Open Access Full Text Article

Small-angle X-ray scattering analysis of ionic domain features in graft-type polymer electrolyte membranes

Nguyen Manh Tuan^{1,2}, Nguyen Huynh My Tue^{1,2}, Vo Thi Kim Yen^{1,2}, Nguyen Nhat Kim Ngan^{2,3}, Dinh Tran Trong Hieu^{1,2}, Hoang Anh Tuan^{1,2}, Doan Quoc Huy^{1,2}, Tran Duy Tap^{1,2,*}



Use your smartphone to scan this QR code and download this article

ABSTRACT

Introduction: Although poly(styrene sulfonic acid) (PSSA)-grafted poly(ethylene-cotetrafluoroethylene) polymer electrolyte membranes (ETFE-PEMs) are potential polymer electrolyte membranes for fuel cells, there are only a few reports on the effect of synthesis steps and grafting degree (GD) on the features of ionic domains. These ionic features are related to the conductance and thus directly affect the fuel cell performance. Accordingly, this work reports SAXS analysis to determine the features of ionic domains, including domain sizes and interdomain distances, in ETFE-PEMs according to GDs. Methods: ETFE-PEMs were prepared via the irradiation of polystyrene onto the original ETFE matrix (grafted-ETFE) and subsequent sulfonation. The structural features of the ionic domains were investigated by the Ornstein–Zernike (OZ) and Teubner-Strey (TS) models based on the fitting of small-angle X-ray scattering (SAXS) profiles. Results: According to the OZ model, the polystyrene (PS) and PSSA grafts can be ordered up to 0.8 and 1.1 nm, respectively. Moreover, the TS model suggested that the interdomain distances of the PS and PSSA grafts were approximately 0.7 and 1.1 nm, respectively. **Conclusion:** The above SAXS results suggest that the grafted-ETFE films have the capacity for self-organization of graft domains. Moreover, phase separation occurred strongly at the sulfonation step, leading to the self-organization of ionic domains at larger dimensions compared to those of the corresponding graft layers.

Key words: Polymer electrolyte membrane, fuel cells, graft polymerization, SAXS

¹Faculty of Materials Science and Technology, University of Science, Ho Chi Minh City, 227 Nguyen Van Cu, District 5, Ho Chi Minh City, Vietnam

²Vietnam National University, Ho Chi Minh City, Vietnam

³*Faculty of Physics and Engineering* Physics, University of Science, Ho Chi Minh City, Vietnam

Correspondence

Tran Duy Tap, Faculty of Materials Science and Technology, University of Van Cu, District 5, Ho Chi Minh City, Vietnam

Vietnam National University, Ho Chi Minh City, Vietnam

Email: tdtap@hcmus.edu.vn

History

- Received: 2024-04-12
- Accepted: 2024-05-31
- Published Online: 2024-6-xx

DOI:



INTRODUCTION

- ² Proton exchange membrane fuel cells (PEMFCs) are ³ eco-friendly electrochemical devices with high con-4 version efficiency (~ 65%) that are suitable for trans-⁵ portation applications and portable devices ^{1,2}. There 6 were 19,000 fuel cell electric vehicles (FCEVs) oper-7 ating in the U.S., Japan, Europe, South Korea, and ⁸ China as of 2019¹. The two most popular FCEVs at ⁹ present are Hyundai Nexo and Toyota Mirai¹. The 10 polymer electrolyte membrane (PEM) is an impor-Science, Ho Chi Minh City, 227 Nguyen 11 tant component of PEMFCs that directly affects fuel 12 cell performance because of its proton conductance ¹³ and ability to prevent gas diffusion through the PEM. 14 Nafion is a commercial PEM, but it has low proton 15 conductance at low relative humidity (RH) (< 50%) ¹⁶ and high temperature (> 80 $^{\circ}$ C) and is expensive to ¹⁷ produce^{1,3}. This has motivated researchers to find al-18 ternative PEMs with suitable electrochemical proper-¹⁹ ties at a reasonable price. 20 Recently, poly(styrene sulfonic acid) (PSSA)-grafted
 - 21 poly(ethylene-co-tetrafluoroethylene) (ETFE) poly-22 mer electrolyte membranes (ETFE-PEMs) have 23 emerged as potential PEMs because some of the

performance parameters of ETFE-PEMs are comparable to or better than those of conventional Nafion 25 membranes^{3,4}. The ETFE-PEMs were prepared by 26 irradiating polystyrene onto the ETFE matrix to 27 obtain the polystyrene-grafted ETFE (grafted-ETFE) 28 and then performing sulfonation on the grafted 29 film³⁻¹³. This process allows us to introduce a 30 large amount of sulfonic acid groups to the ETFE matrix to form proton conductive channels while 32 retaining useful properties, such as thermal stability 33 and mechanical strength, of the original films^{3,5}. The ³⁴ features of the ETFE-PEMs were studied in detail 35 using different approaches, such as Fourier trans-36 form infrared (FT-IR) spectroscopy^{14,15}, positron 37 annihilation lifetime spectroscopy^{16,17}, small-angle X-ray scattering (SAXS)^{17–19}, tensile strength²⁰, ³⁹ and X-ray photoelectron spectroscopy (XPS)²¹. 40 Among these methods, SAXS is the most suitable approach for examining the microstructures and 42 phase features of PEMs at different scales at the 43 same time (the same SAXS profiles). Some works 44 (using SAXS analysis) have reported the high-order 45 microstructures of ETFE-PEMs, including the sizes 46

Cite this article : Tuan N M, Tue N H M, Yen V T K, Ngan N N K, Hieu D T T, Tuan H A, Huy D Q, Tap T D. Small-angle X-ray scattering analysis of ionic domain features in graft-type polymer electrolyte membranes. Sci. Tech. Dev. J. 2024; 27():1-13.

Science & Technology Development Journal 2024, 27():1-13

Copyright

© VNUHCM Press. This is an openaccess article distributed under the terms of the Creative Commons Attribution 4.0 International license.



- 47 and interdomain distances of ionic layers with large ⁴⁸ dimensions^{3–13}. These ionic domains have clear 49 phase separation with the hydrophobic polymer 50 backbone and are related directly to the conductance of membranes^{13,22}. However, there are only a few 51 reports on ionic layers at low dimensions (subnano-52 to nanolevels)^{8,13}. In the graft-type PEM system, a 53 water channel is expected to be created around the 54 55 ionic domains¹⁵. Accordingly, the structural parameters of ionic domains are necessary to understand 56 the structure-conductance relationship, which can 57 58 control the PEM performance in PEMFCs.
- The ionic domain sizes and interdomain distances of 59 PEMs have been studied by the analysis of small-angle 60 61 X-ray scattering (SAXS) profiles using Guinier¹³, Debye-Bueche (DB)/combined with Teubner-Strey 62 (TS)^{23,24}, and Ornstein-Zernike (OZ) models^{25,26}. 64 However, there have been no reports on the ionic domains of ETFE-PEMs using the OZ^{25,26} and TS models²⁷⁻²⁹, although these are effective approaches for 66 determining the microstructural parameters of mem-67 68 branes. Accordingly, this study focuses on the domain sizes and interdomain distances of grafted-ETFE films and ETFE-PEMs using the OZ and TS models. The 70 OZ and TS models were used for fitting the SAXS pro-71 72 files because the OZ model is suitable for describing 73 the correlation length or domain size of inhomogene-⁷⁴ ity systems^{25,26}, while the TS model is suitable for ex-75 tracting structural information from two immiscible phase systems^{27–29}. Similar to OZ, the Guinier³⁰ and 76 77 DB³¹ models are also utilized to determine the cor-78 relation length or domain size in the above films and 79 membranes for comparison.

80 EXPERIMENTAL

81 Materials and ETFE-PEM preparation

The original ETFE films (50 mm in thickness) were 82 purchased from Asahi Glass Co. Ltd., Japan. The 84 ETFE-PEMs were prepared using the same synthetic process described in a previous study³. The synthetic 85 procedure is shown in Scheme 1. A Co⁶⁰ gamma radiation source with an absorbed dose of 15 kGy 87 under an argon atmosphere was used for irradiating 88 polystyrene onto the original ETFE films to create 89 polystyrene-grafted ETFE (grafted-ETFE) films. The 90 91 grafting degree (GD) is determined as the percent-⁹² age of the grafting polymer weight and the original film weight: GD(%) = 100(Wg -Wo)/Wo. Here, Wg 93 ⁹⁴ and Wo are the weights of the grafted-ETFE film and ⁹⁵ the pristine film, respectively. The original ETFE film ⁹⁶ was cut to a size of 6x8 cm² and weighed prior to the 97 irradiation process. After grafting with polystyrene

solution, the surface of the grafted ETFE film was 98 cleaned to remove the homopolymer and the resid- 99 ual monomers prior to weight measurement. In this 100 work, the GD was controlled by varying the monomer 101 concentration and grafting time while maintaining 102 other conditions of irradiation and grafting, such as 103 the irradiation dose, temperature, and solvent. Finally, the grafted-ETFE films were immersed in 0.2 105 M chlorosulfonic acid solution at 50 °C for 6 hours 106 for sulfonation to obtain the ETFE-PEMs. 107

108

125

141

SAXS measurements

Scheme 2 illustrates the SAXS measurements. The 109 SAXS profiles were measured at room temperature 110 and 60% relative humidity using Mo-K α radiation 111 (wavelength, l = 0.07 nm) (Rigaku NANO-Viewer, 112 Japan) at the National Institute of Material Science 113 (NIMS) in Japan. The sample-detector distance was 114 35 cm. The Q-range of the SAXS profiles was Q = 1.0 - 11510.0 nm^{-1} . Here, Q is the magnitude of the scattering momentum transfer, equaling $4\pi \sin(\theta)/\lambda$, where 117 2θ is the scattering angle and λ is the incident X-ray 118 wavelength. The scattering intensities were circularly 119 averaged and corrected using the secondary standard 120 of glassy carbon (provided by Argonne National Lab- 121 oratory, USA) to obtain the absolute intensities ^{5,32}. 122 More details on the SAXS measurements can be found 123 in our previous work⁵. 124

SAXS analysis

In our previous works^{9,13}, field emission scan- 126 ning electron microscopy (FE-SEM) measure- 127 ments showed that ionic domains have different 128 sizes/shapes. Moreover, PSSA chains were not mixed 129 with the amorphous phase of the ETFE matrix, 130 leading to membranes having two immiscible phase 131 systems^{12,21}. Therefore, the OZ model (suitable 132 for describing inhomogeneity systems)^{25,26} and TS 133 model (suitable for describing two immiscible phase 134 systems)²⁷⁻²⁹ were used in this work. To enrich the results, we modeled the morphology of the ionic 136 domains using the popular Guinier³⁰ and DB³¹ models. Similar to the OZ model, the Guinier and 138 DB models are suitable for studying inhomogeneity 139 systems^{30,31}. 140

OZ model

The OZ model is applicable for describing material 142 regions with random shapes ^{25,26} and is suitable for 143 extracting the sizes of grafted polystyrene layers of 144 grafted ETFE films and the ionic domains of ETFE-PEMs. According to OZ theory^{25,26}, the scattering 146



Scheme 1: Synthetic process and chemical structures of ETFE, grafted-ETFE, and ETFE-PEM.



Scheme 2: Illustration of the SAXS measurements.

¹⁴⁷ intensity near Q = 0 is given by:

$$I_{OZ}(q) = \frac{I_{OZ}(0)}{1 + \zeta_{OZ}^2 \cdot q^2}$$
(1)

¹⁴⁸ where ζ_{OZ} is the correlation length or domain size ¹⁴⁹ and $I_{OZ}(0)$ is the scattering intensity at Q = 0. The ¹⁵⁰ fitting parameters follow the least square law. The fit-¹⁵¹ ting was performed at least four times, and the fitting ¹⁵² parameters were averaged. A similar fitting procedure ¹⁵³ was also applied to the Guinier, DB, and TS models. ¹⁵⁴ Table 1 shows the averaged fitting parameters of the ¹⁵⁵ OZ, Guinier, and DB models to compare the results ¹⁵⁶ of domain sizes using different models, while Table 2 ¹⁵⁷ shows those of the TS models to discuss interdomain ¹⁵⁸ distances.

159 Guinier model

¹⁶⁰ In 1939, Guinier proposed an approximation equa-¹⁶¹ tion to determine the radius of gyration R_g for samples with solid spherical molecules as well as ¹⁶² ionomers ³⁰. The radius of gyration is the square root ¹⁶³ of the average squared distance of each scatterer from ¹⁶⁴ the particle center. This size is not fixed for objects ¹⁶⁵ with the same volume but different shapes. According to Guinier theory ³⁰, the scattering intensity near ¹⁶⁷ Q = 0 is given by: ¹⁶⁸

$$I_g(q) = I_g(0) \exp\left(-\frac{1}{3}q^2 R_g^2\right)$$
(2)

where $I_g(0)$ is the scattering intensity at Q = 0.

DB model

The DB model is used to determine the correlation 171 length or domain size of inhomogeneous systems. 172 The Debye-Bueche model is suitable for determining 173 these structural parameters in a sharp two-phase system, where both the sizes and shapes of the phases are 175 random. This model follows an exponential decay of 176

169

170

177 the electron density correlation function. The relevant $_{178}$ expression from this model is as follows 31 :

$$I_{DB}(q) = \frac{A^2}{\left(1 + \zeta_{DB}^2 q^2\right)^2}$$
(3)

¹⁷⁹ where A depends on the system in question and ζ_{DB} 180 is called the correlation length or domain size.

TS model 181

The TS model is applicable for describing two-phase 182 systems with distinct boundaries and has been used 183 for the intermeshing of hydrophobic and hydrophilic 184 structures when the particle shape is not well de-185 186 fined²⁷⁻²⁹. In this case, the clear phase separation of 187 ionic regions and the ETFE backbone was described ¹⁸⁸ in a previous study²². In the TS model, the pair cor-¹⁸⁹ relation function $\gamma(\mathbf{r})$ in real space is assumed to have ¹⁹⁰ the following form:

$$\gamma(r) = \frac{d_{TS}}{2\pi r} exp\left(-\frac{r}{\xi_{TS}}\right) \sin\left(\frac{2\pi r}{d_{TS}}\right) \tag{4}$$

¹⁹¹ where d_{TS} is the domain periodicity or interdomain ¹⁹² distance and ξ_{TS} is a correlation length that has been ¹⁹³ attributed to the dispersion of d_{TS} . Then, the scatter-¹⁹⁴ ing intensity profile, $I_{TS}(q)$, can be expressed as fol-195 lows:

$$I_{TS}(q) = \frac{1}{a_2 + c_1 q^2 + c_2 q^4}$$
(5)

¹⁹⁶ where $a_2 > 0$, $c_1 < 0$, and $c_2 > 0$. The TS model is ¹⁹⁷ suitable for a single broad scattering maximum and a 198 power law decay of -4 at large scattering angles. Furthermore, a_2 , c_1 , and c_2 are also parameters used to fit one-dimensional SAXS profiles and can also be used ²⁰¹ to calculate the correlation length (ξ_{TS}) and domain ²⁰² spacing (d_{TS}) via the following equations:

$$\xi_{TS} = \left[\frac{1}{2} \left(\frac{a_2}{c_2}\right)^{1/2} + \frac{c_1}{4c_2}\right]^{-1/2}$$
(6)
$$d_{TS} = 2\pi \left[\frac{1}{2} \left(\frac{a_2}{c_2}\right)^{1/2} - \frac{c_1}{4c_2}\right]^{-1/2}$$
(7)

²⁰³ The fitting of the SAXS profiles using equation (5) was performed to extract the structure parameters and 204 205 pair correlation function.

RESULTS 206

207 The plots of the best-fit OZ models for the SAXS pro-208 files of the grafted-ETFE films with GDs of 36 and 209 61% are shown in Figure 1a,b. The OZ models (orange ²¹⁰ lines) are plotted by the fitting regions with a Q-range ²¹¹ of 2.0–3.5 nm⁻¹. A screening process was carried out

to determine good fitting regions as good as the suit- 212 able fitting parameters of $I_{OZ}(0)$ and ζ_{OZ} . The suit- 213 able region for fitting is between the ionic peak and the 214 Porod region ^{5,7,8}. In this work, several Q-regions are ²¹⁵ selected for the fitting process, and the fitting parame- 216 ters of $I_{OZ}(0)$ and ζ_{OZ} are averaged. This procedure is 217 applied similarly for the Guinier, DB, and TS models. 218 The grafted polystyrene domain sizes of the grafted 219 ETFEs (with GDs of 36 and 61%) are approximately 220 0.78 nm. Figure 1c,d shows the plots of the Guinier 221 models for the SAXS profiles of the similar films. The 222 Guinier models (green lines) are plotted by the fitting 223 regions with a Q-range of $1.9-2.8 \text{ nm}^{-1}$. The grafted 224 polystyrene domain sizes extracted from the Guinier 225 model were also nearly 0.78 nm. The plots of the DB 226 models are shown in Figure 1e,f. The pink lines rep- 227 resent the DB models with the fitting regions having 228 a Q-range of 1.2–2.7 nm⁻¹. The grafted polystyrene 229 domain sizes extracted from the DB model can be or- 230 dered up to approximately 0.80 nm. The structural 231 parameters extracted from each model are shown in 232 Table 1.

A similar fitting procedure was applied for the SAXS 234 profiles of the ETFE-PEMs with GDs of 36 and 61%. 235 Figure 2a,b illustrates the best-fitting OZ model for 236 the SAXS profiles of the ETFE-PEMs. The fitting re- 237 gions have a Q-range of 1.5–2.5 nm⁻¹. The ionic do- 238 main sizes extracted from the OZ model are approx- 239 imately 1.07 nm. The plots of the Guinier model for 240 fitting the SAXS profiles of the ETFE-PEMs are shown 241 in Figure 2c,d. The Guinier model was applied for the 242 region with a Q-range of $1.3-2.0 \text{ nm}^{-1}$. The results of 243 the Guinier model still show that the ionic domains 244 can be ordered up to 1.12 nm. The plots of the DB 245 model are shown in Figure 2e,f. The fitting regions 246 have a Q-range of 0.9-1.7 nm⁻¹. Similar to the re- 247 sults of the OZ and Guinier models, the domain sizes 248 extracted from the DB model are approximately 1.11 249 nm. The structural parameters extracted from each 250 model are shown in Table 1. 251

233

Figure 3a,b shows the plots of the TS model for fit- 252 ting the SAXS profiles of the grafted ETFEs with a GD 253 of 36% and the related correlation (gamma) function 254 γ (r). This model was applied for fitting a peak with a 255 Q-range of $4.2-8.4 \text{ nm}^{-1}$. In this case, the TS model 256 allows us to extract the correlation distance between 257 grafted polystyrene domains of nearly 0.71 nm. The 258 correlation function shows an intensive peak at 0.8 259 nm and further peaks at approximately 1.6 and 2.3 260 nm. These peaks represent the correlation distances 261 between grafted polystyrene domains. The plots of the 262 best-fitting TS model and the related correlation func- 263 tion of the grafted ETFE with a GD of 61% are shown 264



Figure 1: The plots of OZ, Guinier, and DB model fitting for the SAXS profiles of grafted-ETFE films with GDs of 36 and 61%. The fitting is conducted in several Q-ranges and the obtained fitting parameters are averaged. The fitting parameters are represented in Table 1.



Figure 2: The plots of OZ, Guinier, and DB model fitting for the SAXS profiles of the ETFE-PEMs with GDs of 36 and 61%. The fitting is conducted in several Q-ranges and the obtained fitting parameters are averaged. The fitting parameters are represented in Table 1.

Sample	Microstructures	Model	Domain size (nm)	Ref
Grafted-ETFE 36%	Grafted polystyrene do- main	OZ	0.78 ± 0.05	This study
		Guinier	0.77 ± 0.01	
		DB	0.80 ± 0.01	
Grafted-ETFE 61%	Grafted polystyrene do- main	OZ	0.77 ± 0.03	This study
		Guinier	$\textbf{0.77} \pm \textbf{0.01}$	
		DB	0.81 ± 0.01	
ETFE-PEM 36%	Ionic domain	OZ	1.07 ± 0.06	This study
		Guinier	1.12 ± 0.01	
		DB	1.11 ± 0.01	
ETFE-PEM 61%	Ionic domain	OZ	1.15 ± 0.05	This study
		Guinier	1.14 ± 0.01	
		DB	1.11 ± 0.01	
Poly(ethylene oxide)-block- poly((vinyl benzyl)trimethyl- ammonium chloride)	Hard phase	OZ	\approx 3.8–5.9	26
Poly(N-isopropyl acrylamide) (pNIPAAm)	Polymer-network mesh size	OZ	≈ 1.010	33
Nafion	The packing of two aligned backbones	OZ	pprox 0.5–0.7	34

Table 1: Domain sizes were extracted from fitting for the SAXS profiles using the OZ, Guinier, and DB models of grafted-ETFE films and the ETFE-PEMs having GDs of 36 and 61% and compared with those of other membranes

²⁶⁵ in Figure 3c,d. The fitting region has a Q-range of 4.2–
²⁶⁶ 8.6 nm⁻¹. The results from the TS model show that
²⁶⁷ the intergrafted polystyrene domains are nearly 0.74
²⁶⁸ nm in length. The derived correlation function shows
²⁶⁹ the first, second, and third peaks at approximately 0.9,
²⁷⁰ 1.7, and 2.7 nm, respectively. The fitting results can be

271 seen in Table 2.

Figure 4a,b shows the plots of the best-fitting TS 272 model for the SAXS profiles of ETFE-PEM (GD = 273 36%) and the derived correlation function $\gamma(\mathbf{r})$. The 274 fitting region has a Q-range of $2.7-5.5 \text{ nm}^{-1}$. In this 275 case, the correlation distance between the ionic do-276 mains extracted from the TS model is approximately 277 1.13 nm. The relative correlation function shows an 278 279 intense peak at 1.2 nm and a further peak at approxi-280 mately 2.4 nm. The plots of the TS model and related correlation function of ETFE-PEM (GD = 61%) are 281 282 shown in Figure 4c,d. The fitting by the TS model 283 was applied for the region with a Q-range of 2.8-²⁸⁴ 5.7 nm⁻¹. The interionic domain distance is approx-285 imately 1.06 nm. The derived correlation function shows the first peak at 1.2 nm and the second peak ²⁸⁶ at nearly 2.3 nm. The fitting results can be seen in Ta- ²⁸⁷ ble 2. ²⁸⁸

The above results of SAXS analysis indicate that four 289 models, OZ, Guinier, DB, and TS, are applicable for 290 the ionic domains of ETFE-PEMs. The TS model re- 291 quires the SAXS peak for fitting, while this is not nec- 292 essary for the OZ, Guinier, and DB models. The fit- 293 ting results presented in Table 1 and Table 2 lead to 294 the conclusion that the domain size and domain dis- 295 tance of the ionic aggregates are independent of the 296 GD. However, increasing the number of ionic groups 297 according to GD should improve the proton conduc- 298 tance¹⁵. The results shown in Table 2 suggest that the 299 domain distances in the ETFE-PEMs are lower than 300 those in the other PEMs^{35–37}. In other words, the 301 ionic groups in the ETFE-PEMs are more densely ag- 302 gregated. 303





Sample	Microstructures	Domain dis- tance (nm)	Ref
Grafted-ETFE 36%	Grafted polystyrene domain	0.71 ± 0.01	This study
Grafted-ETFE 61%	Grafted polystyrene domain	0.74 ± 0.01	This study
ETFE-PEM 36%	Ionic domain	1.13 ± 0.01	This study
ETFE-PEM 61%	Ionic domain	1.06 ± 0.02	This study
Polyimide and poly(ethylene glycol) doped with an ionic liquid	Ionic liquid	≈ 9.0-15.0	35
Sulfonated polyphenylenes composed of m- and p- phenylene groups with sulfonic acid substituents (SPP- QP).	Hydrophilic domain	≈ 7.0-8.0	36
ETFE-PEM cross-linked with 1,3-diisopropenylbenzene	Ionic domain	≈ 1.5	37

 Table 2: Domain distances extracted from the TS model of the grafted-ETFE films and the ETFE-PEMs with GDs of 36 and 61% and compared with those of other membranes



Figure 4: Plots of the TS model and derived gamma function of the ETFE-PEMs: a, b) with a GD of 36%; c, d) with a GD of 61%. The fitting is conducted in several Q-ranges and the obtained fitting parameters are averaged. The fitting parameters are represented in Table 2.

DISCUSSION

The domain sizes of the polystyrene grafts extracted 305 306 from the OZ, Guinier, and DB models for the grafted-307 ETFE films with GDs of 36% (0.78-0.80 nm) and 61% (0.77-0.81 nm) are highly similar. A similar 308 case is true for the ETFE-PEMs with GDs of 36% 309 (1.07-1.12 nm) and 61% (1.11-1.15 nm). In other 310 words, the domain sizes at the different GDs (36% 311 312 and 61%) of both the grafted-ETFE film and the 313 ETFE-PEMs are similar. This result indicates that the grafted-ETFE films and the ETFE-PEMs can accom-314 315 modate more PS and PSSA chains with small changes ³¹⁶ in their domain sizes ¹³. The ionic domain sizes of 317 the ETFE-PEMs are greater than those of the cor-318 responding polystyrene graft domain sizes. This re-319 sult can be attributed to the phase separation of PSSA 320 grafts from the backbones of the ETFE matrix at the ³²¹ sulfonation step¹³. These PSSA grafts can be con-³²² nected, aggregated, and shelf-organized to form ionic ³²³ domains. As reported previously^{13,23,24}, the struc-

tural features of these ionic domains, including do- 324 main sizes, strongly affect the conductance of mem- 325 branes for fuel cells. For example, the conductance 326 of ETFE-PEM (GD = 34%) is 5 times greater than 327 that at GD = 19%. This significant increase in con- 328 ductance was elucidated by the short-range distances 329 of the ordered ionic nanochannels, which allowed 330 the creation of water channels. These water chan- 331 nels are favorable for high proton conductance even 332 at low relative humidity¹³. The domain sizes ex- 333 tracted from the OZ model for poly(ethylene oxide)- 334 block-poly((vinyl benzyl)trimethyl-ammonium chlo- 335 ride) (3.8–5.9 nm)²⁶, poly(N-isopropyl acrylamide) 336 (pNIPAAm) (1-10 nm)³³, and Nafion (0.5-0.7 nm)³⁴ are shown in Table 1 for comparison. In this case, 338 the domain sizes of polystyrene grafts are greater than 339 those of the packing of two aligned backbones of 340 Nafion membranes. 341

The TS model allows us to describe a system with clear ³⁴² phase separation with interdomain distances of approximately 0.7 and 1.1 nm for grafted polystyrene ³⁴⁴ 345 domains and ionic domains, respectively. In addition, ³⁴⁶ the derived correlation function shows that the nearest correlation distances of the grafted polystyrene do-347 mains and ionic domains are approximately 0.8 and 348 1.2 nm, respectively. As shown in Tables 1 and 2, the 349 change in structural parameters determined from the 350 TS model did not vary with GD, as determined by 351 the OZ, Guinier, and DB models for both the grafted-352 ETFE films and the ETFE-PEMs¹³. In addition, the peak features observed in the plots of the TS model 354 (Figure 3 and Figure 4) provide further information 355 on the size distribution of ionic domains, which could not be obtained by the OZ, Guinier, and DB mod-357 els. Accordingly, the TS model is the most suitable 358 approach for observing the ionic domains of ETFE-359 PEMs. The structural parameters extracted from the 360 TS model for polyimide and poly(ethylene glycol) 361 doped with an ionic liquid (9-15 nm)³⁵, sulfonated 362 polyphenylenes composed of m- and p-phenylene 363 groups with sulfonic acid substituents (SPP-QP) (7-364 8 nm)³⁶, and ETFE-PEM cross-linked with 1,3-365 diisopropenylbenzene (1.5 nm)³⁷ are shown in Ta-366 ble 2 for comparison. The domain distances of the 367 ETFE-PEMs are lower than those of the ETFE-PEMs 368 cross-linked with 1,3-diisopropenylbenzene. This re-369 sult suggested that the aggregation and concentration 370 of PSSA grafts are hindered by cross-linking with 1,3-371 diisopropenylbenzene. The obtained results in Ta-372 bles 1 and 2 indicate that the domain sizes and in-373 terionic domain distances of the ETFE-PEMs can be 374 controlled at irradiation grafting step 13. Based on the 375 results of the fitting models, we propose a model for 376 the microstructural features of ETFE-PEM consisting 377 of PS and PSSA graft domains (Figure 5). 378 The above results indicate that the simultaneous ap-379 plication of the OZ, Guinier, DB and TS models is 380 necessary to evaluate both the domain sizes and dis-381 tances of the ionic domains. However, as shown in 382 Figure 1 and Figure 2, the fitting is only applied in the 383 384 limited Q-range for the case of the OZ and Guinier 385 models. Further evaluation of the features of the ionic domains in the ETFE-PEMs at lower and higher GDs 386 using SAXS analysis is necessary to understand the 387

³⁸⁷ using SAXS analysis is necessary to understand in ³⁸⁸ structure-conductance relation.

389 CONCLUSIONS

The domain sizes and interdomain distances of the PS
and PSSA grafts of the grafted-ETFE films (~ 0.8 nm)
and the ETFE-PEMs (~ 1.1 nm) were determined by
the OZ and TS models and compared to those of the
Guinier and DB models via SAXS profile fitting. The
domain sizes and interdomain distances did not vary
with GDs of 36 and 61%, respectively, indicating that

both the grafted films and membranes can accommo- 397 date more PS and PSSA chains with small changes 398 in their dimensions. The ionic domain sizes of the 399 ETFE-PEMs can be controlled at the irradiation graft- 400 ing step. The ionic domain sizes of the ETFE-PEMs 401 were greater than the corresponding polystyrene graft 402 domain sizes of the grafted ETFE films, which can 403 be explained by the phase separation of the PSSA 404 grafts from the backbones of the ETFE matrix at 405 the sulfonation step. Note that the PSSA grafts in 406 the ETFE-PEMs can be connected, aggregated, and 407 shelf-organized to form ionic domains at low dimen- 408 sions, which is much lower than those in the ETFE- 409 PEMs cross-linked with 1,3-diisopropenylbenzene (~ 410 1.5 nm) and commercial Nafion membranes (2-5 411 nm). The features of the ionic domains of the ETFE- 412 PEMs under various RH conditions are progressing. 413 414

ACKNOWLEDGMENTS

This research is funded by the Vietnam National 416 Foundation for Science and Technology Development 417 (NAFOSTED) under grant number 103.99-2020.59. 418

415

419

LIST OF ABBREVIATIONS

DB: Debye-Bueche	42			
ETFE: Poly(ethylene-co-tetrafluoroethylene)	42			
ETFE-PEMs: Poly(styrene sulfonic acid) (PSSA)-	422			
grafted poly(ethylene-co-tetrafluoroethylene) (ETFE)				
polymer electrolyte membranes				
FCEV: Fuel cell electric vehicles				
FT-IR: Fourier transform infrared				
GD: Grafting degree				
grafted-ETFE: Polystyrene-grafted ETFE	42			
NIMS: National Institute of Material Science				
OZ: Ornstein-Zernike	430			
PEM: Polymer electrolyte membrane				
PEMFCs: Proton exchange membrane fuel cells				
pNIPAAm: Poly(N-isopropyl acrylamide)				
PS: Polystyrene				
PSSA: Poly(styrene sulfonic acid)				
RH: Relative humidity				
SAXS: Small-angle X-ray scattering				
SPP-QP: Sulfonated polyphenylenes composed of	43			
m- and p-phenylene groups with sulfonic acid sub-	439			
stituents	440			
TS: Teubner-Strey	44			
XPS: X-ray photoelectron spectroscopy				
CONFLICT OF INTEREST	44			

The authors declare that they have no conflicts of interest. 444





446 DATA AVAILABILITY STATEMENT

⁴⁴⁷ The data sets are not publicly available but are avail-⁴⁴⁸ able from the corresponding author upon reasonable⁴⁴⁹ request.

450 AUTHORS CONTRIBUTION

Tran Duy Tap: Conceptualization, Project adminis-451 452 tration, Funding acquisition, Supervision, Resources, 453 Investigation, Methodology, Data curation, Formal 454 analysis, Supervision, Validation, Visualization, Writ-455 ing - original draft, Writing - review & editing. Nguyen Manh Tuan: Investigation, Methodology, 456 Data curation, Formal analysis, Validation, Visual-458 ization, Writing - original draft, Writing - review & 459 editing. Nguyen Huynh My Tue, Vo Thi Kim Yen, Nguyen Nhat Kim Ngan, Dinh Tran Trong Hieu, 460 Hoang Anh Tuan, Doan Quoc Huy: Visualization, 461 Validation, Writing- review & editing. 462

463 REFERENCES

- Wang Y, Seo B, Wang B, Zamel N, Jiao K, Adroher XC.
 Fundamentals, materials, and machine learning of polymer electrolyte membrane fuel cell technology. Energy AI.
 2020;1:100014;Available from: https://doi.org/10.1016/j.egyai.
 2020.100014.
- Nasef MM. Radiation-grafted membranes for polymer electrolyte fuel cells: current trends and future directions. Chem
 v. 2014;114(24):12278-12329;Available from: https://doi.
 org/10.1021/cr4005499.
- 473 3. Duy TT, Sawada SI, Hasegawa S, Katsumura Y, Maekawa
- Y. Poly (ethylene-co-tetrafluoroethylene)(ETFE)-based graft type polymer electrolyte membranes with different ion ex-
- type polymer electrolyte membranes with different ion ex-change capacities: relative humidity dependence for fuel

cell applications. J Membr Sci. 2013;447:19-25;Available from: 477 https://doi.org/10.1016/j.memsci.2013.07.041. 478

- Hao LH, Hieu DTT, Luan LQ, Phuong HT, Dinh VP, Tuyen LA, Hong PTT, Man TV, Tap T D. Electron and gamma irradiationinduced effects in poly (ethylene-co-tetrafluoroethylene)
 films. J. Appl. Polym. Sci. 2022;139(29):e52620;Available from: https://doi.org/10.1002/app.52620.
- Tap TD, Sawada SI, Hasegawa S, Yoshimura K, Oba Y, Ohnuma M, Katsumura Y, Maekawa Y. Hierarchical structure-property relationships in graft-type fluorinated polymer electrolyte membranes using small- and ultrasmall-angle X-ray scattering analysis. Macromolecules. 2014;47(7):2373-83;Available from: https://doi.org/10.1021/ma500111x.
- Tap TD, Nguyen LL, Hien NQ, Thang PB, Sawada SI, Hasegawa
 S, Maekawa Y. Humidity and temperature effects on mechanical properties and conductivity of graft-type polymer
 electrolyte membrane. Radiat Phys Chem. 2018;151:186-191;Available from: https://doi.org/10.1016/j.radphyschem.
 2018.06.033.
- Tap TD, Nguyen LL, Zhao Y, Hasegawa S, Sawada SI, Hung NQ, Tuyen LA, Maekawa Y. SAXS Investigation on morphological change in lamellar structures during propagation steps of graft-type polymer electrolyte membranes for fuel cell applications. Macromol Chem Phys. 2020;221(3):1900325;Available from: https://doi.org/10.1002/macp.201900325.
- Tap TD, Nguyen LL, Hasegawa S, Sawada SI, Luan LQ, Maekawa
 Y. Internal and interfacial structure analysis of graft-type fluorinated polymer electrolyte membranes by small-angle
 X-ray scattering in the high-q range. J Appl Polym Sci.
 2020;137(35):49029;Available from: https://doi.org/10.1002/
 app.49029.
- Hao LH, Tap TD, Hieu DTT, Korneeva E, Tiep NV, Yoshimura 508 K, Hasegawa S, Sawada SI, Man TV, Hung NQ, Tuyen LA, 509 Phuc DV, Luan LQ, Maekawa Y. Morphological characterization of grafted polymer electrolyte membranes at a surface layer for fuel cell application. J Appl Polym Sci. 512 2022;139(14):51901;Available from: https://doi.org/10.1002/ 513 app.51901. 514
- 10. Hieu DTT, Hao LH, Long TH, Tien VV, Cuong NT, Man TV, Loan 515 TTH, Tap TD. Investigation of chemical degradation and wa- 516

- 517 ter states in the graft-type polymer electrolyte membranes. Polym Eng Sci. 2022;62(9):2757-2768;Available from: https:// 518 519 doi.org/10.1002/pen.26059.
- 520 Long TH, Hieu DTT, Hao LH, Cuong NT, Loan TTH, Man TV, 11.
- Tap TD Positron annihilation lifetime spectroscopic analy-521
- 522 sis of nation and graft-type polymer electrolyte membranes
- for fuel cell application. Polym Eng Sci. 2022;62(12):4005-523
- 4017;Available from: https://doi.org/10.1002/pen.26162. 524
- 525 **12**. Tap TD, Long TH, Hieu DTT, Hao LH, Phuong HT, Luan LQ, Man TV. Positron annihilation lifetime study of subnano level 526 free volume features of grafted polymer electrolyte mem-527 branes for hydrogen fuel cell applications. Polym Adv Technol. 528
- 2022;33(9):2952-2965;Available from: https://doi.org/10.1002/ 529 pat 5761 530 Tap TD, Hasegawa S, Yoshimura K, Yen VTK, Tue NHM, Tuan 531 13.
- 532 NM, Hieu DTT, Tuan HA, Hao HL, Nguyen LL, Phuong HT, Luan LO, Man TV, Maekawa Y. Phase separation and water chan-533 nels in graft-type polymer electrolyte membranes for hydro-534 gen fuel cell. Int J Hydrog Energy. 2024;59:777-790;Available 535 536 from: https://doi.org/10.1016/j.ijhydene.2024.02.082.
- 537 Dinh TTH, Lam HH, Tran TD, Le OL, Huvnh TP, Luu AT, Pham KN, Tran DT. FT-IR analysis of the water states 538 of the poly(styrene sulfonic acid)-grafted poly(ethylene-539 co-tetrafluoroethylene) copolymer. Minist Sci Technol Viet-540 541 nam. 2022;64(2):3-9:Available from: https://doi.org/10.31276/ 542 VISTE.64(2).03-09.
- 543 15. Hieu ĐTT, Hao LH, Danh TT, Long TH, Cuong NT, Man TV, Loan
- TTH, Tap TD. Study on the mechanism of graft polymerization 544 and sulfonation of proton exchange membranes for fuel cell. 545 VJST B. 2022;64(6);Available from: https://b.vjst.vn/index.php/ 546 547 ban b/article/view/1282.
- Tue NHM, Long TH, Hieu DTT, Hao LH, Yen VTK, Tuan NM, 548 16 Phuong HT, Luan LQ, Hong PTT, Man TV, Tap TD. Effects 549 of source correction on positron annihilation lifetime spec-550 troscopic analysis of graft-type polymer electrolyte mem-551 552 branes. Sci Technol Dev J. 2023;26(4):press-press;Available 553 from: https://doi.org/10.32508/stdj.v26i4.4052.
- 554 17 Tap TD. Study on the structures of polymer electrolyte mem-
- 555 brane for fuel cell applications using small and ultrasmall angle X-ray scattering. VJST B. 2018;60(8):8-11;Available from: 556 https://b.vist.vn/index.php/ban_b/article/view/624.
- 557
- 558 18 Nguyen LL, Hao LH, Hai LV, Ngan NNK, Cuong NT, Tuyen LA, Phuc PT, Phuong HT, Luan LQ, Hue NTN, Tap TD. Application 559
- 560 of small-angle X-ray scattering to evaluate the impact of elec-
- 561 tron density fluctuation on the micro structures of proton exchange membrane in fuel cell, VJST B, 2020;62(1);Available 562
- from: https://b.vjst.vn/index.php/ban_b/article/view/941. 563 564 19 Lam HH, Dinh TTH, Tran HL, Dang VH, Tran TD, Tran VM, Le QL, Huynh TP, Pham TTH, Tran DT. Investigation of the lamel-565 566 lar grains of graft-type polymer electrolyte membranes for hy-567
- drogen fuel cell application using ultrasmall-angle X-ray scattering. VNU J Sci Nat Sci Technol. 2021;37(4);Available from: 568 569 https://doi.org/10.25073/2588-1140/vnunst.5216.
- 570 **20**. Yen VTK, Hieu DTT, Hao LH, Long TH, Tue NHM, Tuan NM, Cuong NT, Loan TTH, Man TV, Tap TD. Characterization of 571 572 graft-type polymer electrolyte membranes at low grafting degrees for fuel cells. Sci Technol Dev J. 2023;26(2):2799-573 2807:Available from: https://doi.org/10.32508/stdi.v26i2.4051. 574
- Hao LH, Hieu DTT, Danh TT, Long TH, Phuong HT, Man TV, 575 21. Tuyen LA, Ngoc PK, Tap TD. Surface features of polymer elec-576 577 trolyte membranes for fuel cell applications: an approach using S2p XPS analysis. Sci Technol Dev J. 2021;24(3):2100-578 2109;Available from: https://doi.org/10.32508/stdj.v24i3.2556. 579
- 580 22. Zhao Y, Yoshimura K, Sawada S, Motegi T, Hiroki A, Radulescu A, Maekawa Y. Unique structural characteristics of graft-581 582 type proton-exchange membranes using SANS partial scattering function analysis. Macromolecules. 2022;55(16):7100-583
- 584 7109;Available from: https://doi.org/10.1021/acs.macromol. 585 2c00333.
- 586 23. Balog S, Gasser U, Mortensen K, Gubler L, Scherer GG. Nanoscale morphology graft copolymer 587 in

proton-exchange membranes cross-linked with DIPB 588 J Membr Sci. 2011;383(1-2):50-59;Available from: 589 https://doi.org/10.1016/j.memsci.2011.08.031. 590

- 24. Ding YS, Hubbard SR, Hodgson KO, Register RA, Cooper SL. 591 Anomalous small-angle X-ray scattering from a sulfonated 592 polystyrene ionomer. Macromolecules. 1988;21(6):1698-593 1703:Available from: https://doi.org/10.1021/ma00184a028. 594
- 25 Nishikawa K, Kasahara Y, Ichioka T. Inhomogeneity of mix-595 ing in acetonitrile aqueous solution studied by small-angle X-596 ray scattering, J Phys Chem B. 2002;106(3):693-700;Available 597 from: https://doi.org/10.1021/jp011964v.
- 26 Amann M, Diget JS, Lyngsø J, Pedersen JS, Naravanan T, Lund 599 R. Kinetic pathways for polyelectrolyte coacervate micelle for-600 mation revealed by time-resolved synchrotron SAXS. Macro-601 molecules. 2019:52(21):8227-8237:Available from: https://doi. 602 org/10.1021/acs.macromol.9b01072. 603
- Teubner M, Strey R. Origin of the scattering peak in mi-27 604 croemulsions. J Chem Phys. 1987;87(5):3195-3200;Available 605 from: https://doi.org/10.1063/1.453006. 606
- 28 Schubert KV, Strey R, Kline SR, Kaler EW. Small an-607 gle neutron scattering near Lifshitz lines: transition 608 from weakly structured mixtures to microemulsions 609 J Chem Phys. 1994;101(6):5343-5355;Available from: 610 https://doi.org/10.1063/1.467387. 611
- 29 Endo H, Mihailescu M, Monkenbusch M, Allgaier J, Gomp-612 per G, Richter D, Jakobs B, Sottmann T, Strey R, Grillo I. Ef-613 fect of amphiphilic block copolymers on the structure and 614 phase behavior of oil-water-surfactant mixtures. J Chem Phys. 615 2001;115(1):580-600;Available from: https://doi.org/10.1063/ 616 1 1377881 617
- Putnam CD, Hammel M, Hura GL, Tainer JA. X-ray solu-618 tion scattering (SAXS) combined with crystallography and 619 computation: defining accurate macromolecular structures, 620 conformations and assemblies in solution. O Rev Biophys. 621 2007;40(3):191-285;Available from: https://doi.org/10.1017/ 622 \$0033583507004635 623
- Grady BP, Matsuoka H, Nakatani Y, Cooper SL, Ise N. Influence 624 31 of the sample preparation method of the ultrasmall-angle 625 X-ray scattering of lightly sulfonated polystyrenes. Macro- 626 molecules. 1993;26(15):4064-4066;Available from: https://doi. 627 org/10.1021/ma00067a055. 628
- 32. Zhang F, Ilavsky J, Long GG, Quintana JP, Allen AJ, 629 Jemian PR. Glassy carbon as an absolute intensity 630 calibration standard for small-angle scattering. Met-631 all Mater Trans A. 2010;41:1151-1158;Available from: 632 https://doi.org/10.1007/s11661-009-9950-x. 633
- Habicht A, Schmolke W, Goerigk G, Lange F, Saalwaechter K, 33. 634 Ballauff M, Seiffert S. Critical fluctuations and static inhomo-635 geneities in polymer gel volume phase transitions. J Polym Sci 636 B: Polym Phys. 2015;53(16):1112-1122;Available from: https: 637 //doi.org/10.1002/polb.23743. 638
- Shi C, Liu T, Chen W, Cui F, Liu L, Cai Y, Li Y. Interaction, 34. 639 structure and tensile property of swollen nation membranes. 640 Polymer. 2021;213:123224;Available from: https://doi.org/10. 641 1016/j.polymer.2020.123224. 642
- Woo E, Coletta E, Holm A, Mun J, Toney MF, Yoon DY, Frank CW. 35. 643 Polyimide-PEG segmented block copolymer membranes with high proton conductivity by improving bicontinuous nanos-645 tructure of ionic liquid-doped films. Macromol Chem Phys. 646 2019;220(9):1900006;Available from: https://doi.org/10.1002/ 647 macp.201900006. 648
- Shiino K, Otomo T, Yamada T, Arima H, Hiroi K, Takata S, 36. 649 Mivake J. Mivatake K. Structural investigation of sulfonated 650 polyphenylene ionomers for the design of better perform-651 ing proton-conductive membranes. ACS Appl Polym Mater. 652 2020;2(12):5558-5565;Available from: https://doi.org/10.1021/ 653 acsapm.0c00895. 654
- 37. Balog S, Gasser U, Mortensen K, Gubler L, Scherer 655 GG. Nanoscale morphology in graft copolymer 656 membranes cross-linked with DIPB. proton-exchange 657 Membr Sci. 2011;383(1-2):50-59;Available from: 658

659 https://doi.org/10.1016/j.memsci.2011.08.031.