Target Complex Program for Research of NAS UKRAINE

«Development of scientific bases for hydrogen production, storage and use in autonomous energy supply systems»

Development of proton-exchange systems for fuel cells based on polymer membranes and oligomeric ionic liquids

project № 20-21

2019-2021

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Institute of Macromolecular Chemistry, the NAS of Ukraine

November 2021

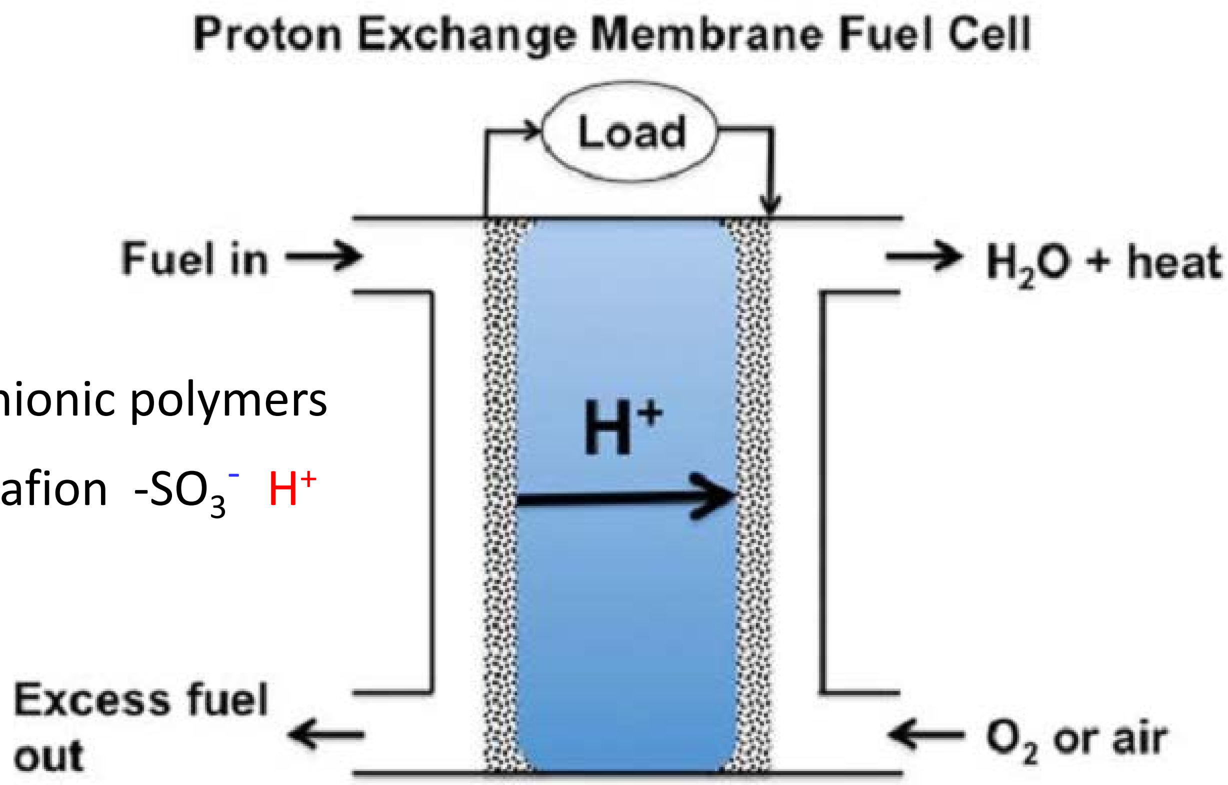
Project goal – development of methods for creating the proton exchange systems for polymer electrolyte hydrogen fuel cells based on polymer membranes in combination with protic oligomeric ionic liquids (OILs) for operation in the temperature range of 100-200^{o}C, as well as establishing ways to control their structure and properties.

Research idea – synthesis of ionic oligomers capable of both performing the functions of proton donors and a heterogeneous ionic conductivity medium and creating on their basis the film ion-conducting proton exchange membranes with anhydrous conductivity mechanism.

Polymer electrolyte fuel cell with proton-exchange polymer membrane (PEM)

Anionic polymers

Nafion -SO_3^- H^+



Anode: $H_2 \rightarrow 2\,H^+ + 2\,e^-$

Cathode: $\frac{1}{2}\,O_2 + 2\,e^- + 2\,H^+ \rightarrow H_2O$

Cell: $H_2 + \frac{1}{2}\,O_2 \rightarrow H_2O$

JOURNAL OF POLYMER SCIENCE, PART B: POLYMER PHYSICS **2013**, *51*, 1727–1735

General structure of the research

1. Synthesis of linear protic cationic OILs with two types of basic centers in their composition

2. Synthesis of star-like protic cationic organosilicon OILs including those with two types of basic centers in their composition

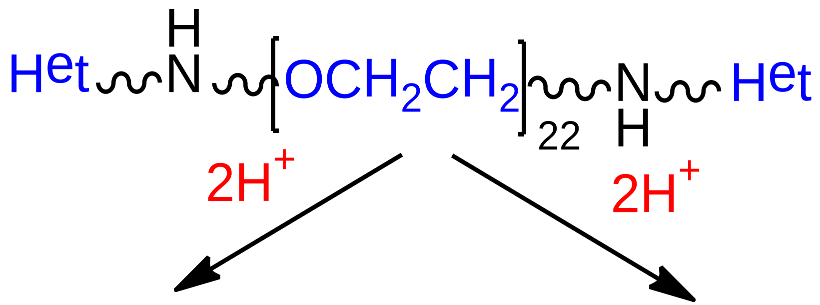
3. Synthesis of hyperbranched protic anionic oligoester OILs

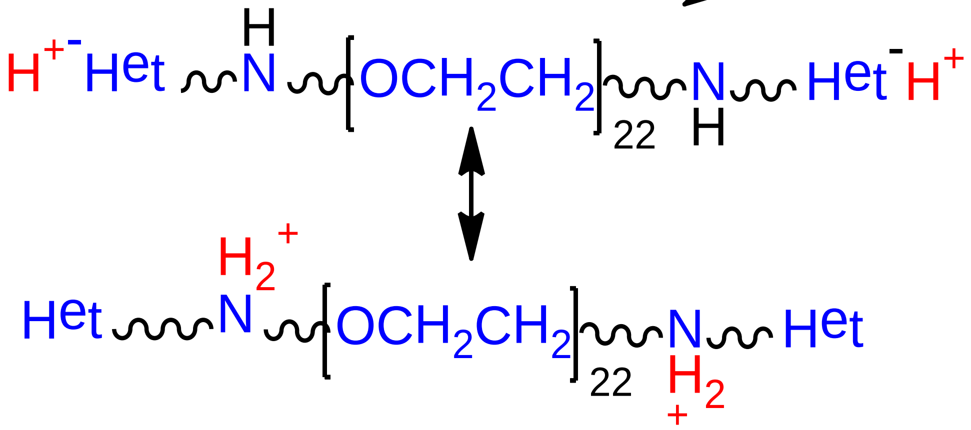
4. Obtaining PEMs based on the synthesized OILs with anhydrous proton-conducting mechanism

5. Study of structure and the thermophysical properties of the synthesized OILs and PEMs

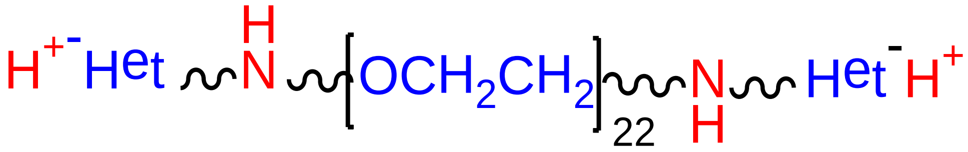
6. Study of ionic conductivity of the synthesized OILs and PEMs in anhydrous conditions

Synthesis of linear protic cationic OILs



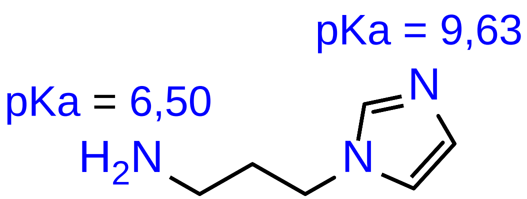


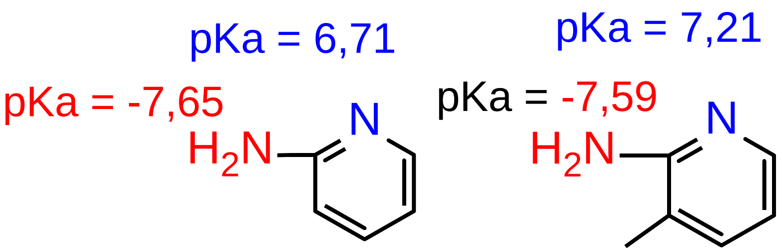
Two types of ionic centers



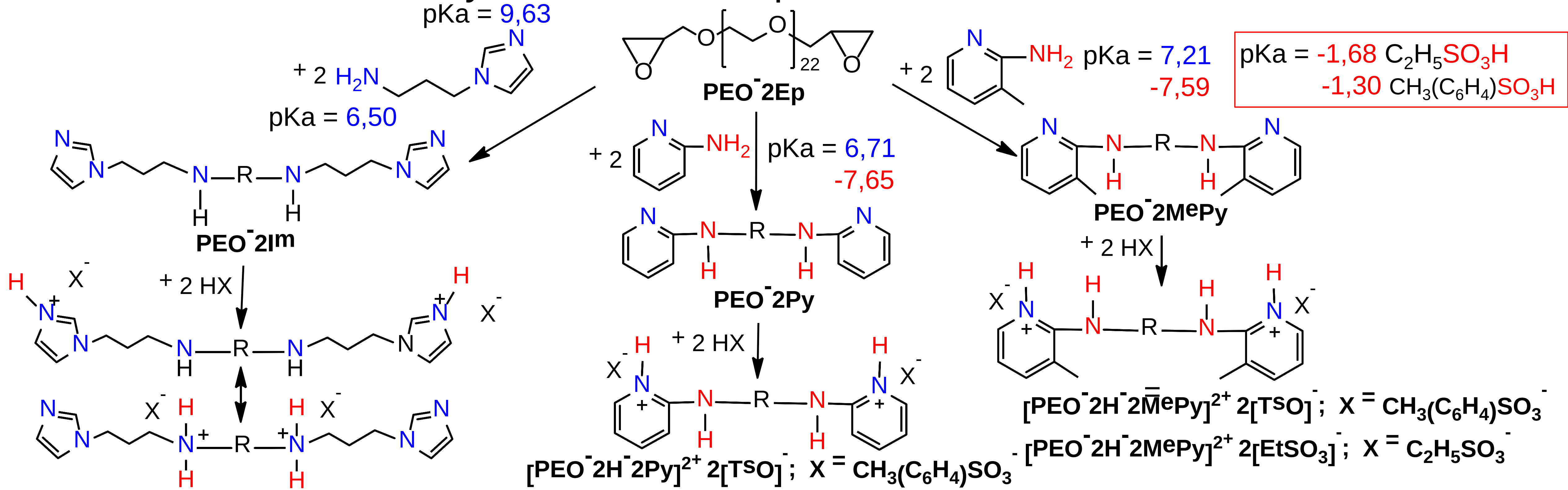
Enhancement of proton acidity of the secondary amino group in the case of protonation of the conjugated nitrogen-containing heterocycle

Initial nitrogen-containing heterocycles (Het)





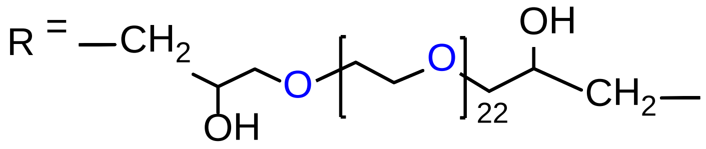
Synthesis of linear protic cationic OILs



[PEO-2H-2Py]$^{2+}$ 2[EtSO$_3$]$^-$; X = $C_2H_5SO_3^-$

[PEO-2H-2Im]$^{2+}$ 2[TSO]$^-$; X = $CH_3(C_6H_4)SO_3^-$

[PEO-2H-2Im]$^{2+}$ 2[EtSO$_3$]$^-$; X = $C_2H_5SO_3^-$



Secondary amino group:

Δ pKa = -2,27 $C_2H_5SO_3^-$

-2,65 $CH_3(C_6H_4)SO_3^-$

Pyridinium heterocycle:

Δ pKa = 7,98 $C_2H_5SO_3^-$

7,60 $CH_3(C_6H_4)SO_3^-$

Secondary amino group:

Δ pKa = 10,18 $C_2H_5SO_3^-$

9,80 $CH_3(C_6H_4)SO_3^-$

Imidazolium heterocycle:

Δ pKa = 8,52 $C_2H_5SO_3^-$

8,14 $CH_3(C_6H_4)SO_3^-$

Secondary amino group:

Δ pKa = -2,14 $C_2H_5SO_3^-$

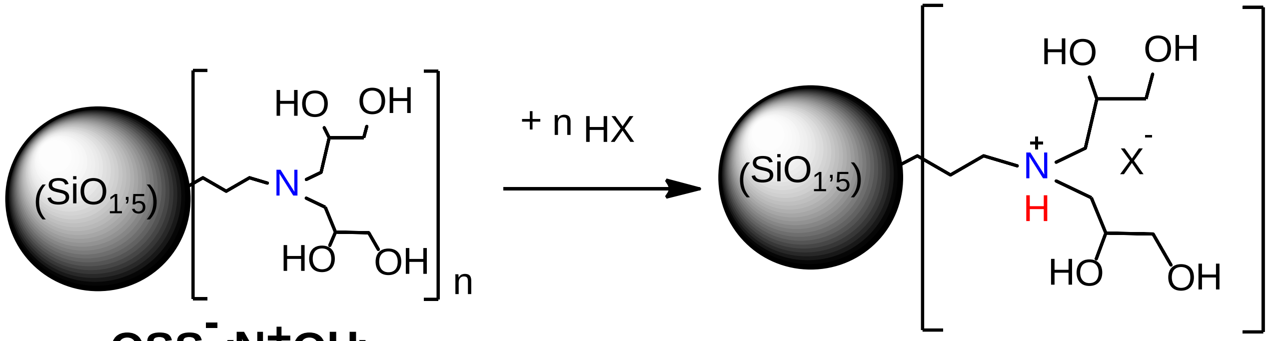
-2,52 $CH_3(C_6H_4)SO_3^-$

Pyridinium heterocycle:

Δ pKa = 7,70 $C_2H_5SO_3^-$

7,32 $CH_3(C_6H_4)SO_3^-$

Synthesis of star-like protic cationic organosilicon OILs



OSS⁻(N⁺OH)

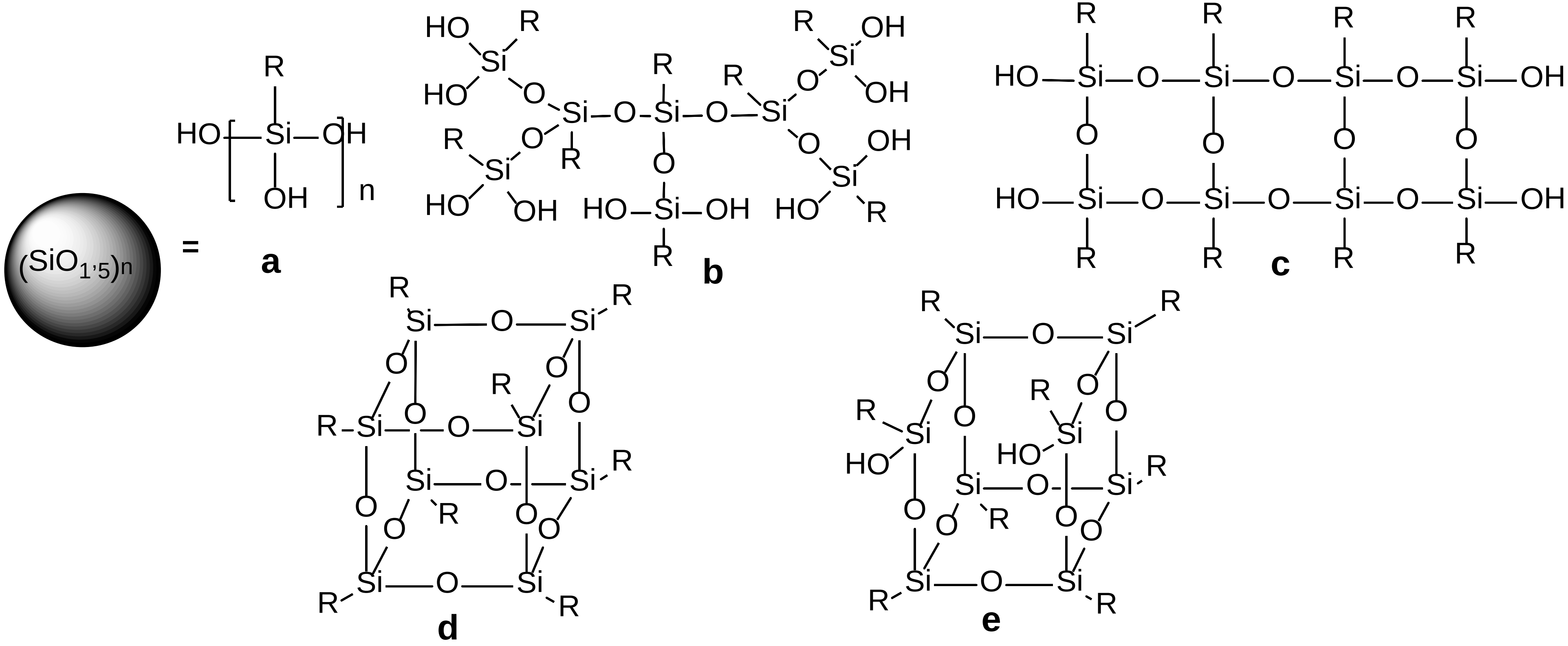
pKa = 8,18

$OSS[NH^+OH]^{n+}$ n $EtSO_3^-$; X^- = $C_2H_5SO_3^-$

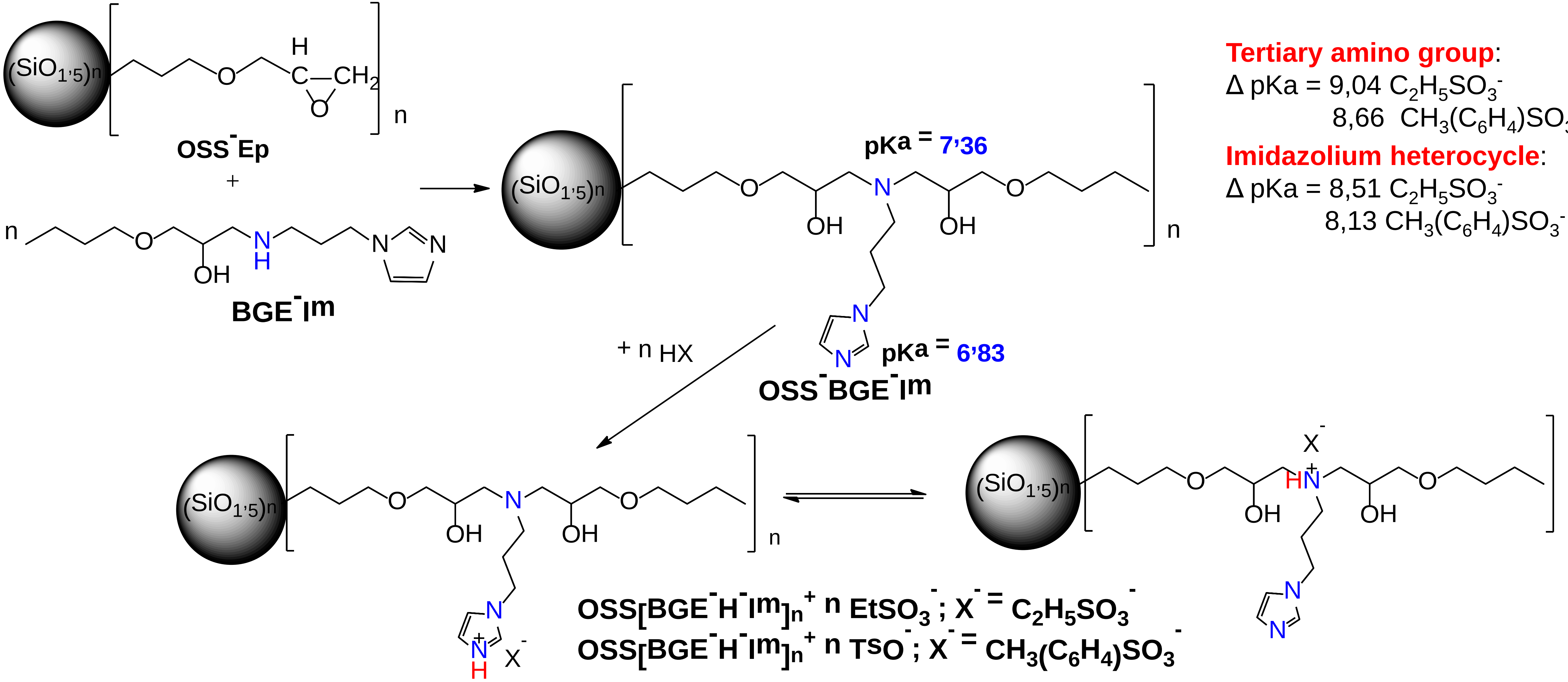
$OSS[NH^+OH]^{n+}$ n TSO^-; X^- = $CH_3(C_6H_4)SO_3^-$

Δ pKa = 9,86 $C_2H_5SO_3^-$

9,48 $CH_3(C_6H_4)SO_3^-$



Synthesis of star-like protic cationic organosilicon OILs with two types of basic centers



Tertiary amino group:

Δ pKa = 9,04 $C_2H_5SO_3^-$

8,66 $CH_3(C_6H_4)SO_3^-$

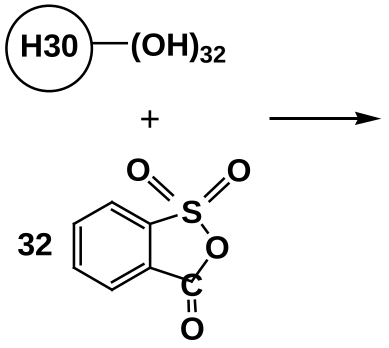
Imidazolium heterocycle:

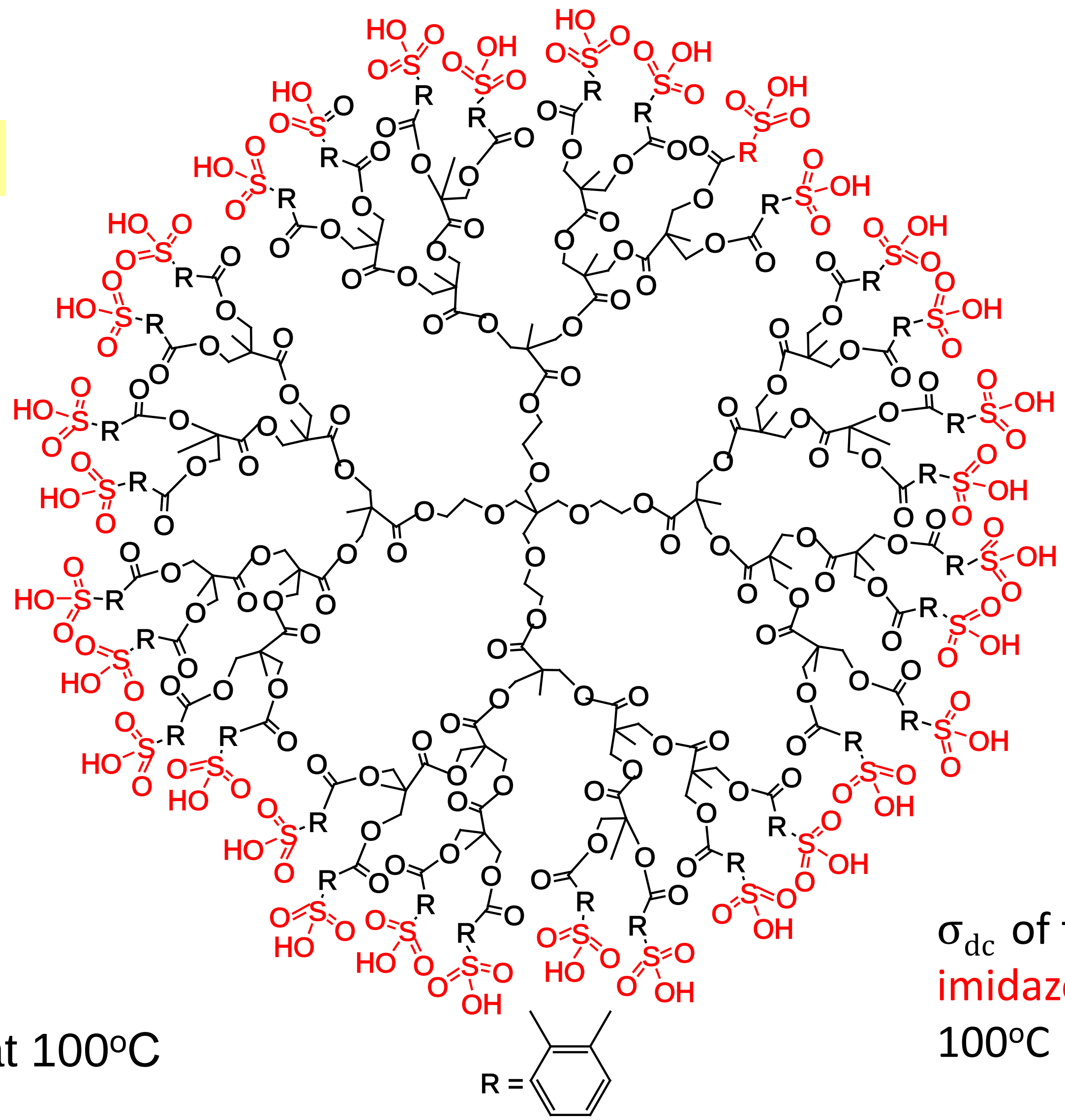
Δ pKa = 8,51 $C_2H_5SO_3^-$

8,13 $CH_3(C_6H_4)SO_3^-$

Synthesis of the starting oligomeric proton donor of hyperbranched structure

Boltorn™ H 30





= 

pKa = -1,02

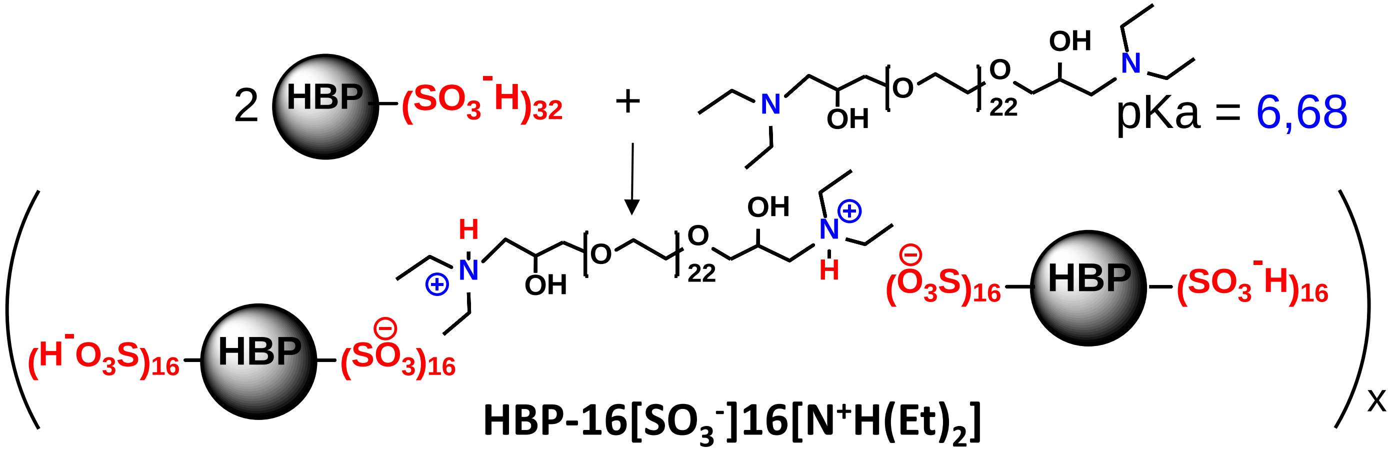
T_d = 230ºC

σ_{dc} = 1,67·10^{-4} S/cm at 100ºC

SO_3-H content 27%

σ_{dc} of the proton donor in the form of imidazolium IL is 3,22·10^{-3} S/cm at 100ºC

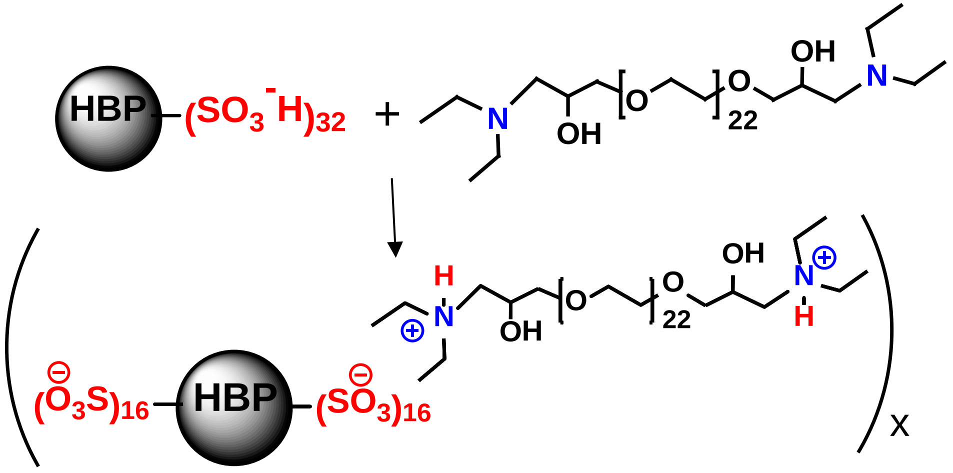
Synthesis of hyperbranched protic anionic oligoester OILs



Δ pKa = 8,66

HBP-16[SO_3^-]16[$N^+H(Et)_2$]

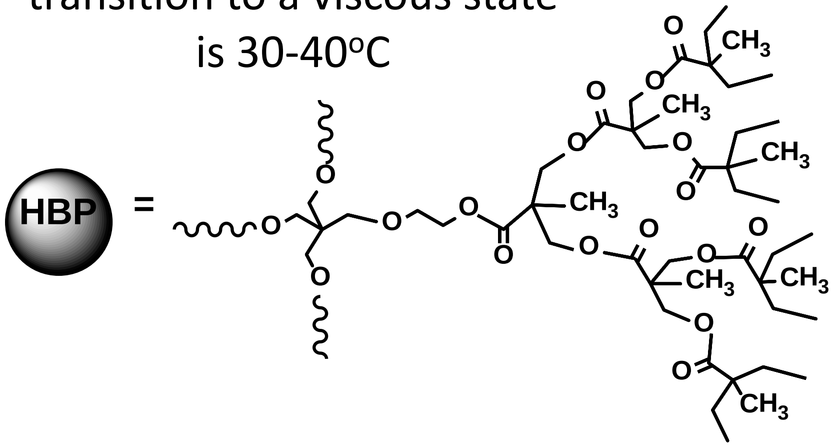
Degree of neutralization of sulfonic acid groups ***50%***



HBP-32[SO_3^-]32[$N^+H(Et)_2$]

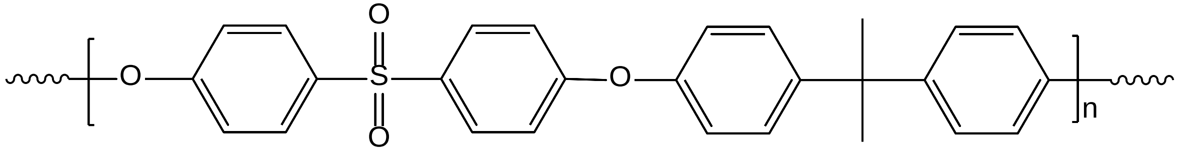
Degree of neutralization of sulfonic acid groups ***100%***

The temperature of the transition to a viscous state is 30-40°C



Initial commercially available thermally robust porous polymer membranes

Polysulfone membrane



Porosity ***80%***

Thickness ***70 μm***

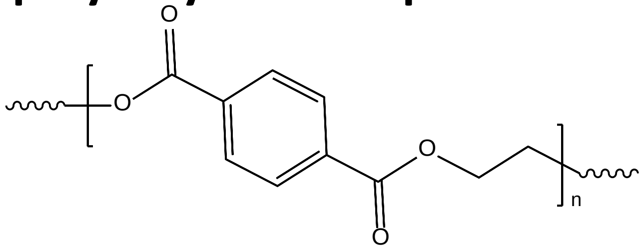
MM ***77000-84000 g/mol***

Glass transition temperature ***190-230°C***

Melting point ***255-400°C***

Temperature of the onset of thermo-oxidative degradation ***≥500°C***

Track polyethylene terephthalate membrane



Porosity ***20%***

Pore diameter ***0,1*** (left fig.) and ***1,0*** (right fig.) ***μm***

Thickness ***10 μm***

Glass transition temperature ***70°C***

Melting point ***250°C***

Temperature of the onset of thermo-oxidative degradation ***350°C***

Preparation of PEMs

Impregnation

Porous polysulfone or track polyethylene terephthalate membrane → **Impregnating with OIL solution** → **Drying, vacuum** → **PEM**

Increase in weight:
Polysulfone 100-125%
Polyethylene terephthalate 30-60%

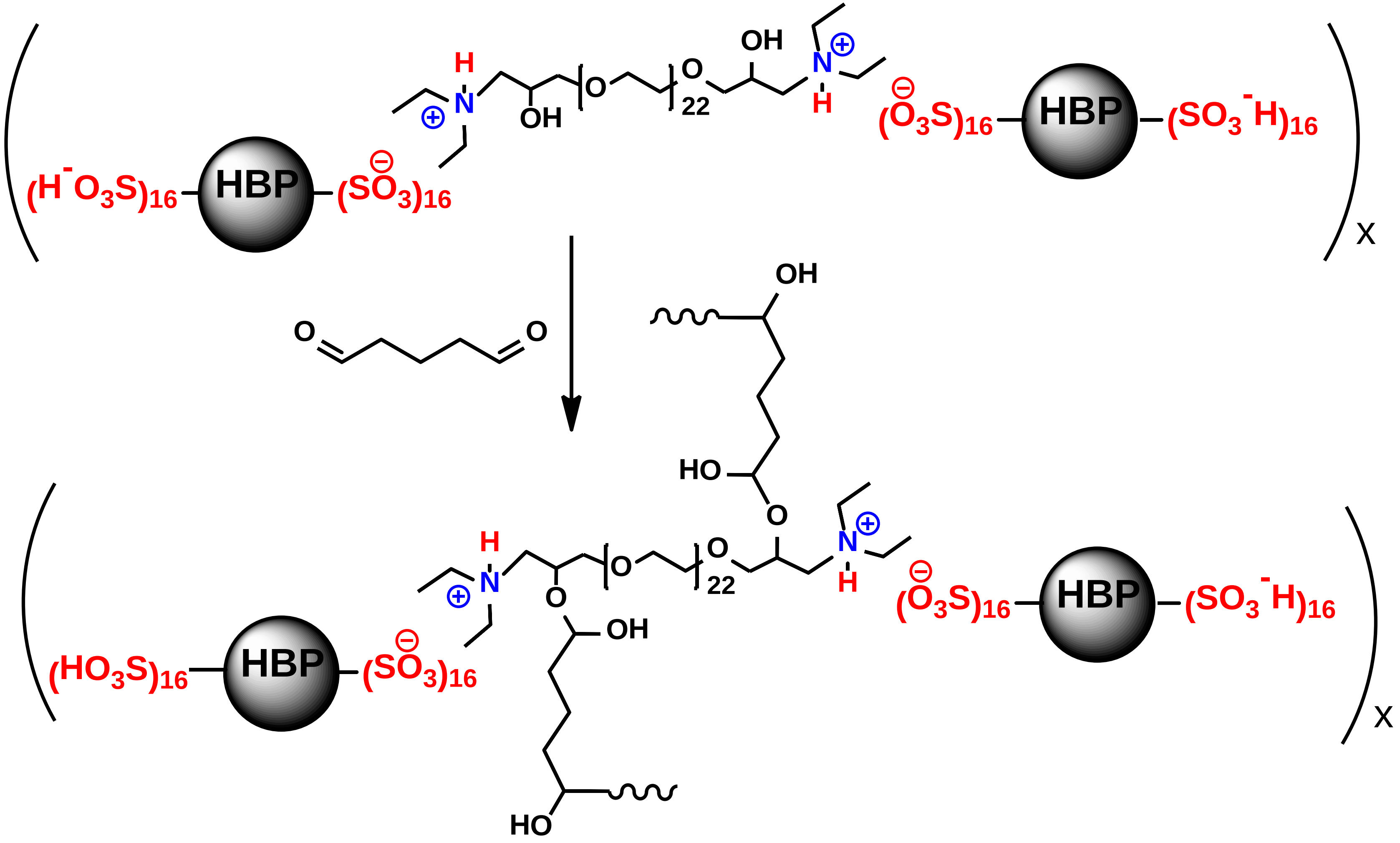
Solution Casting

Dissolving the porous polysulfone membrane → **Mixing with OIL solution** → **Drying, vacuum** → **PEM**

Dopant content *50-60%*

Modification of impregnating solutions of hyperbranched protic anionic oligoester OILs

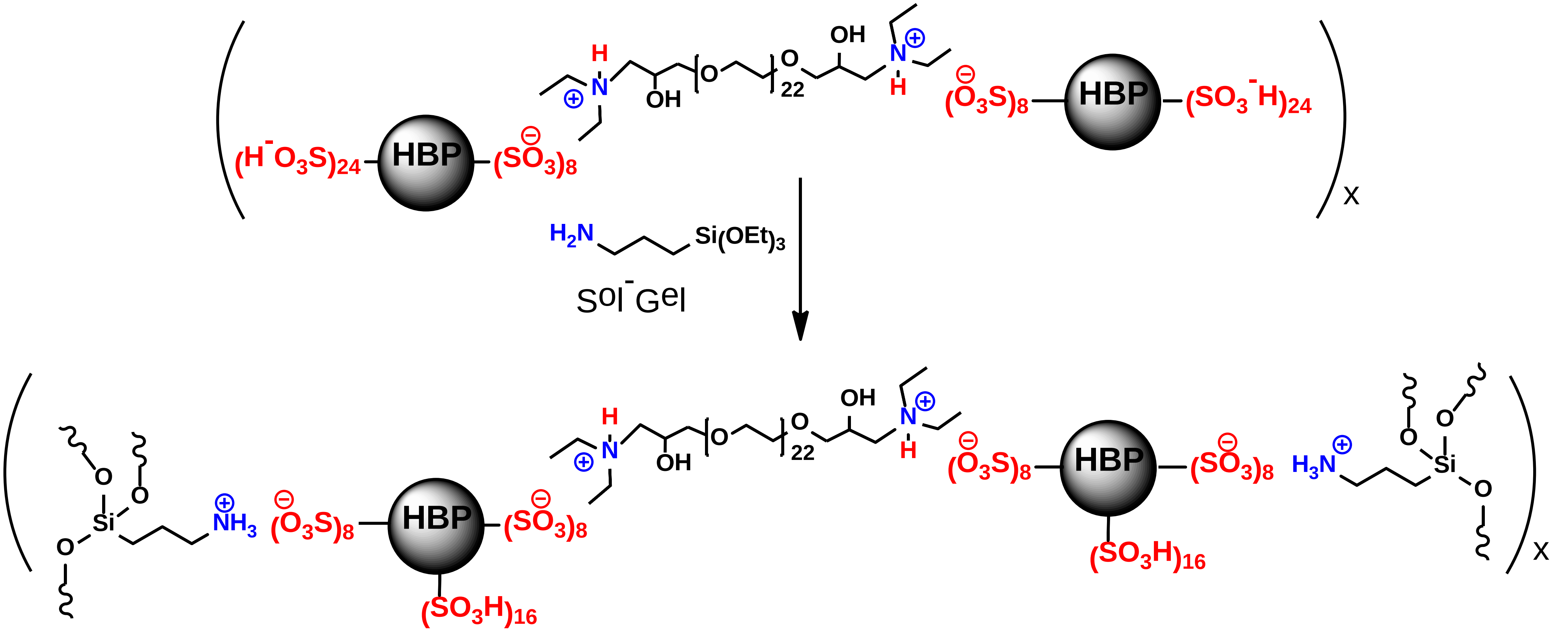
Additional covalent bonding for better trapping the OILs in the PEMs` pores



HBP-16[SO_3^-]16[$N^+H(Et)_2$]-GA

Modification of impregnating solutions of hyperbranched protic anionic oligoester OILs

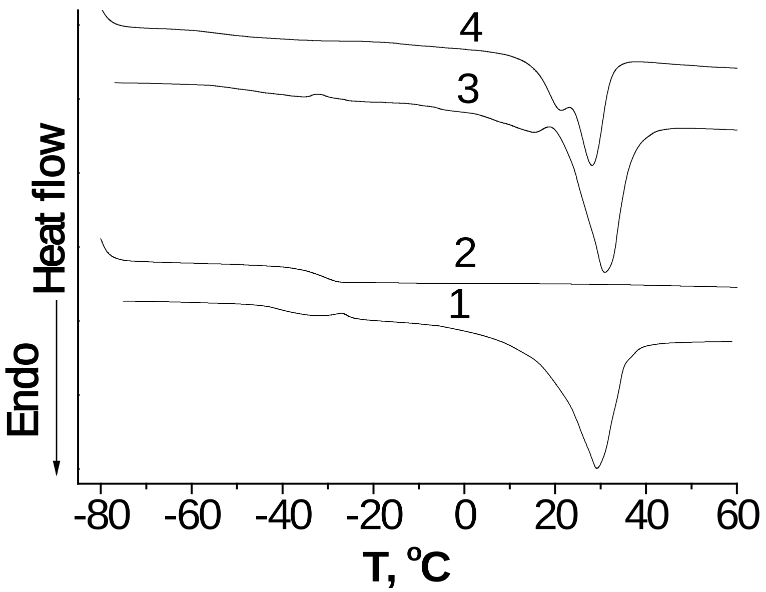
Additional covalent and ionic bonding for better trapping the OILs in the PEMs` pores

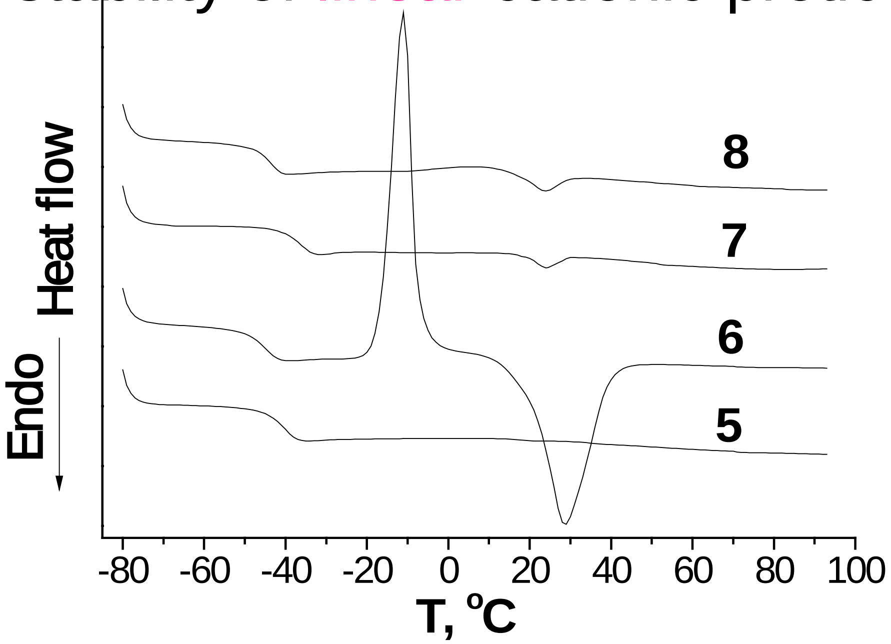


HBP-16[SO_3^-]8[$N^+H(Et)_2$]-Si

Content of the inorganic component $SiO_{1,5}$ is **2,5%wt.**

Thermophysical properties and thermal stability of linear cationic protic OILs

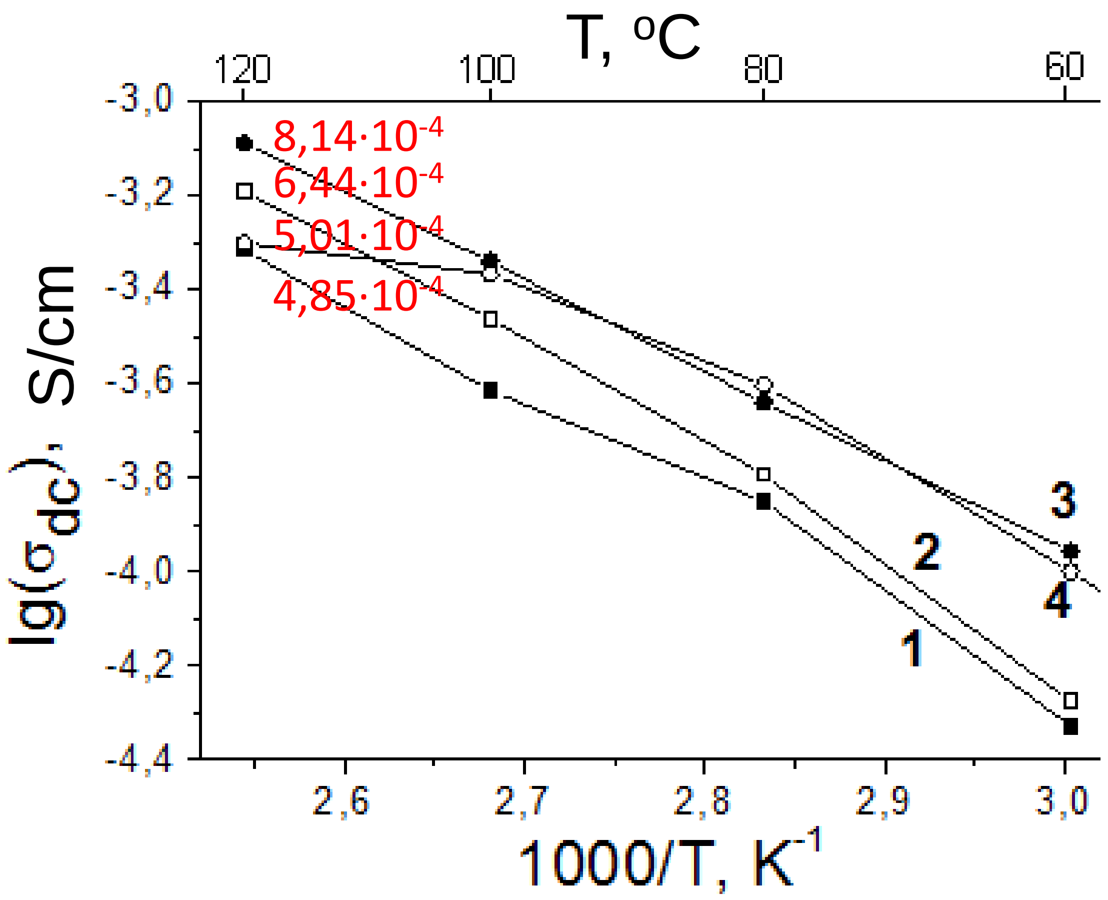


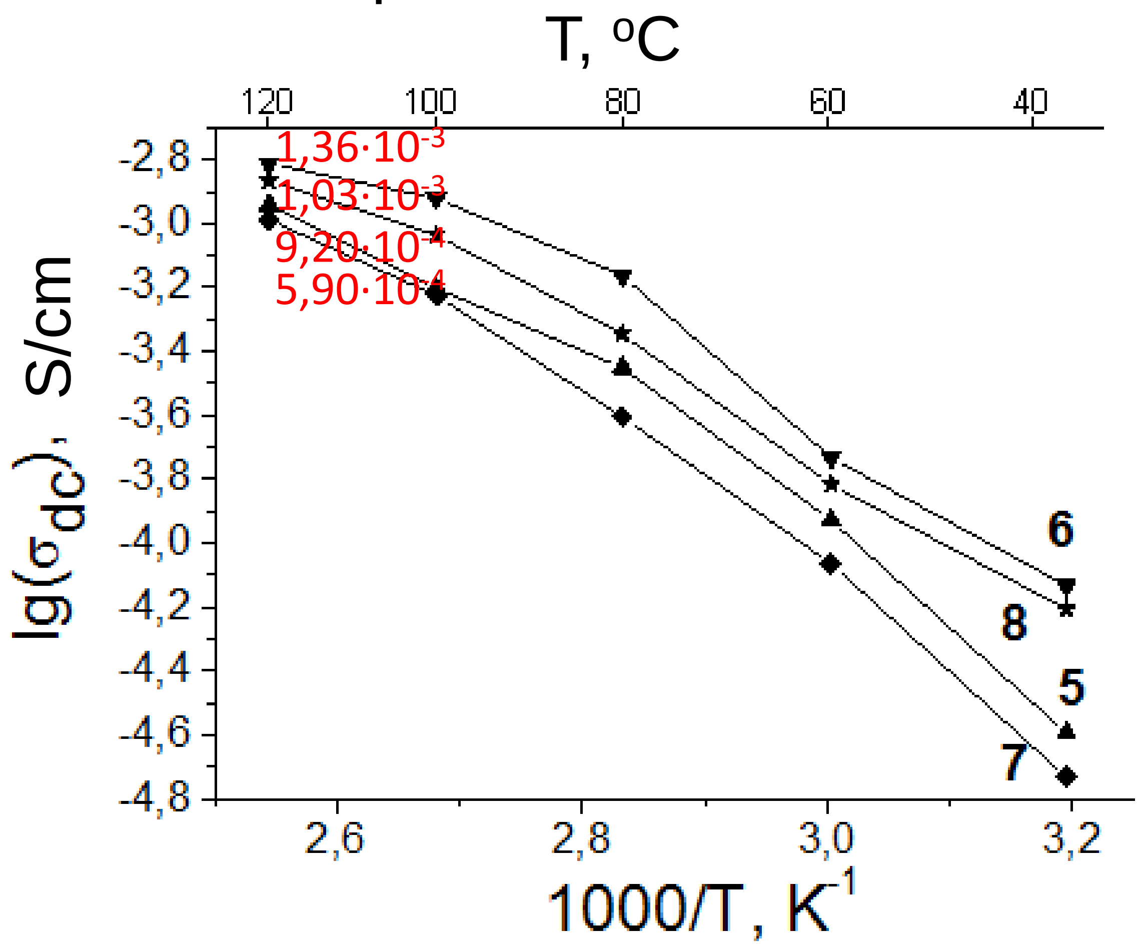


Temperature dependences of heat flows for the synthesized OILs

	OILs	T_g, °C	T_{cc}, °C	T_{m1}, °C	T_{m2}, °C	$T_{d5\%}$, °C
1	$[PEO\text{-}2H\text{-}2Im]^{2+}2[TsO]^-$	- 42.5	- 26.6	18.3	30.2	279
2	$[PEO\text{-}4H\text{-}2Im]^{4+}4[TsO]^-$	- 31.0				282
3	$[PEO\text{-}2H\text{-}2Im]^{2+}2[EtSO_3]^-$	- 44.3	- 32.1	15.3	31.3	287
4	$[PEO\text{-}4H\text{-}2Im]^{4+}4[EtSO_3]^-$	- 54.6	- 16.7	21.0	28.1	291
5	$[PEO\text{-}2H\text{-}2Py]^{2+}2[TsO]^-$	- 40.1				259
6	$[PEO\text{-}2H\text{-}2Py]^{2+}2[EtSO_3]^-$	- 44.8	- 11.0		28.7	274
7	$[PEO\text{-}2H\text{-}2MePy]^{2+}2[TsO]^-$	- 35.9			23.0	288
8	$[PEO\text{-}2H\text{-}2MePy]^{2+}2[EtSO_3]^-$	- 43.5	8.2		23.8	277

Ionic conductivity of linear cationic protic OILs

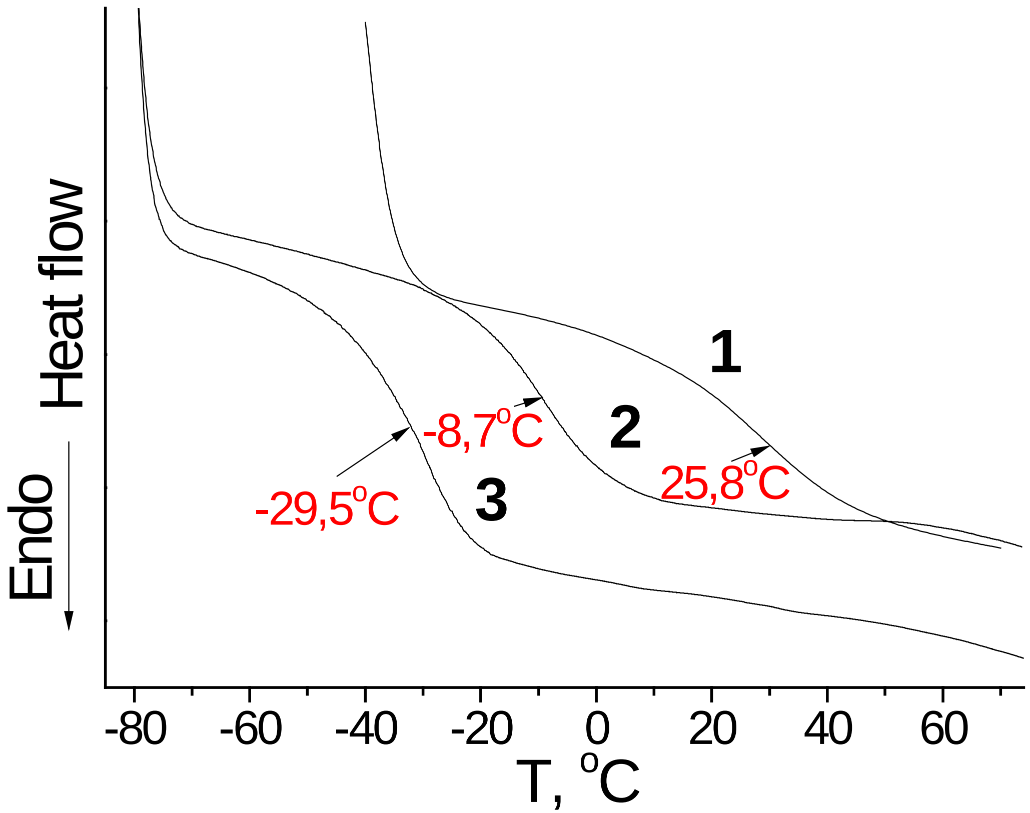




1 – $[PEO\text{-}2H\text{-}2Im]^{2+}2[TsO]^{-}$;
2 – $[PEO\text{-}4H\text{-}4Im]^{4+}4[TsO]^{-}$;
3 – $[PEO\text{-}2H\text{-}2Im]^{2+}2[EtSO_3]^{-}$;
4 – $[PEO\text{-}4H\text{-}4Im]^{4+}4[EtSO_3]^{-}$;

5 – $[PEO\text{-}2H\text{-}2Py]^{2+}2[TsO]^{-}$;
6 – $[PEO\text{-}2H\text{-}2Py]^{2+}2[EtSO_3]^{-}$;
7 – $[PEO\text{-}2H\text{-}2MePy]^{2+}4[TsO]^{-}$;
8 – $[PEO\text{-}2H\text{-}2MePy]^{2+}2[EtSO_3]^{-}$

Thermophysical properties and ionic conductivity of star-like protic cationic organosilicon OILs

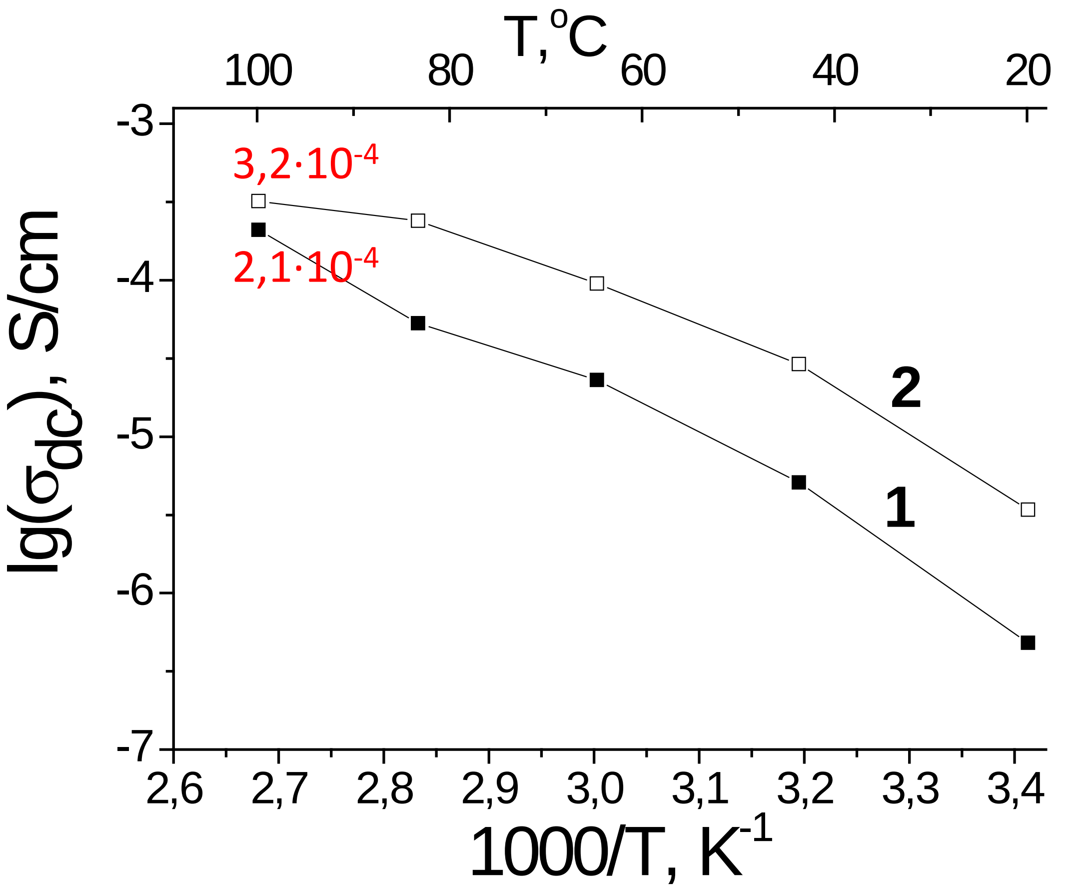


Temperature dependences of heat flows

1 – OSS(N+OH);

2 – $OSS[NH+OH]_n^+$ n TsO^-;

3 – $OSS[NH+OH]_n^+$ n $EtSO_3^-$



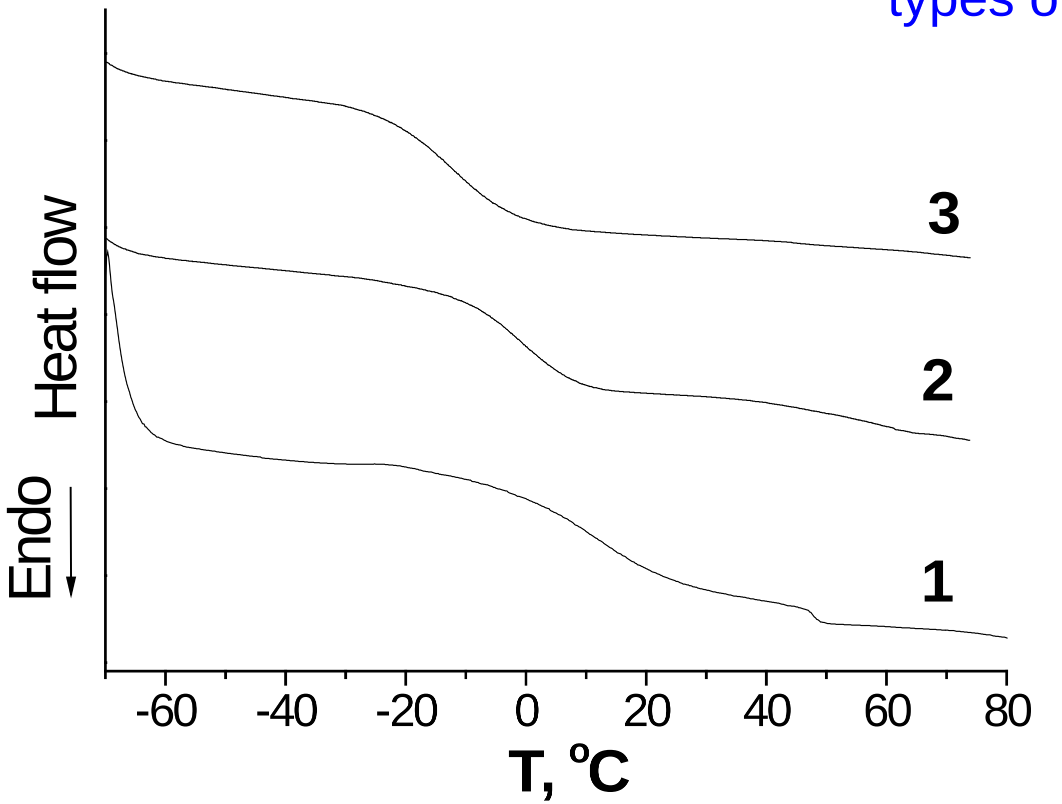
Temperature dependences of ionic conductivity

1 – $OSS[NH+OH]_n^+$ n TsO^-;

2 – $OSS[NH+OH]_n^+$ n $EtSO_3^-$

T_d = 290 °C $OSS[NH+OH]_n^+$ n $EtSO_3^-$;
251 °C $OSS[NH+OH]_n^+$ n TsO^-

Thermophysical properties and ionic conductivity of star-like protic cationic organosilicon OILs with two types of basic centers

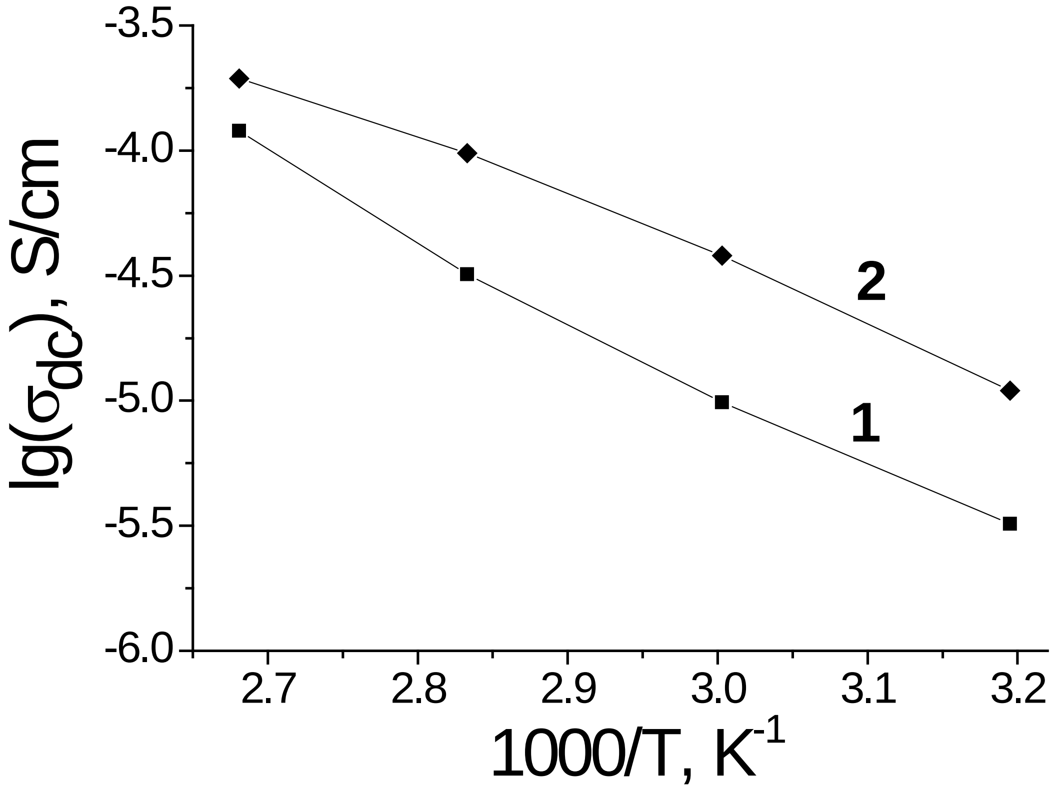


Temperature dependences of heat flows

1 – OSS-BGE-Im;

2 – $OSS[BGE\text{-}Im\text{-}H]_n^+\ n[TsO]^-$;

3 – $OSS[BGE\text{-}Im\text{-}H]_n^+\ n[EtSO_3]^-$



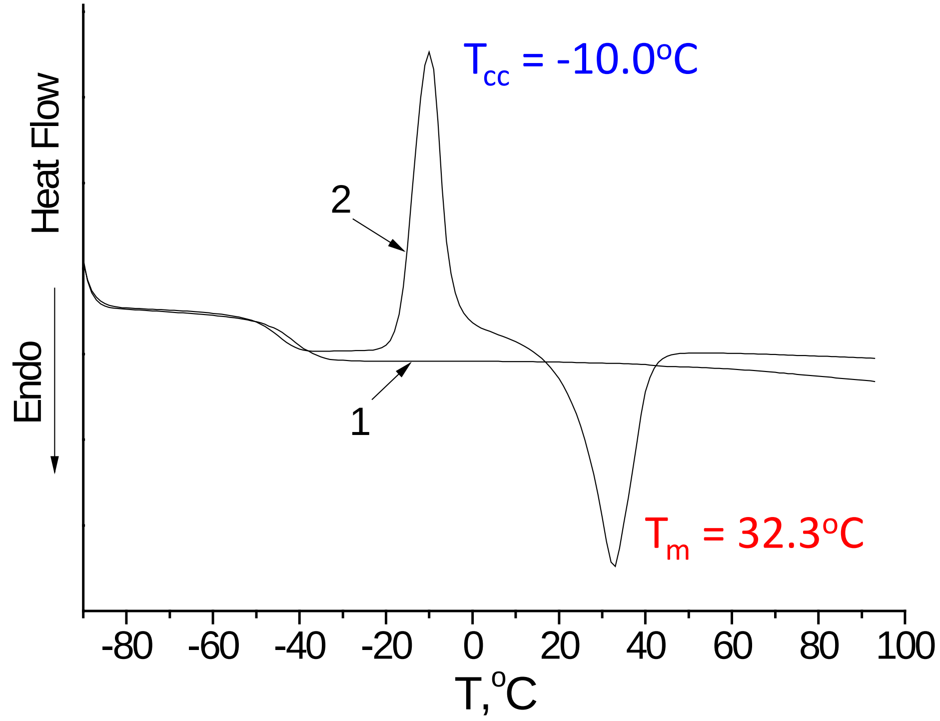
Temperature dependences of ionic conductivity

1 – $OSS[BGE\text{-}Im\text{-}H]_n^+\ n[TsO]^-$;

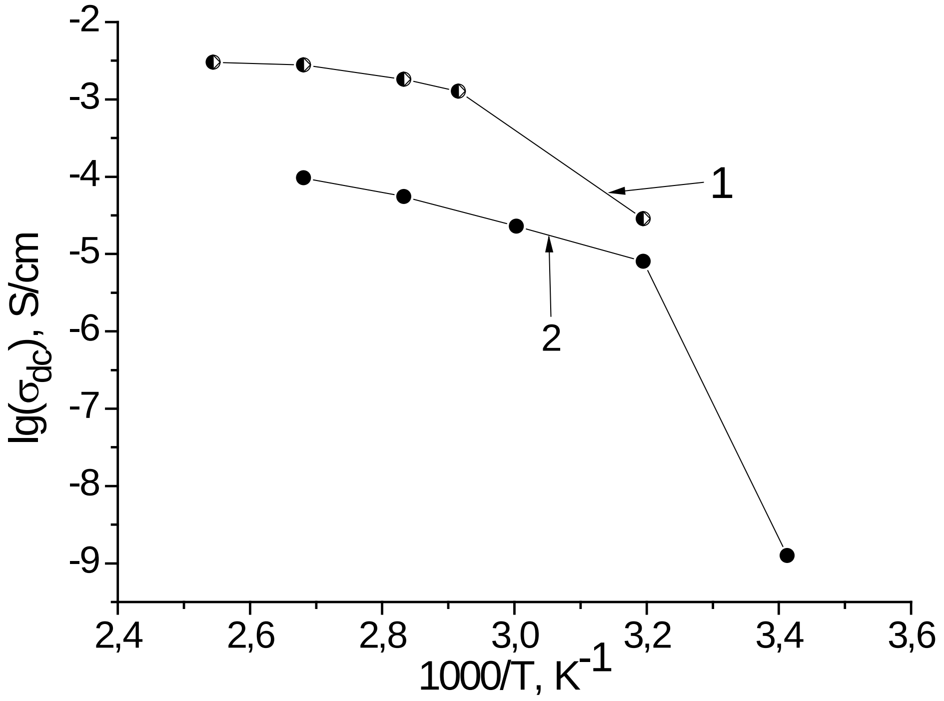
2 – $OSS[BGE\text{-}Im\text{-}H]_n^+\ n[EtSO_3]^-$

T_d = 227 °C OSS-BGE-Im;
201 °C $OSS[BGE\text{-}Im\text{-}H]_n^+\ n[TsO]^-$;
218 °C $OSS[BGE\text{-}Im\text{-}H]_n^+\ n[EtSO_3]^-$

Thermophysical properties and ionic conductivity of protic anionic hyperbranched oligoester OILs



Temperature dependences of heat flows

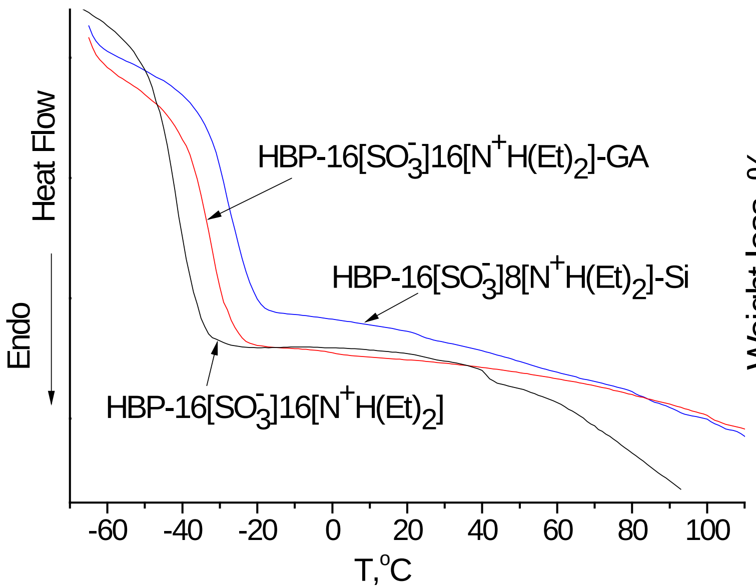


Temperature dependences of ionic conductivity

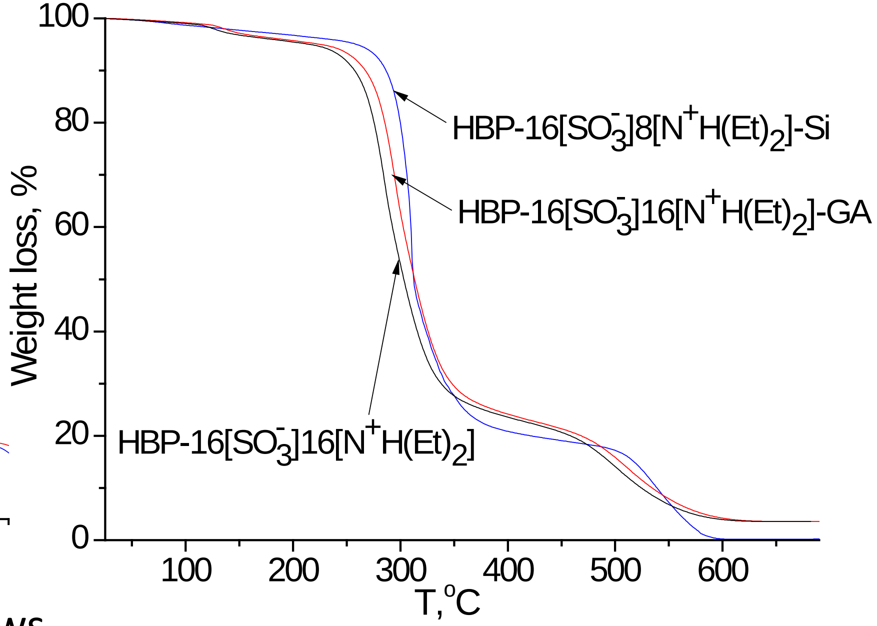
Table. Physicochemical characteristics of the synthesized hyperbranched OILs

N	OIL	Total content of ionic groups, m-equiv/g	T_g, °C	T_d, °C	σ_{dc}, S/cm	
					100°C	120°C
1	HBP-16[SO_3^-]16[$N^+H(Et)_2$]	1,54	-42,2	230	$2{,}79\cdot10^{-3}$	$3{,}02\cdot10^{-3}$
2	HBP-32[SO_3^-]32[$N^+H(Et)_2$]	1,02	-44,9	239	$2{,}95\cdot10^{-4}$	?

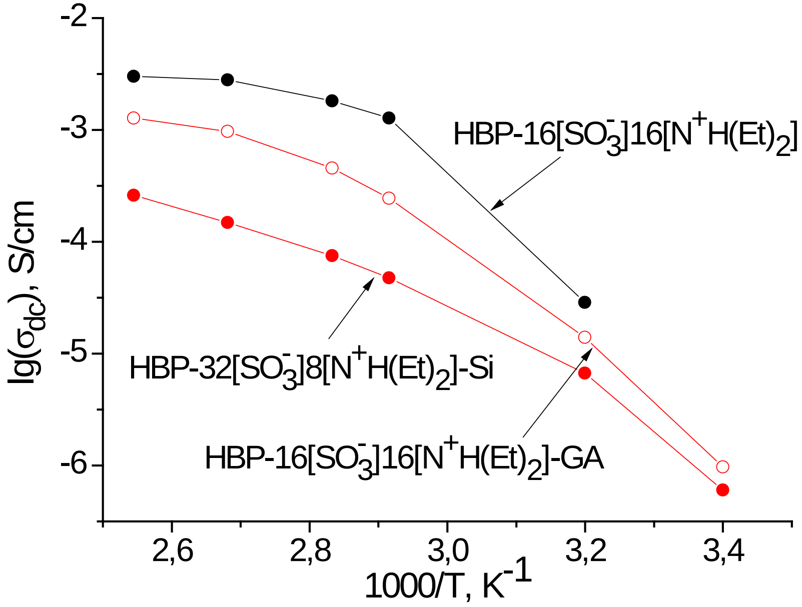
Thermophysical properties and ionic conductivity of protic anionic hyperbranched oligoester OILs with additional covalent and ionic bonding



Temperature dependences of heat flows



Thermogravimetric analysis

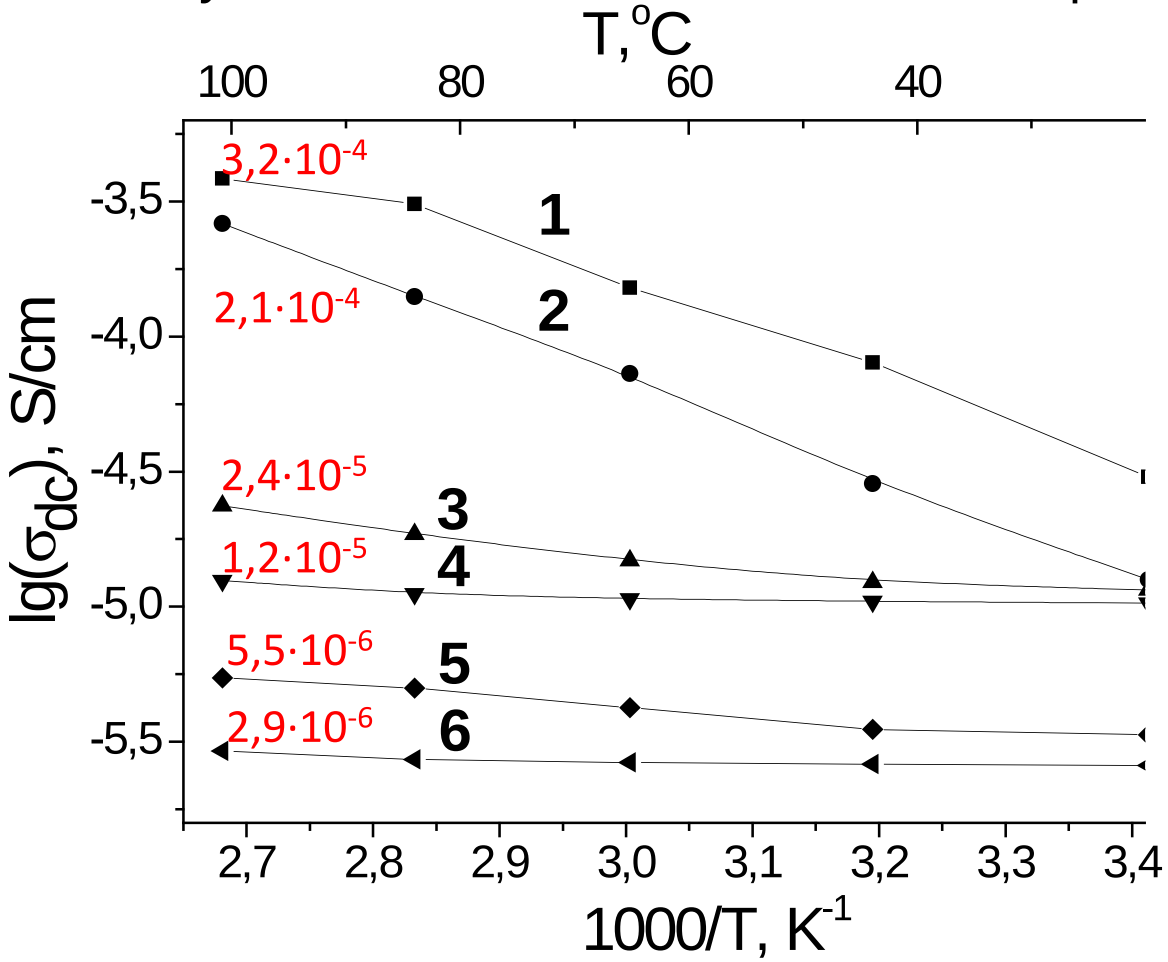


Temperature dependences of ionic conductivity

Table. Physicochemical characteristics of synthesized hyperbranched OILs with additional covalent and ionic bonding

N	OIL	T_g, °C	T_d, °C	σ_{dc}, S/cm	
				100°C	120°C
1	HBP-16[SO_3^-]16[$N^+H(Et)_2$]	-42,2	230	$2{,}79\cdot10^{-3}$	$3{,}02\cdot10^{-3}$
2	HBP-16[SO_3^-]8[$N^+H(Et)_2$]-Si	-27,7	256	$1{,}49\cdot10^{-4}$	$2{,}60\cdot10^{-4}$
3	HBP-16[SO_3^-]16[$N^+H(Et)_2$]-GA	-32,9	243	$9{,}73\cdot10^{-4}$	$1{,}28\cdot10^{-3}$

Ionic conductivity of the PEMs based on the star-like protic cationic organosilicon OILs

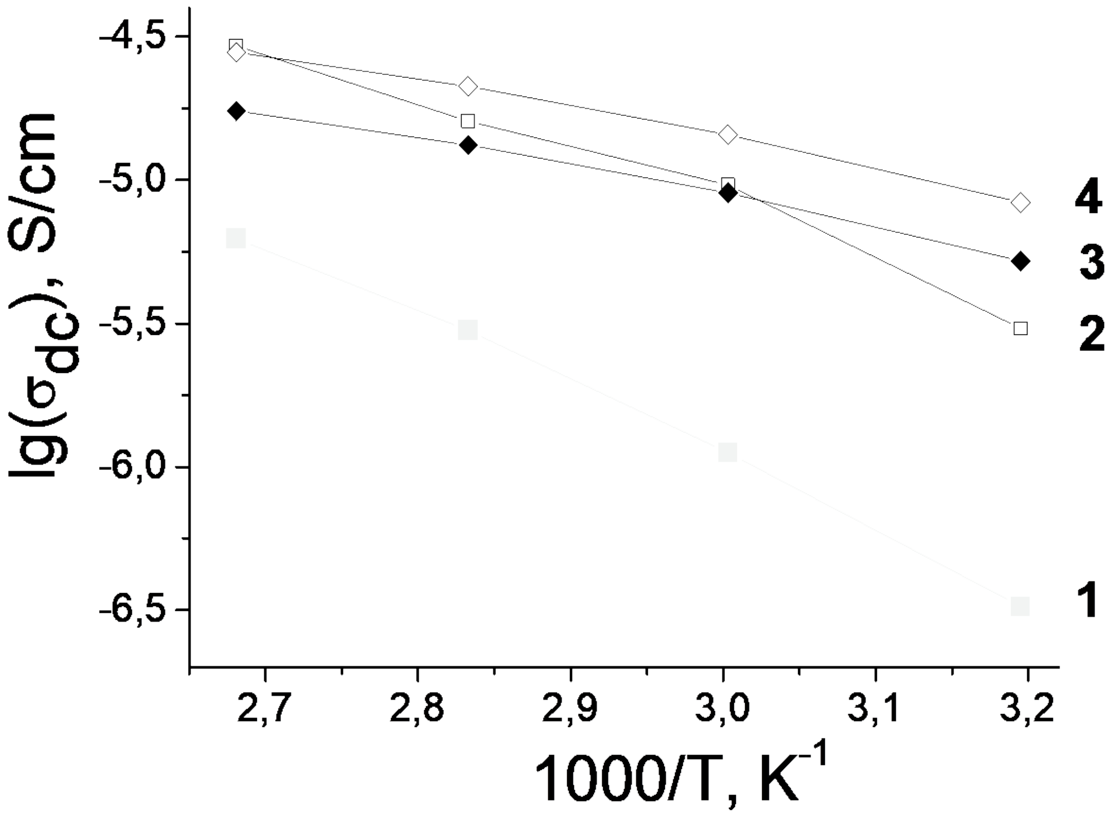


1 – $OSS[NH+OH]_n^+$ n $EtSO_3^-$;
2 – $OSS[NH+OH]_n^+$ n TsO^-;
3 – PETPh1 + $OSS[NH+OH]_n^+$ n $EtSO_3^-$
4 – PETPh1 + $OSS[NH+OH]_n^+$ n TsO^-
5 – PETPh0,1 + $OSS[NH+OH]_n^+$ n $EtSO_3^-$;
6 – PETPh0,1 + $OSS[NH+OH]_n^+$ n TsO^-

The PEMs were obtained by impregnating method

*PETPh1 - track polyethylene terephthalate membrane with pore diameter 1,0 µm
**PETPh0,1 - track polyethylene terephthalate membrane with pore diameter 0,1 µm

Ionic conductivity of the PEMs based on the star-like protic cationic organosilicon OILs with two types of basic centers

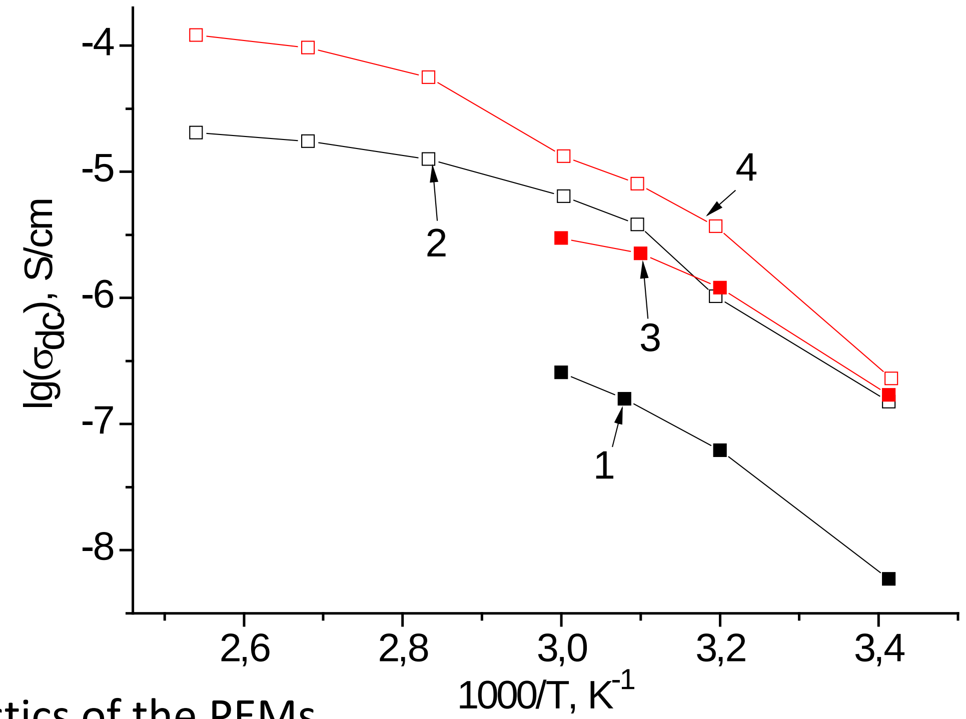


The PEMs were obtained by solution casting method

1 – PS+OSS[BGE-H-Im]$_n^+$ n[TsO]$^-$ dopant content 50%wt.
2 – PS+OSS[BGE-H-Im]$_n^+$ n[TsO]$^-$ dopant content 60%wt.
3 – PS+OSS[BGE-H-Im]$_n^+$ n[EtSO$_3$]$^-$ dopant content 50%wt.
4 – PS+OSS[BGE-H-Im]$_n^+$ n[EtSO$_3$]$^-$ dopant content 60%wt.

*PS – Polysulfone membrane

Ionic conductivity of the PEMs based on the hyperbranched protic anionic oligoester OILs



The PEMs were obtained by impregnating method

Table. Physicochemical characteristics of the PEMs

N	Membrane material	Dopant	Modifying agent	σ_{dc}, S/cm	
				60°C	120°C
1	Polysulfone	$HBP\text{-}16[SO_3]^{-}8[NH(Et)_2]^{+}$-Si	(3-aminopropyl) triethoxysilane	$2{,}57\cdot10^{-7}$	?
2	Polysulfone	$HBP\text{-}16[SO_3]^{-}16[NH(Et)_2]^{+}$-GA	Glutaric aldehyde	$6{,}40\cdot10^{-6}$	$2{,}03\cdot10^{-5}$
3	Polyethylene terephthalate (pore diameter 0,1 μm)	$HBP\text{-}16[SO_3]^{-}8[NH(Et)_2]^{+}$-Si	(3-aminopropyl) triethoxysilane	$2{,}98\cdot10^{-6}$	?
4	Polyethylene terephthalate (pore diameter 0,1 μm)	$HBP\text{-}16[SO_3]^{-}16[NH(Et)_2]^{+}$-GA	Glutaric aldehyde	$1{,}63\cdot10^{-5}$	**$1{,}21\cdot10^{-4}$**

Conclusions

1. Methods for synthesis of linear oligooxyethylene protic cationic OILs were developed. In this direction both introducing the two types of ionic cents with different degrees of ionicity (imidazolium compounds) and strengthening the acidity of the secondary amine group by protonating the conjugated heteroaromatic cycle (pyridinium compounds) in the composition of the OILs were realized.
2. Methods for synthesis of protic cationic organic-inorganic OILs of star-like structure with different degrees of ionicity of ionic groups based on a mixture of fully and partially condensed polyhedral and open-chain oligomeric silsesquioxanes were proposed.
3. Methods for synthesis of protic anionic oligoester OILs of hyperbranched structure with oligooxyethylene counterparts were developed. For better trapping them in the pores of the PEMs they were modified with glutaric aldehyde or (3-aminopropyl) triethoxysilane (followed by sol-gel process).
4. The structure and thermophysical properties of the OILs were studied by the method of dynamic scanning calorimetry. It was shown that depending on the composition the synthesized compounds can be characterized by both a completely amorphous structure (facilitating proton conductivity) and presence of a crystalline phase formed by oxyethylene component.
5. According to the data of thermogravimetric analysis the obtained compounds are thermally stable up to 200 -280 ^{o}C and the dielectric relaxation spectroscopy data indicate a proton conductivity level of 10^{-3} S/cm at 100-120 ^{o}C in absence of humidification that indicates their prospects as anhydrous proton-conducting media for PEMs.
6. Methods for preparation of PEMs by impregnating the track polyethylene terephthalate and porous polysulfone membranes with the OILs solutions, as well as by mixing the polysulfone with the OILs in a solution followed by film casting were developed.
7. The developed PEMs are characterized by thermal stability up to 250-290 ^{o}C and ionic conductivity of 10^{-6}-10^{-4} S/cm at 100-120 ^{o}C under anhydrous conditions. The obtained membranes according to these characteristics are at the level of the best domestic and foreign analogues of this type.

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Thank you for your attention!