single entity, without relying entirely on hydrogen bonds [43]. During this process, the proton and its associated water molecules move together, while unbound water molecules diffuse in the opposite direction. This results in a concentration gradient across the membrane, which facilitates the diffusion of both hydrated hydrogen ions and water molecules. For proton transport via the vehicle mechanism, the membrane's microstructure must contain continuous clusters of hydrated ions to provide pathways. However, under low-water-content conditions, the insufficient quantity and connectivity of these ion clusters hinder continuous proton transport, significantly reducing proton conductivity [44].

Proton transport is a complex process, typically occurring through both hopping and vehicle mechanisms. To enhance proton transport, three main approaches can be taken: increasing water content, optimizing proton transport channels, and increasing the number of proton carriers. Although increasing water content may appear to be the simplest method, doing so indiscriminately can lead to fragmented hydrophobic domains and decreased continuity of hydrophilic domains. This limitation not only reduces the extent of improvement but also compromises the mechanical stability of the membrane. Consequently, optimizing proton transport channels and increasing the number of proton carriers are more practical strategies.

i) **Optimizing Proton Transport Channels**: Improving proton transport channels can enhance the utilization of acid–water interactions, thereby increasing proton conductivity while maintaining appropriate water content [45]. Broadly speaking, proton transport channels refer to hydrophilic domains formed by acidic groups in the polymer chains. Under hydration, these acidic groups dissociate, generating proton carriers that migrate with the aid of hydrodynamic forces. In fact, proton transport channels can take various forms. When certain segments of a polymer's main chain, side chain, or functional groups exhibit differing hydrophilic and hydrophobic properties, microphase separation can occur, creating nanoscale interpenetrating regions [46, 47].

    However, traditional PEM materials like perfluorosulfonic acids or sulfonated hydrocarbon polymers tend to form "dead zones" that interrupt channel continuity, impeding smooth proton migration. Adding fillers—such as nanofibers, nanotubes, graphene, or metal-organic frameworks (MOFs)—can help eliminate these dead zones, transforming the convoluted channels into streamlined highways for proton transport.

    For example, Li et al. [48] developed bio-inspired caterpillar-like alumina fibers loaded with amine groups. These composite fibers were incorporated into sulfonated poly(ether sulfone) (SPES) to create a PEM that can achieve a proton conductivity of 0.263 S/cm at 80 °C and 100% relative humidity (RH), while also improving methanol permeability, thermal stability, and swelling resistance. Liu et al. [49] achieved similar results by synthesizing a ferricyanide coordination polymer that formed a proton-conducting paramagnetic composite with phosphotungstic acid. By applying a magnetic field during the polymer casting process, they aligned the proton transport channels vertically, overcoming phosphotungstic acid loss. This design, supported by redox cycling of cyanide, produced a PEM with a maximum power density of 1107 mW/cm^2 and exceptional durability.

ii) **Increasing Proton Carriers**: Adding more proton carriers is another effective way to improve proton conductivity. Proton carriers generally fall into three categories: acidic, basic, and acid–base pair carriers. Acidic carriers, the earliest developed proton carriers, offer relatively high proton conductivity (10^{-2}–10^{-1} S/cm). They use acidic functional groups like $-SO_3H$ or $-PO_3H_2$ to donate protons, thereby facilitating proton transport. However, excessive acidic groups can lead to excessive water absorption and swelling, which reduces acid concentration and dimensional stability, ultimately affecting the overall performance of the membrane [50]. Basic carriers, on the other hand, act as proton acceptors (e.g. $-NH_2$ or $-NH^-$), initially capturing free H^+ ions to form $-NH_3^+$. These then form intermediates such as $-NH_3^+ \ldots OH^- \ldots H^+$, allowing H^+ ions to dissociate and transfer. Although basic carriers can transport protons, the strong electrostatic interactions between the basic groups and H^+ ions make proton dissociation more difficult, resulting in proton conductivities of less than 10^{-2} S/cm [51].

In contrast, acid–base pair carriers, a newer class of proton carriers, contain both acidic and basic groups. The electrostatic interactions between these groups facilitate proton hopping from acidic donor sites to basic acceptor sites. The electrostatic pairing also lowers the energy barrier for proton migration, thereby accelerating the process [52]. For instance, Sun et al. [53] synthesized double-shelled nanotubes with a carboxylate inner shell and an imidazole outer shell, which were then incorporated into sulfonated poly(ether ether ketone) (SPEEK) membranes. The imidazole outer shell formed acid–base pairs with both the inner shell and the SPEEK matrix, significantly enhancing proton hopping. The resulting membrane exhibited a proton conductivity of 0.336 S/cm at 80 °C and 100% RH, twice that of the original SPEEK membrane.

Similarly, Chen's team [54] combined sulfonic acid–functionalized graphitic carbon nitride nanosheets with sulfonated aromatic polymers. The acid–base pairs between the nanosheets and the matrix promoted sulfonate group dissociation and hydrogen-bond network formation. This "zipper-like" interface interaction induced phase separation and created long-range ionic pathways, resulting in excellent fuel cell performance of 717 mW/cm at 80 °C and 100% RH. Qu et al. [55] developed an acid–base composite membrane made from a carboxyl-containing polyimide and a basic polybenzimidazole for high-temperature PEM applications. Through electrostatic interactions and a continuous hydrogen-bond network, this membrane exhibited improved proton conductivity and enhanced phosphoric acid retention.

1.2.3.2 Classification of PEM

PEMs are a critical component of PEMFCs, directly determining the fuel cell performance. Consequently, PEMs must meet the following criteria [56, 57]:

1) High proton conductivity without electron conduction.
2) Excellent mechanical strength and dimensional stability, maintaining integrity under operational conditions.
3) Outstanding chemical and thermal stability, resisting degradation in harsh environments.
4) Low fuel crossover, effectively blocking reactants.
5) Low cost.

PEMs can be broadly categorized into homogeneous membranes and composite membranes based on their composition.

i) **Homogeneous Membranes**: Homogeneous membranes consist of a single type of material and can be further divided into fully fluorinated, partially fluorinated, and nonfluorinated membranes based on their polymer fluorine content. Nafion, the most common fully fluorinated sulfonic acid membrane, has a structure as shown in Figure 1.6a. Its hydrophobic PTFE backbone provides mechanical strength, while the hydrophilic side chains, terminated with sulfonic acid groups, offer proton transport sites. The distinct hydrophilic–hydrophobic nature of its main and side chains leads to phase separation in the microstructure, forming proton transport channels approximately 5–10 nm in diameter. High sulfonic acid group content endows Nafion with excellent proton conductivity, exceeding 100 mS/cm at 80 °C [59]. Thanks to its PTFE backbone, Nafion also boasts good mechanical, chemical, and thermal stability. However, Nafion's performance is highly sensitive to temperature and water content. Its low glass transition temperature limits its operating temperature to

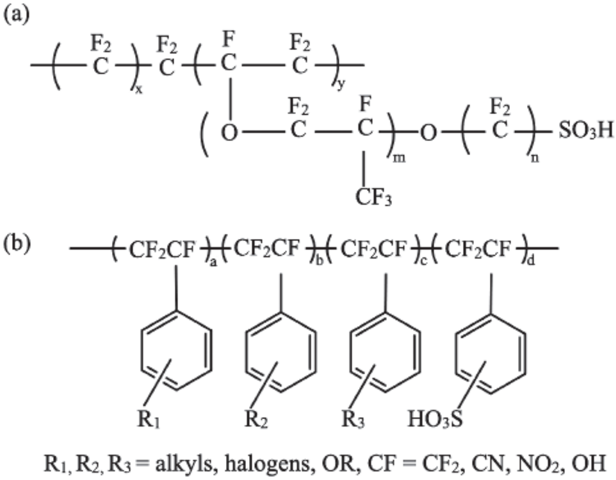

Figure 1.6 Structural formula of (a) Nafion and (b) BAM-3G. Source: Adapted from Basura et al. [58].

below 80 °C, and its proton conductivity drops significantly under low-humidity conditions due to reduced phase separation. Additionally, its high cost and significant fuel crossover impede further application [60–62].

To lower costs and simplify fabrication, researchers have increasingly turned to non-perfluorinated sulfonic acid PEMs. Partially fluorinated sulfonic acid PEMs are one example. These materials are similar to fully fluorinated membranes, with PTFE or polyvinylidene fluoride (PVDF) backbones and non-fluorinated aromatic groups in the side chains. For instance, the BAM-3G series PEMs from Canada's Ballard Power Systems are synthesized by copolymerizing substituted trifluorostyrenes and sulfonated trifluorostyrenes, as shown in Figure 1.6b. These membranes feature low sulfonic acid content, high efficiency, and extended lifetimes (up to 15,000 hours for single cells) at a fraction of Nafion's cost, making them more accessible [58].

Another major category of homogeneous membranes is non-fluorinated sulfonic acid PEMs, which mainly include sulfonated aromatic polymers such as SPEEK, SPES, sulfonated polyimides, and sulfonated polybenzimidazoles [63–66]. Compared to aliphatic polymers, these polymers contain a higher proportion of rigid aromatic groups in their molecular backbones, providing the membranes with good mechanical properties and thermal stability. They can easily be sulfonated to introduce sulfonic acid groups, are derived from widely available materials, and have relatively simple preparation methods. Moreover, the absence of costly fluorination steps significantly reduces their production costs. However, due to shorter side chains, less-pronounced phase separation, and a lower sulfonic acid group content compared to perfluorosulfonic acid membranes, nonfluorinated sulfonic acid PEMs generally exhibit lower proton conductivity [67]. Additionally, they tend to have high humidity requirements and limited durability, which remain challenges to overcome.

ii) **Composite Membranes**: Whether fully fluorinated, partially fluorinated, or nonfluorinated sulfonic acid membranes, each type has its own strengths and weaknesses, making it difficult to find a homogeneous PEM that excels in all aspects. Modifying a homogeneous PEM—such as by incorporating fillers—can produce composite membranes that address these limitations. Composite membranes offer unique advantages over homogeneous membranes, including the ability to integrate the benefits of the fillers and to tailor performance improvements for specific needs. Depending on the nature of the filler, modification methods can be categorized as either organic–inorganic or organic–organic approaches.

a) **Organic–Inorganic Modification**: Introducing inorganic components can effectively enhance proton conductivity, particularly for sulfonated polymers under low-humidity conditions. Common inorganic fillers include silica [68], heteropoly acids [69], carbon materials [34], and MOFs [70]. These fillers can improve water retention, dimensional stability, mechanical strength, and methanol permeability to varying degrees. Inorganic fillers can be introduced by methods such as doping, sol-gel processes, or in situ synthesis.

For example, Yan et al. [71] prepared sulfonated mesoporous silica frameworks with controlled channel sizes of approximately 0.5 nm, slightly larger than the diameter of H_3O+ ions (0.28 nm) and slightly smaller than methanol molecules (0.4 nm). These molecular sieve-like membranes, when combined with Nafion, showed methanol permeability three orders of magnitude lower than Nafion. Pei et al. [72] introduced CeO_2-based core–shell micro/nanostructures rich in tourmaline into perfluorosulfonic resin, resulting in a composite membrane with excellent proton conductivity and chemical stability. At 80 °C and 100% RH, the composite membrane achieved a maximum power density of 1006 mW/cm^2, higher than Nafion's 906 mW/cm^2 under the same conditions. Additionally, CeO_2 helps scavenge hydroxyl radicals, slowing degradation and improving the membrane's durability.

b) **Organic–Organic Modification**: Organic modifications involve incorporating functional organic materials into the polymer matrix. This approach can compensate for the inherent shortcomings of the polymer matrix while selectively enhancing specific properties. Organic fillers can be divided into small organic molecules and macromolecular organic substances [73–75].

Small organic molecules include covalent-organic frameworks, hydrogen-bonded organic frameworks, and ionic liquids (ILs), while macromolecular organic fillers include PVDF, polyvinyl alcohol, and sulfonated polymers. These fillers interact with the polymer matrix through various mechanisms, supplementing missing functions and enhancing existing performance. For instance, Sun's group [41] hydrogen-bonded Nafion with polyvinyl alcohol and then post-modified it with 4-carboxybenzaldehyde to produce a repairable PEM. This PEM demonstrated superior mechanical stability (with a tensile strength of 20.3 MPa and strain of 380%), improved proton conductivity (0.11 S/cm at 80 °C, 1.2 times that of Nafion), and resistance to methanol permeation. Under methanol fuel cell conditions, the membrane could self-heal mechanical damage up to tens of microns in size.

Zhao and co-workers [76] embedded Nafion nanofibers into a polybenzimidazole matrix to create a Nafion/polybenzimidazole composite membrane. The polybenzimidazole provided high ion selectivity, while the fibrous Nafion ensured high proton conductivity and low cost. Compared to Nafion 212, the composite membrane, with only 40 wt% Nafion, exhibited a 58-fold reduction in vanadium crossover and achieved 99.8% coulombic efficiency and 80.0% energy efficiency at a high current density of 210 mA/cm^2 in vanadium redox flow batteries.

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