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He, Chenfeng; Guiver, Michael D.; Mighri, Frej; Kaliaguine, Serge

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Surface orientation of hydrophilic groups in sulfonated poly(ether ether ketone) membranes

Chenfeng He[a], Michael D. Guiver[b], Frej Mighri[a], and Serge Kaliaguine[a]*

[a]Department of Chemical Engineering, Laval University, 1065 avenue de la Medecine, Quebec, Quebec, G1V 0A6, Canada

[b] National Research Council, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada

[*]Corresponding author. serge.kaliaguine@gch.ulaval.ca

phone: +1 418-656-2708, fax: +1 418-656-3810

Abstract

Sulfonated poly(ether ether ketone) copolymers (SPEEK) with a range of sulfonate contents (SC 77%-51%) were synthesized via nucleophilic substitution polycondensation from hydroquinone and sulfonated hydroquinone. Membranes obtained by solvent casting from dimethylacetamide onto glass surfaces were analyzed for surface behaviour. The surfaces of a membrane were hydrophobic in air, but hydrophilic in water. This surface behaviour was corroborated by water contact angle vs. time, using sessile drop measurements. Hydrophilic sulfonic group aggregates on SPEEK chain and various media contacting with the top or bottom surfaces of the membrane during the fabrication process caused differences in surface behaviour. Angle-dependent XPS showed that there was a higher atomic S/C ratio of the bottom surface than on the corresponding top surface. The hydrophilic sulfonic groups were in higher concentration within the membrane, with the concentration gradually decreasing towards the surface for SPEEK-HQ-80 and SPEEK-HQ-70 membranes. Acidification with strong acid and higher temperature induced a more hydrophilic surface on a membrane than a milder acidification process. The depth profile at the membrane surface was examined by a combination of contact angle, XPS and ATR-FTIR.

KEYWORDS: *surface molecular reorientation, wetting, PEM, sulfonated poly(ether ether ketone), SPEEK*

1. Introduction

Extensive efforts have been made to develop potential alternatives for Nafion® in PEM application [1]. Aromatic polymers with sulfonic acid groups and their sulfonated derivatives have attracted considerable interests due to their excellent thermal and chemical stability. Sulfonated derivatives of poly(ether sulfone) (SPES) [2], polyimide (SPI) [3], polyimidazole [4], polyphenylene [5], and polybenzimidazole [4] are among poly(aryl ether ketones) (PAEK) being investigated as PEM materials.

PAEKs are of considerable interest due to the combination of their chemical stability, physical and mechanical properties. As a class of promising PAEK for PEM, aromatic sulfonated poly(ether ether ketone) (SPEEK) has been widely investigated. The two main approaches to introduce sulfonic acid groups into this type of polymer are (a) the post-sulfonation of existing polymers, or (b) the direct copolymerization of sulfonated monomers [1]. The sulfonation reaction of commercial Victrex PEEK, yielding sulfonated poly(ether ether ketone), has been thoroughly investigated by various groups [6-9]. The post-sulfonation process is advantageous due to the availability of inexpensive commercial polymers, such as PEEK, and because of a relatively simple sulfonation procedure that can be scaled up. Challenges, however, may be encountered in both the precise control of the sulfonation sites location and the degree of sulfonation (DS), resulting in a random and less-defined distribution of sulfonic acid groups along the polymer chain. Moreover, harsh reaction conditions, i.e., elevated temperatures, extended reaction time and strongly-acidic sulfonation agents, may be required for the sulfonation process, which could lead to side reactions and polymer degradation [1].

Copolymers synthesized by direct copolymerization exhibit advantages in the controllability of the sulfonate content (SC) and sulfonation sites location, leading to more defined chain structures in comparison with the postsulfonation method [10]. Nevertheless, the compatibility between the solvent and reactants, such as potassium carbonate, monomers, intermediates, oligomers and growing polymer chains under the reaction conditions, is essential for a successful copolymerization. The solvent is chosen from the solubility of reactants, the solubility of high molecular weight polymer during polymerization process and the reactivity of the monomers. Moreover, the direct copolymerization process using sulfonated monomers is hampered by the limited availability or purity of sulfonated monomers.

The presence of a certain amount of water in sulfonated PEMs is vital for proton transport through the membrane. However, excessive water uptake in a PEM leads to unacceptable dimensional change [11] dimensional mismatch with the electrodes and delamination of catalyst layers from the PEM [12]. On the other hand, a loss of conductivity occurs at elevated temperatures (above 80 ^{o}C) due to dehydration. These issues may result in a reduction of mechanical properties [13] or poor membrane electrode assembly (MEA) performance and durability [1].

The unique character of Nafion® originates from the combination of a highly hydrophobic perfluoropolymer backbone and flexible side chains bearing exceptionally hydrophilic and super acidic sulfonic acid groups. The surface of Nafion®, however, transforms from a hydrophobic surface in the presence of air or water vapor atmosphere [14, 15] into a hydrophilic surface when in contact with liquid water. This transformation is supported and elucidated by simulation models and experimental results. The highly incompatible hydrophobic backbone and hydrophilic side chain constituents separate the polymer matrix into micro-phases, which lead the sulfonic acid groups to cluster into hydrophilic domains and the polymer backbone to form hydrophobic domains [1]. In some polymer systems, the composition of the membrane surface differs, sometimes dramatically, from the composition within the bulk, resulting in a material with distinct surface properties, such as wettability and adhesion. Differences of the surface free energy of the components within a polymer may explain the overall surface morphology in which the lower surface energy component of polymer preferentially aggregates towards the polymer-air interface [16, 17].

Until now, there has been no comparative investigation of partially sulfonated SPEEK prepared by the direct copolymerization process with the same composition as that originating from a post-sulfonation process of commercial Victrex PEEK. In this study, a series of SPEEK copolymers based on hydroquinone bearing various sulfonate contents were first synthesized by copolymerization using hydroquinone as an alternative to post sulfonated SPEEK. Flexible, transparent and tough membranes were prepared by the solution casting. To better understand the effects of water on SPEEK membranes and the swelling of PEM, we investigated the differences in hydrophilicity between two surfaces of a membrane, and, between the surface and the bulk of these membranes. Furthermore, the change in membrane hydrophilicity upon contacting with water vapor and liquid water was investigated. The depth profiles of membrane surfaces were examined by contact angle, XPS, ATR-FTIR and FTIR, providing the surface information from 0.5 nm to 1 μm to the surface. It was observed that sulfonic groups aggregated within the membrane. The hydrophilicity of the membrane surface in contact with liquid water may be of practical importance in PEM fuel cells because liquid water is produced in traditional fuel cells application. Attempts were first initiated to interpret the composition difference between the glass-polymer surface and air-polymer surface of the same membrane.

2. Experimental Section

2.1. Chemicals and Materials.

All chemicals were purchased from Sigma-Aldrich or Fluka. Hydroquinone (HQ) ReagentPlus^{TM}, $\geq$99% was purified by sublimation under vacuum. 4,4’-Difluorobenzophenone (DFK) 99% was used as obtained. 2,5-Dihydroxybenzenesulfonic acid potassium salt (SHQ), technical grade, was purified by recrystallization using ethanol/water (1/1,v/v). Potassium carbonate (anhydrous) was dried at 100 ^{o}C in a vacuum oven for 12 h. Anhydrous dimethyl sulfoxide (DMSO) 99.9%, 1-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc), 2-propanol (also designated as isopropanol (IPA)) and toluene were used without further purification.

2.2. SPEEK Synthesis

2.2.1. Synthesis of Copolymer SPEEK

The copolymers of SPEEK in potassium form were synthesized using DFK and HQ, with various stoichiometric amounts of SHQ. The copolymer of SPEEK was denoted as SPEEK-HQ-XX, where XX refers to the molar ratio of SHQ to DFK (in percentage). In a typical copolymerization represented by SPEEK-HQ-70, SHQ (21 mmol, 4.7935 g), HQ (9 mmol, 0.9910 g), DFK (30 mmol, 6.5460 g) and potassium carbonate (34.5 mmol, 4.7682 g) were precisely weighed and transferred into a 250 mL three-neck flask equipped with a mechanical stirrer, Dean-Stark trap and an argon gas inlet. 80 mL of DMSO and 40 mL of toluene were added. The mixture was refluxed at 150 ^{o}C for 4 h, following which the toluene was removed, allowing the temperature to slowly increase to 175 ^{o}C. After a polymerization time of 24 h, the viscous mixture was vacuum filtered overnight, and then, the collected transparent dark red solution was poured into excess cold IPA under strong mechanical stirring to obtain a string-like polymer product. The resulting polymer fibers were washed thoroughly a few times using fresh IPA and cold water successively. The copolymer SPEEK-HQ-70 in potassium form was dried in a vacuum oven at 120 ^{o}C for 24 h.

2.2.2. Synthesis of Post SPEEK

The post sulfonation of PEEK (Victrex PLC) was run using concentrated sulfuric acid according to the procedure described elsewhere [9, 18]. The process was detailed in supporting information.

2.3. Membrane Fabrication

SPEEK copolymer (4 g) was dissolved in DMAc (20 mL) under stirring overnight. A uniform and transparent polymer solution without bubbles was obtained, which was then filtered through a stainless steel pressure filter (Millipore) and cast using a doctor blade onto a clean glass plate (21 cm × 29.7 cm). The cast membrane solution was placed flat in a covered container at 60 ^{o}C with a slow argon purge for ~20 h. The resulting membrane was removed from the glass plate by immersing it in cold water. The membrane was stored in water at room temperature for 24 h, with the water being changed several times to remove residual solvent. The SPEEK membrane in the potassium form was converted to the acid form by placing it into 1 M H_2SO_4. Two acidification processes were used. One was acidification by 1 M H_2SO_4 at room temperature for 24 h. Another one was acidification by 1 M H_2SO_4 at room temperature for 21 h, followed by acidification at 84-90 ^{o}C for 2 h. After acidification, the membrane was immersed in water at room temperature for 24 h, with several changes of fresh water, until the wash water was at pH 7. Membranes in either the potassium or acid form were dried in ambient air in a fume hood overnight, and then laid flat in a vacuum oven at 60 ^{o}C for 12 h. The temperature was slowly increased to 120 ^{o}C and maintained at that temperature for 24 h. Finally, the membranes were stored in a dessicator prior to characterization.

2.4. Characterization and Tests

Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) and fourier transform infrared spectroscopy (FTIR) spectra of homogenous membranes were recorded at 45^{o} of incidence angle from 4000-500 cm^{-1} using a Thermo Nicolet Magna-850 (Thermo Scientific, Madison, WI) and a Thermo-Nicolet 760 FTIR, respectively. The Golden-Gate (diamond IRE) ATR accessories (Specac Ltd., London, U.K.) were used for ATR-FTIR measurement. ATR correction was applied for all resulting ATR-FTIR spectra using Thermo Nicolet Omnic software to illustrate the different penetration depths of the various wavelength. A liquid-nitrogen-cooled narrow-band Mercury Cadmium Telluride (MCT) detector was used for all spectra measurements. The sample chamber of Thermo-Nicolet 760 FTIR was purged with CO_2- and

H_2O-free air before measurement. A thin film (0.01mm) was used for FTIR measurements. All membrane samples were dried in vacuum-oven at 120 °C for 24 h and kept in a dessiccator prior to measurements. A sample was measured using at least three different pieces from the same membrane and the average was reported. Each spectrum was obtained from the acquisition of 128 scans at 4 cm^{-1} resolution from 4000 to 750 cm^{-1} using a Happ-Genzel apodization.

^1H-NMR spectra were recorded in DMSO-d6 using a Varian Unity Inova spectrometer at a resonance frequency of 399.96 MHz for ^1H. Signals from DMSO-d_6 were used as the reference for ^1H (2.50 ppm (DMSO)). The sulfonate content (SC) was calculated from ^1H-NMR as shown elsewhere [19].

The solubility of SPEEK-HQ both in potassium and proton forms was tested in DMSO, DMAc and NMP. 2% (polymer/solvent, g/g) polymer solution was prepared at room temperature (20 °C), followed by standing over night. The solution was then heated progressively at regular 5 °C accumulation and kept constant for one hour. The temperature at which the transparent solution was obtained was recorded.

Both initial contact angles of water on membranes and contact angle vs. wetting time (300 s) were measured at room temperature by the sessile drop analysis method, using a FTA 200 (First Ten Angstroms, USA) goniometer. The volume of water drop was about 10 μL. The drop image was recorded with a camera, followed by the shape of water drop analysis and calculation of contact angle using the FTA 32 software. The value of contact angle was obtained by averaging at least five drops of water on separated spots of the same membrane. The contact angles of water on membranes were measured on pictures and averaged by the right and the left contact angle of the same drop.

The chemical compositions of membrane surfaces were determined by Angle-dependent X-ray photoelectron spectroscopy (XPS) using Axis Ultra DLD system. Both sides of the membranes were examined at take-off angles of 30^o, 45^o, 60^o and 90^o.

Crystallization within the membrane was observed under a ZEISS Axioskop-40 using polar lenses at room temperature. The membranes were first heated to 300 ^oC at a heating rate of 50 ^oC /min, and then cooled down in ambient air and the crystal formation was recorded.

3. Results and Discussion

3.1. Polymerization of Copolymer SPEEK-HQ

The synthesis of poly(arylene ether)s by nucleophilic aromatic substitution polycondensation in polar solvents was first proposed in an early patent [20]. Later, McGrath and coworkers reported the synthesis and the detailed mechanism of condensation of poly(arylene ether sulfone)s via potassium carbonate in aprotic polar solvents [21, 22]. The polarity of typically used aprotic polar solvents is listed in Table S1.

The synthesis of fully sulfonated PEEK by copolymerization was first reported for gas dehumidification membrane materials [23] and later reported for proton conducting membranes [24]. Nevertheless, initial efforts to synthesize partially sulfonated PEEK (SHQ/DFK 40:100) via copolymerization were unsuccessful [25]. The failure of the attempted synthesis of SPEEK with

SHQ/DFK 40:100 was reported using DMSO as solvent. It was suggested that the poor solubility of non-sulfonated PEEK oligomers in very polar DMSO solvent (Dielectric constant 46.68 in Table S1) resulted in the precipitation of oligomers from the copolymerization mixture, leading to the termination of polymer chain growth and failure of polymerization.

In our work, a series of copolymers SPEEK bearing various sulfonate contents (80-45%) was synthesized from hydroquinone and sulfonated hydroquinone by nucleophilic aromatic substitution polycondensation with DFK under solution polymerization conditions as shown in Fig. S1. Depending on the expected sulfonate content of SPEEK, we used DMSO or NMP as the solvent for different SPEEK polymerization. Both SPEEK bearing 70% sulfonate content in potassium form (SPEEK-HQ-70K) and SPEEK bearing 80% sulfonate content in potassium form (SPEEK-HQ-80K) were obtained. Using the same procedure, however, the first attempt to synthesize SPEEK bearing 60% sulfonate content in potassium form (SPEEK-HQ-60K) encountered challenges in recovering the polymer products. In our work, after filtration of the polymerization mixture through a filter paper under water vacuum overnight, a resulting 40 mL gel was collected and a very viscous slurry remained on the filter paper. The gel was heated at about 80 ^{o}C and poured into excess cold IPA under strong mechanical stirring. Fine string-like polymer product and milky liquid on the top layer were obtained; the latter was evaporated by a rotary evaporator to remove IPA. The resulting concentrated mixture was poured into NMP (about 50% volume of gel). The gel mixture was heated at 100 ^{o}C and then the resulting solution was cast on a Petri dish and dried in a fume hood for a few days. The initial membrane was obtained and further dried under vacuum at 120 ^{o}C for 24 h. The membrane was re-dissolved into NMP at 100 ^{o}C and poured into excess cold IPA under strong mechanical stirring. String-like fibers were obtained.

A second attempt was made for SPEEK-HQ-60K synthesis using a similar process [23]. To prevent the resulting polymer solution from gel formation in DMSO, the polymer mixture was directly poured into excess cold IPA under strong mechanical stirring, and off-white fibers were obtained.

In solution polymerization, premature precipitation of intermediates and oligomers from the copolymerization mixture may occur due to the poor solubility of reactants and the growing chain during polymerization. This results in termination of the polymer chain growth, and leads to failure of polymerization. PEEK is a semi-crystalline polymer; the introduction of sulfonic groups onto PEEK decreases its crystallinity and improves its solubility in polar approntic solvents, such as DMSO and NMP. These solvents were therefore employed for nucleophilic aromatic substitution polycondensation via solution polymerization. Oligomers and polymers bearing various sulfonate contents exhibit different solubilities in various solvents possessing various polarities [6, 26]. Compared to high SC SPEEK, low SC SPEEK exhibited higher crystallinity and solubility in relatively lower polarity solvents. Proper solvent polarity was therefore essential for a successful direct synthesis of SPEEK bearing various sulfonate contents. In order to achieve high molecular weight polymer, a less polar solvent compared to DMSO (Dielectric constant 46.68 at 20 °C in Table S1), such as NMP (Dielectric constant 32.2 at 20 °C in Table S1), and higher reaction temperatures [27] were desirable to prevent premature precipitation of the semi-crystalline polymer.

In our work, the initial attempts to synthesize SPEEK with SCs of 50% and 40% were unsuccessful, using the similar process and DMSO as solvent as in reference [23]. Besides the polymer obtained, the presence of oligomers of SPEEK-HQ-50K and SPEEK-HQ-40K was inferred from GPC curves as shown in Fig. S2. These oligomers are similar to those found in reference [25]. In Fig. S2, the small peaks at elution volume about 19.3 mL and 19.4 mL suggest the oligomers of SPEEK-HQ-40K and SPEEK-HQ-50K bearing M_n 5400 and M_n 3100 g/mol relative to polystyrene standard, respectively. To prevent premature precipitation of oligomers of the semi-crystalline polymer during polymerization, a less polar and higher boiling point solvent, NMP, was employed to increase the solubility of reaction intermediates. It provides higher solubility and compatibility with the potassium biphenolate, oligomers and growing polymer chains. It moreover results in higher polymerization temperature to increase the polymerization rates. Other than using DMSO [25], NMP and a higher reaction temperature (190 ^{o}C) were used for the successful synthesis of SPEEK with SC of 45% in our work. High molecular weight polymer and the absence of oligomers were confirmed in Fig. S2, exhibiting M_n 53.8 kg/mol compared to polystyrene standard.

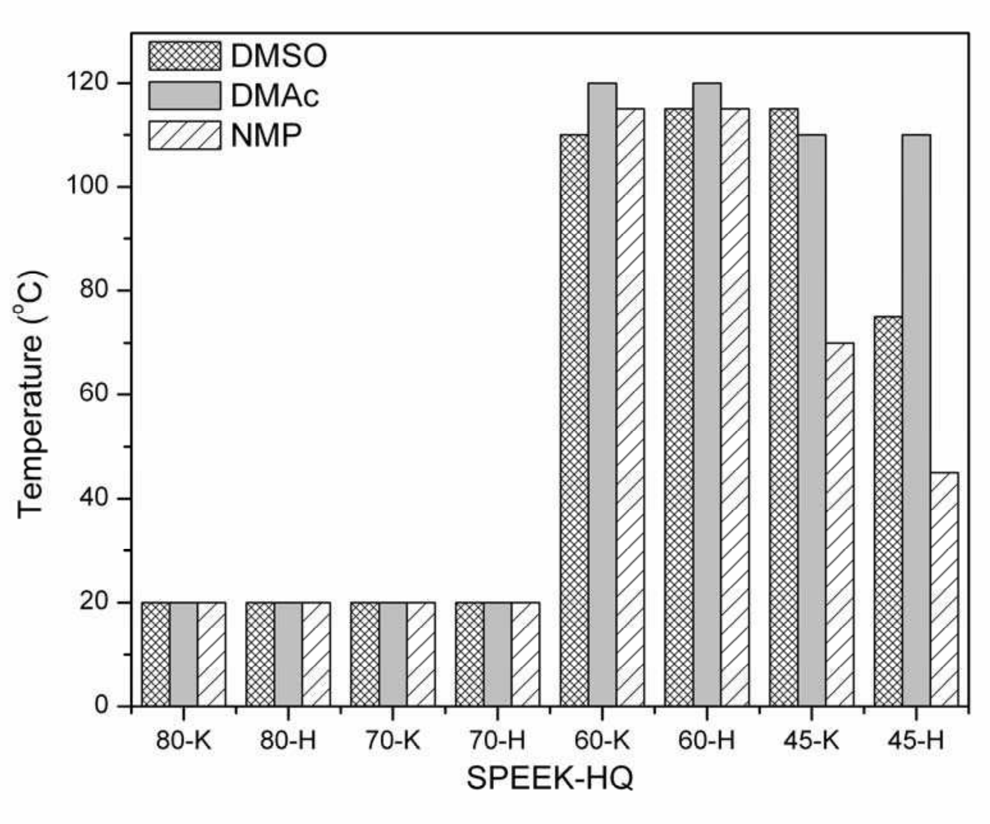

Fig.1. The temperature required to obtain transparent solutions of SPEEK-HQ both in potassium and proton forms in various aprotic polar solvents.

The solubility test of copolymer SPEEK-HQ, both in potassium and proton forms, showed that SPEEK-HQ-80 and SPEEK-HQ-70 dissolved well into DMSO, DMAc and NMP at room temperature (20 ^{o}C). Transparent solutions were obtained. As shown in Fig. 1, SPEEK-HQ-60K and SPEEK-HQ-60H were partly soluble at room temperature and the solutions were cloudy. The transparent solutions of SPEEK-HQ-60H and SPEEK-HQ-60K in various solvents were obtained at temperature in the range of 110-120 ^{o}C depending on the solvent used. On cooling, all SPEEK-HQ-60K and SPEEK-HQ-60H solutions recurred to be cloudy. At room temperature, a light gel of SPEEK-HQ-45 was formed in all solvents. It was observed that SPEEK-HQ-45K showed more severe tendency of gel formation than SPEEK-HQ-45H. Furthermore, the trend of gel formation of solvents was DMSO>DMAc>NMP. Fig. 1 shows that NMP was the best solvent for SPEEK-HQ-45 in both potassium and proton forms.

The synthesis of copolymer SPEEK based on hydroquinone was confirmed by FTIR (Fig. 2). The strong characteristic absorption band at 1025 cm^{-1} was attributed to the S=O stretching vibration. The other bands of sulfur-oxygen were attributed as follows: asymmetric O=S=O stretch at 1253 cm^{-1}, symmetric O=S=O stretch at 1081 cm^{-1}, and S−O stretch at 709 cm^{-1}. Fig. 2 shows that the absorption band at 1081 cm^{-1} increases with sulfonate content.

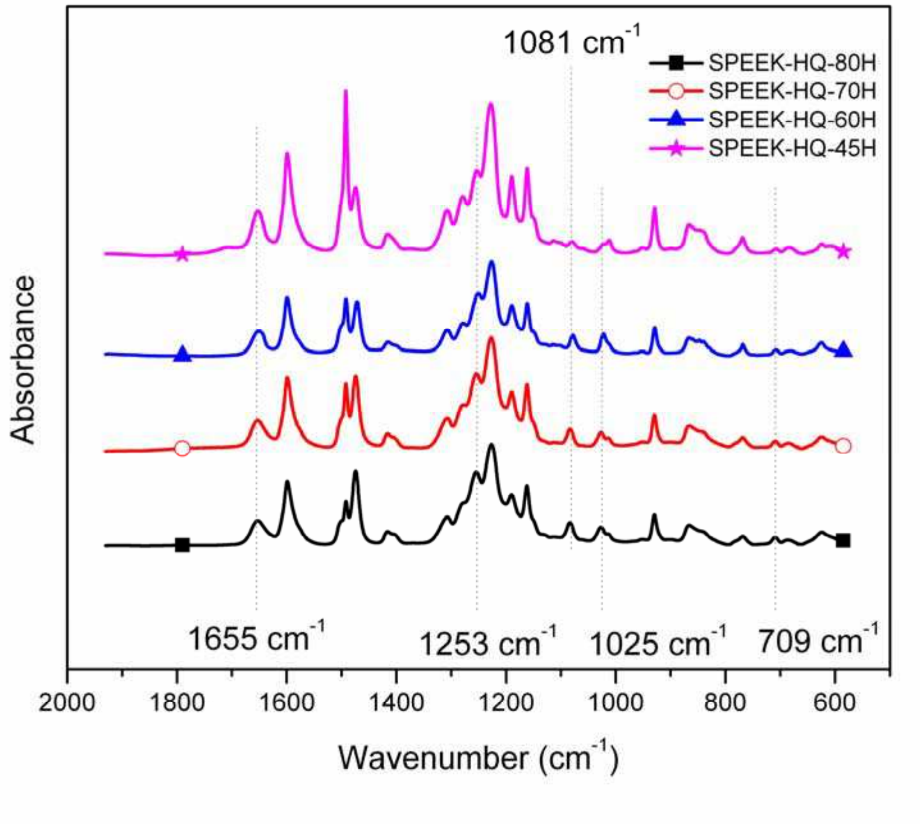

Fig.2. The fingerprint region of FTIR spectra of copolymer SPEEK-HQ in proton form with different sulfonate contents.

The polymerization was further confirmed by ^{1}H-NMR and the SC values were calculated from ^{1}H-NMR. The nomenclature of the aromatic protons for the SPEEK repeat unit was shown elsewhere [9, 19]. The results are summarized in Table S2. It was found that the calculated SC was in relatively good agreement with the experimentally targeted value.

The molecular weights of SPEEK in potassium form or proton form were determined both by viscosity measurements and by GPC. Given the existence of polyelectrolyte effect of ionomer in polar solvents, an inorganic salt, LiBr, was dissolved in the polar solvent NMP and the solution was used as solvent to depress the polyelectrolyte effect of SPEEK solution. A distinct polyelectrolyte effect is observed in Fig. S3, which reports measured viscosity values as functions of polymer concentration in both pure NMP and LiBr solution in NMP. It demonstrates that 0.05 M LiBr/NMP successfully depresses the polyelectrolyte effect of SPEEK-K in NMP, leading to the reduced viscosity (η_{red}) and the inherent viscosity (η_{inh}) intersecting correctly at the viscosity axis for extrapolation to infinite dilution as shown in Fig. S3.

. Table S3 shows the molecular weight relative to the standards, polydispersity index (PDI), reduced viscosity and inherent viscosity of SPEEK copolymers. From these data, it may be concluded that high molecular weight copolymer SPEEK based on hydroquinone was synthesized.

3.2. Characterization of Copolymer SPEEK-HQ

3.2.1. Thermal Stability and Glass Transition Temperature of Copolymer SPEEK-HQ

The thermal stability and glass transition temperature of copolymer SPEEK-HQ were investigated by TGA and DSC and the results are shown in supporting information. It was found that both increased monotonously with sulfonation content for the proton and potassium forms of copolymer SPEEK-HQ.

3.2.2. Crystallization

The presence and disappearance of crystalline regions within SPEEK-HQ-45K membrane is shown in Fig. 3. The sample was first heated at a rate of 50 ^{o}C/min to 300 ^{o}C, and then cooled down to room temperature in ambient air, at which temperature crystallinity was observed (Fig. 3a). The sample was then heated again continuously at the same heating rate to 150 ^{o}C, 200 ^{o}C, 250 ^{o}C, 300 ^{o}C, 330 ^{o}C and 350 ^{o}C. The membrane began to lose its crystallinity at 250 ^{o}C (Fig. 3d) and the crystallinity disappeared completely at 330 ^{o}C (Fig. 3f). The membrane was further heated to 350 ^{o}C (Fig. 3g), and then cooled down in ambient air to room temperature and no crystallinity was observed subsequently (Fig. 3h).

The crystallinity of post-sulfonated SPEEK in sodium form (post-SPEEK-Na) produced via ion exchange from post-sulfonated SPEEK-H was reported in the literature [7]; it was monitored by DSC in melted and quenched samples below 9% sodium sulphonate content [7]. Compared with the crystallinity of post-sulfonated SPEEK-Na in reference [7], the copolymer SPEEK-HQ-

K produced in this work bearing a much higher potassium sulphonate content (45%) exhibited crystallinity under a polarized lense microscope, as shown in Fig. 3.

This crystallinity differences between copolymer SPEEK-HQ-K and post-sulfonated SPEEK-Na may be related to a lower polydispersity index of copolymer SPEEK-HQ compared to that of post-sulfonated SPEEK although the polydispersity index of SPEEK-Na is not reported in ref. [7].

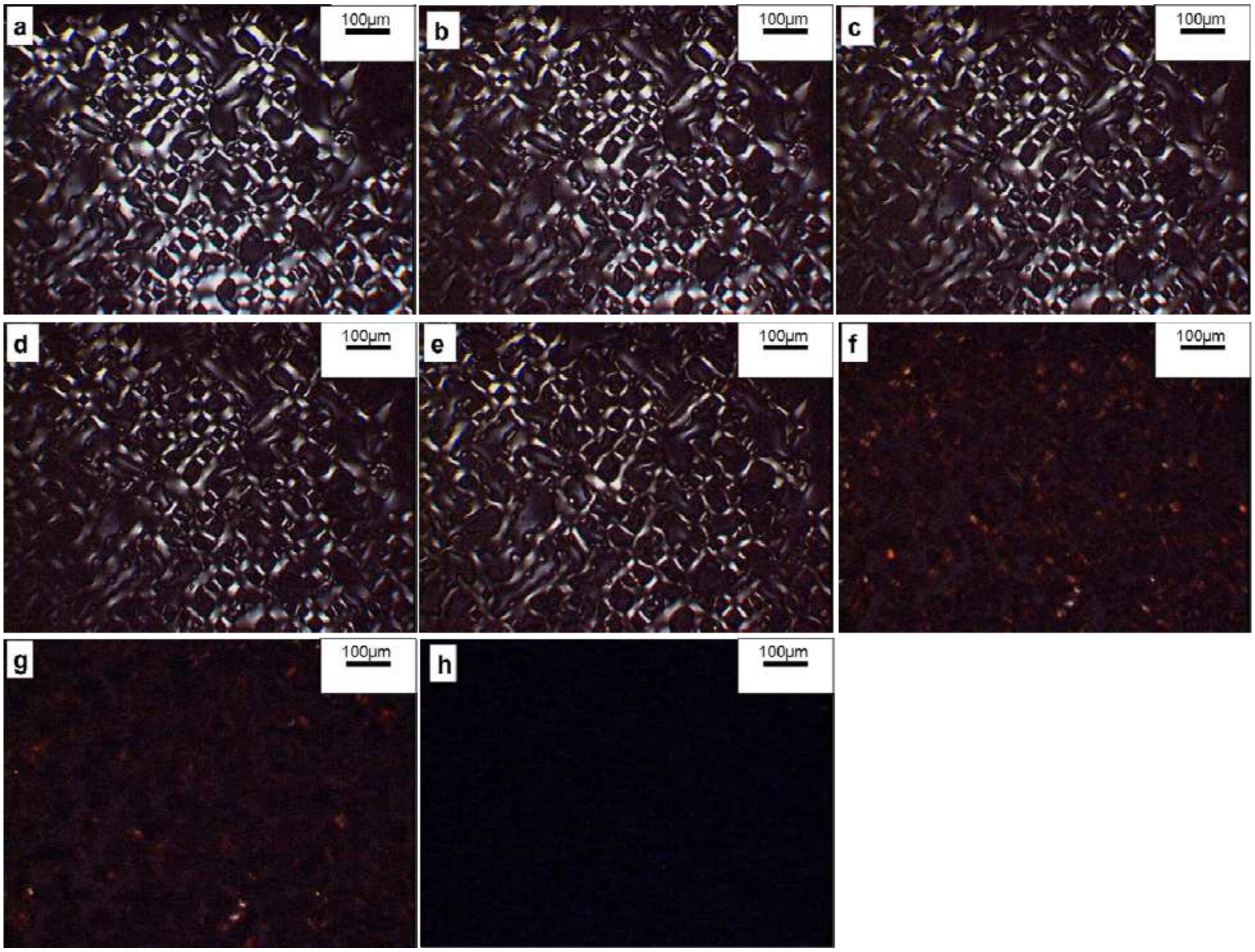

Fig. 3. Observation of crystallinity within copolymer SPEEK-HQ-45K membrane under microscope using polar lenses.

a. Heating at rate 50 ^{o}C/min to 300 ^{o}C, and then cooled in ambient air to RT, crystallinity is observed.
b. Heating at rate 50 ^{o}C/min, crystallinity is still observed at 150 ^{o}C.
c. Heating at rate 50 ^{o}C/min to 200 ^{o}C, crystallinity is still observed.
d. Heating at rate 50 ^{o}C/min to 250 ^{o}C, membrane begins to lose crystallinity.
e. Heating at rate 50 ^{o}C/min to 300 ^{o}C, membrane begins to lose crystallinity.
f. Heating at rate 50 ^{o}C/min to 330 ^{o}C, membrane loses crystallinity completely.
g. Heating at rate 50 ^{o}C/min to 350 ^{o}C, no crystallinity is observed.
h. Cooled in ambient air to RT, no crystallinity is observed.

3.3. Surface Behavior of Copolymer SPEEK-HQ Membrane

Langmuir [28] proposed that the surface properties of a solid are determined by the specific arrangement of atoms at the surface rather than the configuration of a macromolecule as a bulk. This infers that whether a polymer surface is hydrophilic or hydrophobic depends on the presence or absence of the hydrophilic moieties located at the interface. The hydrophilicity of a surface cannot be predicted from the presence or absence of hydrophilic moieties in the molecules. About surface configuration, he further observed: (1) The surface configuration involves the motion of short-range forces. It depends on the nature and arrangement of the atoms which constitute the actual surface, and not on the arrangement of the underlying molecular layers. (2) Contacting with various media, a surface layer may undergo a nearly instantaneous reversal of surface configuration orientation.

The surface of a solid, especially for a polymer surface, is significantly different from the bulk of the same material. This difference involves surface dynamics, surface reconstruction and their changes due to change of the surrounding medium [29-32].

3.3.1. Membrane Surface Characteristics at Less Than 0.5 nm Thickness: Wetting Behavior

The unique characteristics of Nafion® originate from its phase separation into hydrophobic domains and highly hydrophilic channels. In contact with air, Nafion® exhibits a hydrophobic character, swelling much however during hydration. This phenomenon was initially referred to as ‘Schroeder’s paradox’ [14, 15, 33-35] indicating that Nafion® showed differences in water uptake from liquid water compared to saturated water vapor under otherwise identical conditions. This was a consequence of a complex interfacial behavior and this puzzling feature resulted from the microstructural transition of Nafion® occurring when the environment changed from water vapor to liquid water [15], i.e., Nafion® micelles at the surface facing a vapor phase tended to align parallel to the surface and formed a thin hydrophobic fluorine layer [14, 36]. Nafion® micelles at the surface facing liquid water phase, however, tended to break up and align perpendicular to the membrane surface, leading to hydrophilic sulfonic acid groups facing the membrane surface [14, 36].

This morphology transition was corroborated by complementary measurements of contact angle and surface topography by grazing-incidence small-angle X-ray scattering (GISAXA) or atomic force microscopy (AFM) in water vapor and under liquid water [14, 15, 36]. The various morphologies of Nafion® in contact with a vapor phase or liquid water were elucidated and established from the fact that water contact angle of Nafion® is more than 100° in water vapor, thus existing as an hydrophobic surface, but it is about 30^{o} in liquid water, exhibiting an hydrophilic surface [14, 15, 37].

Similar to Nafion®, sulfonated poly(aryl ether ether ketone ketone)s (SPEEKK) show a hydrophobic main chain matrix and hydrophilic sulfonic acid group phase. The difference is only in the existence of less pronounced phase separation, less connected hydrophilic channels and more dead-end channels in SPEEKK compared to Nafion® [38]. It is reasonable to postulate that SPEEK-HQ exhibits similar microstructure to SPEEKK with, maybe, minor morphology differences due to a more rigid backbone and less phase separation between hydrophobic and hydrophilic domains of SPEEK-HQ. The lower flexibility of SPEEK-HQ backbone and random position of the sulfonic acid groups on the main chain result in small sulfonic clusters [39]. Furthermore, strongly hydrophilic sulfonic acid groups attached to the hydrophobic main chain of SPEEK-HQ severely disadvantage the hydrophobic character of the hydrophobic domains of SPEEK-HQ, leading to poorer and indistinct phase separation of SPEEK-HQ compared with Nafion®. It may therefore be expected that the surface configuration transformation observed in Nafion® when the environment changed from water vapor to liquid water also occurs in SPEEK. This postulate was indeed confirmed by the water contact angle evolution of SPEEK-HQ membranes during wetting, which is shown in Figs. 4-6.

In general, the decreasing water contact angle values were found to correspond to an increasing surface energy that results from -SO_3K groups being changed to -SO_3H units. It is shown in this study (Figs. 4-6) that the bottom surfaces of all membranes exhibit lower contact angle and higher surface energy compared to the corresponding top surface.

The contact angle of a water droplet on the surface of a membrane provides the information about the outermost two or three monolayers of molecules on the surface. In this case it is determined by the presence of ionic or polar (which is $–SO_3K$ or $–SO_3H$) sites on the surface of SPEEK-HQ-K and SPEEK-HQ-H membranes. Changes in the contact angle as the water droplet remains on the surface provide the information about the structure changes of that surface when immersed in water.

Values of contact angles and the droplet base area (the area between a water droplet and the membrane interface) as a function of droplet interaction time are shown in Figs. 4 and 5. All SPEEK-HQ membranes, in the potassium salt or proton form, top surface or bottom surface, behave in a similar way. The initial contact angles at which the water droplet touches on the membrane surface are above 80^o and 70^o, indicating high hydrophobicity for SPEEK-HQ in both the potassium salt form and proton form. These initial values range from 90.8^o to 76.4^o (Fig.4) and 85.1^o to 73.3^o (Fig.5) respectively. Upon exposure to water, however, the contact angle dramatically decreases (by $5\text{-}18^o$) in a few seconds as the water droplet interacts strongly with the surface. Afterwards, the contact angle falls slowly over 300 s measurement. Meanwhile, the water droplet base area increases. This indicates that the water molecules are spreading on the membrane, which is resulting from the attraction or interaction between water molecules and SO_3K or SO_3H groups within the membrane, leading to water penetrating into the surface. Differences in the contact angle at the initial stage and final stage of 300 seconds reflect changes in structure of the membrane surface in two different media, namely water vapor and liquid water respectively. The membrane surface transformed from hydrophobic in humid air to hydrophilic in liquid water during wetting. A similar phenomenon during wetting was also observed and similarly interpreted in a Nafion® membrane [37]. The final angle is of more practical significance for PEM in fuel cells because liquid water is the medium in the environment of a fuel cell.

Figs. 4 and 5 show that SPEEK-HQ-60K and SPEEK-HQ-80H top and bottom surfaces exhibited the most dramatic decreases in contact angle at the water droplet touching on the membrane surface, compared to other membranes in the same form. The dramatic decrease of contact angle exhibited that a rapid molecular rearrangement occurred when the water droplet touched on the membrane surface.

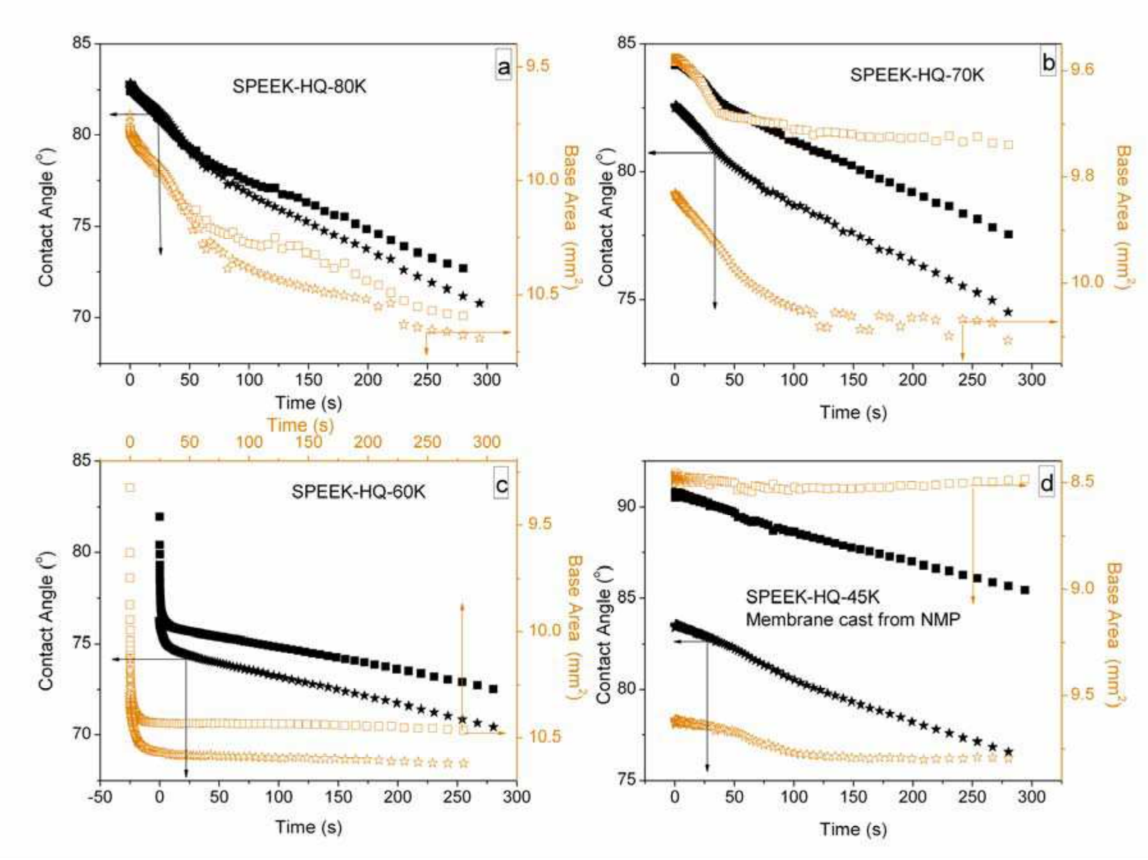

Fig. 4. Water contact angle (■) of the top surface and (★) of the bottom surface; drop base area (□) on the top surface and (☆) on the bottom surface of a membrane vs. time on SPEEK-HQ-K membrane

annealed at 120 °C for 24 h. Membranes were cast using DMAc unless otherwise indicated

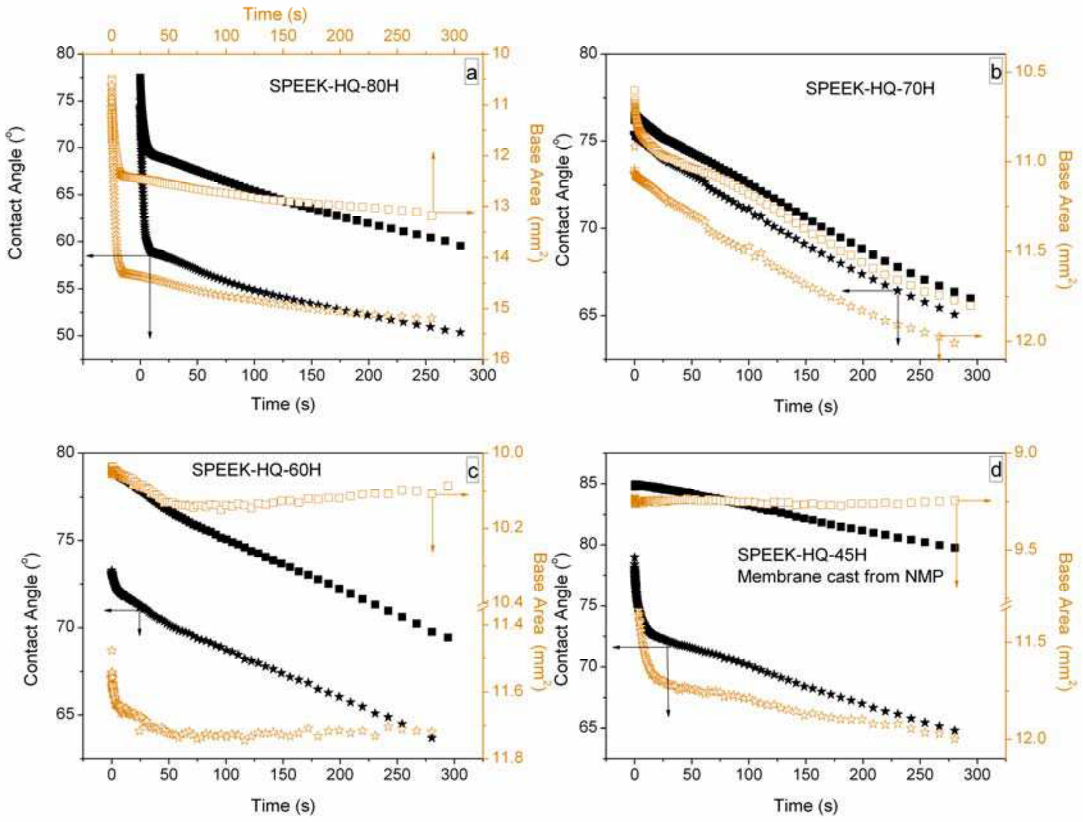

Fig. 5. Water contact angle (■) of the top surface and (★) of the bottom surface; drop base area (□) on the top surface and (☆) on the bottom surface of a membrane vs. time on SPEEK-HQ-H membrane annealed at 120 °C for 24 h. Membranes were cast using DMAc unless otherwise indicated.

Indeed, from Figs. 4 and 5, the bottom surface of a copolymer SPEEK-HQ membrane shows a lower initial and lower final water contact angle than its top surface. The bottom surface of a membrane is therefore more hydrophilic compared to its corresponding top surface. Changes in contact angle as a water droplet remains on the surface provide information about the structure transformation of that surface as it becomes wet. The transformation of SPEEK-HQ surface from being hydrophobic in air to being hydrophilic in liquid water was observed during membrane wetting in this study.

Upon deposition of a water drop, water diffuses into the membrane causing the membrane to swell underneath the water drop. This creates a differential expansion between a top wet layer and a bottom dry layer, causing the membrane to adsorb water and buckle [37]. The corresponding flexure goes through a maximum with time [37]. Macroscopic swelling, also referred to as bulk swelling, is defined as the large-scale expansion of ionomer membranes in an area of at least 1 mm^2 [40].

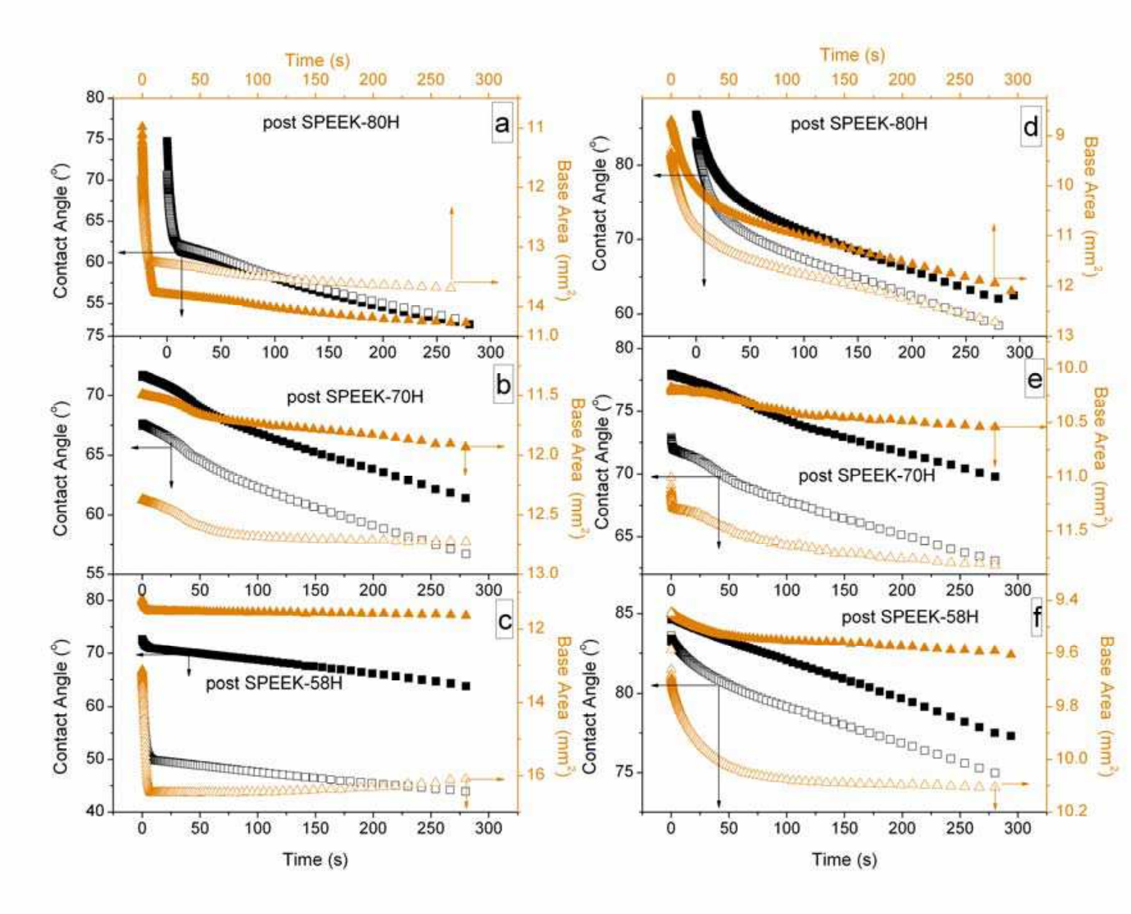

Fig. 6. Water contact angle (■) of the top surface and （□） of the bottom surface; drop base area (▲) on the top surface and (△) on the bottom surface of a membrane vs. time on post-SPEEK-H

membrane annealed at 120 °C for 24 h. Figs. 6a-c and Figs. 6d-f show the membranes cast using DMAc and NMP, respectively.

It is well known that the character of a PEM is depending on the solvent used for membrane casting [19]. The results shown in Fig. 6 indicate that post-sulfonated SPEEK in proton membrane cast from DMAc provides a lower initial and final contact angle than when NMP is used for membrane casting. This suggests that the membranes cast from DMAc exhibit higher surface energy and have a stronger affinity to the MEA than those cast from NMP.

It is observed in Fig. 5 that SPEEK-HQ-70H membrane exhibits less contact angle difference between the top and the bottom surface compared to SPEEK-HQ-80H and SPEEK-HQ-60H. Furthermore, the initial contact angle of SPEEK-HQ-70H is a little lower than that of SPEEK-HQ-80H. This suggests that the SPEEK-HQ-80H surface exhibits higher hydrophobic character than that of SPEEK-HQ-70H surface. Thus the morphological transformation of the membrane surface upon wetting could be increased by the degree of sulfonate content as well as the treatment method [41].

3.3.2. Membrane Surface Characteristics at Less Than 2-3 nm Thickness: Surface Composition by XPS

The chemical composition of dry membrane surface was determined using XPS at take-off angles of 30°, 45°, 60° and 90°, which provided information on membrane depth profiling. The results of atomic ratio S/C are reported in Fig. 7 for some of the above discussed membranes. The bottom surface of a membrane, which was in contact with the glass plate during casting, exhibits a higher sulfur atomic concentration compared with its corresponding top surface contacted with argon (air) during casting, implying a higher sulfonic acid content. As discussed below, this phenomenon could be explained by a micro-phase separation of SPEEK during membrane preparation.

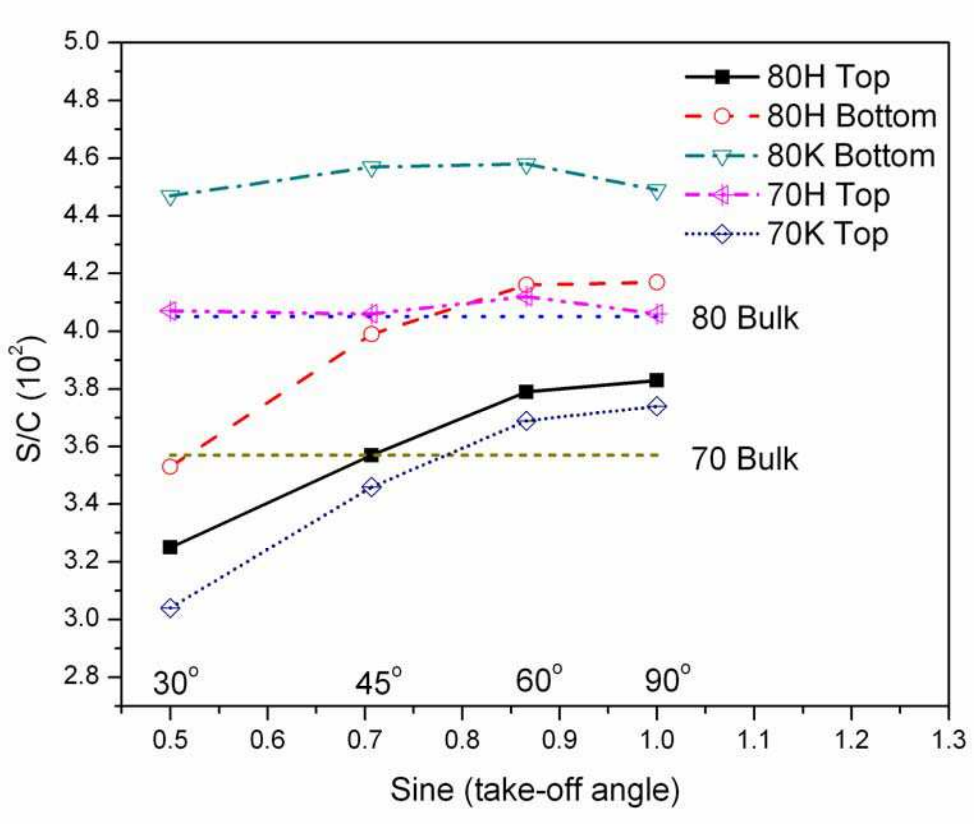

Fig.7. S/C vs. sine (take-off angle) of copolymer SPEEK-HQ membrane using angle-dependent XPS.

In a polar solvent such as DMAc, polyelectrolyte ionomer SPEEK-HQ-K molecules surrounded by solvent molecules exist as random coils of dissociated polyanion chains, accompanied by dissociated K^+ ions. Macromolecular coils interweave and penetrate into each other to distribute uniformly in the entire polymer solution. A depiction of a macromolecular coil of SPEEK-HQ-K in DMAc is illustrated in Fig. 8.

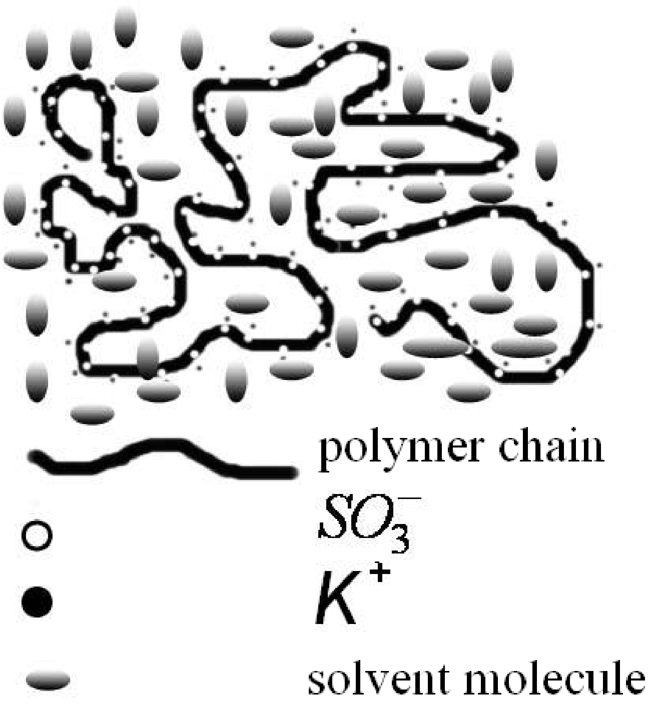

Fig. 8. Schematic cartoon of a random copolymer SPEEK-HQ-K chain in a polar solvent.

The unique properties and performance of perfluorinated sulfonic acid polymer electrolyte membranes result from their complex microstructure. Exposed to water or other hydrophilic solvents, a polymer electrolyte exhibits nanoscale segregation into two sub-phases, i.e., hydrophilic domains and hydrophobic domains [42]. Employing small-angle X-ray scattering (SAXS) data and water self-diffusion coefficients obtained by pulsed-field-gradient (PFG-NMR), a microstructure model of sulfonated poly (aryl ether ether ketone ketone) (SPEEKK) was proposed, involving a cubic hydrophilic channel system in a hydrophobic matrix [38]. This involves an inverted-micelle aggregate of which hydrophilic sulfonic acid heads assemble in contact with the surrounding hydrophobic polymer chain clusters. It was suggested that SPEEK exhibited similar microstructure conformation in a polar solvent DMAc [38]. A packing sphere model of the sulfuric groups in post-sulfonated SPEEK, similar to Nafion® [43], either isolated or in small spherical clusters of two or three interacting sulfonic groups, was further proposed quite recently by Wu et al. [39]. The flexible perfluoroalkylether (PFAE) side chain in Nafion® provides the possibility for forming lamella clusters, leading to rod-like [14] or plate-like [39, 44] hydrophilic domains. However, the rigidity of SPEEK backbones restricts this possibility, leading to the formation of smaller clusters. These small clusters would absorb water to form spherical hydrophilic domains [39] that have smaller, more branched and more dead-end channels than Nafion®. This microstructure difference leads SPEEKK or SPEEK to show poorer fuel cell behavior than that of Nafion® [38, 39, 45].

The membrane fabrication starts with dissolution of the potassium salt of SPEEK in a polar solvent such as DMAc. SPEEK molecules are arranged in spherical aggregates (Fig. 9a). In those the sulfonic groups (-, so_3^-) are either isolated or in a small spherical cluster of two (●) or three (●)interacting sulfonic groups. Here (▬) is hydrophobic matrix fusing with DMAc molecules and (+) is potassium cation (K^+) [39]. The first step of membrane fabrication is to cast a polymer solution (potassium salt form) onto a glass plate, followed by a second step of drying at 60 ^{o}C under constant argon slow purging (Fig. 9b). During the slow evaporation of solvent DMAc, more concentrated SPEEK solution gradually forms and molecular chains approach closer to each other, accompanied by dissociated K^+ ions diffusing to the outer and inner polyanion to balance the electrostatic forces until a primary membrane forms. During this process, hydrophilic sulfonic acid groups or spherical clusters are being absorbed onto the glass plate to reduce the polymer-glass substrate interfacial energy, while hydrophobic matrix is driven to the polymer-argon interface. The primary membrane is dried in vacuum oven at 120 ^{o}C and kept constant for 24 h (Fig. 9c). During this process, both sides of a membrane are contacting with vacuum that is zero surface tension medium. Lower free energy component, or hydrophobic phase, is driven and migrates to the vacuum-polymer interface.

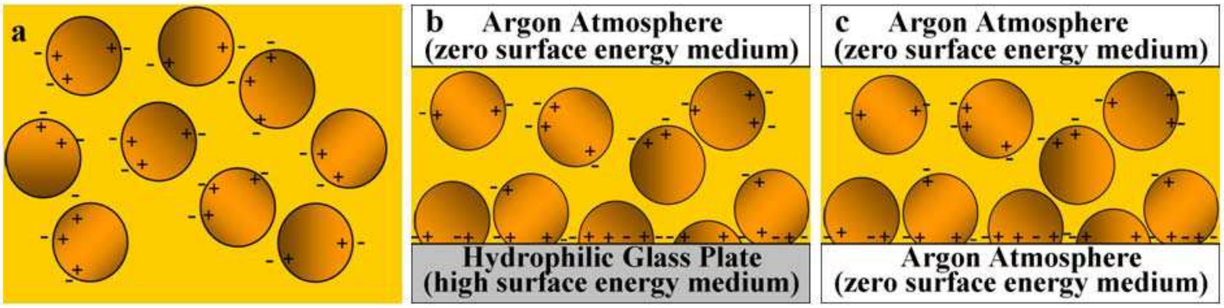

Fig.9. Schematic illustration of membrane fabrication.

This process is dominated by the parameters of both a constant heating rate and slow argon purging rate, leading to solvent slow evaporation. This results in sufficient time for polymer molecules in solution to reach the equilibrium of evolved conformation of SPEEK. The interaction of backbones of ionomer molecules is driven by the thermal movement of polymer chains during drying. With the increasing ionomer concentration, the ionomer molecules shrink gradually in solution and aggregate together to form bigger aggregates, fusing into each other to form more concentrated solution. The molecular chains are thus curling closer gradually and forming membrane which may be considered to be a compact nearly dried solution [45].

During membrane casting where the polymer is close to the glass substrate, the hydrophilic sulfonic acid heads, which possess higher surface free energy are attracted to the hydrophilic glass plate, whose water contact angle is about 35^o. Hydrophilic sulfonic acid groups are adsorbed onto the glass plate, thus reducing the polymer-glass substrate interfacial energy. The conformation of the adsorbed molecules on the glass plate is different from those mobile molecules being free in the overlying solution. It should be noted that no completely spherical aggregates are adsorbed to the glass plate surface, and that the hydrophilic core of sulfonic acid group regions are in contact with the glass plate (Fig. 9b). Therefore, sulfonic group aggregates are more concentrated towards the glass substrate compared with the top surface, which was towards the argon (air), or with the bulk membrane (Fig. 9b).

Argon gas may be regarded as a zero surface energy medium [30] that showed a strong attraction to the hydrophobic domains of a membrane to reduce the polymer-argon interfacial energy, leading to more hydrophobic atomic groups preferentially being exposed to the top surface of the membrane (Fig. 9b). Compared to the bottom surface, the polymer-argon interface is enriched in the hydrophobic domains (Fig. 9b). The different contacting media used in membrane fabrication, hydrophilic glass plate or hydrophobic argon, give rise to differences between the bottom surface and top surface of a membrane. The XPS results shown in Fig. 7 indeed indicate that the sulfur atomic concentration is significantly higher on the bottom surface of the SPEEK-HQ-80H membrane than on its top surface. It seems thus that the vacuum annealing of the membrane (120 ^{o}C, 24 h in vacuum) did not erase these differences. Siemann investigated the solvent casting process for various polymer/solvent systems, including polycarbonates / methylene chloride, polyvinylidene fluoride / acetone, polyimides / dimethylformamide and polyethersulfone / methylene chloride, etc. It was reported that the difference in properties of the two sides of a cast membrane was maintained, even after drying with residual solvent content lower than 0.5 % [46].

Both sides of a membrane exhibited less sulfur on the outer surface detected at take-off angle 30^o, compared with the depth of the membrane at photoelectrons take-off angle 45^o. It can be seen in all cases that the lowest S/C is at 30^o take-off angle, and S/C increases with higher take-off angles. This infers that the hydrophilic sulfur component aggregates gradually within the membrane and is in higher concentration in the bulk than on the membrane surface. The only exception is SPEEK-HQ-70H top surface, which shows only minor changes in S/C with take-off angle. It could probably be attributed to the stronger acidification condition used for SPEEK-HQ-70H membrane compared with any other membranes in this study. The stronger acidification condition was 1 M H_2SO_4 at room temperature for 21 h, followed by acidification at 80-90 ^oC for 2 h. The tendency of hydrophilic sulfur to aggregate within the membrane was perhaps mitigated by the acidification at higher temperature.

Gibbs [47] reported that in a multi-component system, components of lower surface free energy would exhibit the tendency to enrich the surface of a condensed phase. He suggested that the differences in the surface free energy of various components within a polymer membrane may dominate the overall surface morphology, whereby the lower surface energy segment resided near the polymer-air interface [16, 17, 48-50].

During the second step of membrane drying at 60 ^oC on the glass plate (Fig. 9b), until a thick viscous polymer solution evolved into a primary solid membrane, the hydrophilic glass substrate gave rise to higher sulfur atom concentration at the bottom surface of a membrane than at its corresponding top surface. After the membrane was peeled from the glass plate, the membrane was left into a vacuum oven for further drying process in which temperature was increased gradually up to 120 °C and kept constant for 24 h. During this process, both sides of the membrane were towards vacuum (Fig. 9c), which is a zero surface tension medium [30]. Thermodynamically, the lower free energy component, i.e., hydrophobic phase, was driven and migrated to the vacuum-polymer interface at both sides of the membrane during this drying process. This segregation effect was found to be enhanced by annealing [29, 51] and it is believed that the temperature is a crucial variable in affecting the surface morphology and composition in many cast membrane systems [51]. In our work, except for the SPEEK-HQ-70H top surface, this effect results in reinforcing the segregation of hydrophilic groups between the surface and the bulk, leading to a lower sulfur atomic concentration of the outermost surface than in the bulk.

Similar to our finding, Kim et al. investigated surface fluorine enrichment in the 6FCN-35 membranes [52], i.e., disulfonated poly(arylene ether benzonitrile) copolymers containing hexafluoroisopropylidene diphenol, whose molar ratio of unsulfonated benzonitrile to the disulfonated sulfone monomer was 65:35. They also found that surface fluorine, lower surface energy group, was enriched on the air-contacting surface to about 38%, doubling the 17% of fluorine content of the bulk membrane. The glass-contact surface was found to have close to unchanged fluorine content about 15%. The differences of fluorine atomic concentration on different sides of a membrane were attributed to the low surface free energy of the hexafluoroisopropylidene moiety, which provided a thermodynamic driving force for the self-assembly at the air-polymer interface, leading to fluorine hydrophobic groups enrichment, on the air-contacting membrane surface [52].

3.3.3.Membrane Surface Characteristics at Less Than 1 μm: Relative Content of Sulfonic Groups by ATR-FTIR

In this study the information about the membrane surface within less than 1 μm was investigated using ATR-FTIR (Fig. 10).

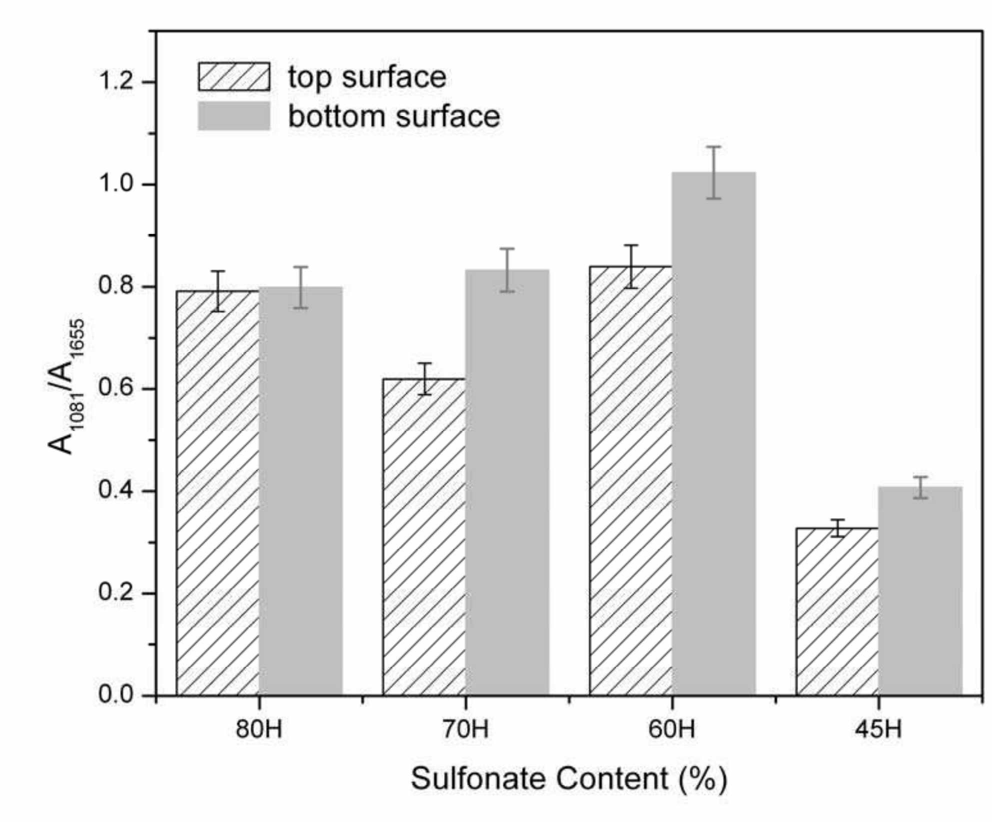

Fig. 10. A_{1081}/A_{1655} ratio of ATR-FTIR peaks area vs. sulfonate content of copolymer SPEEK-HQ in proton form.

The strong FTIR absorbance band at 1655 cm^{-1} was attributed to stretching vibration of –C=O– on phenyl rings while the 1081 cm^{-1} characteristic strong absorption band was attributed to symmetric O═S═O (Fig. 2). It is shown in Fig. 2 that the absorption band at 1081 cm^{-1} increases in intensity upon higher sulfonate content of SPEEK-HQ-H membranes. However, the absorption band at 1655 cm^{-1} remains relatively constant because –C=O– group was introduced from DFK monomer, which was in the same amount for all SPEEK-HQ synthesis. The area ratio of absorption band at 1081 cm^{-1} (A_{1081}) over the absorption band at 1655 cm^{-1} (A_{1655}) would exhibit the relative amount of sulfonic acid group of the membrane. ATR-FTIR spectra of both sides of the same SPEEK-HQ-H membrane were recorded using at least three pieces of a membrane at the same side. The values of A_{1081}/A_{1655} and its 5% error are plotted in Fig. 10. It is confirmed by the results shown in Fig. 10 that the bottom surface of a SPEEK-HQ-H membrane exhibits higher sulfur content compared to its corresponding top surface.

4. Conclusions

SPEEK-HQ copolymers bearing various sulfonate contents (SC) ranging from 77% to 51% were synthesized using hydroquinone. Polymerization was confirmed both by FTIR and ^{1}H-NMR. Flexible, transparent and tough membranes were obtained by solution casting of SPEEK-HQ copolymer in salt form. The membranes in acid form were obtained by acidification of cast SPEEK-HQ-K.

The surface characteristics of copolymer SPEEK-HQ membranes were studied by contact angle, XPS and ATR-FTIR. It was shown that upon exposure of membranes to water vapour, hydrophobic groups tend to cluster on the membrane surface and form a hydrophobic layer on the outermost surface, whereas $–SO_3H$ groups preferably aggregate within the membrane bulk. The surface transforms very quickly from hydrophobic in the air to hydrophilic in liquid water. It was also found that the bottom surface of a membrane (which was in contact with the glass plate during casting) is more hydrophilic than its top surface (which was in contact with argon during casting). The surface characteristics of SPEEK-HQ membranes were shown to be determined by the sulfonate content as well as by the treatment process.

It is believed that the study of dynamic evolution of surface characteristics of amorphous glassy polymer membranes as exemplified in the present study would be especially significant in order to understand the ageing process of these membranes. It is indeed known that the physical ageing of polymers is strongly dependant on membrane thickness [53]. Thus the evolution with time of the membrane properties of an asymmetric film prepared by phase inversion will be strongly affected by the characteristics of its surface layer and its dynamic changes under working as well as during preparation and storage.

Appendix A. Supplementary material

Additional experimental details and figures are available in the online version.

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