

Synthesis and Properties of Sulfonated Poly(arylene ether nitrile) Copolymers Containing Carboxyl Groups for Proton-Exchange Membrane Materials

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ABSTRACT: A series of sulfonated poly(arylene ether nitrile) copolymers containing carboxyl groups were synthesized via a nucleophilic aromatic substitution reaction from phenolphthalein, hydroquinone sulfonic acid potassium salt, and 2,6-difluorobenzonitrile in *N*-methyl pyrrolidone (NMP) with K_2CO_3 as a catalyst. The synthesized copolymers had good solubility in common polar organic solvents and could be easily processed into membranes from solutions of dimethyl sulfoxide, NMP, *N,N'*-dimethyl acetylamine, and dimethylformamide. Typical membranes in acid form were gained, and the chemical structures of these membranes were characterized by Fourier transform infrared analysis. The thermal properties, fluorescence properties, water uptake, ion-exchange capacity, and proton conductivities of these copolymers were also investigated. The results indicate that they had high glass-transition temperatures in the range 151–187°C and good thermal stability, with the 10 wt% loss temperatures ranging from 330 to 351°C under nitrogen. The copolymers showed characteristic unimodal ultraviolet–visible (UV–vis) absorption and fluorescence emission, and the UV–vis absorption, fluorescence excitation, and emission peaks of the copolymers were obvious. Moreover, the copolymer membranes showed good water uptake and proton conductivities at room temperature and 55% relative humidity because of the introduction of both sulfonic acid groups and carboxyl groups into the copolymers, whose contents were in ranges 18.45–67.86 and 3.4×10^{-4} to 3.0×10^{-3} s/cm, respectively. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40213.

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INTRODUCTION

As efficient and clean energy devices, fuel cells can convert chemical energy into electrical energy by the electrochemical reaction of oxygen and hydrogen. During the past several years, proton-exchange membrane fuel cells (PEMFCs) have drawn great attention for applications in vehicular transportation, cogeneration systems, distributed residences and institutions, and also some portable devices, such as computers and mobile communication equipment.¹ Proton-exchange membranes (PEMs) are one of the core components in PEMFCs, the major roles of which are as electrolytes for the transport of protons from the anode to the cathode and as a diaphragm material for preventing oxygen and hydrogen gases from mixing. In the early stages, perfluorinated sulfonic acid copolymer membranes consisting of polytetrafluoroethylene main chains and perfluoroaliphatic ether side chains tethered with sulfonic acid groups, such as DuPont's Nafion and Solvay Solexis's Aquivion, are the most common PEMs as a result

of their outstanding chemical and mechanical stabilities and their high proton conductivities.^{2–4} There is no doubt that these membranes also have some disadvantages such as a high cost, low operation temperature, and high fuel permeability.^{5,6} Therefore, it is of interest to investigate the synthesis and properties of less expensive and more versatile polymer electrolytes.

High-performance polymers such as poly(aryl ether sulfone)s and poly(aryl ether ketone)s^{7–11} have become important alternative candidates for PEMs because of their excellent thermal, mechanical, and dielectric properties and oxidative resistance. Consequently, these high-performance polymers containing pendant acidic functions, such as sulfonated poly(arylene ether sulfone) and sulfonated poly(arylene ether ketone),^{12–18} have been studied largely and have become promising alternative PEM materials in recent years. For instance, D. S. Kim et al.¹⁹ and Y. S. Kim and coworkers^{20,21} synthesized a series of sulfonated poly(arylene ether sulfone) copolymers by the direct

copolymerization of biphenol, disulfonated-activated aromatic halide monomers, and precursor-activated aromatic halide monomers. Xiao and coworkers^{22,23} and Gao and coworkers^{24,25} synthesized poly(phthalazinone ether sulfone)s and poly(phthalazinone ether ketone)s containing sulfonic acid groups by both direct polymerization reactions and postsynthesis sulfonation reactions. However, these copolymers, with their high sulfonic acid content, have a tendency to swell at high temperatures and relative humidities (RHs), and this leads to a decrease in the mechanical strength of the membranes.

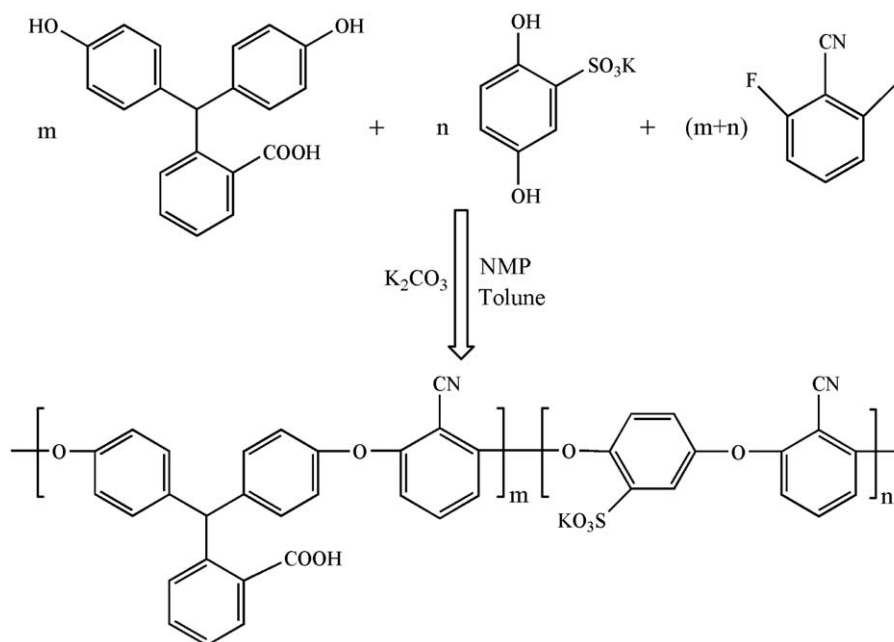
As a class of superengineering plastic, poly(arylene ether nitriles) (PENs) are well-known for their outstanding mechanical properties, high thermal stability, excellent chemical resistance, and good film-forming ability and processability.^{26–28} Recently, our group reported the synthesis, water uptake, and proton conductivities of sulfonated poly(arylene ether nitrile) copolymers (SPENHs) obtained by the direct copolymerization of hydroquinone sulfonic acid potassium salt (SHQ), bisphenol A, and 2,6-difluorobenzonitrile (DFBN).²⁹ However, in this study, we synthesized a series of sulfonated poly(arylene ether nitrile) copolymers containing carboxyl groups (SPENH-COOHs) from phenolphthalein (PPL), SHQ, and DFBN, and thus, carboxyl groups as pendant groups were also introduced into the copolymers. This would not only increase the water uptake and proton conductivities of the membranes but also enhance the fluorescence properties of the copolymers; this indicates that the copolymers could also be used as polymeric light-emitting materials, such as photovoltaic devices,³⁰ field effect transistors,³¹ and electrochromics.³² In addition, in this study, we also concretely investigated their chemical structures, solubility, thermal properties, fluorescence properties, water uptake, ion-exchange capacity (IEC), and proton conductivities and compared the water uptake and proton conductivities of these copolymers with those of the SPENHs.

EXPERIMENTAL

DFBN and SHQ were obtained from Aldrich. Phenolphthalein, hydrochloric acid, and zinc were supplied by Chengdu Haihong Chemicals. *N,N'*-Dimethylacetamide [DMAc; analytical reagent (AR)], *N,N'*-dimethylformamide (DMF; AR), *N*-methyl pyrrolidone (NMP; AR), dimethyl sulfoxide (DMSO; AR), tetrahydrofuran (THF; AR), chloroform (CHCl₃; AR), acetone (AR), toluene (AR), potassium carbonate (K₂CO₃; AR), sodium hydroxide (NaOH; AR), and sodium chloride (NaCl; AR) were purchased from Tianjin BODI Chemicals. All of the materials were used without further purification. The synthesis of PPL was implemented according to the literature.³³

Synthesis of SPENH-COOH

As depicted in Scheme 1, the SPENH-COOH copolymers were synthesized through a nucleophilic aromatic substitution reaction from PPL and SHQ with DFBN in NMP solvent with K₂CO₃ as a catalyst based on a similar procedure in the literature.³⁴ A series of SPENH-COOH copolymers with different contents of carboxyl and sulfonic acid groups were obtained by the alteration of the molar ratios of PPL to SHQ. The specific molar ratios and synthesis conditions are shown in Table I. In a typical reaction, DFBN (0.15 mol, 20.85 g), PPL (0.105 mol, 33.6 g), SHQ (0.045 mol, 10.26 g), and K₂CO₃ (0.2 mol, 27.6 g) were mixed in a 250-mL, three-necked, round-bottomed flask equipped with a condenser, a Dean-Stark trap, and an overhead mechanical stirrer with 80 mL of NMP and 20 mL of toluene. The mixture was heated to about 150°C, and the temperature was maintained for 2 h to distill the dehydrating agent. Then, the temperature was gradually increased to 195°C for about 2 h until the reaction mixture displayed the rod-climbing phenomenon. Subsequently, the mixture was poured into water to precipitate the product. The product was washed thoroughly with boiling water to remove residual solvent and salt. Finally, the



Scheme 1. Synthetic route of the SPENH-COOH copolymers.

Table I. Synthesis Conditions and Physical Properties of the SPENH-COOH Copolymers

Polymer	PPL/S HQ molar ratio	Dehydration time at 150°C (h)	Polymerization time at 195°C (h)	Yield (%)	η_{inh} (dL/g)
SPENH-COOH-70	70:30	2	2	95.4	0.83
SPENH-COOH-50	50:50	2	2	94.7	0.95
SPENH-COOH-30	30:70	2	2	94.0	1.37

collected copolymer was dried at 120°C *in vacuo* overnight. The yield was the ratio of practical production to theoretical production in percentage terms. The yields of the SPENH-COOH copolymers are displayed in Table I, and they were all higher than 94.0%.

Preparation of the Membranes

An amount of 1 g of the copolymer in the potassium salt form (SPENH-COOH) was dissolved in 20 mL of DMF solvent. The obtained solution was cast onto a clean glass plate and then dried in an oven at 80, 100, 120, and 160°C (1 h each) to evaporate the solvent. The acid form membranes (SPENH-COOH) were obtained by the immersion of the corresponding potassium form SPENH-COOH membranes in a 2 mol/L HCl solution for 24 h at room temperature; the membranes were denoted as SPENH-COOH-70, SPENH-COOH-50, and SPENH-COOH-30, respectively. Afterward, these membranes were immersed in deionized water for another 24 h, during which period the water was replaced with clean water a few times to remove excess acid. These SPENH-COOH membranes were yellow and transparent, and their thickness was in the range 60–80 μm .

Characterization of the Membranes

Fourier transform infrared (FTIR) spectra of the SPENH-COOH membranes were recorded on a Shimadzu 8000S spectrophotometer. Differential scanning calorimetry (DSC) analysis was performed on TA Instruments DSC-Q100 modulated thermal analyzer at a heating rate of 10°C/min and a nitrogen flow rate of 50 mL/min from room temperature to 350°C. Thermogravimetric analysis (TGA) was carried out on a TA Instruments TGA-Q50 at a heating rate of 20°C/min from room temperature to 800°C under nitrogen.

Fluorescence Properties

The ultraviolet–visible (UV–vis) absorption spectra were recorded on a UV2501-PC spectrophotometer. Fluorescence excitation and emission spectra were monitored on a Hitachi F-4600 FL spectrophotometer. They were measured in NMP solutions at a concentration of 1.5 mg/mL at room temperature.

Water Uptake

The water uptake was measured by the immersion of the SPENH-COOH membranes in deionized water for about 24 h at room temperature. Subsequently, the water was wiped from the surface of the membranes with filter paper, and the membranes were weighed immediately. Afterward, the membranes were dried at 80°C *in vacuo* for 12 h, and the weight of the dry membranes was measured. The water uptake was calculated by the following equation:

$$\text{Water uptake(\%)} = \frac{\omega_{\text{wet}} - \omega_{\text{dry}}}{\omega_{\text{dry}}} \times 100\%$$

where ω_{wet} and ω_{dry} are the weights of wet and dry membranes, respectively.

IEC

The IEC was measured via traditional titration. The SPENH-COOH membranes were dried at 80°C *in vacuo* overnight, and then, they were weighed immediately. Afterward, these membranes were soaked in a 1 mol/L NaCl solution for 24 h at room temperature so that the hydrogen ions (H^+ 's) could be exchanged by sodium ions (Na^+ 's). Finally, the solution was titrated with a 0.1 mol/L NaOH solution. The IEC was calculated by

$$\text{IEC} = \frac{C_{\text{NaOH}} \times V_{\text{NaOH}}}{W_d} \times 100\%$$

where C_{NaOH} , V_{NaOH} , and W_d represent the molarity of the NaOH solution, the consumed volume of the NaOH solution in the titration process, and the weight of the dry membranes, respectively.

Proton Conductivity

The proton conductivity was evaluated in air atmosphere at room temperature and 55% RH. The SPENH-COOH membranes were immersed in deionized water for 24 h before the test. The impedance measurements were performed on a CS350 (Wuhan CorrTest Instrument Corp., Wuhan, China) electrochemical workstation coupled with a computer. The membrane sample was clamped between two stainless steel electrodes with area of 1 cm^2 . The impedance spectra of the copolymer membranes were recorded from 10^7 to 1 Hz. The resistance values related to the membranes' proton conductivities were derived from the high-frequency intercept of the impedance with the real axis. The proton conductivity (σ) was calculated by the following relationship:

$$\sigma = \frac{d}{RS}$$

where d is the thickness of the membrane, S is the cross-sectional area of the membrane perpendicular to the current flow, and R is the resistance of the membrane.

RESULTS AND DISCUSSION

Characterization of the SPENH-COOH Copolymers

The inherent viscosities (η_{inh} 's) of all of the SPENH-COOH copolymers were measured with an Ubbelohde viscometer in NMP solvent at 30°C, and the values are shown in Table I. It was obvious that the η_{inh} increase with increasing SHQ monomer was due to the increase of chemical interaction between

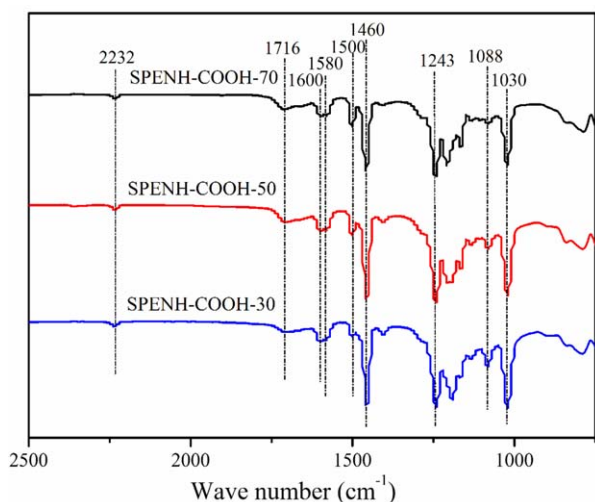


Figure 1. FTIR spectra of the SPENH-COOH copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the sulfonic acid groups.²⁹ Meanwhile, we observed that the η_{inh} values of all of the SPENH-COOH copolymers were higher than 0.8 dL/g; this indicated that the synthesized copolymers had high molecular weights. Moreover, the good film-forming properties of all of the copolymers also confirmed the high molecular weight of the products.

FTIR spectroscopy is a convenient method for characterizing the chemical structure of the copolymers. The FTIR spectra of SPENH-COOH copolymers are shown in Figure 1. The characteristic absorption bands at 1460, 1500, 1580, and 1600 cm^{-1} were observed and were assigned to the stretching vibration of the benzene rings. The absorption band at 2232 cm^{-1} was attributed to the symmetric stretching vibration of nitrile groups. Characteristic absorption bands of the aromatic sulfonate symmetric and asymmetric stretching vibrations were observed at 1030 and 1088 cm^{-1} .²⁹ A characteristic absorption band at 1716 cm^{-1} was clearly observed; this corresponded to the stretching vibration of carboxyl groups.³⁵ In addition, the characteristic absorption band of the aromatic ether was obtained at 1243 cm^{-1} . All of these data indicate that the SPENH-COOH copolymers were synthesized successfully, as shown in Scheme 1.

Solubility of the SPENH-COOH Copolymers

The solubility behaviors of the synthesized SPENH-COOH copolymers were evaluated in all kinds of solvents by the disso-

lution of 40 mg of the SPENH-COOH copolymers in 1 mL of solvent. The results are summed up in Table II. As shown, SPENH-COOH-70 had excellent solubility in some polar organic solvents, such as DMAc, DMSO, DMF, and NMP, at room temperature, and both SPENH-COOH-50 and SPENH-COOH-30 could also be dissolved in the aforementioned solvents by heating. In addition, SPENH-COOH-70 could be dissolved in some low-boiling solvents, such as THF and CHCl_3 , and acetone by heating. However, SPENH-COOH-50 and SPENH-COOH-30 could not be dissolved in these low-boiling solvents. All in all, all of the SPENH-COOH copolymers exhibited good solubility. The bulky pendent groups, such as carboxyl and sulfonate groups, probably hindered the dense packing of the polymer chains because of a reduction in the chain interactions through an increase in the chain distances. Therefore, the polymer chains could be solubilized more easily by the solvent molecules.³⁵ Nevertheless, it was apparent that the solubility of SPENH-COOH-70 was better than those of SPENH-COOH-50 and SPENH-COOH-30. This was due to the fact that the solubility of the copolymers was also influenced by the chemical interaction between the sulfonic acid groups.²⁹ SPENH-COOH-70 had fewer polar sulfonic acid groups than SPENH-COOH-50 and SPENH-COOH-30; this resulted in a great decrease in the chemical interaction between sulfonic acid groups. Consequently, SPENH-COOH-70 was penetrated more easily by the solvent molecules.

Thermal Properties

The thermally induced phase-transition behavior of all of the SPENH-COOH copolymers was investigated with DSC under nitrogen, and the DSC curves are shown in Figure 2. The glass-transition temperatures (T_g) are listed in Table III, and they were in the range 151–187°C. As shown in Figure 2, it is clear that the T_g values of the SPENH-COOH copolymers increased with decreasing PPL units. This was mainly due to the following reasons:

1. The content of carboxyl groups affected the T_g values of the SPENH-COOH copolymers, and the decrease of the carboxyl groups resulted in the increase in T_g because of the fact that the carboxyl groups were the flexible side groups.³⁴
2. The content of sulfonic acid groups also influenced the T_g values of the SPENH-COOH copolymers, and the increase in the sulfonic acid groups led to an increase in T_g because of the increase in the intermolecular interactions by pendant ions, which enhanced the molecular bulkiness and raised the rotation activation energy of the polymer molecular segment.³⁶

Table II. Solubility of the SPENH-COOH Copolymers

Polymer	Solubility ^a						
	NMP	DMAc	DMF	DMSO	CHCl_3	Acetone	THF
SPENH-COOH-70	++	++	++	++	+	+	+
SPENH-COOH-50	+	+	+	+	–	–	–
SPENH-COOH-30	+	+	+	+	–	–	–

^a ++, soluble at room temperature; +, soluble by heating; –, insoluble.

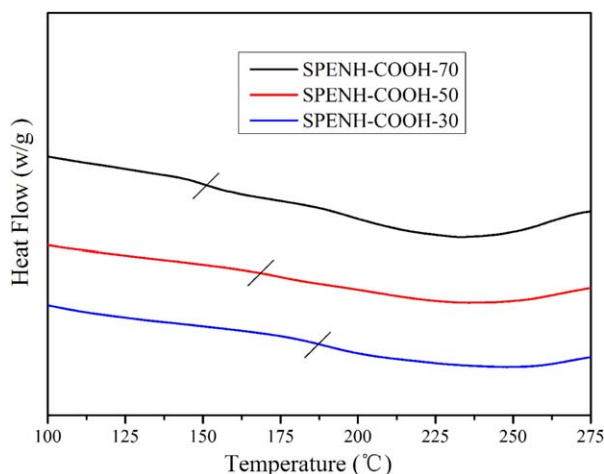


Figure 2. DSC curves of the SPENH-COOH copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Furthermore, the formation of endothermic curves in the range 200–275 °C (Figure 2) was due to the decomposition of the carboxyl groups of the SPENH-COOH copolymers.

The thermal stability of the SPENH-COOH copolymers was evaluated by TGA under nitrogen, and the TGA curves are displayed in Figure 3. In addition, the 5% weight loss temperatures ($T_{d5\%}$'s), 10% weight loss temperatures ($T_{d10\%}$'s), and char yield (C_y) values are summarized in Table III. As shown in Figure 3, the TGA curves of all of the SPENH-COOH copolymers showed three distinguishable transition steps; these corresponded to the loss of carboxyl groups, the decomposition of sulfonic acid groups, and the degradation of the main chain of the polymers. As shown in Table III, $T_{d5\%}$ and $T_{d10\%}$ were in the range 267–285 and 330–351 °C, respectively. According to Figure 3 and Table III, we clearly observed that the thermal stability of the SPENH-COOH copolymers decreased with increasing PPL units. This was due to the fact that the carboxyl groups were dissociated more easily than the sulfonic acid groups, which decomposed rapidly from the benzene ring when the temperature reached nearly 250 °C. Furthermore, the C_y values of all of the SPENH-COOH copolymers shown in Table III were in the range 49.10–58.21%. All in all, these results indicate that the SPENH-COOH copolymers exhibited good thermal stability.

Fluorescence Properties

The UV-vis absorption, fluorescence excitation, and emission spectra of the SPENH-COOH copolymers were measured in NMP solution at room temperature. Figure 4 displays the

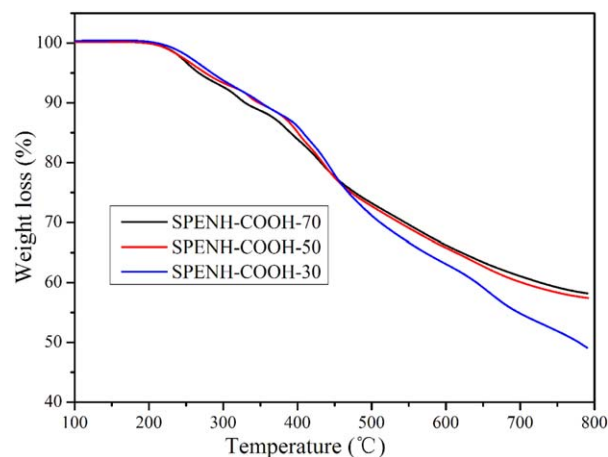


Figure 3. TGA curves of the SPENH-COOH copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

UV-vis absorption spectra of the SPENH-COOH copolymers, and Table III lists the wavelengths of maximum absorbance [$\lambda_{\max}(\text{abs})$'s]. Clearly, all of the SPENH-COOH copolymers exhibited characteristic unimodal UV-vis absorption, and a strong absorption peak was observed at about 316 nm. This mainly corresponded to the absorption peak of the copolymer backbone. The fluorescence excitation spectra monitored on emission at 370 nm, and the emission spectra recorded on excitation at 330 nm are shown in Figure 5. The wavelengths of maximum excitation [$\lambda_{\max}(\text{ex})$] and emission [$\lambda_{\max}(\text{em})$] are summarized in Table III. As shown in Figure 5(a) and Table III, three excitation peaks for all of the SPENH-COOH copolymers were observed at about 231, 284, and 334 nm, respectively, and the first two peaks were much weaker than the third one. As shown in Figure 5(b) and Table III, there was only one strong emission peak at approximately 372 nm for each SPENH-COOH copolymer; this was attributed to the introduction of conjugated units into the copolymer backbone. In general, the UV-vis absorption, fluorescence excitation, and emission peaks were not evidently altered with the change in the molar ratios of PPL and SHQ, and all of the SPENH-COOH copolymers exhibited good fluorescence properties.

Water Uptake and IEC

The hydrophilic nature of the SPENH-COOH copolymers were evaluated by the water uptake measurement. The water within the membranes was the main carrier to transport the protons, so it was a necessary condition to ensure the proton conductivity. The water uptake as a function of the sulfonic acid group

Table III. Thermal and Fluorescence Properties of the SPENH-COOH Copolymers

Polymer	Thermal properties				Fluorescence properties (nm)		
	T_g (°C)	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	C_y (%)	$\lambda_{\max}(\text{abs})$	$\lambda_{\max}(\text{em})$	$\lambda_{\max}(\text{ex})$
SPENH-COOH-70	151	267	330	58.21	316	372	231, 284, 330
SPENH-COOH-50	169	276	348	57.43	316	370	231, 283, 334
SPENH-COOH-30	187	285	351	49.10	316	372	230, 286, 334

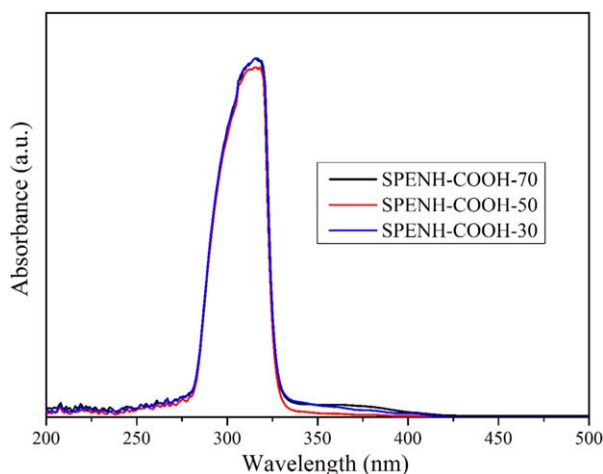


Figure 4. UV-vis absorption spectra of the SPENH-COOH copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

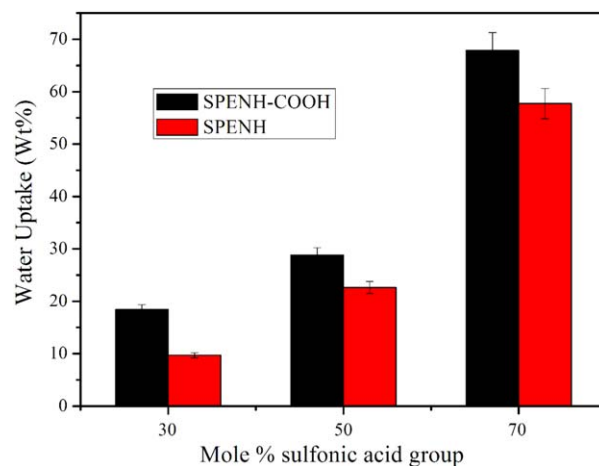


Figure 6. Influence of the sulfonic acid group content on the water uptake of the SPENH-COOH and SPENH membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

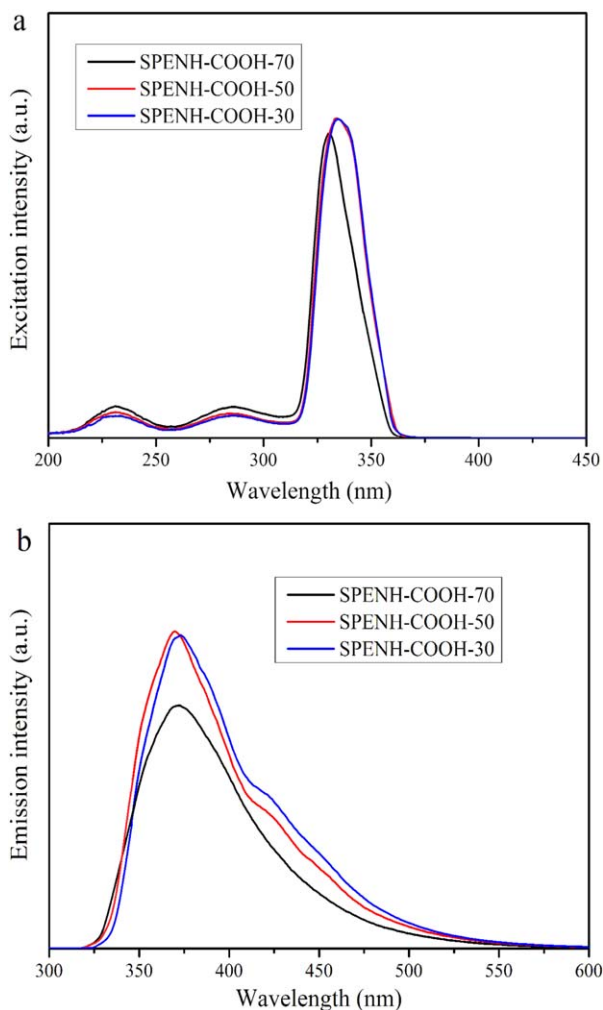


Figure 5. (a) Fluorescence excitation and (b) emission spectra of the SPENH-COOH copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

content is shown in Figure 6. We observed that the water uptake of all of the SPENH-COOH membranes increased gradually with increasing sulfonic acid group content. These SPENH-COOH membranes had water uptakes of 18.45, 28.79, and 67.86% for SPENH-COOH-70, SPENH-COOH-50, and SPENH-COOH-30, respectively. In addition, the water uptake of the SPENH membranes reported in our previous work²⁹ is also shown in Figure 6. It was obvious that the water uptakes of the SPENH-COOH membranes were higher than those of the corresponding SPENH membranes; this was because the hydrophilic phase of the SPENH-COOH membranes arose from both the sulfonic acid groups and carboxyl groups, whereas the hydrophilic phase of the SPENH membranes just resulted from the sulfonic acid groups. Compared with the Nafion117 membrane, which had a water uptake of 35% at room temperature,³⁷ the SPENH-COOH-30 membrane possessed a higher water uptake of 67.86%. In addition, the theoretical calculated IEC values in millimoles of SO_3H per gram and measured IEC values in millimoles of SO_3H plus millimoles of COOH per gram of the SPENH-COOH membranes as a function of the sulfonic acid group content are displayed in Figure 7. As shown, they increased with increasing sulfonic acid group content, and the measured IEC values were still lower than the calculated IEC values despite the introduction of carboxyl groups into the copolymers; this was due to the fact that the hydrophilic nature of the carboxyl groups was much weaker than that of the sulfonic acid groups and so the carboxyl groups have a slight effect on the IEC of the SPENH-COOH membranes.

Proton Conductivity

The proton conductivities of the SPENH-COOH membranes as a function of the sulfonic acid group content was measured at room temperature, and the results are shown in Figure 8. For comparison, the proton conductivities of the SPENH membranes reported in our previous literature²⁹ are also displayed in Figure 8. It was clear that the proton conductivities of the SPENH-COOH membranes increased with increasing sulfonic acid group content. More specifically, the proton conductivities

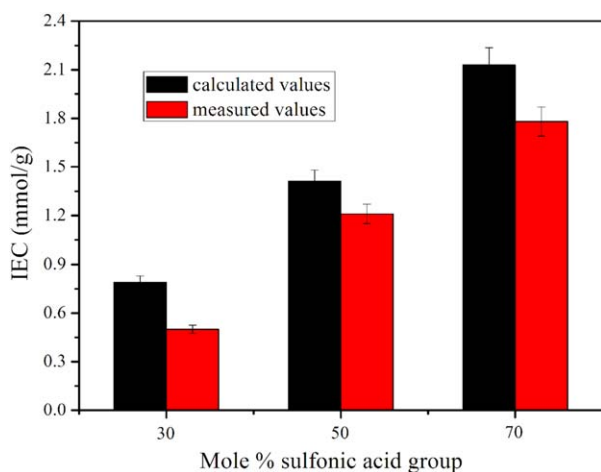


Figure 7. Influence of the sulfonic acid group content on the IEC of the SPENH-COOH membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increased from 3.4×10^{-4} s/cm for the SPENH-COOH-70 (IEC = 0.50 mmol/g) to 1.9×10^{-3} s/cm for the SPENH-COOH-50 (IEC = 1.21 mmol/g) and then increased to 3.0×10^{-3} s/cm for the SPENH-COOH-30 (IEC = 1.78 mmol/g); this value was lower than that of the Nafion 117 membrane at room temperature.³⁸ This was probably because of the two reasons:

1. The RH of the environment was different during the test, and the proton conductivity of Nafion 117 was measured at 100% RH, whereas those of the SPENH membranes were measured at 55% RH.
2. The SPENH-COOH membranes showed less obvious hydrophilic/hydrophobic phase separation than the Nafion 117 membrane because of the increased stiffness of the aromatic backbone, the shorter ionic side chains, and the lower acidity of the carboxyl and sulfonic acid groups.¹⁵

Compared with the SPENH membranes, the hydrophilic phase of which only arose from the sulfonic acid groups, the corre-

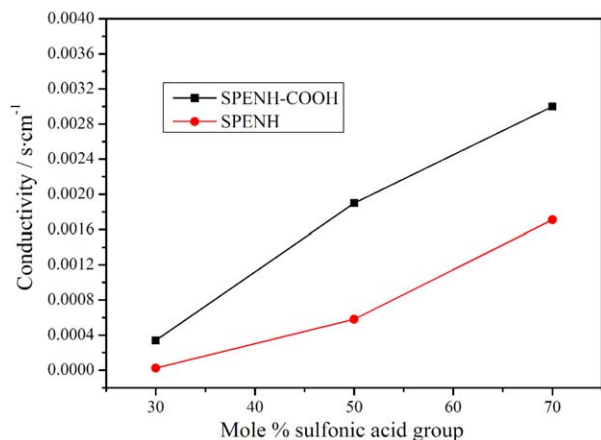


Figure 8. Influence of the sulfonic acid group content on the proton conductivities of the SPENH-COOH and SPENH membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sponding SPENH-COOH membranes had a bit higher proton conductivities. This was because both the sulfonic acid groups with a strong hydrophilicity and the carboxyl groups with a slight hydrophilicity were introduced into the SPENH-COOH copolymers. It was certain that the proton conductivities of the SPENH-COOH membranes increased with increasing temperature and RH of the environment, and even the SPENH-COOH-30 membrane showed a proton conductivity comparable to that of Nafion117. On the whole, the result was very favorable for the PEM application.

CONCLUSIONS

A series of SPENH-COOH copolymers were synthesized successfully from PPL, SHQ, and DFBN via nucleophilic substitution polycondensation. These SPENH-COOH copolymers exhibited good solubility in common polar organic solvents, such as DMAc, DMSO, DMF, and NMP, and they have good film-forming properties. The chemical structures of the SPENH-COOH membranes were characterized by FTIR spectroscopy. The T_g , $T_{d5\%}$, and $T_{d10\%}$ values of the SPENH-COOH copolymers increased with decreasing PPL units. The UV-vis absorption, fluorescence excitation, and emission peaks of the copolymers were obviously due to the introduction of conjugated units into the copolymer backbone. In addition, the SPENH-COOH membranes with high sulfonic acid group content exhibited good water uptake, IEC, and proton conductivities, and the water uptake and proton conductivities of the SPENH-COOH membranes were higher than those of the corresponding SPENH membranes at room temperature. All of these attributes make the SPENH-COOH membranes with high sulfonic acid group contents attractive as PEM materials for fuel cell applications.

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