

Cation and anion exchangers from nanofibrous polystyrene for fast water treatment

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Abstract - The main goal of this study was to prepare and characterize ion exchangers on nanofibrous polystyrene matrix. Starting nanofibers were sulfonated and crosslinked at the same time by sulfuric acid. Strongly acidic cation exchanger was obtained in such a way. Anion exchanger was prepared by reaction of ethylene diamine with sulfochlorides on nanofibers acquired from sulfogroups. The polymer matrix was made from polystyrene nanofibers prepared by Nanospider™ technology from regenerated polystyrene.

Various types postpolymerization reactions and other methods of crosslinking were studied. Greatly diverse behavior between nano- and microsize materials was observed. The sorption properties of nanofibrous ion exchangers were compared to the granular ion exchangers resulting in rapidly faster kinetics of fibrous ion exchangers.

The starting polymer matrix was polystyrene because the common ion exchangers are based on this polymer^{1,2}. The nanofibers of polystyrene were prepared by Nanospider™ technology.

In principle the electrospinning by Nanospider™ is a modified process for the production of nanofibers and nanofiber layers via the electrostatic fiber spinning of polymer solutions¹⁷. As opposed to other methods in the public domain, Nanospider™ technology does not utilize jets or capillaries for the production of fibers, but utilizes a rotating drum partially submerged in a polymer solution. The main advantage of this technology is the significant increase in production capacity.

Polystyrene nanofibers prepared by Nanospider™ technology can be spun from mixture of aromatic solvents and polar aprotic solvents. We used aromatic solvents based on the natural terpenoids¹⁰. This solvents are pretty cheap, ecological and environmental friendly¹¹. Also we can use recycled expanded polystyrene, its foams (extruded polystyrene) or copolymers of polystyrene (like acrylonitrile butadiene styrene or maleic anhydrid) can be used as a starting material for spinning.

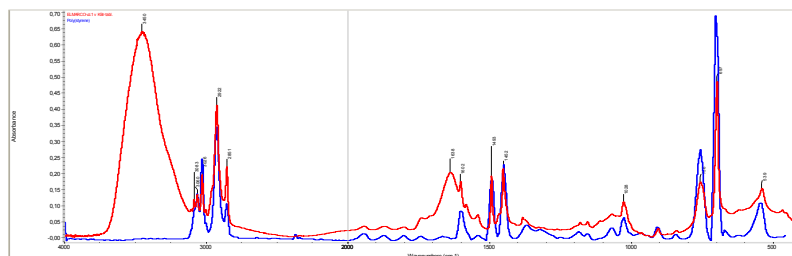


Figure 1 Infrared spectra of nanofibrous polystyrene made by Nanospider technology (red) and polystyrene standard (blue).

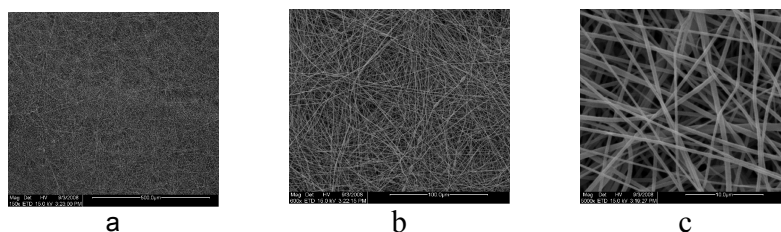


Figure 2 Polystyrene nanofibers prepared by Nanospider™ technology – starting material: recycled polystyrene, spun from aromatic solvents based on the aromatic terpenoids^[10] – the fiber diameter is about 90 to 350 nm; a) magnification 150, b) magnification 600, c) magnification 5000

As a sulfonated polystyrene is water soluble crosslinking for ion exchange purposes before, during or after introduction ionogenic groups is indispensable. Crosslinking during the electrospinning, analogical to crosslinking of polyvinylalcohol was not successful. Also radiation crosslinking did not give desirable effect. The ratio of agent and initiator was 2:1. Either the concentration of agent was too low to reach the crosslinking effect or the high concentration disturbed the process of electrospinning. Peppas, Regas and Valkanas^{12,13,14} described suspension polymerization with Friedel-Crafts catalysts. But the polystyrene nanofibers compared to another polystyrene material (like microfibers) showed diametrically different behaviour of nanofibers. So these methods can not be applied for the nanofibrous material.

Sulfonation of polystyrene by sulfuric acid is the standard method for introduction strongly acidic cation exchanging groups. This reaction is simple in the case of crosslinked copolymer styrene divinylbenzene particles used for production common ion exchanger. By noncrosslinked PS nanofibers is necessary to find optimal conditions for preparation product having acceptable exchange capacity but still insoluble in water. At higher degree of substitution is product soluble without crosslinking. Fortunately by sulfonation of PS with sulfuric acid proceeds in small extent crosslinking. Sulfogroups Kucera and Jancar⁵ published „sulfonation of polymers“ possibility of crosslinking by sulfone crosslinkages in their review. Because of the presence of relatively highly reactive $-SO_3H$ groups, crosslinking reaction between the molecules of the sulfonated product occur.

As we knew it is possible to sulfonate non-crosslinked polystyrene nanofibers to the low conversion of functional groups^{2,3}, we started optimizing sulfonation for the purpose of crosslinking.

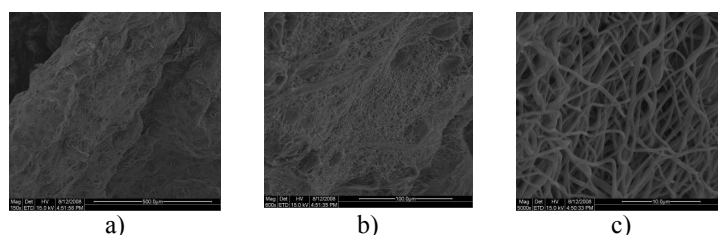


Figure 3 Nanofibrous polystyrene sulfonated and crosslinked by sulfobridges; a) magnification 150, b) magnification 600, c) magnification 500

After successful sulfonation crosslinking and functionalization the polystyrene nanofibers increase their diameter from about 350 nm to 500 nm. The weight of nanofibrous samples increases to 150%. Sulfones are very stable compounds. The

nanofibrous polystyrene is then insoluble in common organic solvents like toluene or acetone also by heating. Their decomposition can be achieved only by melting with alkaline hydroxides^{15,16}.

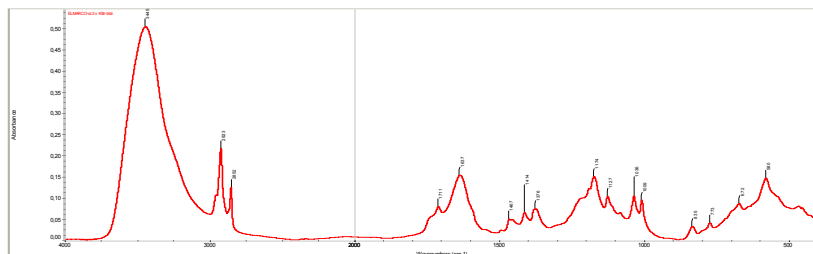


Figure 4 Infrared spectra of nanofibrous polystyrene strong acid cation exchanger crosslinked by sulfone bridges

Ar-SO₂-Ar 1360 – 1335 cm⁻¹, 1170 – 1160 cm⁻¹ s
-SO₃- H⁺ 2600, 2250, 1680 cm⁻¹, 1230 – 1120 cm⁻¹, 1120 – 1025 cm⁻¹ s

These spectra show the presence of sulfo groups (peaks at 2600, 2250, 1680 cm⁻¹, 1230 – 1120 cm⁻¹, 1120 – 1025 cm⁻¹) and sulfone crosslinkages (peaks at 1360 – 1335 cm⁻¹, 1170 – 1160 cm⁻¹). This nanofibrous product swells significantly in solution treated (when we immerse the sample into the water its weight increases more than 25 times). After drying this matter is very fragile.

Polystyrene nanofibers with sulfone crosslinkages and sulfone functional groups were analyzed with Elementar vario EL III.

Sample	%C	%H	%S
A	35.67	6.055	14.75
B	36.18	6.072	14.88
C	46.95	5.442	14.071
D	46.95	5.496	14.219

Table 1 Elemental analysis of crosslinked sulfonated nanofibrous polystyrene

These samples show high concentration of sulfur, two times higher than strong acid cation exchangers (~ 5%). Part of its sulfur is in the form of sulfon.

The physical and chemical properties of this material can be improved by adding crosslinking agent into the sulfonating solution. This crosslinking agent (e.g. formaldehyde) introduces methylene bridges beside of sulfone bridges.

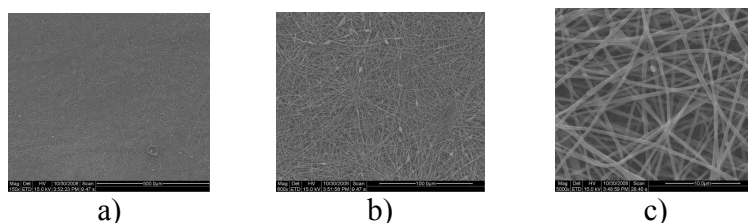


Figure 5 Polystyrene nanofibers crosslinked with methylene bridges; a) magnification 150, b) magnification 600, c) magnification 5000

This product differs from sulfon crosslinked polystyrene especially in physical properties – in micro scale the diameter of nanofibers does not chase (200 – 350 nm) and

in macro scale the membrane keeps its elastic properties also after drying. The swelling behavior enables water uptake under 1g per 1g of dry material. This material is very stable in high temperature, it does not change its morphological structure after 2 hours in 220°C.

Functionalization of sulfone crosslinked polystyrene with sulfone functional groups proceeds during sulfonation, as it can be seen in infrared spectrum of this material. The ion exchange capacity of sulfone crosslinked nanofibrous polystyrene is around 5,2 meq/g.

Functionalization of methylene crosslinked material proceeds similarly to functionalization of common granular ion exchangers, in hot concentrated sulfuric acid. The ion exchange capacity of this methylene crosslinked polystyrene nanofibrous is around 1 meq/g.

Sulfonated polystyrene we can convert to anion exchanger via sulfochloride derivatives followed by reaction with di/polyamine. This way is more environmentally friendly and not so hazardous as chloromethylation with chloro methyl methyl ether. The ion exchange capacity of this nanofibrous polystyrene anion exchangers is 1,3 meq/g.

Method for measuring ion exchange capacity was acid-base titration. Ion exchange capacity (IEC) is the measure of the number of replaceable H⁺ ions per unit mass of the exchange material. The effluent was collected in a flask, and measured by titration to a phenolphthalein end-point against a known molarity solution.

Sample	type	Functional group	Ion exchange capacity [meq / g dry matter]
FNF - 1	Nanofibers	-SO ₃ H ⁻	5,5 – 6,2
FNF – 2	Nanofibers	-SO ₃ H	6,1-6,3
FNF – 3	Nanofibers	--SO ₃ H	4,8 – 5,9
FNF – 4	Nanofibers	--SO ₃ H	3,9- 4,2

Table 2 The ion exchange capacity related to the neutralizing solution. Neutralizing solution after sulfonation of nanofibrous polystyrene is for FNV 1 – methanol, for FNV 2 it is hot saturated hydroxide in ethanol, FNV 3 – ethanol, FNV 4 – ethanol mixed with acetone

Trade mark	Company	Type	Functional group	Ion exchange capacity	
				[meq / g dry exchanger]	In data sheet of material
HCR-S/S	Dowex	resin	-R-SO ₃ ⁻	5,0	2 eq /l
K-5P	Promion	microfibers	-COOH	5,3	3-8 meq /g dry matter
K-1	IPOC ^a	microfibers	-R-SO ₃ ⁻	2,4	3 meq /g dry matter
FNF*	Elmarco ltd.	nanofibers	-R-SO ₃ ⁻	5,2	3,8 meq /g

Note: ^a Institute of Physical Organic Chemistry of the National, Academi of Science of Belarus; ^bEvaluated in MEGA a.s.

Table 3 Comparison of ion exchange capacity between granular and fibrous ion exchangers

Compared to the granular ion exchangers, fibrous sulfonic cation exchanger exhibits excellent kinetic features. These features are expressed by no lag in acid-base titration in comparison with granular ion exchangers. The half-time of sorption by fibrous ion-exchangers is more than 20 times shorter⁷.

This features allow water treatment even in filtration through 10- or 20-mm filtering bed at a high flow velocity⁶. The use of thin-fiber close-packed fibrous ion exchangers

considerably simplifies control of the permeability and hydrodynamic resistance of filtering beds to ensure the required conditions for water treatment.

All the tested fibrous sulfonic cation exchangers, irrespective of the bed height, are more efficient sorbents for preparation of deeply purified water than the granular resin.

The use of the filtering beds prepared from close-packed thin-fiber ion exchangers can be promising in development of small high-performance filtering units for deep water purifying. In water purification we can use the advantage of selectivity of chosen functional groups (e.g. for fast and specific sorption of highly toxic or radioactive pollutants like Hg, U, Cd) Further potential applications are as support of catalytically active metal ions or in biotechnology. In nuclear engineering we can decontaminate the surface selectively, treat small volumes of concentrated solutions or big volumes with low concentration of radioactive substances. We can utilize preconcentration of ions on the surface of nanofibrous ion exchangers in analytical chemistry (chromatography etc.).

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