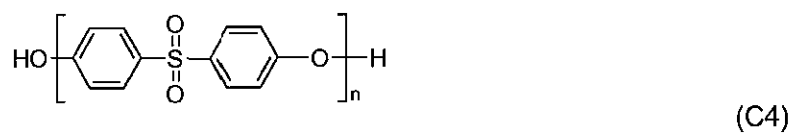
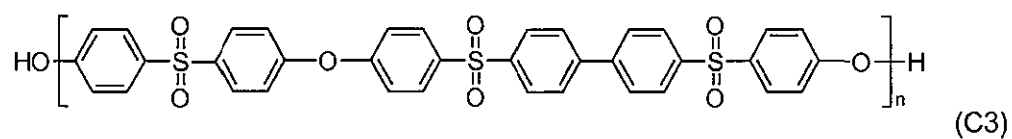
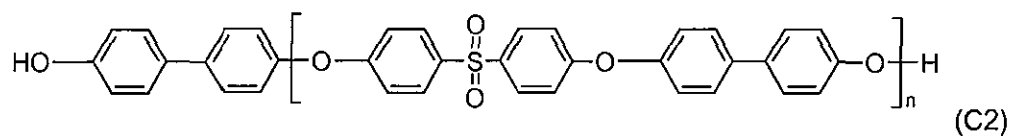


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C) Dioles



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with n, m each ranging from 1 to 100.

Polymer compositions, membrane manufacturing and processing

The present copolymers are preferably used as anti-adhesion additives in polymer compositions, such as compositions for membranes, especially water processing or gas separation membranes.

Manufacturing of ultra filtration membranes often includes solvent induced phase separation (SIPS). The present copolymers are preferably employed as additives in this process.

In the SIPS process, the educt polymers (e.g. selected from polyvinyl pyrrolidone, vinyl acetates, cellulose acetates, polyacrylonitriles, polyamides, polyolefines, polyesters, polysulfones, polyethersulfones, polycarbonates, polyether ketones, sulfonated polyether ketones, polyamide sulfones, polyvinylidene fluorides, polyvinylchlorides, polystyrenes and polytetrafluoroethylenes, copolymers thereof, and mixtures thereof; preferably selected from the group consisting of polysulfones, polyethersulfones, polyvinylidene fluorides, polyamides, cellulose acetate and mixtures thereof, especially including poly ether sulfone) are dissolved in a suitable solvent (e.g. N-methylpyrrolidone, dimethylacetamide or dimethylsulfoxide) together with the additive(s). In a next step, a porous polymeric membrane is formed under controlled conditions in a coagulation bath. In most cases, the coagulation bath contains water as coagulant, or the coagulation bath is an aqueous medium, wherein the matrix forming polymer is not soluble. The cloud point of the polymer is defined in the ideal ternary phase diagramm. In a bimodal phase separation, a microscopic porous architecture is then obtained, and water soluble components (including polymeric additives) are finally found in the aqueous phase.

In case that the polymeric additive is simultaneously compatible with the coagulant and the matrix polymer(s), segregation on the surface results. With the surface segregation, an enrichment of the additive is observed. The membrane surface thus offers new (hydrophilic) properties compared to the primarily matrix-forming polymer, the phase separation induced enrichment of the additive of the invention leading to antiadhesive surface structures.

An important property of the novel surface modifying additive is the formation of a dense coverage combined with a strong anchoring effect to the polymeric matrix. In many cases, a surface structure is obtained by micro-structured self-assembling monolayers (SAM), which hinder the adhesion of microbes.

The present copolymers combine structural elements, which encourage detachment of fouling. These copolymers are especially useful as a blending additive, since they contain an antifouling segment and an anchor, the combination of which is especially useful for membrane applications; the silicone moiety further is a good "sticking polymer" to

polysulfone, thus providing structural stability and contributing to the low leaching properties.

The present copolymers combine low energy segments and hydrophilic segments.

- 5 Phenomenologically, these segments reassemble to form nano-scaled structures in the topography of the membranes surface. In case of simultaneous self assembling of the copolymers during the SIPS process, the membrane surfaces are covered by substructures leading to reduced fouling properties of the membrane either by added topographic (relief and/or area dimension) or surface energy structuring moieties (by electrostatic interaction with the ambient media).

- Antifouling properties of the present polymer compositions, especially of the membranes, may be enhanced by further incorporation of one or more antimicrobial or bacteriostatic agents into the composition. A preferred agent is an oligodynamic metal, especially silver in ionic and/or metallic form. Optionally, the silver component may be accompanied by zinc oxide as co-component. Useful silver components include silver colloids, silver glass, silver zeolites, silver salts, elemental silver in form of powder or microparticles or nanoparticles or clusters. An advantageous method of preparing an antimicrobial membrane includes in situ formation of elemental silver particles in the casting solution containing one or more (co)polymers of the present polymer composition in dissolved form. Elemental silver particles, especially those incorporated into semipermeable membranes and/or polymer matrices close to the final article's surface, may be transformed into silver halogenide particles such as AgCl, AgBr, AgI, e.g. by treatment with a hypohalogenide solution (e.g. of NaOCl).

- 25 A typical process for the preparation of a solution to prepare membranes is characterized by the following steps:

1. Solving matrix polymers for a membrane's dope in a suitable solvent, typically NMP, DMA, DMSO or mixtures of them.
- 30 2. Adding pore forming additives such as PVP, PEG, sulfonated PES or mixtures of them
3. Heating the mixtures until a viscous solution is obtained; typically temperatures at 5-250 °C, preferred 25-150 °C, mostly preferred 60-90 °C.
4. Adding the anti-adhesion silicone-polyurethane additive to the dope at 5-250 °C, preferred 25-150 °C, and mostly preferred 60-90 °C. Optionally other additives e.g. silver containing compounds may be added in the same step.
- 35 5. Stirring of the solution/suspension until a mixture is formed within 1-15 h, typically the homogenization is finalized within 2 h.
6. Casting the membrane dope in a coagulation bath to obtain a membrane structure. Optionally the casting could be outlined using a polymeric support (non-woven) for stabilizing the membrane structure mechanically. To test the bioactivity for the application a standard procedure in flat membrane fabrication is used.
- 40 7. Analysis of the membrane for additive content.

The following examples illustrate the invention. Unless otherwise stated, room temperature denotes an ambient temperature of 20-25°C; molecular weight data (such as Mw, Mn) are as determined by gel permeation chromatography; and water contact angle (WCA) measurements are performed according to the static sessile drop method.

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Abbreviations used in the examples and elsewhere:

L	litre
NMP	N-methylpyrrolidone
PD	Polydispersity
10 PEG	Polyethyleneglycol
PES	Polyethersulfone
PVP	Polyvinylpyrrolidone
thf	Tetrahydrofuran
w%, wt%	percent by weight

15

Components used in the examples:

20 **A) Diisocyanates**

HDI: 1,6-Hexamethylene diisocyanate (Desmodur H® , commercial product from Bayer, Germany)

25 TDI: 2,4-Toluenediisocyanate (commercial product from Aldrich, Germany)

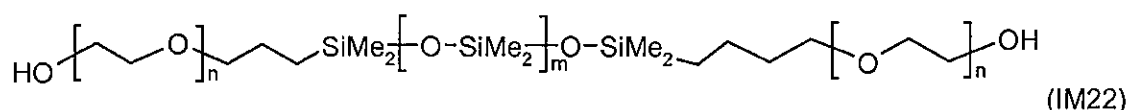
MDI: Diphenylmethane-4,4'-diisocyanate (Desmodur 44 MC®, commercial product from Bayer, Germany)

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B) Diol 1

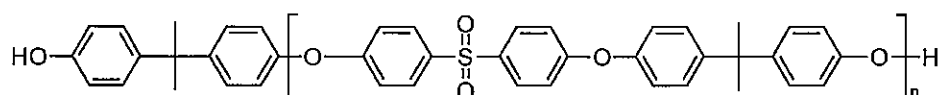
PEG 2000 (Fluka; $m = 45$)

- 5 Poly dimethylsiloxane; $m = 10$ available as IM 11® (IM11)
 $m = 50$ available as IM 15® (IM15)
 each from Wacker, Germany.

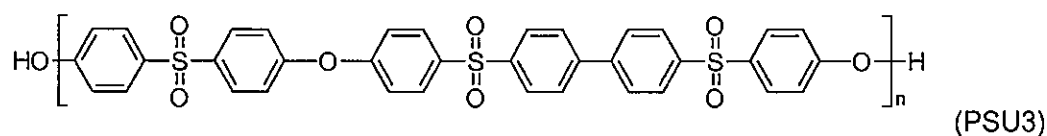
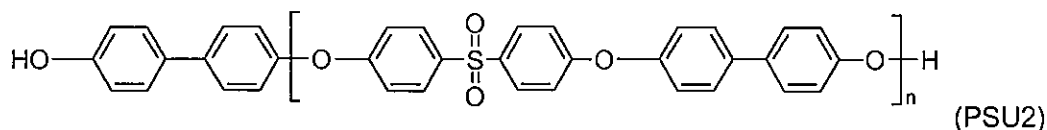


- 10 Poly dimethylsiloxane-b-polyethylenoxide: IM 22®, available from Wacker, Germany.

C) Diol 2



- 15 $M_n = 4 \text{ kDa}$, $M_w = 6-7 \text{ kDa}$ (PSU1)



- 20 $\text{HO}-\left[\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-\text{O}\right]_n-\text{H} \quad (\text{PSU4})$

Ultrason® 2020 PSR (commercial product from BASF, Germany) (PSU5)

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D) Further polymers and solvents:

Tetrahydrofurane: commercial product from Aldrich, Germany.

N-methylpyrrolidone (NMP): commercial product from Aldrich, Germany.

Polyvinylpyrrolidone (PVP): Luvitec® PVP 40 K commercial product from BASF, Germany.

Example 1: Preparation of the siloxane-block-polyurethane:

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Instruments: 250 ml Erlenmeyer glass tube, magnetic stirrer, heat plate, condenser, internal thermometer

Diol components are mixed in 120 ml of tetrahydrofurane (thf) at 25 °C. According to the sum of the OH-numbers of the diol components, the diisocyanate component is added in one dosage. Solid diisocyanate components are added as a solution in 30 ml of thf. After stirring the mixture for 5 minutes, the catalysts (1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU): 0.1 g; and dibutyl tin dilaurate: 0.1 g) are added. The well observable NCO-absorption vibration at 2325 cm⁻¹ is used for monitoring the progress of the reaction. The reaction mixture is stirred for 15 h at 25 °C; subsequently, all volatile components are evaporated using a rotary evaporator and high vacuum pump. The crude polymeric compounds are characterized by elemental analysis, ¹H-NMR and gel-permeation chromatography. The following table 1 shows the amounts of reactants used and the characterization of the polymers obtained.

20 Tab. 1: Composition of copolymers (amounts [g] refer to component in column left)

Sample	Diol 1	[g]	Diol 2	[g]	Diisoc.	[g]	NCO/OH
A1.0	IM15	7.5	IM22	7.5	HDI	0.99	1.0
A1.1	IM15	7.5	IM22	7.5	HDI	0.99	1.0
A2.0	PSU1	10	IM22	5	HDI	0.98	1.0
A2.1	PSU1	10	IM22	5	HDI	0.98	1.0
A3.0	PSU1	10	IM15	5	HDI	0.61	1.0
A4.0	PSU1	10	IM22	5	MDI	0.61	1.0
A5.0	PSU1	10	IM22	5	TDI	0.61	1.0
A6.0	PSU5	10	IM22	5	MDI	0.80	1.0
A7.0	IM11	15	IM22	30	HDI	7.39	1.2
A8.0	IM22	15	-	-	HDI	2.03	1.5
A9.0	IM22	15	-	-	MDI	2.01	1.0

Characterizations of the polyurethane block copolymers:

25 Gel permeation chromatography (GPC) in tetrahydrofurane and polystyrene as reference; elementary analysis (EA) and ¹H-NMR spectroscopy in d₆-dimethylsulfoxide as solvent. Results are shown in table 2.

Tab. 2: Copolymer characteristics

Sample No.	GPC (Da)				Elemental Analysis			1H-NMR (d ₆ -DMSO)		
	Mn	Mw	Mp	PD	%C	%H	% Si	$\frac{\text{CH}_3\text{Si}}{\text{CH}_3\text{C}}$	$\frac{\text{C}_2\text{H}_4\text{O}}{(\text{CH}_3)_2\text{C}}$	$\frac{(\text{CH}_3)_2\text{Si}}{\text{C}_2\text{H}_4\text{O}}$
A1.0	14885	19755	23382	1.32						
A1.1	19440	31743	25567	1.63	40.2	8.5	24.6			0.92
A2.0	9843	23039	23796	2.34						
A2.1	6493	16933	16116	2.61	62.6	6.2	10.6	1.45	1.94	0.75
A3.0	5714	14920	15144	2.61	56.7	6.4	10.0	0.58		
A4.0	6034	10404	9701	1.72						0.71
A5.0	4321	6676	6145	1.55						0.71
A6.0	43609	66279	64782	1.52						
A7.0	18598	38802	40358	2.09						
A8.0	16596	31026	27402	2.35	44.7	8.7	15.7			0.71
A9.0	11365	22902	18933	2.01						0.71

The silicon(tenside) polyurethanes show typical molecular mass distributions with Mn: 5-18 kDa; Mw 14-36 and a poly dispersity of 1.9-2.9.

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Example 2: Membranes

The following procedure is carried out in the preparation of membranes:

- 10 Place N-methylpyrrolidone (NMP) (70 ml) in a three-neck flask with agitator. Add polyvinylpyrrolidone Luvitec® PVP 40 K (6 g) to the NMP and increase the temperature to 60°C and stir until a homogeneous clear solution is obtained. Mix required amount of the polyurethane of the invention (additive of example 1; 5 w% in respect to polyethersulfone, 0.9 g) to 6 g of NMP and sonicate for 20 minutes and add the solution to the
- 15 PVP solution and stir until the solution is homogeneous. Add polyethersulfone Ultra-son® 2020 PSR (PES, 18 g) to the solution and stir until a viscous solution is obtained. Degas the solution overnight at room temperature (30-40°C). Reheat the membrane solution to 70°C. Cast membrane on the glass with a casting knife (200 µm) at room temperature and allow dry time of 30 second before immersion. Cast membrane in
- 20 water bath of 25°C. After 10 minutes of immersion, rinse membrane with hot water (65-75°C, 30 minutes). Membrane preparation should form a continuous film having micro structural characteristics of UF membranes; a continuous film (at least 10 X 15 cm size) with a top thin skin layer (1-2 microns) and a porous layer underneath (thickness: 100-150 microns) is obtained characterized by: Void breadth on top: 2.0 µm; skin layer:
- 25 1.2 µm; thickness: 120 µm; pore size under skin layer: 1-3 µm.

Physical-chemical performance of the membrane:

Analysis of silicone-polyurethane additives in the surface of the membrane is carried out using a variety of surface characterizing techniques. Scanning electron microscope/energy dispersive X-ray spectroscopy (SEM/EDX) to visualize the morphology and get a qualitative information of Silicon distribution and therefore additive distribution on the surface, X-ray photoelectron spectroscopy (XPS) to get quantitative information of the silicon content in the surface (1-4 monolayers = 2-10 nm). This information allows the determination of an enrichment factor of the polymeric additive in the surface of the membrane) and matrix-assisted laser desorption ionization as a mass spectrometry (MALDI-MS) imaging technique in which the sample, often a thin tissue section, is moved in two dimensions while the mass spectrum is recorded. Here qualitative information on the nature of the additive (dimethylsiloxane- and polyethyleneglycol-fragments) and their distribution on the surface are available. Topographical microdomains of additive by lateral phase separation in the coverage might be observed thereby in a resolution of 420x420 nm².

15

Characterization of membranes by SEM/EDX and XPS:

The membranes are characterized by XPS (X-Ray Photoelectron spectroscopy). The obtained concentration of silicon atoms in the 2-10 nm deepness of the surface indicates a high enrichment based over the theoretical silicon in bulk material at 5 w% initial additive loading to polyethersulfone (enrichment factor $EF = w\% \text{ Si at surface} / w\% \text{ Si calculated}$).

Results are compiled in the following table 3; Si concentrations [Si] are given in % by weight, as sampled over 3 points of 0.5 mm² each, in bulk (calculated) or at surface (2-10 nm).

Tab. 3: Membrane characteristics

Membrane	Additive [w%]	[Si] calculated	[Si] surface	EF
M1	A1.0 [5]	1.2	11.8	9.6
M2	A8.0 [5]	0.8	9.8	12.5
M3	A2.1 [5]	0.5	7.1	13.5
M4	A3.0 [5]	0.5	8.9	17.8
M6	A1.0 [5]			
M7	A1.0 [10]			
M8	A2.0 [5]			
M9	A2.0 [10]			
M10	A4.0 [5]			
M11	A5.0 [5]			
M12	none	0		

The XPS measurements indicate the polymeric additives enrichments on the surface of membranes (2-10 nm deepness) depending on the type of additive with a factor of 10-18 (calculated from an average of 5 w% additives in respect to PES).

- 5 A SEM/EDX analysis is carried out for the membrane M1 containing the additive A1.0 at the surface. The even distribution of the additive is also recognized in resolution of 420x420 nm² of an area 100x100 μm by MALDI-ToF SIMS, mapping silicon of membrane surface M1. The characteristic fragments for silicon and PEG (mass fragment m/z 45) are observed. The Si/PEG-ratio suggests a homogenous distribution of the
10 additive on the surface.

Characterization of membranes by water contact angle and water flux:

- Water flux is performed in a dead-end filtration cell (110 ml capacity, membrane area
15 1.59×10⁻³ m²) connected to a feed reservoir with a nitrogen cylinder as a pressure source. The filtration cell consists of a cylindrical vessel, equipped with a porous support on which membrane is placed. A stirrer is installed in the cell and a speed of 400 rpm is maintained during the test. Experiments are operated at constant pressure (100 kPa) and permeate is collected in a beaker placed on an electronic balance. A pres-
20 sure transducer is connected to the upstream side of membrane to measure the pressure in the cell. Both balance and pressure transducers are connected to a computer for data recording. Membranes are moisted with ethanol before flux measurement. Results for membranes M6 to M11 and M12 (comparison) are average values obtained from 5 measurements [WCA] or 3 measurements [water flux]. Membranes of the inven-
25 tion show a high water contact angle of more than 68° and a good water flux.

Example 3: Anti-adhesion performance

- Two tests are applied to assess anti-adhesion properties of the membrane's surfaces.
30 a) Protein adhesion; the recovery of flux the membranes of the invention is determined in relation to a membrane without additive: Surfaces are contacted with BSA (bovine serum albumine) as a model protein. BSA adhesion reduces the water flux; the flux can be recovered by rinsing with water (Jw) or by additional chemical treatment (Jc) with
35 sodium hydroxide. Flux recovery (normalized to the initial water flux) indicates the membrane's ability to self-cleaning and reduction of fouling.

Instruments: X-flow membrane cell, UV-vis spectrometer

- 40 Procedure:
Water flux and BSA filtration are performed using a non-commercial experimental prototype Perspex crossflow module of channel dimensions of 3 mm high, 25 mm width and 110 mm length. A feed pressure of 100 kPa is obtained using a peristaltic feed

pump (Master flux Model 7529-00 by Cole Parmer) and adjusted by a ball valve situated at the module outlet. With the channel dimension given, a cross flow velocity of 0.2 m/s is maintained for all experiments. A pressure transducer (Labom Diff. Pressure transmitter CP1310) connected to both feed and permeate sides of the membrane is used to measure the TMP (trans membrane pressure); a balance is used to monitor the permeate flux.

The experiment consists of four main stages: initial water flux, fouling, water rinse and chemical cleaning. This sequence is repeated 3 times for each membrane. In a typical run, a membrane strip of appropriate dimension is cut out from a flat sheet and mounted in the cross flow cell; polypropylene backing is used as support. The membrane is pre-compacted at 125 kPa until a constant flux is obtained. Then the pressure is reduced to 100 kPa and the initial water flux (J_i) is measured (for about 1 hour). Then the ultrafiltration experiments are performed with 0.5 wt% BSA (pH is adjusted to 4.9-5.1 by drop-wise addition of 0.1 M HCl) solution at constant pressure of 50 kPa and constant flux of about 41 ± 3 L/m²h for 90 minutes. Constant flux is achieved by using a Gilson pump in the permeate line. Then the membrane is rinsed with water for 15 minutes (1 L/min) and pure water flux is measured (J_{w1}). Chemical cleaning is done by rinsing membrane with a 0.2 wt% NaOH solution for 15 minutes and after buffering the cell, water flux is measured again (J_{c1}). The cycle is repeated 3 times. Flux recovery and resistance removal for different membranes are estimated. Samples from permeate are withdrawn for analysis by UV spectrometer to estimate the rejection. Membranes samples of the invention are taken from permeate/retentate to examine the release of the active component.

The following table 4 shows the flux of membranes of the invention relative to the flux observed with a membrane (M12) containing no copolymer of the invention (recovery after 3 cycles).

Tab. 4: Flux recovery after 3 cycles using water rinsing and addl. chem. cleaning (J_c)

Membrane	Additive (% to PSU)	J_c
M6	A1.0 (5)	1.64
M7	A1.0 (10)	1.05
M8	A2.0 (5)	1.34
M9	A2.0 (10)	1.49
M10	A4.0 (5)	1.07
M11	A5.0 (5)	1.32

The present membranes show good flux recovery.

b) Anti-adhesion of bacteria: Relative adhesion effects are quantified using antibody-antigen reactions to monitor bacteria adhered to the surface. Testing of *Escherichia coli* and *Staphylococcus aureus* is conducted according to DIN EN ISO/EC 17025.

- The samples are incubated with test cell system. Loose cell material is removed in defined washing steps. Adhered cells on the sample surface are detected in an immune assay using antigen-antibody reactions. The adhesion is monitored by a relative semi-quantitative cell unit counting. Thereby a first-anti-body reaction occurs on the adhered
- 5 test cell system; docking on this first level antibody, a specific enzyme is fixed by a secondary antibody. After addition of a colouring substrate, an enzyme catalysed colouring reaction occurs; coloration is proportional to the amount of adhered cells. Compared to the blank (membrane without polyurethane additive) the relative adhesion is evaluated. Each sample is independently measured nine times. The test result for the sample is
- 10 normalized to the blank (comparative) sample's average.
- The relative adhesion results as quotient of the average data of the samples and the comparative blank sample. Multiplication by 100 results in relative adhesion in percentage unit. Samples with a relative adhesion > 100% demonstrate increased adhesion of test bacteria. Materials with a relative adhesion of <100 % demonstrate decreasing
- 15 adhesion (adhesion reduction). Results are compiled in the below table 5.

Tab. 5: Adhesion of E. coli (Ec) or S. aureus (Sa) relative to comparative membrane

Membrane	Additive	% adhesion Ec	% adhesion Sa
M1	A1.0	- 14	- 40
M2	A8.0	- 42	- 8
M3	A2.1	- 44	- 3
M4	A3.0	- 45	- 22

- Membranes of the invention effectively inhibit bacterial adhesion.
- 20

Example 4: Copolymers used in flat sheet membranes

- Siloxane block-urethane copolymers are prepared according to example 1. The ratio
- 25 between the different diols and the type of isocyanates used are reported in the table below:

Copolymer	IM22 (g)	IM15 (g)	PSU (g)	MDI 4,4' (g)	HDI (g)
B	20	/	40	/	4.0
C	10	/	40	/	3.1
D	10	/	40	5.95	/
E	15	/	30	5.38	/

Table 6: Copolymer's composition

These copolymers have been characterized by GPC and elemental analysis:

Copolymer	Mw (Da)	Mn (Da)	Mp (Da)	PD	Elemental analysis
B	9033	3811	7286	2.37	C: 63%; H: 6.58%; N: 1.37%; O: 16.8%; S: 3.54%; Si: 5.3%
C	10161	3454	9112	2.94	C: 66.3%; H: 5.64%; N: 1.38%; O: 15.6%; S: 4.15%; Si: 3.3%
D	9527	3129	7470	3.04	C: 68.6%; H: 6.50%; N: 1.41%; O: 15.5%; S: 4.1%; Si: 2.8%
E	18633	4467	13372	4.17	C: 64.9%; H: 6.8; N: 1.48; O: 15.4%; S: 3.7%; Si: 4.3%

5

Table 7: GPC (PS calibration) and elemental analysis of copolymers

These additives have been used at 5 % b.w. to prepare flat sheet membranes according with the procedure described in example 2.

10

The membranes are characterized by XPS (X-Ray Photoelectron spectroscopy). A high enrichment based over the theoretical silicon in bulk material at 5 w% initial additive loading to polyethersulfone (enrichment factor $EF = w\% \text{ Si at surface} / w\% \text{ Si calculated}$).

15

Results are reported in the following table; Si concentrations [Si] are given in % by weight, as sampled over 3 points of 0.5 mm² each, in bulk (calculated) or at surface (2-10 nm).

20

Membrane	Copolymer	Si% in the bulk	Si% on surface	EF	XPS Elemental analysis
MA2	B	0.25%	3.8%	15.2	C: 72.1%; S: 3.4% N: 2.0%; O: 18.7%; Si 3.8%
MA3	C	0.15%	3.7%	24.7	C: 72.9%; S: 3.1% N: 2.2%; O: 18.0%; Si 3.7%
MA4	D	0.10%	3.9%	39	C: 71.4%; S: 3.0% N: 2.6%; O: 19.4%; Si 3.9%
MA5	E	0.19%	4.4%	23.2	C: 70.1%; S: 2.9% N: 2.4%; O: 20.1%; Si 4.4%

Table 8: Si concentration in flat sheet membranes bulk and on surface. Enrichment factor as ratio between Si on surface and in the bulk.

5

XPS measurements show that the enrichments of polymeric additives on membrane surface is changing on the basis of the additive chemical composition and structure. In general additive with lower Si content exhibit a higher surface enrichment (EF).

- 10 Membranes are then characterised by contact angle, flux recovery after water or chemical cleaning and water flux. The procedure for water and chemical flux test is described on pag 13-14 (Case PF70441).

	JW	JC	Water Flux (L/m ² h)	Contact angle (°)
MA2	0.72	0.94	190±40	92±5
MA3	0.62	0.85	220±60	83±4
MA4	0.84	1.01	200±40	84±2
MA5	0.63	0.85	180±40	86±2
Control (PES)	0.42	0.74	280±30	61±7

- 15 Table 9: Flux recovery after 3 cycles of water(JW) or chemical cleaning (JC). Contact Angle (°) and water flux.

- 20 Membranes functionalized with siloxane block-urethane copolymers of the invention show better flux recovery after both water and chemical cleaning (compared with standard non flat sheet PES membrane).

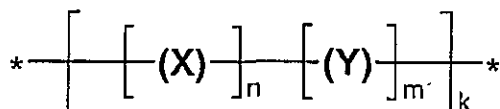
Water flux is in the same range of standard PES membrane which means that these additives do not significantly impact membrane pore structure. Contact angle for functionalized membranes is higher if compared with standard PES (membrane surface is more hydrophobic), this is reflection these additives' behavior to self-enrich on membrane surface as can be detected by and higher amount of Si on surface if compared with the bulk.

5

Claims:

1. Polymer composition comprising

a) an oligo- or polyurethane of the formula I

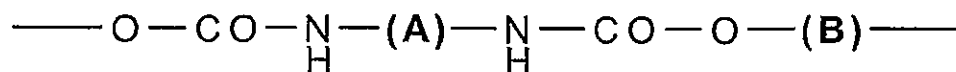


(I)

wherein k and n independently are numbers from 1 to 100,

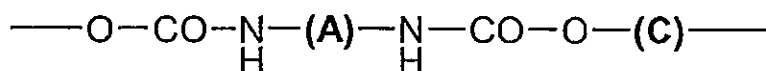
m is from the range 1-100,

(X) is a block of formula



(II)

and (Y) is a block of the formula



(III),

(A) is a residue of an aliphatic or aromatic diisocyanate linker,

(B) is a residue of a linear oligo- or polysiloxane containing alkanol end groups, and optionally further containing one or more aliphatic ether moieties, and

(C) is an aromatic oligo- or polysulfone block;

or a mixture of such oligo- or polyurethanes; and

b) one or more further organic polymers selected from the group consisting of polyvinyl pyrrolidone, polyvinyl acetates, cellulose acetates, polyacrylonitriles, polyamides, polyolefines, polyesters, polysulfones, polyethersulfones, polycarbonates, polyether ketones, sulfonated polyether ketones, polyamide sulfones, polyvinylidene fluorides, polyvinylchlorides, polystyrenes and polytetrafluoroethylenes, copolymers thereof, and mixtures thereof; preferably selected from the group consisting of polysulfones, polyethersulfones, polyvinylidene fluorides, polyamides, cellulose acetate and mixtures thereof.

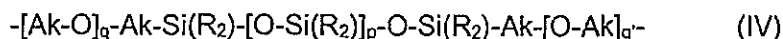
2. Polymer composition according to claim 1, wherein the molecular weight (Mn) of the compound of formula I is from the range 1500 to 100000, wherein n and m each are

from the range 1 to 50, and k is from range 1 to 20.

3. Polymer composition according to any of claims 1 or 2, where in the oligo- or polyurethane of the formula I

(A) is a divalent residue selected from C₂-C₁₂alkylene and Ar;

(B) is a divalent residue of an oligo- or polysiloxane of the formula



wherein Ak stands for C₂-C₄alkylene, R stands for C₁-C₄alkyl, and each of p, q and q' independently is a number selected from the range 0-50;

- 5 (C) is a diphenyl sulfone monomer or linear oligomer or polymer block containing 1-50 moieties phenyl-SO₂-phenyl, and optionally further 1-50 further moieties Ar, which moieties are, in case of the oligomer or polymer, linked together by spacers Sp;
Ar is -Ph-Sp-Ph-;
Ph is phenyl or phenyl substituted by C₁-C₄alkyl; and
10 Sp independently is selected from direct bond, -O-, C₁-C₃alkylene.

4. Polymer composition according to any of claims 1 to 3, comprising the oligo- or polyurethane of formula I in an amount of 0.1 to 25 % by weight of the total polymer composition, especially in a homogenous phase or within the same phase enriched at the
15 surface.

5. Polymer composition according to any of claims 1 to 4, further comprising one or more antimicrobial or bacteriostatic agents, especially silver in ionic and/or metallic form such as silver colloid, silver glass, silver zeolite, silver salts, elemental silver in
20 form of powder, microparticle, nanoparticle or cluster.

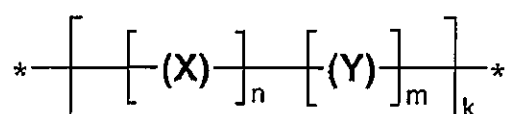
6. Membrane, especially semipermeable membrane, comprising a polymer composition of any of claims 1 to 5.

- 25 7. Membrane of claim 6, showing an at least 8-fold enrichment of silicon, especially an 8- to 25-fold enrichment of silicon, in the section 2-10 nm from the membrane surface over the membrane's average silicon content.

8. Process for the preparation of a membrane, especially a semipermeable membrane
30 for water treatment or and gas separation purposes, which process comprises incorporation of a polymer composition according to any of claims 1 to 5 into the membrane material.

9. Use of the polymer composition according to any of claims 1 to 5 for the preparation
35 of an antimicrobial membrane, especially for water separation or gas separation purposes.

10. Oligo- or polyurethane compound of the formula I

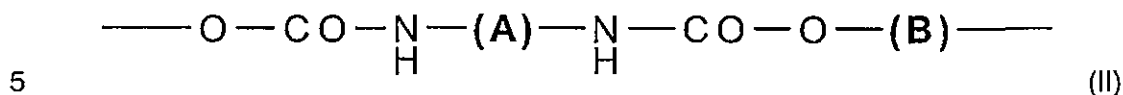


(I)

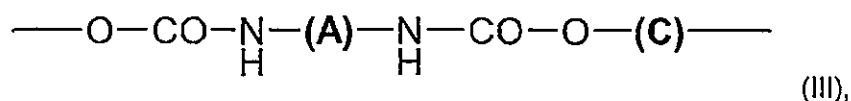
wherein k and n independently are numbers from 1 to 100,

m is from the range 1-100,

(X) is a block of formula



and (Y) is a block of the formula



(A) is a residue of an aliphatic or aromatic diisocyanate linker,

(B) is a residue of a linear oligo- or polysiloxane containing alkanol end groups, and optionally further containing one or more aliphatic ether moieties, and

(C) is an aromatic oligo- or polysulfone block;

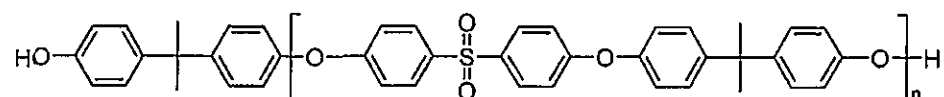
especially for use as an antimicrobial or anti-bioadhesive additive.

11. Compound according to claim 10, the molecular weight (Mn) of the compound of formula I being from the range 1500 to 100000, especially from the range 4000 to 25000, wherein n and m are from the range 1 to 50, and k is from range 1 to 20.

12. Use of an oligo- or polyurethane according of formula I as described in any of claims 1 to 5 or 10 to 11 as an additive imparting antiadhesive or bacteriostatic properties to a polymer composition, especially to a polymer membrane.

13. Compound, especially according to claim 10, which is selected from

a) poly(polydimethylsiloxane-block-co-polyethersulfonyl)urethane derived from a polyethersulfone of formula



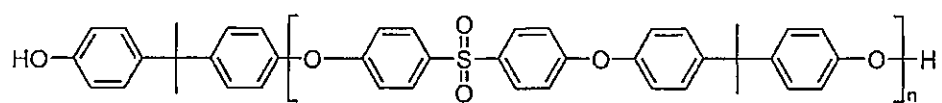
and polydimethylsiloxane of formula



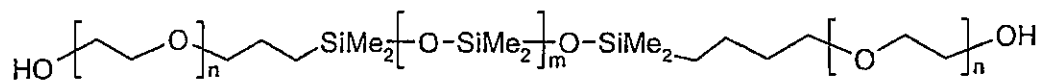
in a molar ratio ranging

from 3:1 to 1:1, where m in both formulas is from the range 5 to 80, and 1,6-hexamethylene diisocyanate as linker;

b) poly(polydimethylsiloxane-block-co-polyethylenoxid-block-co-polyethersulfonyl)urethane derived from a polyethersulfone of formula



and polydimethylsiloxane of formula



in a molar ratio ranging from 3:1 to 1:1, wherein n and m are from the range 5 to 80,

5 and hexamethylene diisocyanate as linker.