Polymer Electrolyte Membranes Fuel Cell

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The development of sulfonated hydrocarbon polymer (SHP)-based polymer electrolyte membranes (PEMs) has been pursued in order to overcome drawbacks of the perfluorosulfonic acid ionomer-based PEMs in fuel cell applications. To improve the proton conductivity of SHP-based PEMs without deterioration in physicochemical stability, control of polymeric architecture is necessary to form distinct phase-separated structures between the hydrophilic and hydrophobic domains. By pursuing rational design strategies for the copolymer architectures, it will be possible to develop high-performance SHP-based PEMs in fuel cell applications. This study focused on the synthetic procedures which underlie structure-engineered copolymers and their PEM properties.

polymer electrolyte membrane fuel cell
perfluorinated sulfonic acid ionomer
sulfonated hydrocarbon polymer
phase-separation

1. Introduction

Recently, interest in eco-friendly alternative energy has increased due to the depletion of fossil fuels and environmental pollution, many countries are making great efforts to develop renewable energy technologies that can replace fossil fuels [1]. In particular, studies that utilize hydrogen as an energy source are being actively conducted [2][3][4]. As the most abundant element in the universe, there are clearly no concerns with its depletion. The fuel cell is an eco-friendly energy conversion device that can generate electrical energy by the electrochemical reaction between the fuel supplied (mainly hydrogen) and oxidizers [5]. Unlike conventional power generation technologies, fuel cells can efficiently utilize hydrocarbon-based energy sources without emission of noise or vibration. Furthermore, since combustion process is not required, harmful substances such as nitrogen oxides (NO_x) and sulfur oxides (SO_x) are not generated during operation [6]. As shown in **Table 1**, fuel cells can be classified according to the type of electrolyte they use, and include alkali fuel cells (AFCs), molten carbonate fuel cells (MCFCs), solid oxide fuel cells (SOFCs) and polymer electrolyte membrane fuel cells (PEMFCs) [7][8][9][10].

Table 1. Classification of fuel cells.

AFC	MCFC	SOFC	PEMFC	
Electrolyte	Aqueous solution of potassium hydroxide soaked in a matrix	Liquid solution of lithium, sodium and/or potassium carbonates, soaked in a matrix	Yttria stabilized zirconie	Solid organic polymer, poly-perfluorosulfonic acid

AFC	MCFC	SOFC	PEMFC	
Fuel	Pure H_2	H_2, CO, CH_4, other	H_2, CO, CH_4, other	Pure H_2
Charge carrier	OH^-	CO_3^{2-}	O^{2-}	H^+
Operating temperature	90–100 °C	600–700 °C	600–1000 °C	50–100 °C
Efficiency	60%	45–47%	35–43%	53–58%
Application	Military, Space	Electric utility, Large distributed generation	Auxiliary power, Electric utility, Large distributed generation	Backup power, Portable power, Small distributed generation, Transportation

In particular, PEMFCs have been studied intensively due to their high energy efficiency (even at low temperature) and the numerous applications they have proven suitable for, such as electric vehicles and portable devices (**Figure 1**a). Among the various components that constitute PEMFCs, polymer electrolyte membranes (PEMs) that provide a pathway for proton transport and prevent the permeation of the supplied fuels and electrons are regarded as the key component [11]. It is well known that protons can be transported from the anode to the cathode through the interconnected ionic clusters formed by phase separation between hydrophilic–hydrophobic domains in PEMs [12][13]. Therefore, the polymers used in PEMs should have hydrophobic segments that can maintain the membrane stability and hydrophilic segments containing fixed anionic groups that can transport protons [14]. Due to the high selectivity of PEMs regarding the target molecules, the possible wide application of PEMs as solid or gel-type electrolytes in various energy conversion and storage devices such as solar cells and secondary battery systems have also been recently studied [15][16][17][18][19][20][21][22]. In addition, considerable experimental and theoretical studies have also been performed to elucidate the effective diffusivity for the target molecules in PEMs used in such energy devices [23][24].

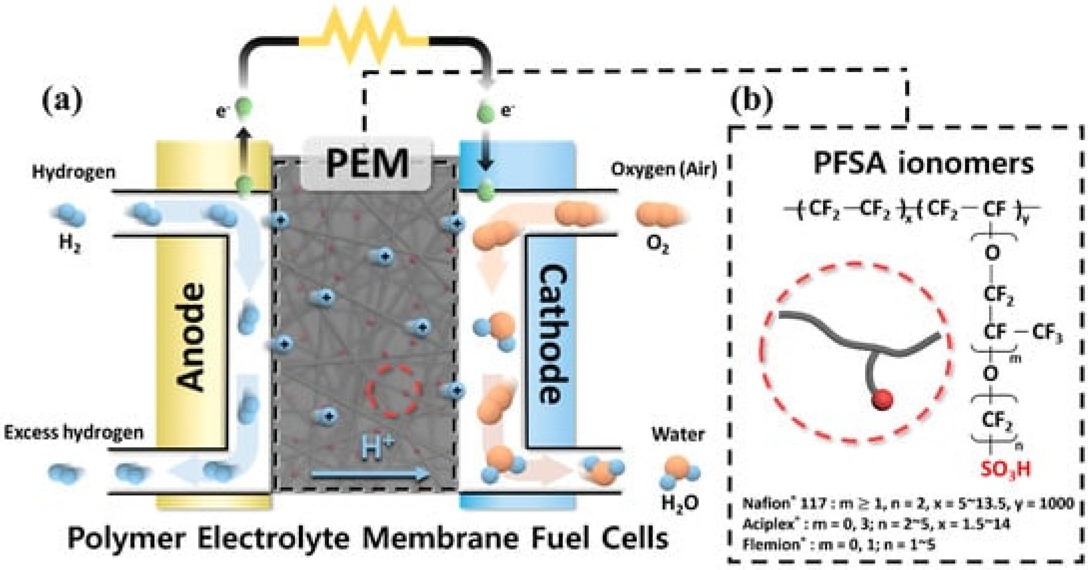


Figure 1. (**a**) Schematic diagram of polymer electrolyte membrane fuel cells. (**b**) Chemical structures of perfluorosulfonic acid ionomers.

After decades of research, perfluorosulfonic acid (PFSA) ionomer-based PEMs such as Nafion®, Aciplex® and Flemion® have been developed and applied in commercialized PEMFC vehicle systems including the Toyota Mirai (2015), the Honda Clarity (2016) and the Hyundai Nexo (2018) [25]. This is because the PFSA ionomers, shown in **Figure 1**b, are composed of a hydrophobic perfluoro backbone and the flexible hydrophilic side chains containing sulfonic acid groups, the interconnected ionic clusters formed by the phase separation between the hydrophobic and hydrophilic domains are well developed (**Figure 2**). Therefore, the PFSA ionomer-based PEMs can maintain high proton conductivity despite their low ion exchange capacity (IEC) and reveal outstanding physical stability even under highly humidified operating conditions. In addition, since the PFSA ionomers are mainly composed of C-F bond having a strong bonding energy (485 kJ/mol at 273 K), the corresponding PEMs exhibit outstanding chemical stability under the harsh operating conditions of PEMFCs [26][27]. Nevertheless, the use of PFSA ionomer-based PEMs still has inherent drawbacks, which include limited operating temperatures due to their low glass transition temperature, expensive manufacturing costs due to the complicated synthetic process and environmental problems caused by production of toxic pollutants (e.g., HF) during the disposal process [28]. These drawbacks have prompted the development of alternative PEMs via different strategies which have included modifying the PFSA-ionomer structure, introducing inorganic/organic composite materials and developing sulfonated hydrocarbon-based polymers [11][29][30].

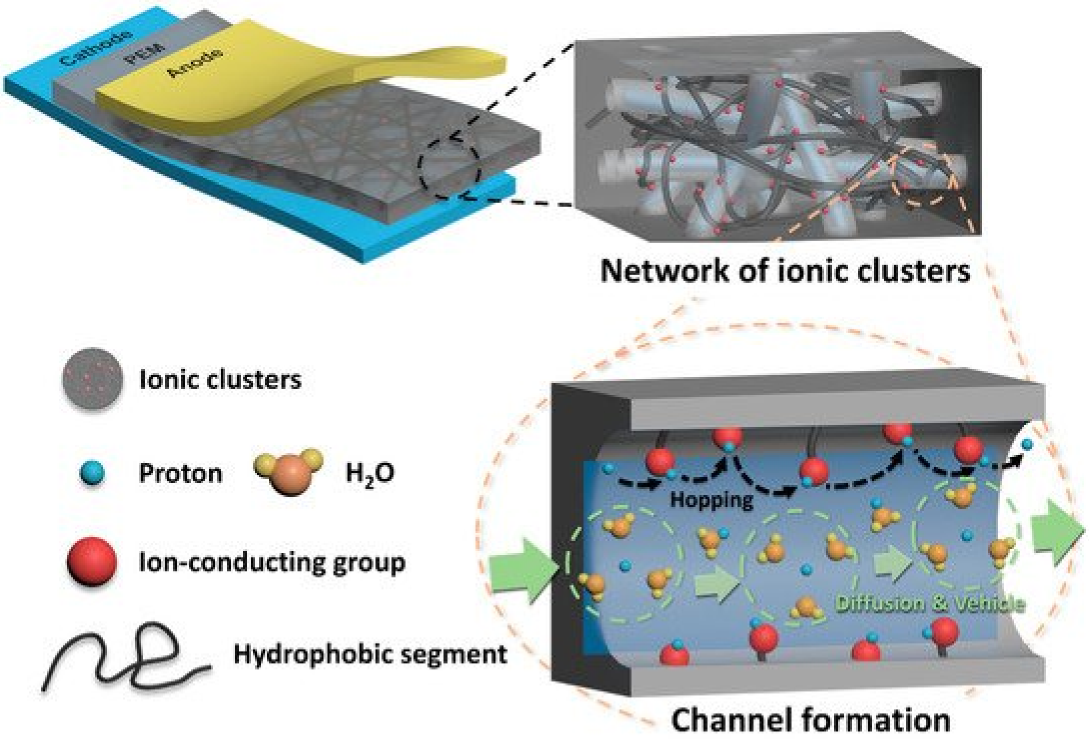
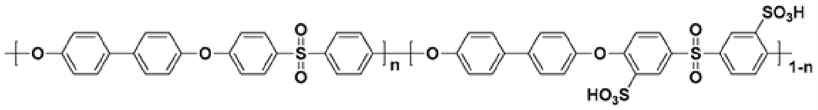
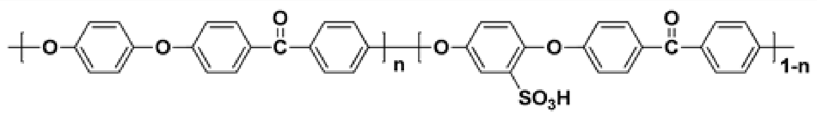
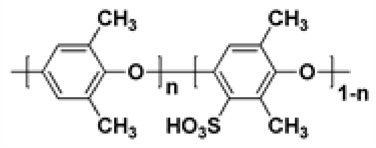
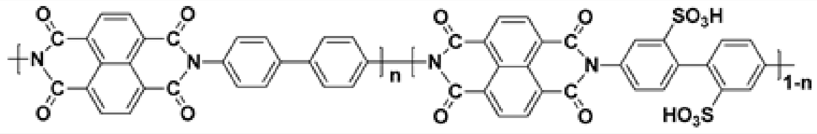


Figure 2. Schematic diagram of ionic clusters formed in polymer electrolyte membranes.

The sulfonated hydrocarbon polymers (SHPs) have been intensively studied due to their outstanding thermal stability, high mechanical strength as well as low fuel cross-over [31][32][33][34]. In addition, it is possible to develop PEMs at low cost due to the relatively convenient synthetic process compared to that of the PFSA ionomers. Moreover, various types of SHPs with different IECs can be obtained by incorporating diverse monomers and/or by post-modification of intermediates [35][36][37]. Representative SHP structures including sulfonated poly(arylene ether sulfone) (SPAES) [38][39][40][41][42][43], sulfonated poly(ether ether ketone) (SPEEK) [44][45], sulfonated poly(phenylene oxide) (SPPO) and sulfonated polyimide (SPI) [46][47] are shown in **Table 2**. Although PEMs with these polymers have been studied as alternatives to the PFSA ionomer-based PEMs due to the advantages described, the proton conductivity of the SHP-based PEMs is generally lower than that of the PFSA ionomer-based PEMs, because the interconnected hydrophilic channels are not as well developed as PFSA ionomer-based PEMs [48]. Typically, SHPs having a high degree of sulfonation (DS) can form large hydrophilic domains, resulting in high proton conductivity. However, when the DS of SHPs is high enough to reach a comparable proton conductivity as that of PFSA ionomer-based PEMs, they do not maintain the necessary high physicochemical stability for PEMFC operation [30][49][50]. To improve the proton conductivity of SHP-based PEMs without the deterioration in physicochemical stability, structural engineering of the SHPs has been conducted to form distinct phase-separated structures of the hydrophilic and hydrophobic domains, similar to those of PFSA ionomers [51][52][53]. It is generally known that control of hydrophilic and hydrophobic segments within SHPs can be achieved by the preparation of block, graft/comb-shaped and densely sulfonated copolymers [54][55][56]. Therefore, this study reports on recent research trends related to the development of SHP-based PEMs showing high performances in PEMFCs by pursuing rational design strategies for the copolymer architectures.

Table 2. Representative structures of sulfonated hydrocarbon polymers used in polymer electrolyte membrane fuel cells.

Polymer	Structure
SPAES[a]	
SPEEK[b]	
SPPO[c]	
SPI[d]	

[a] sulfonated poly(arylene ether sulfone); [b] sulfonated poly(ether ether ketone); [c] sulfonated poly(phenylene oxide); [d] sulfonated polyimide.

2. Structural Engineering of Sulfonated Hydrocarbon Polymers for PEMFC Applications

2.1. Block Copolymer-Based PEMs

In general, sulfonated hydrocarbon polymers synthesized via the nucleophilic aromatic substitution reaction between dihalo monomers with or without sulfonic acid groups and difunctional monomers with nucleophiles (e.g., dihydroxy and dithiol) are composed of randomly distributed hydrophilic and hydrophobic moieties due to the random distribution of hydrophilic sulfonic acid groups (**Figure 3**). Therefore, the PEMs prepared by random copolymers usually exhibit lower proton conductivity compared to the PFSA-based PEMs, especially at low relative humidity (% RH) conditions, due to the low hydrophilic/hydrophobic phase separation behavior which forms the small ion-conducting channels [57][58]. Therefore, structural engineering of SHP-based polymer beginning with the synthetic process is highly required to control the nano-phase structures of the resulting PEMs.

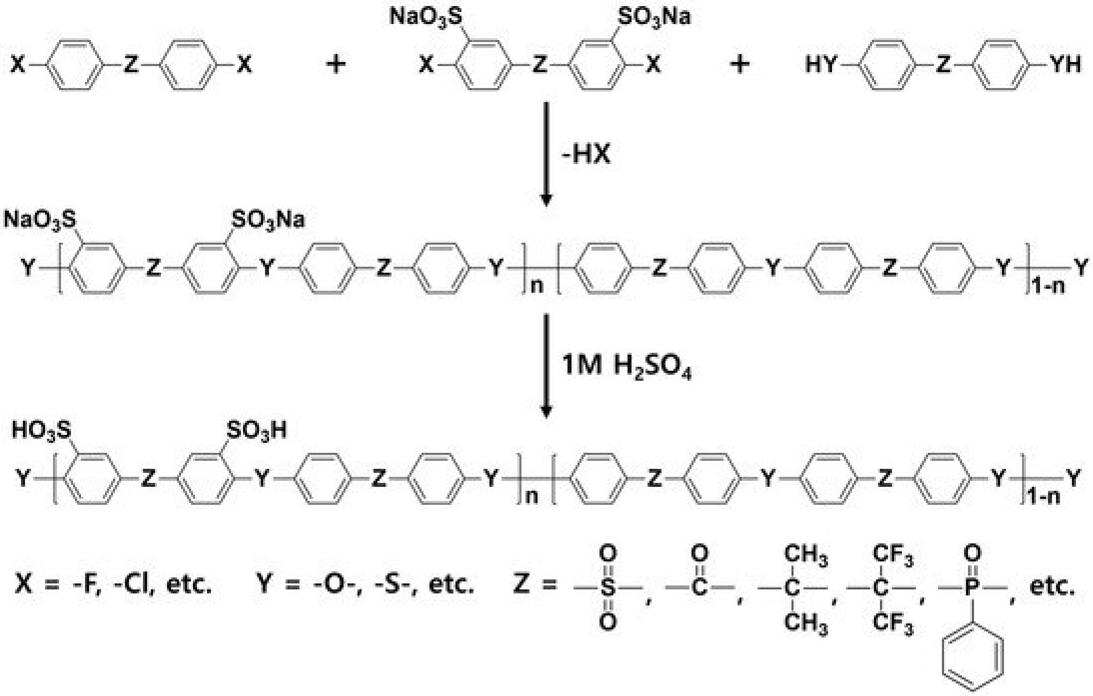


Figure 3. Synthetic procedures of sulfonated hydrocarbon-based random copolymers.

It is well known that block copolymers synthesized by assembling the hydrophilic and hydrophobic oligomers forming di-block, tri-block and multi-blocks can effectively control the nano-phase structure and facilitate the distinct phase separation characteristics of the hydrophilic/hydrophobic moieties [59][60][61][62]. Therefore, the block copolymer-based PEMs are able to exhibit outstanding proton conductivity even under low RH conditions and greatly reduce the conductivity dependence on temperature and humidity changes. In addition, due to the well-defined phase-separated structure, the dimensional and chemical stabilities of the block copolymer-based PEMs can be improved compared to those of the random copolymer-based PEMs having similar ion exchange capacities (IECs).

Representatively, Michael D. Guiver et al. reported development of a PEM with ‘ABA’ type tri-block copolymer (SP3O-*b*-PAES-*b*-SP3O) composed of sulfonated poly(2,6-diphenyl-1,4-phenylene oxide)s (SP3O) as a hydrophilic ‘A’ block and poly(arylene ether sulfone) (PAES) as a hydrophobic ‘B’ block (**Figure 4**a) [63]. Although the IEC value (0.97 meq g^{-1}) of the SP3O-*b*-PAES-*b*-SP3O membrane was found to be smaller than those of other reported hydrocarbon-based PEMs, showing the values from 1.50 to 2.34 meq g^{-1}, the size of the ionic clusters observed by atomic force microscopy (AFM) and transmission electron microscopy (TEM) were 15 nm and 5–10 nm, respectively, and these are comparable to or larger than those of Nafion® 112. Therefore, the proton conductivities of the SP3O-*b*-PAES-*b*-SP3O membrane are comparable to those of Nafion® 112 under low humidity conditions from 30 to 50% RH.

James E. McGrath et al. developed multi-block copolymers using phenoxide-terminated sulfonated poly(arylene ether sulfone) (BPS100) with different chain lengths as the hydrophilic oligomers and poly(arylene ether sulfone) (BPS0) with different chain lengths as the hydrophobic. Two different types of block copolymers were prepared by incorporating different types of perfluoroaryl chain extenders such as hexafluorobenzene (HFB) and decafluorobiphenyl (DFBP), as shown in **Figure 4**b [64]. The resulting multi-block copolymer-based membranes revealed well-defined ion-conducting channels with distinct phase separation between hydrophilic and hydrophobic domains. In addition, the membrane properties including ion conductivity could be adjusted by changing the hydrophilic/hydrophobic block length (e.g., 5k–5k, 10k–10k, 15k–15k, etc.) [65][66]. Furthermore, it was noted that membranes formed using DFBP as the chain extender, BPS100-BPS0-DFBP, showed a more distinct phase-separated structure than with HFB as the chain extender (BPS100-BPS0-HFB). This occurs due to the higher content of fluorine moieties in DFBP, which increases the hydrophobicity of the BPS0 oligomers and the acidity of sulfonic acid groups in the hydrophilic BPS100. This observation indicates that the molecular structure of the chain extender affects the properties of the resulting multi-block copolymer-based PEMs.

The incorporation of highly reactive reagents such as HFB and DFBP as chain extenders can efficiently increase the molecular weight of block copolymer by increasing the reaction rate of hydrophilic and hydrophobic segments. However, the structure of the resulting block copolymer is usually random multiblock copolymers due to the same telechelic functionality of the hydrophilic and hydrophobic oligomers. Recently, Byungchan Bae et al. reported detailed synthetic strategies for the development of alternating multi-block copolymer with high-molecular weight by using hydrophilic and hydrophobic segments with different telechelic functional groups. A transparent and flexible PEM with IEC value of 2.9 meq g^{-1} could be obtained using this alternating multi-block copolymer (X10-Y10), as shown in **Figure 4**c [67]. Interestingly, the proton conductivity of this block copolymer PEM is four times higher than that of PFSA ionomer-based PEMs such as Nafion® and Aquivion® at 80 °C and RH 90%. As well, the conductivity is also comparable to that of the PFSA ionomer-based PEMs even under low RH conditions (≤50%). The distinct phase-separated structure confirmed by TEM as well as the large IEC value of the alternating multi-block copolymer membrane could support its outstanding proton conductivity.

A multi-block copolymer incorporating polyimide (PI) moieties into the main chain was developed by James E. McGrath et al. (**Figure 4**d) [68]. As PI is vulnerable to acidic conditions, a modified PI was adopted to improve the hydrolysis resistance of the PI-based PEMs under fuel cell operating conditions. Multi-block copolymers, utilizing sulfonated poly(arylene ether sulfone)-*b*-polyimide (BPSH-*x*-PI-*x*, where *x* indicated the chain length of the hydrophilic and hydrophobic oligomers, respectively), were synthesized via imidization using hydrophilic BPSH oligomers with amine functional end groups and hydrophobic PI oligomers with anhydride end groups. The experimental IEC of the BPSH-*x*-PI-*x* membrane was found to diminish as the chain lengths of the hydrophilic and hydrophobic moieties increased, although all IEC values showed a similar range from 1.22 to 1.65 (meq g^{-1}). AFM analysis of the BPSH-*x*-PI-*x* membranes indicated that the connectivity and size of the ion-conducting channels were better formed as the chain length of each block increased. Accordingly, water uptake of the membranes increased as the length of each block increased, but it decreased sharply when hydrophilic/hydrophobic chain lengths were each over 20 k (i.e., BPSH-*20*-PI-*20*) due to the enhanced phase separation as well as entanglement between intermolecular chains. In terms of proton conductivity, the BPSH-*15*-PI-*15* membrane possessed moderate ion-conducting channels, and the largest water absorption behavior exhibited the largest conductivity values among the samples and these values were larger than those of Nafion® 112 at 80 °C. Based on these results, it can be concluded that optimizing chain lengths of the hydrophilic/hydrophobic blocks can effectively engineer the ion-conducting channels and thereby control membrane properties [65][69]. Due to the outstanding proton conductivity of the block copolymer-based PEMs by constructing the well-defined phase-separated structures, the MEAs prepared with these PEMs have been tried to apply in fuel cell vehicles operating at low RH conditions. The PEM properties of the above-described block copolymer-based PEMs including IEC, water uptake and proton conductivity are summarized in **Table 3**.

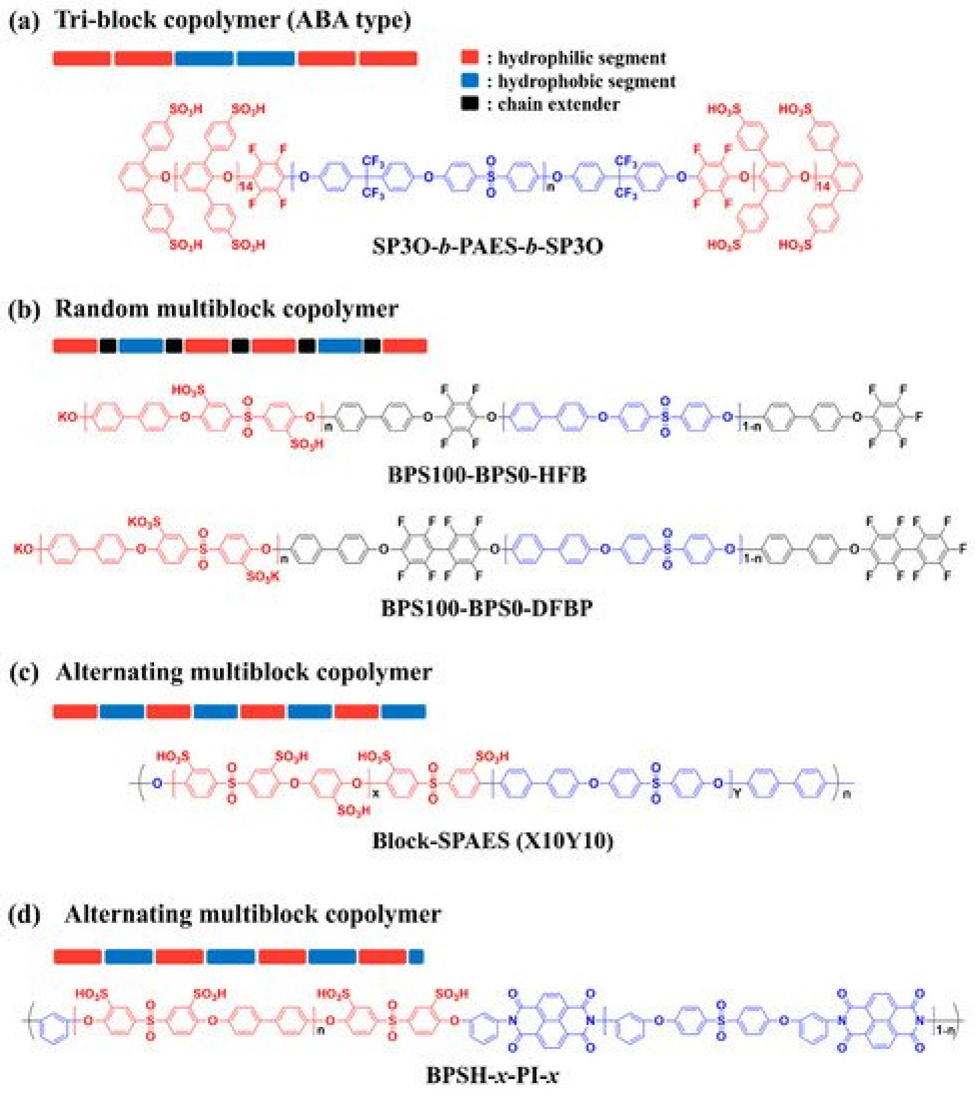


Figure 4. Representative chemical structures of sulfonated hydrocarbon-based block copolymers [63][64][67][68].

Table 3. Properties of block copolymer-based polymer electrolyte membranes.

Sample		IEC (meq g^{-1})	Water Uptake		Proton Conductivity		References
			Value (%)	Conditions (°C, % RH)	Value (mS cm^{-1})	Conditions (°C, % RH)	
SP3O-*b*-PAES-*b*-SP3O	X100	0.97	47.4	20, 100	9	90, 30	[63]
SPAE100-BPS0-HFB	5k–5k	1.30	35	rt, 100	50	30, 100	[64]

Sample		IEC (meq g^{-1})	Water Uptake		Proton Conductivity		References
			Value (%)	Conditions (°C, % RH)	Value (mS cm^{-1})	Conditions (°C, % RH)	
	10k–10k	1.38	68		100		
	15k–15k	1.40	79		110		
SPAE100-BPS0-DFBP	10k–5k	1.83	100		160		
	15k–10k	1.71	90		140		
Block-SPAES	X10Y10	2.90	390	rt, 100	480	80, 90	[67]
BPSH-*x*-PI-*x*	5–5	1.65	59	rt, 100	80	30, 100	[68]
	15–15	1.55	85		100		
	20–20	1.22	57		100		

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