Cation-Exchange Membranes: Comparison of Homopolymer, Block Copolymer, and Heterogeneous Membranes

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ABSTRACT: Three types of sulfonic cation-exchange membranes were compared: (a) homogenous membranes prepared by sulfonation of poly(2,6-dimethyl-1,4-phenylene oxide) or poly[oxy(1,4-phenylene)oxy(1,4-phenylene)carbonyl(1,4-phenylene)] and solution casting of the sulfonated products, (b) membranes prepared by sulfonation of poly[styrene-*block*-(ethene-*stat*-butene)-*block*-styrene] film, and (c) heterogeneous membranes prepared by melt-blending linear polyethylene and particles 10–25 μm particles of sulfonated cation-exchanger followed by compression molding. At the same ion-exchange capacity (IEC), the membranes based on the block copolymer showed considerably higher ionic conductivity than the homogeneous membranes. Though having a higher IEC, the heterogeneous membranes were less conductive than the other investigated membranes. Their advantage consists in the ease of preparation and superior resistance to oxidative environment. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: E66–E72, 2012

Key words: cation-exchange membranes; poly(phenylene oxide); poly(ether ketones); styrene block copolymers; heterogeneous membranes

INTRODUCTION

Ion-exchange membranes are used as active separators in electrochemical processes, such as electrodialysis, electrolysis, and proton exchange fuel cell technology. Cation-exchange membranes contain negatively charged groups (usually sulfonic acid groups) attached by covalent bonds to the polymer backbone.

The largest group of cation-exchange membranes comprises homogeneous membranes consisting of a single polymer or random copolymer. (The same applies to anion-exchange membranes.) These membranes are prepared either by casting a solution of a polymer with ion-exchange groups and evaporating the solvent or by introducing ion-exchange groups into a polymer film. Many homogeneous membranes are based on aromatic polymers which can be easily sulfonated. Promising membranes have been prepared from sulfonated polyetherketones,[1–5] sulfonated polysulfones,[6–8] sulfonated polyimides,[9–11]

and poly(phenylene oxide).[12–14] A general rule reads that while the membranes of medium-sulfonated aromatic polymers show fairly good proton conductivities and acceptable mechanical properties, the membranes of highly sulfonated aromatic polymers swell excessively in water and show poor mechanical strength in the water-swollen state. An alternative to homogeneous membranes is the membranes prepared from two polymers: one polymer imparting to the membrane mechanical strength and controllable swelling properties while the other polymer with charged groups controlling transport properties.

Two-polymer membranes can be prepared by several methods: (a) chemical or radiation-grafting of styrene or styrene-divinylbenzene monomers onto nonfluorinated or partially fluorinated films and subsequent sulfonation,[15–18] (b) by preparing semi-interpenetrating polymer networks by mixing solutions of an ion-exchange polymer (or its precursor) and a matrix polymer, followed by casting and evaporation of the solvent,[19] (c) by blending acid and basic polymers to form ionic crosslinks,[20–22] (d) by blending finely powdered ion-exchange particles with a polymer binder and calendering, extruding, or compression molding the blend,[23–25] or (e) by dispersing ion-exchange particles in a solution of an inert polymer, casting the suspension, and evaporating the solvent.[26]

A technical solution that combines the advantages of homogeneous and two-polymer membranes is the use of block copolymers. The two blocks—one hydrophobic imparting to the membrane mechanical strength and the other containing charged groups—are covalently linked. The immiscibility and covalent linking of two blocks give rise to a well-organized periodic domain microstructure.[27,28] Commercial availability of block copolymers makes them attractive for preparation of ion-exchange membranes. The membranes based on sulfonated poly(styrene-*block*-olefin) copolymers have recently been the subject of several publications.[29–31] Cation-exchange membranes based on block copolymers of sulfonated aromatics other than polystyrene ones have also been described.[32–35]

The aim of this work is to compare the properties of cation-exchange membranes prepared from sulfonated homopolymers or block copolymer and melt-processed heterogeneous membranes.

EXPERIMENTAL

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO; Spolana Neratovice, Czech Republic, M_w = 208,000, by light scattering), poly[oxy(1,4-phenylene)oxy(1,4-phenylene)carbonyl(1,4-phenylene)] (PEEK; Aldrich, nominal M_w = 20,800), poly[styrene-*block*-(ethene-*stat*-butene)-*block*-styrene] (block PS; Aldrich, nominal M_w ∼ 118,000), linear polyethylene (ExxonMobil, EXACT 0210), sulfuric acid (96%, p.a., Lachner, Czech Republic), 1,2-dichlorethane (Aldrich, anhydrous, 99.8%), chloroform (Fluka, puriss. p.a.), N,N-dimethylformamide (DMF; Fluka, purum, 99%), chlorosulfonic acid (Fluka, purum > 98%), iron(II) sulfate heptahydrate (Sigma-Aldrich, puriss. p.a.), and hydrogen peroxide (Fluka, puriss. p.a.) were used as received. Dowex[TM] HCR-S/S (Dow Chemical Company) (sulfonated polystyrene ion-exchanger with predominant particle size of 10–25 μm) and a heterogeneous Ralex[TM] CMP-PES membrane (cation-exchange membrane reinforced with a polyester network) were obtained from Mega (Czech Republic).

PPO sulfonation

PPO was dissolved in 1,2-dichloroethane (45°C) to form a 3% solution. A 5% chlorosulfonic acid solution in 1,2-dichloroethane was slowly added to the polymer solution at 45°C while stirring. The precipitated sulfonated product was removed by filtration, washed thoroughly with distilled water, and left to stand overnight in an excess of aqueous ammonia to transform the product to the NH_4^+ form. Subsequently, the sulfonated PPO (SPPO) product was filtered off, washed with distilled water, and dried.

When the molar ratio PPO monomer unit/ClSO$_3$H was 1 : 0.4, the S and N contents (by elemental analysis) in the product were 6.00 and 2.62%, respectively. For the molar ratio of 1 : 0.5, the S and N contents were 6.89 and 3.01%, respectively, and for the ratio of 1 : 0.55, the S and N contents were 7.31 and 3.19%, respectively.

SPPO membrane preparation

A 15% solution of SPPO (NH_4^+ form) in DMF was cast as a thin film onto a glass plate, and the solvent was slowly evaporated at 80°C. Then the film was removed from the glass plate by immersion into a water bath, washed with water for several days, then immersed into 1M aqueous HCl for 24 h, and then again washed with water. The dry membranes were 95–100 μm thick.

PEEK sulfonation

A 15% solution of PEEK (15 g) in DMF was dissolved in 400 mL of sulfuric acid (96%), and the solution was stirred at 25°C for 4 days. Then it was poured into an excess of ice water, the precipitated sulfonated product (SPEEK) was filtered off, washed thoroughly with distilled water, left to stand in an excess of aqueous ammonia overnight, filtered off, washed with distilled water, and dried. The S and N contents (by elemental analysis) were 6.56 and 2.84%, respectively. The same procedure, but with the solution stirred for 5 days, gave the product with S and N contents 6.83 and 2.98%, respectively, and with the solution stirred for 6 days gave the product with S and N contents 7.10 and 3.10%, respectively.

SPEEK membranes

A 15% solution of SPEEK (NH_4^+ form) in DMF was cast onto a glass plate, and the solvent was slowly evaporated at 80°C. Then the film was removed from the glass plate by immersion in a water bath, washed with water for several days, then immersed into aqueous 1M HCl for 24 h, and then again washed with water. The dry membranes were 95–100 μm thick.

Sulfonated block PS membranes

A 15% solution of block PS in cyclohexane was cast into a Petri dish, and the solvent was evaporated at 40°C. The dry membrane was immersed into a chlorsulfonic acid solution in 1,2-dichloroethane, washed with 1,2-dichloroethane, left to stand in an excess of aqueous ammonia overnight to transform the product to the NH_4^+ form. Before further characterization, it was immersed in 1M aqueous HCl for 24 h
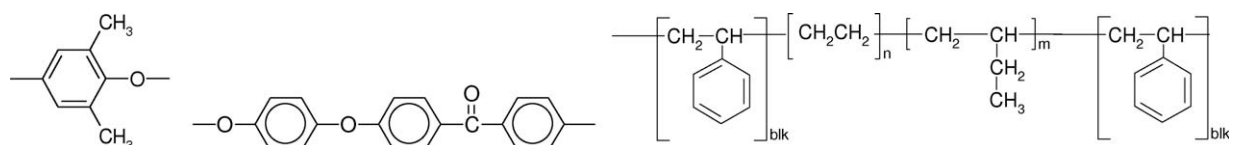
Figure 1 Formulas of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), poly[oxy(1,4-phenylene)oxy(1,4-phenylene)carbonyl(1,4-phenylene)] (PEEK), and poly[styrene-*block*-(ethene-*stat*-butene)-*block*-styrene] (block PS).

and then again washed with water. The dry membranes were 100–105 μm thick.

When the unsulfonated membrane (3 g) was treated with 60 g of a 10% solution of chlorsulfonic acid in 1,2-dichloroethane for 3 h, the S and N contents in the product were 7.11 and 3.04%, respectively, when treated with 60 g of a 5% solution of chlorosulfonic acid in 1,2-dichloroethane for 20 min, the S and N contents were 6.71 and 2.93%, respectively, and when treated with 60 g of a 5% solution of chlorsulfonic acid in 1,2-dichloroethane for 10 min, the S and N contents were 5.91 and 2.56%, respectively.

Heterogeneous membranes

Linear polyethylene (34 wt %) and cation-exchange particles Dowex HCR-S/S with a predominant particle size of 10–25 μm (66 wt %) were blended in a Brabender Plasti-corder PLE 651 at 140°C until the mixture became optically homogeneous, and the torque value reached a constant value. In another experiment, the ratio of linear polyethylene/Dowex HCR-S/S particles was 40 : 60 by weight. The blends were compression-molded between two poly(ethylene terephthalate) films at 140°C and 10 MPa. The resulting membranes were 0.30 mm thick. Before subsequent characterizations, the membranes were conditioned by successive immersion in 1M HCl, 1M NaOH, 1M HCl, 1M NaOH, and 0.1M HCl (for 24 h each). Between the steps, the membranes were washed with deionized water.

NMR

^{1}H-NMR (300.13 MHz) spectra of block PS in CDCl$_3$ were recorded on a Bruker Advance DPX300 at 25°C.

Membrane swelling in water

Membrane strips were immersed into water at 25°C. After 48 h, the strips were removed from water, wiped with tissue paper, weighed, dried in vacuum at 80°C for 8 h, and again weighed. The membrane degree of swelling (DS) in water was calculated using the relationship SW = $(W_S - W_0)/W_0$, where W_S is the weight of a swollen strip, and W_0 is the weight of a dried strip, respectively.

Oxidative stability

Oxidative stability of the membranes was tested by immersing the films into Fenton's reagent (3% aqueous H$_2$O$_2$ containing 4 ppm Fe^{2+} ions) at 70°C. The disintegration time of PPO and block PS membranes and a decrease in weight of heterogeneous membranes were used to evaluate their oxidative stability.

Small angle X-ray scattering

Small angle X-ray scattering (SAXS) experiments were performed using a pinhole camera (Molecular Metrology SAXS System) attached to a microfocused X-ray beam generator (Osmic MicroMax 002) operating at 45 kV and 0.66 mA. The camera was equipped with a multiwire gas-filled area, a detector with a diameter of active area 20 cm (Gabriel design). Experimental setup covered the q range of 0.004–0.17 Å^{-1} scattering vector, $q = (4\pi/\lambda)\sin\theta$, where $\lambda = 1.54$ Å is the wavelength, and 2θ is the angle between the incident X-ray beam and the detector measuring the scattered intensity.

Microscopy

Scanning electron micrographs (SEM) of the prepared membranes were obtained with a Hitachi scanning electron microscope S4700. Membranes dried in desiccator over molecular sieves were immersed into liquid nitrogen, broken, placed in a metal holder, and coated with an Au/Pd layer by vacuum sputtering.

Mechanical properties

Tensile strength testing of membranes in the water-swollen state was carried out with an Instron 5800 R testing machine at room temperature using 5 × 1 cm test specimens. Tensile strength at break and the energy needed to break the specimen were determined at a cross-head speed of 10 mm min^{-1}. The reported results are mean values of five measurements.

Ion exchange capacity

Ion exchange capacity (IEC) was evaluated by potentiometry during the transformation of a membrane

TABLE I
Block PS: ^{1}H-NMR Spectra

Proton type	Chemical shift (ppm)	Proton proportion (%)
Aromatic	6.37–7.22	10.8
CH$_2$	1.08–1.99	74.9
CH$_3$	0.80–0.89	14.3

sample from the H$^+$ to Na$^+$ cycle. The potential response of a Ross combined glass electrode (Orion) was recorded with a Keithley 6514 electrometer of high input impedance (200 TΩ). The potential vale was converted to the concentration of displaced ions in solution using a calibration curve. This series of experiments was performed in a gas-tight cell under argon atmosphere.

Ionic conductivity

The in-plane ionic conductivity of the membrane was measured in the gas-tight cell of a thermostated box in deionized water (relative humidity 100%). A four-electrode arrangement, a frequency Response Analyzer Solartron SI 1250 and Electrochemical Interface Solartron SI 1287 were used to measure the impedance spectra and setting of experimental conditions, respectively.

RESULTS AND DISCUSSION

Sulfonation

Sulfonation of aromatic polymers is an electrophilic substitution reaction, which can be carried out with common sulfonation agents, such as sulfuric acid, sulfur trioxide, or chlorsulfonic acid. The degree of sulfonation must be controlled to prevent obtaining polymers highly swelling or even soluble in water. In this work, three polymers were sulfonated: PPO, PEEK, and block PS. For their formulas, see Figure 1. The composition of block PS was specified using ^{1}H-NMR spectroscopy (Table I); it comprised 12 mol % styrene units, 67 mol % ethene units, and 21 mol % butene units. The degree of sulfonation of PPO was controlled by using different amounts of chlorsulfonic acid and that of PEEK by the reaction time with sulfuric acid. In the case of PEEK, benzene rings bearing electron-withdrawing carbonyl groups are not sulfonated.[36] Block PS sulfonated with sulfuric or chlorsulfonic acid was insoluble in common organic solvents; hence, the sulfonation with ClSO$_3$H of a cast membrane was carried out. Its degree of sulfonation was controlled both by the ClSO$_3$H concentration and by the reaction time. All three polymers were sulfonated to obtain the membranes with an IEC $\sim$ 2.2 meq g^{-1} of dry polymer, which is a compromise between a high IEC and good membrane handling.

Membrane mechanical properties and oxidative stability of membranes

Relevant properties of membranes made of sulfonated polymers and those of the unsulfonated starting materials are given in Table II. Both homopolymers were sulfonated to the degree of sulfonation of $\sim$ 30%. Hence, approximately every third benzene ring carries a sulfonic acid group. On the other hand, almost all benzene rings in block PS underwent sulfonation. Mechanical properties of water-swollen ion-exchange membranes are poorer by an order of magnitude than those of their unsulfonated counterparts, but they allow acceptable handling. Mechanical properties may be considerably improved by reinforcement (see Table II, membrane Ralex).

TABLE II
Properties of Membranes from Unsulfonated and Sulfonated Polymers

Membranes	S content[a] (%)	IEC (meq g^{-1})	DS[b] (%)	SW[c] (%)	Break stress[d] (MPa)	Energy to break[d] (mJ mm^{-3})	Oxidative degradation[e]
PPO	0	0	0	<0.1	32.3	35.7	>150 h
SPPO	6.89	2.22	32.6	72	17.1	8.3	15 min
SPEEK	7.10	2.22	27.1	95	19.2	10.3	N/A
Block copolymer	0	0	0	<0.1	32.8	50.9	>150 h
Sulfonated block PS	7.11	2.22	99.3	135	6.6	6.0	60 min
Linear polyethylene	0	0	0	<0.1	19.0	6180	>150 h
Heterogeneous membrane	9.56	3.05	–	97	1.7	2.6	Weight loss 30 min 2% 60 min 18%
Ralex^{TM} CMP-PES	7.08	2.20	–	41	7.6	375.2	Weight loss 30 min 1% 60 min 8%

^{a} By elemental analysis.
^{b} Degree of sulfonation based on N content. DS 100% corresponds to 1 SO$_3$H per benzene ring.
^{c} Degree of swelling in water (25°C).
^{d} In a water-swollen state.
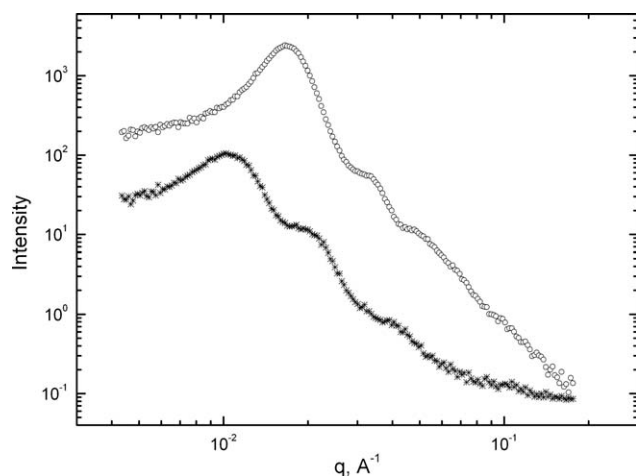^{e} The onset of membrane disintegration in Fenton's reagent.

Figure 2 SAXS profiles for dry sulfonated block PS membrane (upper curve) and for water-swollen sulfonated block PS membrane (lower curve).

Figure 3 SAXS profiles for SPPO membrane (upper curve) and for SPEEK membrane (lower curve).

The investigated membranes differ considerably in their stability in oxidative environment, which is present in many electrochemical devices. While unsulfonated membranes are highly stable in Fenton's reagent, all sulfonated membranes undergo a fast degradation. However, the behavior of sulfonated membranes in Fenton's reagent is different: homogeneous SPPO membrane soon disintegrates. (SPEEK membranes were not tested because they are soluble at 70°C). The sulfonated block PS membranes disintegrate slowly, due to the stability of unsulfonated polyolefin blocks. The heterogeneous membranes, owing to their inert matrix, retain their good mechanical strength at comparable treatment times, which may considerably prolong their lifetime in electrochemical applications.

Membrane morphology

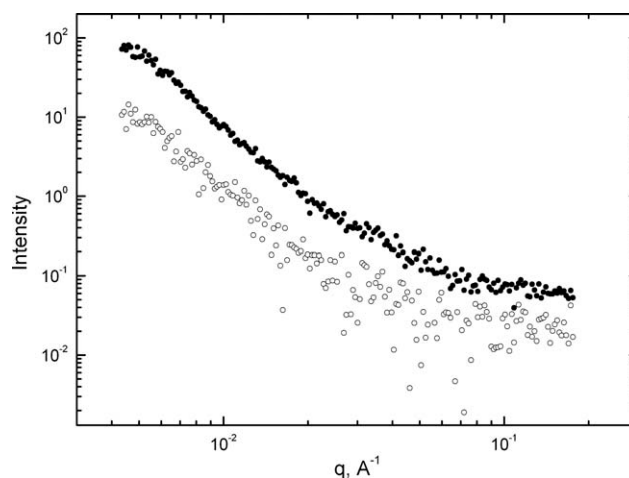SAXS profiles for both dry and water-swollen sulfonated block PS membranes are shown in Figure 2.

They clearly exhibit a periodic nanosized domain microstructure. The microstructure results from the immiscibility of the two highly different blocks: one polar (hydrophilic) and the other one nonpolar (hydrophobic). As expected, the domain microstructure is not shown by homogeneous SPPO and SPEEK membranes (Fig. 3). On a larger scale, sulfonated block PS membranes (SEM micrograph, Fig. 4, left side) and SPPO (Fig. 4, right side) and SPEEK membranes (similar structure, not shown) do not comprise any substantial inhomogeneities.

The structure of heterogenous membranes is complex. In these membranes (Fig. 5), large ion-exchanger particles and adjacent voids can be observed in the membrane cross section. On the surface, there is a skin layer formed predominantly by the matrix polymer with some cracks and few particles penetrating the skin. The skin layer imparts mechanical strength to the membrane but may decrease its conductivity. It is well known that small particles added to a polymer lead to the
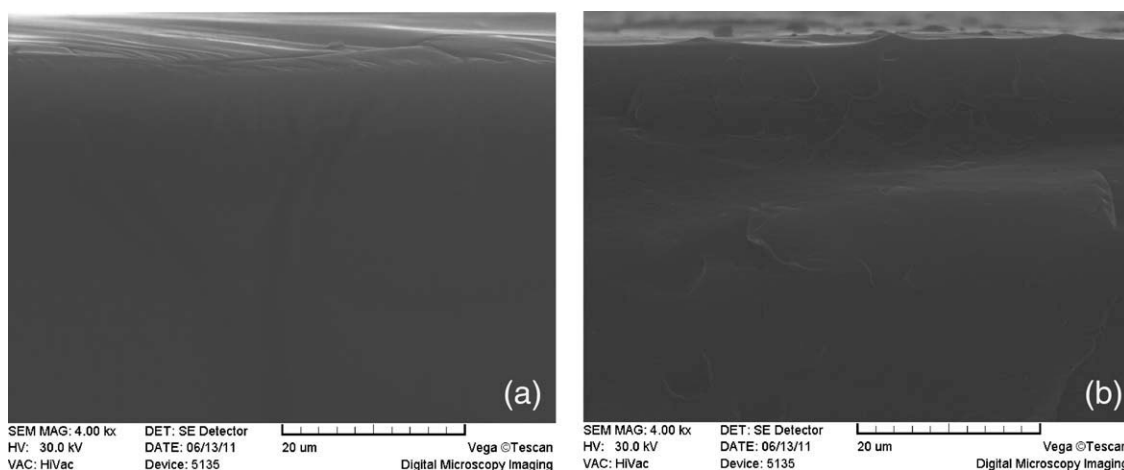

Figure 4 SEM micrographs of cross sections of sulfonated block PS membrane, IEC = 2.22 meq g^{-1} (left side) and SPPO membrane, IEC = 2.22 meq g^{-1} (right side).
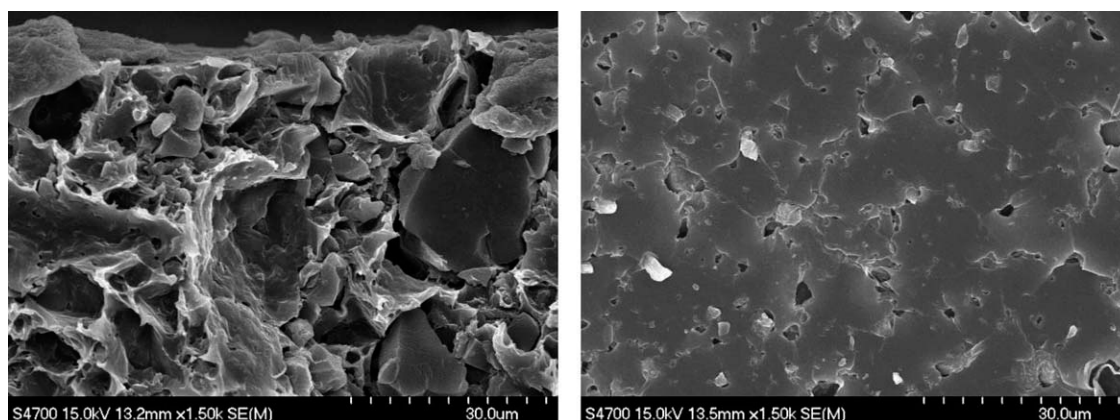
Figure 5 SEM micrographs of a heterogeneous membrane containing 66 wt % of ion-exchange particles: cross section (left side) and surface (right side).

development of specific polymer morphology[37,38] including the formation of a skin layer. The relation between the structure and properties of particulate filled polymers is usually quite complex; always several factors influence properties simultaneously. The most important factors influencing the morphology are the interfacial adhesion between the matrix polymer and fillers and the effect of processing and shaping conditions.

Membrane ionic conductivity

It is well known that ionic conductivities of membranes increase with increasing IEC.[39,40] However, in homogeneous membranes, the limit is set by the membrane mechanical strength. In block PS, sulfonated polystyrene blocks aggregate to form conductive domains within a hydrophobic polyolefin

Figure 6 Dependence of ionic conductivity (30°C) on the ion-exchange capacity of membranes. (1) membranes of block PS; (2) membranes of SPEEK; (3) membrane of SPPO; (4) heterogeneous membranes; (5) heterogenous membrane Ralex[TM].

matrix. Though the total ion-exchange capacities of block PS membranes were similar to those of SPEEK and SPPO, the IEC inside polystyrene domains was very high (ca. 5 meq g^{-1} calculated from the degree of sulfonation). This results in a high conductivity of sulfonated block PS membranes (Fig. 6). High conductivity of block copolymer membranes was observed by Nakabayashi et al.[35] A similar effect can be also found with Nafion membranes, which, despite their low total IEC (0.9 meq g^{-1}), are highly conductive in aqueous medium. Nafion side chains with sulfonic acid groups form distinct ionic phases in a highly hydrophobic matrix.[41] Thus, it may be concluded that the interconnected domains with a high concentration of ion-exchange groups give rise to high ion conductivity. Heterogeneous membranes show lower ionic conductivity than the other investigated types although their IEC is quite high. It plausibly results from the existence of a skin on the membrane surface with a low concentration of ion-exchange particles, and it also may be caused by some isolated particles in the core not forming a percolation path.

CONCLUSIONS

Three types of sulfonic cation-exchange membranes were compared: (a) homogenous membranes, (b) membranes based on a block copolymer, and (c) heterogeneous membranes containing small particles of a cation exchanger. Membranes based on a block copolymer comprised a periodic nanosized domain microstructure. On the surface of heterogeneous membranes, there is a skin layer formed predominantly by the matrix polymer with some cracks. At the same IEC, the membranes based on the block copolymer showed considerably higher ionic conductivity than the homogeneous membranes. Though having a higher IEC, the heterogeneous membranes were less conductive than the other investigated
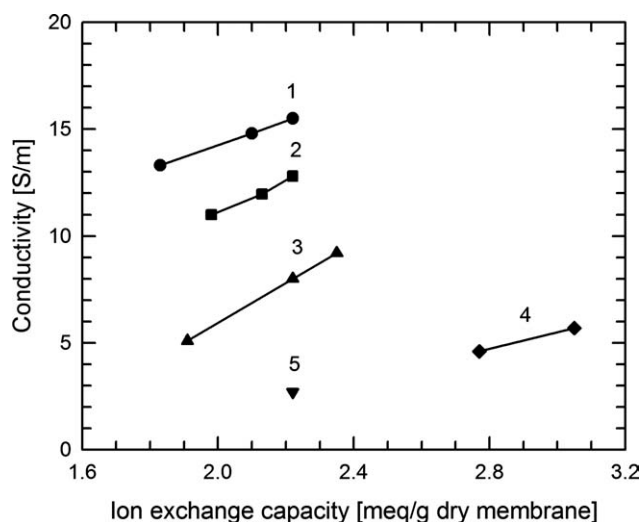
membranes. A high conductivity of membranes based on a block copolymer is explained by the existence of interconnected microdomains with an increased local concentration of sulfonic acid groups and a low conductivity of heterogeneous membranes results mainly from the existence of a skin with a low concentration of these groups. The advantage of heterogenous membranes consists in the ease of preparation and superior resistance to oxidative environment.

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