(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
07 December 2023 (07.12.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/232169 A1

(51) International Patent Classification:
C08J 5/22 (2006.01) *B01J 47/012* (2017.01)
B01D 71/82 (2006.01) *C08F 8/24* (2006.01)

(21) International Application Number:
PCT/CZ2023/050021

(22) International Filing Date:
22 April 2023 (22.04.2023)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PV 2022-238 03 June 2022 (03.06.2022) CZ

(71) Applicants: **USTAV MAKROMOLEKULARNI CHEMIE AV CR, V. V. I.** [CZ/CZ]; Heyrovskeho namesti 1888/2, 16200 Praha 6 (CZ). **VYSOKA SKOLA CHEMICKO-TECHNOLOGICKA V PRAZE** [CZ/CZ]; Technicka 1905/5, 16000 Praha 6 (CZ). **UJV REZ, A.S.** [CZ/CZ]; Hlavni 130, 25068 Husinec, Rez (CZ). **ENVISAN-GEM, A.S.** [CZ/CZ]; 37371 Hůry 149 (CZ).

(72) Inventors: **ZITKA, Jan**; 27343 Zajezd 8 (CZ). **OTMAR, Miroslav**; U koleji 340/22, 16100 Praha 6 (CZ). **PAVLOVEC, Lukas**; 27343 Zajezd 8 (CZ). **BOUZEK, Karel**; Na ruzovem poli 2563, 27201 Kladno (CZ). **HNAT, Jaromir**; Krivoklatska 885, 19900 Praha 9 (CZ). **DOUCEK, Ales**; Ovenecka 348/36, 17000 Praha 7 (CZ). **FILISTEIN, Vaclav**; Budejovicka 139, 38411 Netolice (CZ).

(74) Agent: **HARBER IP S.R.O.**; Dukelskych hrdinu 567/52, 17000 Praha 7 (CZ).

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

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

Published:
— *with international search report (Art. 21(3))*

WO 2023/232169 A1

(54) Title: ANION-EXCHANGE MATERIAL BASED ON BLOCK POLYMER OF STYRENE AND OLEFINS

(57) Abstract: The invention provides a method for preparing an anion-exchange membrane, comprising the following steps: a) subjecting poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) to chloromethylation on the benzene rings in the styrene units to form a chloromethylated poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene); b) casting the chloromethylated poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene- *block*-styrene) into the form of a membrane; c) subjecting the chloromethylated poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) in the form of the membrane to a reaction with 1-methylpyrrolidine to form a quaternary 1,1-dimethylpyrrolidinium salt covalently bound to the benzene rings of the styrene units. Furthermore, an anion-exchange membrane obtainable by this method is provided.

Anion-exchange material based on block polymer of styrene and olefins

Field of Art

The invention relates to a high-capacity anion-exchange material based on the block copolymer poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) bearing quaternary 1,1-dimethylpyrrolidinium groups covalently bound to the aromatic nucleus through one of the methyl substituents of the said 1,1-dimethylpyrrolidinium group.

Background Art

Ion-exchange membranes find application on a laboratory as well as industrial scale. The most important applications include electrochemical desalination of sea and brackish waters, separation of electrolytes from non-electrolytes, purification of pharmaceutical products, use as solid electrolytes and use in other processes. Ion-exchange membranes are produced either as homogeneous membranes, which are a single-phase system, or as heterogeneous membranes, which are formed by a dispersion of ion-exchange particles in a hydrophobic polymer binder (J. Schauer, L. Brožová, Journal of Membrane Science 250 (2005) 151).

Anion-exchange (anex) membranes are usually prepared from chloromethylated cross-linked polystyrene, or by grafting styrene or vinylbenzyl chloride onto a porous membrane and subsequent chloromethylation. The chlorine atom from the chloromethyl group is then subjected to a substitution reaction with a trialkylamine to form a quaternary tetraalkylammonium functional group. Another method for preparing anex membranes involves quaternization of poly(4-vinylpyridine) (G. Merle, M. Wessling, K. Nijmeijer, J. Membr. Sci. 377 (2011) 1).

Carcinogenic and toxic chloroalkyl ethers or bischloroalkyl ethers (e.g. (chloromethyl)methyl ether or bis(chloromethyl)ether) are often used for industrial chloromethylation. Chloromethylation of the block copolymer poly(styrene-*block*-ethylene-*stat*-butylene-*block*-styrene) (PSEBS) having M_w 30,000 g.mol^{-1} by a reaction with (chloromethyl)methyl ether catalyzed by $ZnCl_2$ is described in document EP 2157105A1. The thus prepared precursor is subsequently reacted with a solution of trimethylamine, resulting in PSEBS bearing quaternary

tetramethylammonium groups attached to the benzene ring of the styrene unit via a covalent bond through one of the methyls. Also reported in the literature is chloromethylation of a PSEBS block copolymer having M_w 89,000 g.mol^{-1} and a styrene content of 28.6 wt.% without the use of (chloromethyl)methyl ether (R. Vinodh, A. Ilakkiya, S. Elamathi and D. Sangeetha, Mater. Sci. Eng. B: Solid-State Mater. Adv. Technol. **167** (2010) (1), 43). Paraformaldehyde with hydrogen chloride, and $ZnCl_2$ as a catalyst, were used for this reaction. The resulting chloromethylated polymer was subsequently subjected to a quaternization reaction with triethylamine. Membranes prepared from this material showed a low ionic conductivity (0.69 mS.cm^{-1}) and ion-exchange capacity (0.578 meq.g^{-1}), which corresponds to roughly 20% chloromethylation, assuming that the subsequent formation of the quaternary tetraalkylammonium salt takes place almost quantitatively. A similar procedure with a PSEBS copolymer having M_w of 118,000 g.mol^{-1} and a styrene content of 29 wt. % according to the publication Q. H. Zeng, Q. L. Liu, I. Broadwell, A. M. Zhu, Y. Xiong and X. P. Tu, J. Membr. Sci. **349** (2010) (1-2) 237 also showed a degree of chloromethylation of about 20% with a maximum chlorine content of 1.75 %, and the membrane resulting from a reaction with trimethylamine also had a low ionic conductivity of 9.37 mS.cm^{-1} at 80 °C. Chloromethylation of PSEBS copolymer using (chloromethyl)methyl ether and subsequent quaternization reaction with trimethylamine is also described in other publications (J. Zhou, J. Guo, D. Chu, R. Chen, J. Power Sources **219** (2012) 272); L. Sun, J. Guo, J. Zhou, Q. Xu, D. Chu, R. Chen, J. Power Sources **202** (2012) 70; J. Žitka, J. Peter, B. Galajdová, L. Pavlovec, Z. Pientka, M. Paidar, J. Hnát, K. Bouzek, Desalination Water Treat. **142** (2019) 90). A quaternization reaction of chloromethylated PSEBS with 1,4-bicyclo[2.2.2]octane is also described in the literature (J. Hnát, M. Plevová, J. Žitka, M. Paidar, K. Bouzek, Electrochim Acta **248** (2017) 547). When using chloromethyl(methyl) ether, a tendency to side reactions is mentioned in the literature, which in the case of styrene polymers leads to cross-linking (R. C. Fuson, C. H. McKeever, Chloromethylation of Aromatic Compounds, Organic Reactions, John Wiley & Sons, Inc., 2004). Chloromethylation of the PSEBS block copolymer without the use of (chloromethyl)methyl ether followed by a reaction with trimethylamine is described in patent document CZ305138. Another drawback of these membranes known in the art lies, as described in the above-mentioned publications, in their limited stability in an alkaline environment.

Disclosure of the Invention

The present invention provides a method for preparing anion-exchange (anex) membranes containing or consisting of a block copolymer poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene), in which the benzene rings of the styrene units bear a quaternary 1,1-dimethylpyrrolidinium group covalently attached via one of its methyls (formula I), said method comprising the following steps:

– subjecting poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) to chloromethylation on the benzene rings in the styrene units to form a chloromethylated poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene);

– casting the chloromethylated poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) into the form of a membrane;

– subjecting the chloromethylated poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) in the form of the membrane to a reaction with 1-methylpyrrolidine to form a quaternary 1,1-dimethylpyrrolidinium salt covalently bound to the benzene rings of the styrene units.

In a preferred embodiment, the block copolymer poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) used as a starting copolymer for the chloromethylation has a number average molar mass of 10,000 to 1,000,000 $g.mol^{-1}$ and a weight percent of styrene in the range of 10 to 70%.

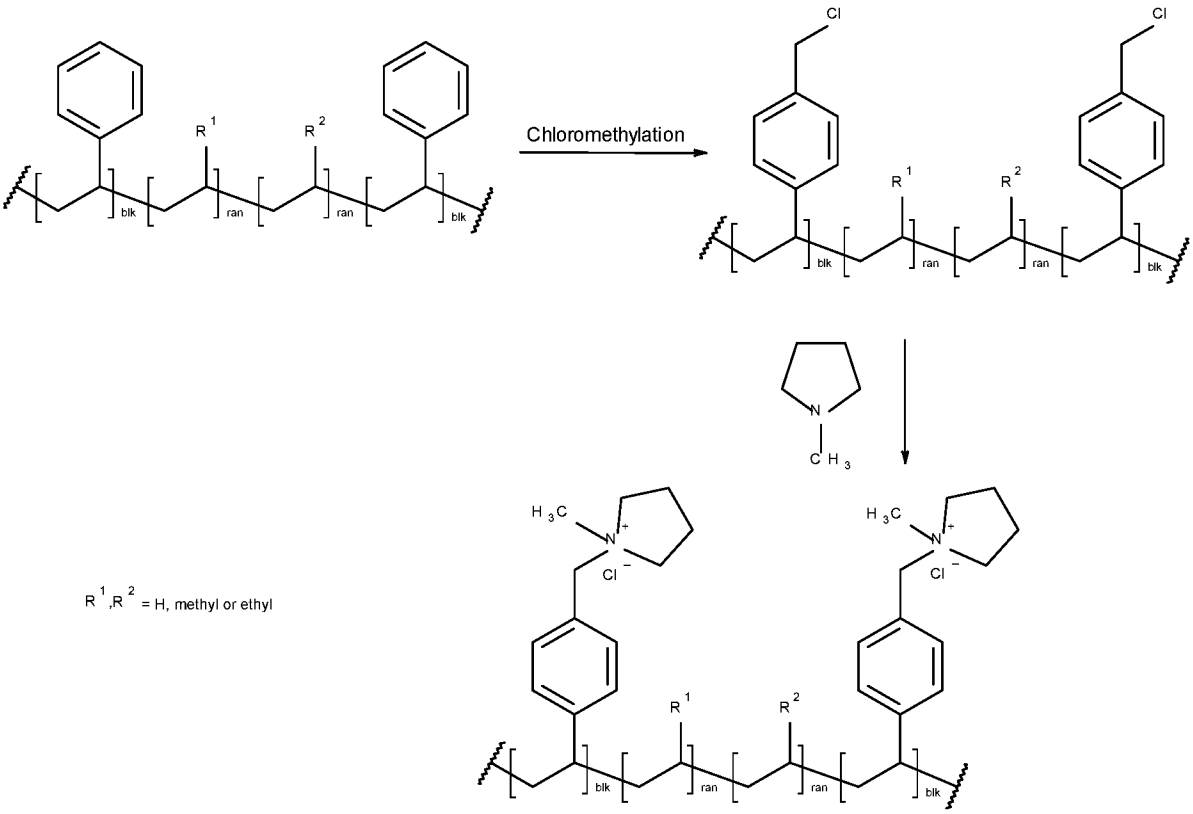
In a preferred embodiment, the starting copolymer is a poly(styrene-*block*-ethylene-*stat*-butylene-*block*-styrene) copolymer (PSEBS).

Chloromethylation can preferably be carried out by the process described in the patent document CZ305138, i.e. by bringing the starting block copolymer poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) into a reaction with dimethoxymethane, with a reagent selected from the group PCl_3, $SOCl_2$ and $SiCl_4$, and with a $ZnCl_2$ catalyst, at a temperature within the range of 10°C to 65°C, for at least 2 hours, in some embodiments for 2 to 24 h, in other embodiments for 24 hours to 1 month.

In a preferred embodiment, water and/or C1-C4 alcohol is used as a suitable solvent for the reaction step of the chloromethylated membrane with 1-methylpyrrolidine. These solvents ensure good solubility of the reagents and wettability of the membrane without dissolving it.

Preferably, the reaction of the membrane with 1-methylpyrrolidine is carried out at a temperature within the range of 20°C to 65°C, more preferably for at least 24 hours to 48 hours.

The preparation procedure can be illustrated by the following reaction scheme, which, however, does not limit the scope of protection:

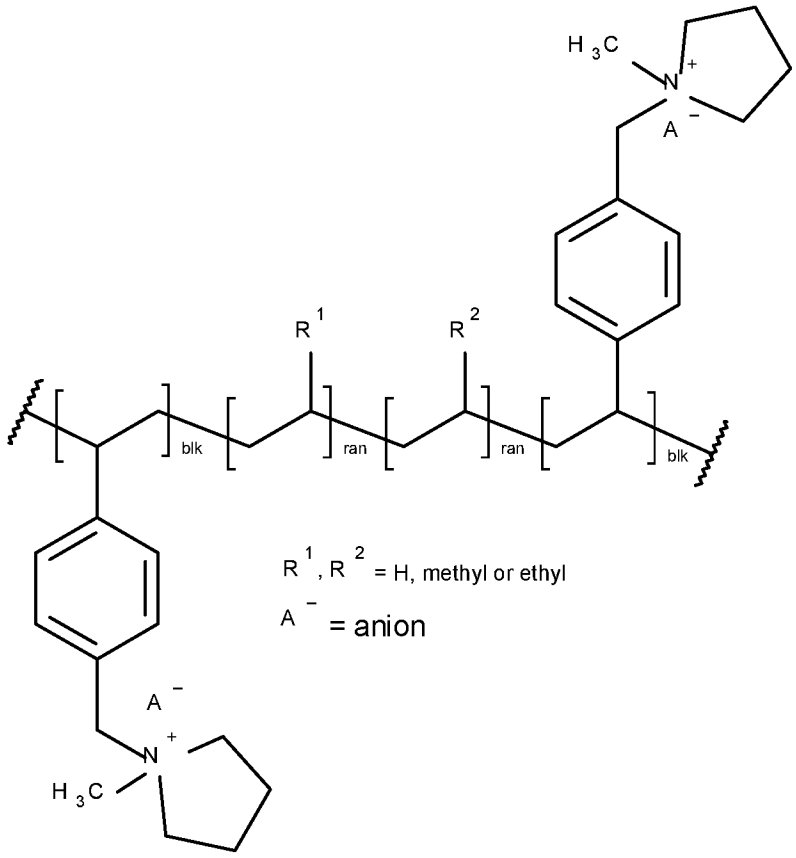


Afterwards, an anion exchange step can be performed, i.e. the chloride anion can be exchanged for another anion.

The present invention further provides an anion-exchange membrane containing or consisting of a block copolymer poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene), in which the benzene rings of the styrene units carry quaternary 1,1-dimethylpyrrolidinium

group covalently attached to the benzene ring via one of the methyls. The membrane is obtainable by the method according to the invention.

The block copolymer can be represented schematically by formula I:



Formula (I)

The membranes of the invention are highly ion-conductive, have good mechanical properties even in the dry state, and are usable, for example, in applications for ion-exchange materials, such as solid electrolytes, ion-exchange membranes, ion-exchange binders and catalyst carriers. High ionic conductivity refers to a conductivity of at least 50 $mS.cm^{-1}$ in the hydroxide cycle at a temperature of 25 °C.

Preferably, the content of styrene units is in the range of 10 to 70 wt.%, more preferably 20 to 40 wt.%, and the content of alkylene units of each type is in the range of 10 to 50 wt.%, based on the weight of the starting poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) without the bound 1,1-dimethylpyrrolidinium groups.

Preferably, the alkylene is butylene and ethylene.

Preferably, the content of 1,1-dimethylpyrrolidinium groups is in the range of 0.8 to 3.2 mmol.g^{-1}, more preferably 0.9 to 1.9 mmol.g^{-1}, based on the weight of unswollen block copolymer with the bound 1,1-dimethylpyrrolidinium groups and with a chloride counterion, according to formula I. The chloride counterion is a counterion that is formed during the preparation reaction and is used here as a reference counterion. Membranes with other counterions can be prepared by the anion exchange step, and the content of 1,1-dimethylpyrrolidinium groups can be converted (re-calculated) to the content relative to the copolymer with the reference counterion.

The membranes obtainable by the method according to the present invention can be preferably used for the preparation of homogeneous or microheterogeneous membranes, impregnation of electrodes in electrochemical devices or as catalyst carriers.

Examples of carrying out the Invention

Example 1

5 g of PSEBS block copolymer with a styrene content of 29 wt.%, i.e. 1.45 g (0.0139 mol), was dissolved in 95 g of chloroform, and 10 g (0.131 mol) of dimethoxymethane, 1.8 g (0.0132 mol) of $ZnCl_2$ and 2 g (0.0146 mol) of PCl_3 were added. $ZnCl_2$ was dispersed by stirring for 1 h and the mixture was then heated at 60 °C for 24 h. Then the reaction mixture was diluted with 100 g of chloroform and precipitated into 2 L of ethanol. The precipitated polymer was filtered off, washed with 2 L of ethanol and dried at room temperature. Chlorine content 4.56 wt.%. Degree of chloromethylation 49%. The product was soluble in toluene and chlorinated solvents.

Example 2

5 g of block copolymer PSEBS with a styrene content of 29 wt. %, i.e. 1.45 g (0.0139 mol), was dissolved in 95 g of chloroform, and 10 g (0.131 mol) of dimethoxymethane, 1.8 g (0.0132 mol) of $ZnCl_2$ and 2 g (0.0146 mol) of PCl_3 were added. $ZnCl_2$ was dispersed by stirring for 1 h. The mixture was then left at room temperature of (20°C) for 27 days. After 27 days, the mixture was diluted with 100 g of chloroform and precipitated into 2 L of ethanol. Subsequently, the polymer was filtered off, washed with 2 L of ethanol and dried at room

temperature. Chlorine content 5.38 wt. %. Degree of chloromethylation 59%. The product was soluble in toluene and chlorinated solvents.

Example 3

The chloromethylated polymer prepared according to Example 2 was dissolved into a 5% solution in tetrahydrofuran, cast onto a Teflon pad and covered with a petri dish to slow down the solvent evaporation. Under these conditions, the solvent was evaporated at laboratory temperature after 48 h. The thus prepared membrane weighing about 1 g was embedded in 100 ml of a 35% ethanol solution of 1-methylpyrrolidine in a reaction vessel. The vessel was tightly closed and heated at 60 °C for 24 h. Then the membrane was removed and immersed in 0.5 L of 1M HCl for 1 h. The membrane was removed, washed with demineralized water and dried at room temperature. Conversion to the OH^- phase was performed by immersing the membrane in 1 L of 1M NaOH for 1 h and then washing with distilled water. The ionic conductivity in the OH^- phase of the membrane at 30 °C is 42.3 $mS.cm^{-1}$.

Example 4

The chloromethylated polymer prepared according to Example 2 was dissolved into a 5% solution in tetrahydrofuran, cast onto a Teflon pad and covered with a petri dish to slow down the evaporation of the solvent. Under these conditions, the solvent was evaporated at laboratory temperature after 48 h. The thus prepared membrane weighing about 1 g was embedded in 100 ml of a 10% ethanol solution of 1-methylpyrrolidine in a reaction vessel. The vessel was tightly closed and left at a laboratory temperature of 25°C for 48 h. The membrane was then removed and immersed in 0.5 L of 1M HCl for 1 h. The membrane was again removed, washed with demineralized water and dried at laboratory temperature. Conversion to the OH^- phase was performed by immersing the membrane in 1 L of 1M NaOH for 1 h and then washing with distilled water. The ionic conductivity in the OH^- phase of the membrane at 30 °C is 30.2 $mS.cm^{-1}$.

Example 5: Determination of chlorine content

In the procedure according to the present invention, the membrane is first cast, and only on the finished membrane, the reaction of the chloromethyl group with 1-methylpyrrolidine is performed to form a charged 1,1-dimethylpyrrolidinium functional group. The reaction is almost quantitative. The reaction in the solvent is important because it allows the membrane to

swell, which ensures that the reagent reaches all the chloromethyl groups.

In order to demonstrate that the chloromethyl groups are almost completely removed and replaced by 1,1-dimethylpyrrolidine groups, an elemental analysis of the membranes converted from the Cl^- phase to the OH^- phase was performed. The conversion to the OH^- phase was carried out according to the procedure described in J Appl Electrochem (2012) 42:545–554, section 2.3 “pretreatment of the membrane”. The membrane is immersed for 24 hours in demineralized water, then it is immersed in 0.1M NaOH for 2 hours, then it is immersed in 0.1M HCl overnight, then it is immersed in 0.1M NaOH for 4 hours and finally is immersed in demineralized water for 24 hours. After each immersion step, the membrane was washed with demineralized water. The amount of HCl and NaOH relative to the theoretical content of charged functional groups in the membrane is in the range of 10 to 100.

The chloromethylated membrane before reaction with 1-methylpyrrolidine had a chlorine content of 5.09 ± 0.01 %. After the reaction with 1-methylpyrrolidine, carried out according to Example 3, the chlorine content was 2.45 ± 0 %. After conversion to the OH^- phase, the chlorine content was 0.11 ± 0 %.

Another chloromethylated membrane before reaction with 1-methylpyrrolidine had a chlorine content of 2.61 ± 0.02 %, i.e. it was a membrane with a lower content of chloromethyl groups. After the reaction with 1-methylpyrrolidine according to Example 3, the chlorine content was 2.28 ± 0.02 %. After conversion to the OH^- phase, the chlorine content was 0.11 ± 0 %.

The same residual chlorine content for both the low and high chloromethylated membranes suggests that the residual chlorine is a systematic phenomenon, which may be due in part to measurement error, in part due to the conversion reaction from the chloride to hydroxide form exhibiting equilibrium, and in part due to the fact that even the conversion of chloromethyl groups is not completely quantitative (only almost quantitative).

Example 6: Determination of ion exchange capacity

The ion exchange capacity was evaluated by spectrophotometric determination of the molar amount of nitrate ions exchanged by a membrane sample of known weight. Before the measurement, the membrane samples were immersed in 0.1 $mol.dm^{-3}$ NaOH for 4 hours, then in 0.1 $mol.dm^{-3}$ HCl for 12 hours, and then in 0.1 $mol.dm^{-3}$ NaOH for 4 hours. After each immersion step, the membrane was washed with demineralized water. The membrane samples were subsequently placed in 1 L of 1 $mol.dm^{-3}$ KNO_3 solution for 24 hours. Five samples with dimensions of 1×1 cm^2 were measured for each membrane. Each of the samples was then

thoroughly rinsed with demineralized water and transferred to 0.1 L of 0.1 mol.dm^{-3} NaCl solution for a period of 24 hours. The ion exchange capacity was calculated based on the determined amount of nitrate ions and the weight of the dry sample.

Results:

For the membrane prepared according to Example 3, the ion exchange capacity IEC = 1.48 ± 0.04 mmol/g was recorded.

For the membrane prepared according to Example 4, the ion exchange capacity IEC = 0.65 ± 0.05 mmol/g was recorded.

Industrial Applicability

Anex membranes (and ion-exchange membranes in general) are used in both laboratory and industrial scale. The most important applications include mainly electrochemical desalination of sea and brackish waters, separation of electrolytes from non-electrolytes, purification of pharmaceutical preparations, use as solid electrolytes and use in other electrochemical processes such as electrodialysis, electrolysis and fuel cells.

CLAIMS

1. Method for preparing an anion-exchange membrane, comprising the following steps:

a) subjecting poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) to chloromethylation on the benzene rings in the styrene units to form a chloromethylated poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene);

b) casting the chloromethylated poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) into the form of a membrane;

c) subjecting the chloromethylated poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) in the form of the membrane to a reaction with 1-methylpyrrolidine to form a quaternary 1,1-dimethylpyrrolidinium salt covalently bound to the benzene rings of the styrene units.

2. Method according to claim 1, further comprising a step of anion exchange on the membrane produced in step c).

3. Method according to claim 1 or 2, wherein the starting block copolymer poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) in step a) has a number average molar mass of 10,000 to 1,000,000 $g.mol^{-1}$ and a weight percent of styrene in the range of 10 to 70%, preferably 20 to 40 %, and the content of alkylene of each type is within the range of 10 to 50 wt.%.

4. Method according to any of claims 1 to 3, wherein the reaction step c) is carried out using water and/or C1-C4 alcohol as a solvent.

5. Anion-exchange membrane obtainable by the method of any one of claims 1 to 4, containing or consisting of a block copolymer poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene), in which the benzene rings of the styrene units carry a quaternary 1,1-dimethylpyrrolidinium group covalently attached via one of its methyls.

6. Anion-exchange membrane according to claim 5, wherein a weight percent of styrene in the range of 10 to 70%, preferably 20 to 40 %, and the content of alkylene of each type is within

the range of 10 to 50 wt.%, relative to the weight of poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) without the 1,1-dimethylpyrrolidinium groups.

7. Anion-exchange membrane according to claim 5 or 6, wherein the alkylene is butylene and ethylene.

8. Anion-exchange membrane according to any one of claims 5 to 7, wherein the content of 1,1-dimethylpyrrolidinium groups is within the range of 0.8 to 3.2 mmol.g^{-1}, preferably 0.9 to 1.9 mmol.g^{-1}, relative to the weight of poly(styrene-*block*-C2-C4-alkylene-*stat*-C2-C4-alkylene-*block*-styrene) with the bound 1,1-dimethylpyrrolidinium groups, and calculated to the form with chloride counterions.

9. Use of the anion-exchange membrane according to any one of claims 5 to 8 for impregnation of electrodes in electrochemical devices, as catalyst carriers, as ion-exchange membranes and binders in electrochemical devices, as solid electrolytes, in ion-exchange applications, and/or in catalytic systems.

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2023/050021

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J5/22 B01D71/82 B01J47/012 C08F8/24
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J G01N B01D C08F B01J

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YU NA ET AL: "Improving the performance of quaternized SEBS based anion exchange membranes by adjusting the functional group and side chain structure", EUROPEAN POLYMER JOURNAL, PERGAMON PRESS LTD OXFORD, GB, vol. 154, 14 May 2021 (2021-05-14), XP086635466, ISSN: 0014-3057, DOI: 10.1016/J.EURPOLYMJ.2021.110528 [retrieved on 2021-05-14] Experimental sections 2.1-2.3 and Fig. 1 ----- -/--	1-9

[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 July 2023	21/07/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Arz, Sandra

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/CZ2023/050021

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	VINODH R ET AL: "A novel anion exchange membrane from polystyrene (ethylene butylene) polystyrene: Synthesis and characterization", MATERIALS SCIENCE AND ENGINEERING: B, ELSEVIER, AMSTERDAM, NL, vol. 167, no. 1, 25 February 2010 (2010-02-25), pages 43-50, XP026915770, ISSN: 0921-5107, DOI: 10.1016/J.MSEB.2010.01.025 [retrieved on 2010-01-26] experimental sections 2.1 - 2-4 and Fig. 1	1-9
A	WO 2015/110096 A1 (USTAV MAKROKOLEKULARNI CHEMIE AV CR V V I [CZ] ET AL.) 30 July 2015 (2015-07-30) the whole document	1-9

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/CZ2023/050021

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2015110096 A1	30-07-2015	CZ 305138 B6	13-05-2015
		WO 2015110096 A1	30-07-2015