Phenolphthalein-Based Cardo Poly(arylene ether sulfone): Preparation and Application to Separation Membranes

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ABSTRACT: Cardo poly(arylene ether sulfone)s are an important type of high performance engineering thermoplastics. They possess unique properties, including good processability, thermal stability, and good insulating and mechanical properties as well as excellent chemical resistance. They are potential candidates for the preparation of ion exchange, water purification, and gas separation membranes. This review focuses on the synthesis of phenolphthalein-based cardo poly(arylene ether sulfone)s, including synthesis of cardo bisphenols and their polymers, and their application to separation membranes. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 1–12, 2013
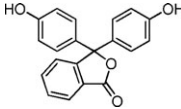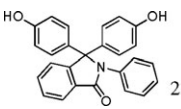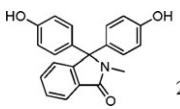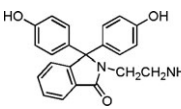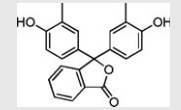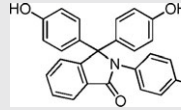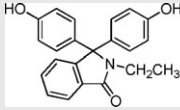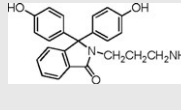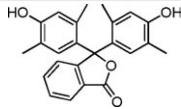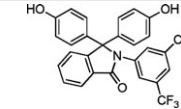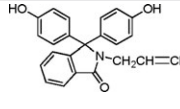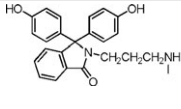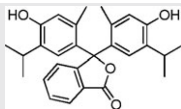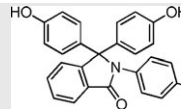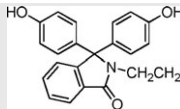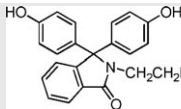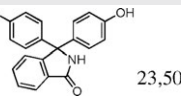
INTRODUCTION

Cardo polymers contain cyclic side groups in repeating units. Such polymers are named after the Latin word "cardo," which means loop, since the pendant cyclic groups can be considered to be loops of the backbone of the polymers.[1] Compared with conventional polymers, cardo polymers possess better thermal stability (high T_g) and mechanical properties as well as solubility in polar solvents, which are important for rigid aromatic polymers. Many polymers with cardo groups have been synthesized, including polyarylates,[2–4] polycarbonates,[5,6] polyimides,[7–9] polyamides,[8,10] poly(arylene ether sulfone)s (PESs),[11–26] poly(arylene ether ketone)s,[11,27] and poly ether oxadiazoles,[28] among others. Of these, cardo PES is of great interest since this is one of the most popular families of high performance engineering thermoplastics. In addition to being flame retardant, PES has many attractive properties, including relatively low cost and good processability, chemical resistance, thermal stability, and good insulating and mechanical properties. Some PESs are commercially available, such as Polysulfone Udel®, Polyethersulfone Victrex®, and cardo polyethersulfone (PES-C). PESs are used in a variety of fields, as adhesives, coatings, fibers, composite matrices, moldings and membranes. Separation membranes function as a selective barrier between two adjacent fractions, regulating the transport of substances between the two sides of the membrane.[29] Membrane separation technology is considered one of the most promising new technologies, and is a high efficiency and low energy consumption process. Separation membranes are divided into three categories: ion exchange membranes (for fuel cells, lithium batteries, etc.), gas separation membranes and membranes for water purification.

Various kinds of cardo groups have been introduced into poly(arylene ether)s, such as phenolphthalein and its derivatives,[12–19,27] 9,9-diarylfluorene,[30,31] cyclohexane,[32] xanthene,[33] decahydronaphthalene,[34] spirodilactam,[35] and so on. Their synthetic methods and basic properties are reported, such as enhanced solubilities, glass transition temperatures, and mechanical properties. These polymers are seldom made into functional materials and applied to specific fields. This is probably due to the difficult preparation of cardo monomers and lack of suitable functionalization methods for these cardo polymers. In recent years, fluorene-based cardo functional polymers have been prepared by several groups and they mostly focus on ion exchange membranes for fuel cells as the main applications.[36–44] Recently, Miyatake et al. reviewed fluorene-containi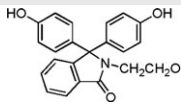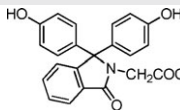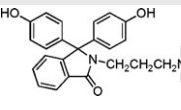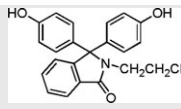ng polymers as ion conductive membranes for fuel cells.[30] There are many advantages of functionalized fluorene-based cardo polymers and they exhibit excellent properties as ion exchange membranes for fuel cells. But the methods to functionalizing the fluorene-based polymers are only limited to sulfonation[30,31,45] or chloromethylation[46–48] on the benzene rings, which are far from enough to satisfy various applications. Up to now, phenolphthalein-based cardo polymers are most widely studied. One of the reasons is the cheap and easily available raw material phenolphthalein, which is a kind of industrial product. Phenolphthalein is a cardo bisphenol and contains a lactone

Table I. Phenolphthalein-Based Cardo Bisphenols

[a]numbers behind the monomer are references including the monomer.

group in its structure, which provides a reaction site to prepare various functional cardo bisphenols. Phenolphthalein-based cardo polymers have greater polarity and asymmetric structures than other cardo polymers, which result in different properties. Phenolphthalein-based polymers possess better solubility than polymers containing fluorene and anthrone groups, because the asymmetric structure leads to less crystallization.[1] This review focuses on monomer synthesis and polymer synthesis of phenolphthalein-based cardo PESs and potential applications to separation membranes.

Synthesis of Phenolphthalein-Based Cardo Monomers

PES is synthesized by polycondensation of bisphenol compounds and aromatic difluoro, dichloro, or dinitro compounds. To synthesize cardo PES, the cardo group is usually introduced as a bisphenol compound, because it is relatively easy to synthesize cardo bisphenol.[11,23,53,54] Phenolphthalein is a common pharmaceutical raw material and an important acid-base indicator in analytical chemistry. It is commercially available and easy to functionalize chemically. Many cardo bisphenols have been synthesized from phenolphthalein (Table I) in one of two routes. A one-step route of synthesis is shown in Scheme 1 where phenolphthalein reacts with a primary amine directly under a N_2 atmosphere at room temperature (or elevated tem-

perature, depending on the activity of the amine).[15,23,53] The primary amine could be an aliphatic amine[12,19,50] or an aromatic amine,[49,52] as well as aqueous ammonia.[53] The reaction proceeds by a condensation reaction to form the desired phthalimidine bisphenol. An excess of amine is used (to saturate the reaction in the forward direction), and solvent is not usually needed. If the amine is a liquid, it is the reactant as well as solvent; if not, the reaction is performed in the melt state. To accelerate the reaction, an acid catalyst could be used. A common catalyst is the preformed hydrochloride salt of the corresponding amine. A higher reaction temperature can also facilitate the reaction. For example, consider the reaction of phenolphthalein and aqueous amine. At room temperature, it takes 20 days for the purple solution to change into a colorless solution, which indicates the complete consumption of phenolphthalein.[53] At 120°C in an autoclave, the solution will turn colorless in 12 h. Although a higher reaction temperature accelerates the consumption of phenolphthalein, it can also lead to more impurities[55]; therefore, the temperature and time of the reaction must be controlled.

A multistep route of synthesis is shown in Scheme 2. First, phenolphthalein is reduced to its acid form (dihydrophenolphthalein) by zinc dust in boiling NaOH solution, which makes it
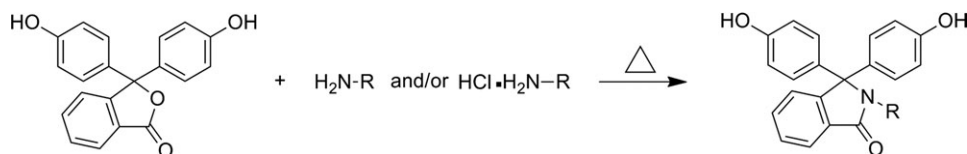
Scheme 1. One-step route synthesis of cardo bisphenols from phenolphthalein.

easier to be activated and form the amide. The carboxyl group of the dihydrophenolphthalein is next activated by N-hydroxysuccinimide (NHS) and dicyclohexylcarbodiimide (DCC) to form the activated ester, which reacts directly with the amine to form the amide, which is then oxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to form the desired bisphenol.[51]

We modified some steps to simplify and optimize the multistep synthesis.[56] First, we used sodium borohydride instead of sodium hydroxide so the reduction reaction would proceed at room temperature and the time needed would be reduced from 96 h to only several hours. We simplified the next two steps (activation and amide formation) into one step with O-(7-Aza-benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HATU) as the condensation agent instead of NHS and DCC. The crude amide product is then used directly without further purification. Although this modified route contains multiple steps, each step is easy to perform. The reaction conditions are more moderate and all steps are performed at room temperature, a distinct advantage over the original synthesis in which high temperature is usually needed. In addition, the product of each step is easy to purify and the yield is high. In some situations, especially for aromatic amines or some special amines, the corresponding bisphenols cannot be synthesized by the one-step route or else the yield of product is low. Thus, the modified synthesis is a better choice in spite of the multiple steps involved.

Synthesis of Phenolphthalein-Based Cardo PES

Poly(arylene ether sulfone) can be synthesized by many routes,[57] including the Ullmann reaction, nickel catalyzed coupling, the Friedel-Crafts electrophilic substitution, and nucleophilic aromatic substitution which is the most widely used method. PES is commonly synthesized via nucleophilic aromatic substitution polycondensation of an activated dihalo or dinitro monomer

with a bisphenol in the presence of a base, which usually is potassium carbonate.[58] The activating group plays an important part in the aromatic substitution reaction because it stabilizes the negative charge that develops through formation of a Meisenheimer complex, which is the rate-determining step.[59] In addition, polar aprotic solvents also stabilize the Meisenheimer complex and are necessary to obtain a high molecular weight polymer. The synthesis of PES via an aromatic nucleophilic substitution reaction involves the reaction of stoichiometric quantities of the monomers and an excess of potassium carbonate in polar aprotic solvents such as N,N-dimethylacetamide (DMAc) or N-methylpyrrolidinone (NMP) at a concentration of about 20% g/mL solids (based on the weight of the monomers and volume of the solvent). Toluene is usually used to remove water formed during the early stage of reaction by azeotropic distillation, the toluene is then removed, and the polymerization reaction proceeds at high temperature under nitrogen for several hours (polymerization temperature and time depend upon the reactivity of the monomers) and the viscosity of the solution increases. Because of the high activity of the cardo bisphenol, cardo PES polymerization could be performed at a lower temperature and in a shorter time. If the difluoro monomer is used, the azeotropic distillation with toluene could be omitted and high molecular weight polymer could be obtained.[16]

Applications to Separation Membranes

Cardo PES is a type of high performance engineering thermoplastic, which is used in many fields. Cardo PES forms films, which means that it could be used as a material for separation membranes. Here, we describe how it could be used in three kinds of separation membranes: ion exchange (for fuel cells or lithium batteries), water purification and gas separation membranes.

Ion Exchange Membranes

With the increasing demand for energy, alternatives to fossil fuels are needed. Fuel cells are electrochemical devices that can
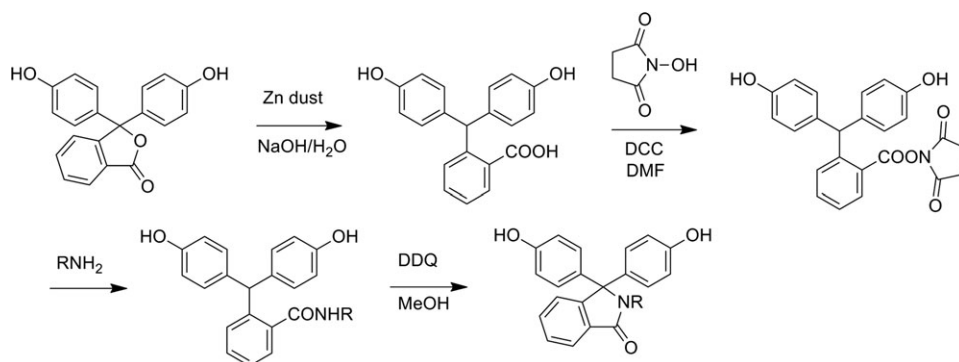
Scheme 2. Multi-step route synthesis of cardo bisphenols from phenolphthalein.
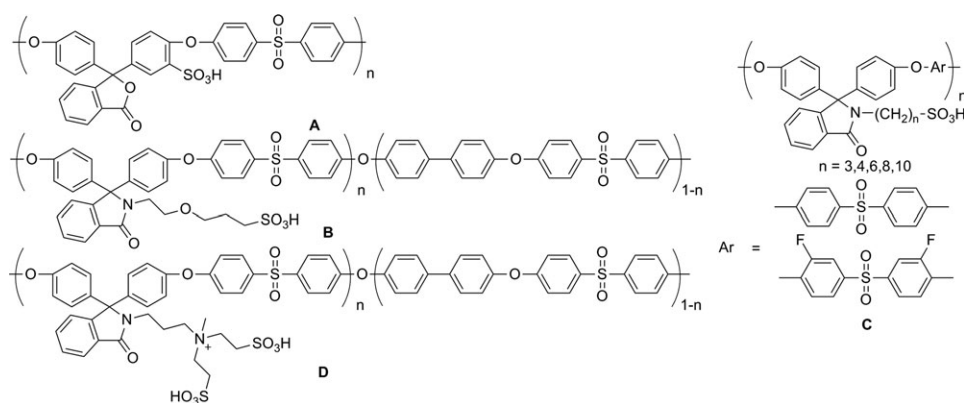
Scheme 3. Chemical structures of cardo PEMs.

convert chemical energy directly into electrical energy. Research activity in polymer electrolyte fuel cells (PEFCs) has increased because PEFCs provide an innovative alternative to current power sources and offer higher efficiencies, renewable fuels, and a lower environmental cost.[60] Automobile companies have announced that fuel cell powered vehicles will be available in the next 5–10 years, and they have already demonstrated some prototypes.[61] Polymer electrolyte membrane for PEFCs must exhibit transportation of ions (protons or hydroxide), act as an electrical insulator and a fuel barrier (oxygen, hydrogen, or methanol), while exhibiting good mechanical properties and stability (chemical, thermal, oxidative, and hydrolytic stability).[62] Depending upon the ions they transport, ion exchange membranes are either proton exchange membranes or hydroxide exchange membranes. Relatively more kinds of proton exchange membranes have been developed in the last few decades. Currently, the most common proton exchange membranes are perfluorosulfonic acid membranes (e.g., Nafion), first commercialized by DuPont, that have excellent proton conductivity, good mechanical and chemical properties, and long-term durability. Perfluorosulfonic acid membranes have some drawbacks, including high cost, low conductivity at elevated temperatures, and high fuel crossover.[63] Many aromatic hydrocarbon ionomers were developed in attempts to solve these problems. Various kinds of sulfonated aromatic hydrocarbons have been studied, including sulfonated poly(arylene ether sulfone)s,[39,64–70] poly(arylene ether ketone)s,[71–74] poly(arylene sulfide sulfone)s,[75–80] polyimides,[81–84] poly(arylene ether nitrile)s,[85,86] polybenzimidazoles,[87–90] and polyphenylenes.[91–95] Among these various materials, cardo PES is one of the most promising candidates for PEFC, because of its special chemical structure, easy functionality, and stability.

Cardo PES Proton Exchange Membranes
Proton exchange membranes (PEMs) are usually made of sulfonated polymers; although, there are other proton conducting groups, such as carboxyl groups[96] and phosphonic acid groups.[97–101] However, sulfonated polymers are the best materials for PEMs because of their strong acidity and ease of introduction of sulfonic acid groups. Li et al. reported the first phenolphthalein-based cardo PES PEM for use in direct methanol fuel cells in 2005.[25] The chemical structure of the sulfonated polymer SPES-C is shown in Scheme 3(A). Li et al. made the

main-chain type PEM by sulfonating commercial cardo PES (PES-C) with concentrated sulfuric acid. The degree of sulfonation (DS) can be controlled by the reaction time and temperature. SPES-C membranes with 70% DS were not water-soluble and had a low degree of swelling. Proton conductivity was 0.011 S/cm at 80°C, 0.0338 S/cm at 110°C, which was lower than that of the benchmark material Nafion 115 membranes under the same conditions. However, the methanol permeability of the SPES-C membrane was considerably lower than that of the Nafion 115 membrane.

Although some properties of the main-chain type sulfonated polymers are useful, their performance is not satisfactory for practical applications. These main-chain aromatic ionomers only achieve good conductivity at high ion exchange capacities (IECs), which causes an excessively high water uptake and a dramatic loss of mechanical properties. With lower IEC, SPES-C has lower water uptake and lower conductivity ($\sigma < 10^{-2}$ S cm^{-1}), which is not acceptable for use in fuel cell. Conversely, if the IEC is increased to obtain higher proton conductivity, the mechanical properties of the membrane deteriorate. Other attempts have been made to improve the performance of PEM instead of increasing IEC. Li et al. blended sulfonated cardo PES with other materials to improve the performance of PEM. Inorganic conductor phosphotungstic acid (PWA) powder, a kind of heteropoly acid, was blended with 70% DS SPES-C.[24] The proton conductivity of the composite membrane was 4.5×10^{-2} S cm^{-1} at 90°C and 6.7×10^{-2} S cm^{-1} at 110°C, which was a large increase compared with the virgin SPES-C. The PWA particles (50–80 nm) were homogeneously distributed within the SPES-C matrix and showed no aggregation, because of the specific interactions between SPES-C and PWA. The conductivity of the blended membrane was constant over 3 months, which means that the PWA particles are stable in the matrix and that the specific interactions decrease the leakage of the water-soluble particles. In another work, Gao et al. blended SPES-C with high DS SPEEK.[21] SPES-C has better mechanical properties and a lower swelling ratio but lower conductivity while high DS SPEEK has higher proton conductivity but swells excessively even dissolved in water at 70°C. Better dimensional stability and greater proton conductivity can be achieved by mixing these two polymers. Pure SPEEK (DS 61.7%) membrane dissolves completely in water at 70°C, and with 40 wt % SPES-C the swelling decreases
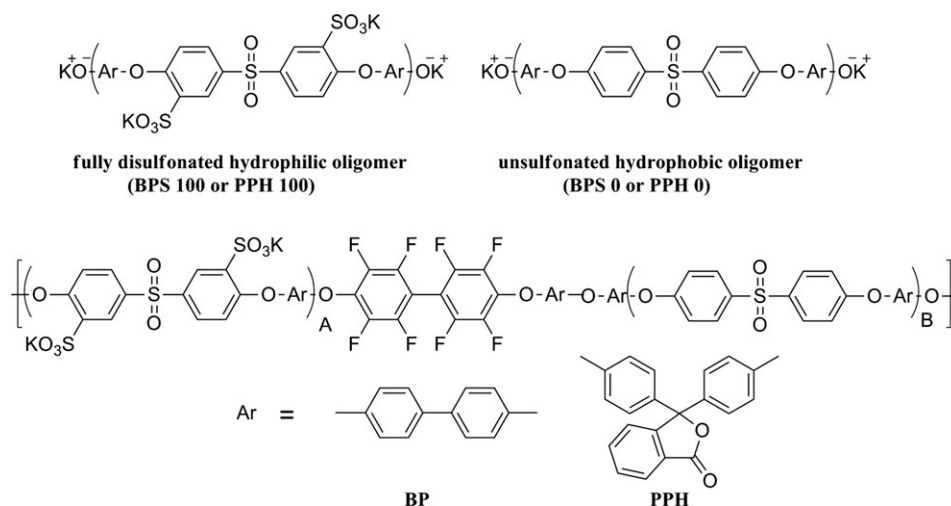
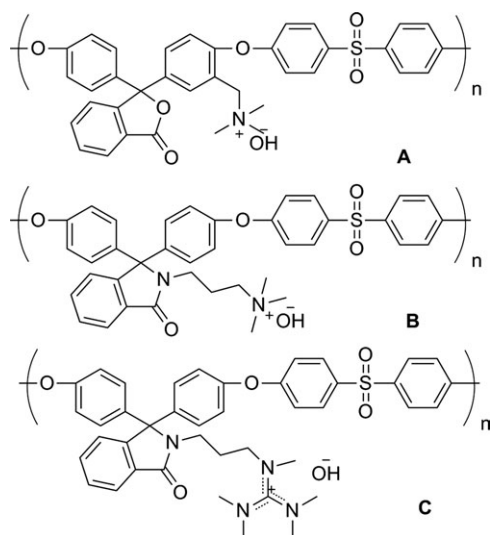**Scheme 4.** Structures of hydrophilic-hydrophobic multiblock copolymers.

to 29.7% at 80°C, due to the excellent dimensional stabilities of phenolphthalein-based cardo PES. The proton conductivity of SPEEK (DS 55.1%)/SPES-C (30 wt %) membrane increases to 0.16 S cm^{-1} at 140°C and 100% RH, comparable with that of Nafion 115.

Another way to improve the performance of PEMs is to locate the hydrophilic sulfonic acid groups at the side chains.[92,102–104] Thus, the main chains can be separated from the side chains and kept in a relatively hydrophobic environment, and better phase separation could be obtained while decreasing the swelling ratio and improving proton conductivity and stability. We designed and synthesized a series of sulfonated side-chain type cardo PESs.[12,15,16] Phenolphthalein has a lactone ring that can be easily modified into other functional bisphenol monomers. We synthesized a hydroxyl-containing cardo bisphenol (PPH-OH) by the condensation reaction of phenolphthalein and 2-aminoethanol.[15] Cardo PES with pendant hydroxyl groups was prepared by polycondensation of PPH-OH and 4,4′-difluorodiphenylsulfone as well as 4,4′-biphenol. The sulfonic acid groups were introduced by reaction of 1,3-propanesultone with the pendant hydroxyl group in the presence of sodium hydride [Scheme 3(B)]. This method of introducing sulfonic acid is better than sulfonation using sulfuric acid, because the position and amount of sulfonic acid groups can be precisely controlled. The side-chain type cardo PES prepared in this manner possesses a higher proton conductivity, lower swelling ratio, and lower methanol permeability than the main-chain type PES with similar IEC. The great performance of the side-chain type PES can be explained by the excellent phase-separated morphologies. The flexible hydrophilic side chains are easy to aggregate and form ionic clusters while the rigid aromatic main chain maintains mechanical properties and resistance to swelling. To further investigate the relationship between the side chain structure and membrane properties, we synthesized cardo PES with different length side chains [Scheme 3(C)].[16] SPES with longer aliphatic side chains exhibit lower water uptake and swelling ratios because its longer aliphatic side chains improve the phase separation of the main chain and sulfonic acid side chains and

lowered IEC. SPESs with longer side chains have lower proton conductivity because of their lower IEC. It is concluded that higher IEC is more important than a longer side chain for proton conductivity in our series of polymers. When fluorine atoms are introduced into the backbone, better performance can be obtained. It indicates that introduction of fluorine groups to the polymer main chain can further improve the hydrophobic properties of the polymer backbone and yield better phase separation. Because of the cardo structure and lactone group of phenolphthalein-based cardo PES, various side chains can be introduced by a facile way, and the side-chain type membranes showed excellent properties for use in fuel cells.

Zwitterion electrolyte materials are reported to increase lithium ion conductivities up to seven times more than the pure polyelectrolyte.[105] Inspired by this idea we synthesized a series of novel zwitterionic polymers aiming to investigate zwitterion effects in PEMs.[12] The structure of the polymer is shown in Scheme 3(D). There are two sulfonic acid groups and one ammonium group in each repeating unit, and investigation of IEC values indicated that each ammonium group interacted with one sulfonic acid group. Because of the strong interaction, the increased packing density of polymer chains results in polymer membranes with lower water uptake and swelling ratio and better oxidative stability. The zwitterionic cardo PES exhibits higher conductivity than side-chain type SPES with similar IEC values, which means that zwitterionic effects could facilitate proton transport as described in the literature.

Building hydrophilic and hydrophobic block copolymers is another efficient way to improve the performance of PEMs.[31,45,69,106,107] Guo et al. synthesized phenolphthalein-based PES hydrophilic-hydrophobic multiblock copolymers (shown in Scheme 4).[20] These copolymers exhibit higher proton conductivity than the random polymer with similar IEC under both fully and partially hydrated conditions via the formation of a nanophase separated morphology. The author found that the volume fraction of the hydrophilic/hydrophobic segments was an important factor for achieving high proton conductivities.

Scheme 5. Structures of cardo HEMs.

Hydrophilic segments serve as the ion conducting channel and hydrophobic segments provide the mechanical properties as the matrix. Cardo block PPH, due to its fully aromatic and bulky structure, contributes significantly to the mechanical properties, thermal and environmental stability of the copolymers. With PPH0 as the hydrophobic segments, they increase the hydrophobicity and change the volume fraction of hydrophobic blocks, thus, improve the phase separation morphology. In addition, PPH with pendant lactone groups provide chemically reactive sites for further modification or grafting reactions to achieve functional polymeric materials.

Cardo Hydroxide Exchange Membrane
In recent years, interest has grown in the development of hydroxide exchange membranes (HEMs) for applications in alkaline fuel cells, because there are some limitations on the use of proton exchange membranes. These include slow electrode kinetics, CO poisoning of Pt and Pt-based electrocatalysts at low temperatures, high cost of the catalysts, and high fuel permeability.[108–110] Hydroxide exchange membrane fuel cells (HEMFCs) have numerous advantages over PEMFCs. In a basic environment, the cathode oxygen reduction overpotential could be significantly reduced, leading to high fuel cell efficiencies. Moreover, catalysts in basic medium are more durable, and the inherently faster kinetics of oxygen reduction reactions in an alkaline fuel cell render it possible to employ nonprecious metals as catalysts instead of noble metals such as Pt and Ru.

Li et al. reported the first phenolphthalein-based cardo hydroxide exchange membrane for direct methanol fuel cells.[26] Because of the easy functionalization ability of the phenolphthalein-based PES, the cardo HEM was made by chloromethylating the commercial polymer PES-C with chloromethyl methyl ether in the presence of zinc chloride. The chloromethylated PES-C was quaternized by trimethylamine followed by hydroxide exchange to yield HEM [Scheme 5 (A)]. The membrane prepared is stable in 1M NaOH solution over 25–70°C and has high hydroxide conductivity and low methanol permeability. As for PEMs, there

are similar drawbacks in main-chain type HEMs. A series of novel side-chain type cardo PES HEMs were prepared by our group.[18,19] We synthesized a tertiary amine-containing bisphenol by reaction of phenolphthalein and *N,N*-dimethyl-1,3-propanediamine. Cardo PES with pendant tertiary amine was made by polymerization of 4,4′-dichlorodiphenylsulfone and the prepared bisphenol. Iodomethane was used to quaternize the PES containing the tertiary amine groups [Scheme 5 (B)]. The advantages of this method are that it avoids the use of the toxic chloromethylation reagent chloromethyl methyl ether, and that the degree and the location of quaternization could be controlled precisely. The side-chain type HEM has higher hydroxide conductivity than the main-chain type quaternized PES. The flexible side chain facilitates formation of a hydrophilic/hydrophobic microphase separation morphology, which ultimately results in better connected ionic domains and a high density of ionic clusters leading to excellent conductivity.

To increase the hydroxide conductivity and stability of cardo HEMs, we introduced guanidinium into the side chain as the hydroxide conducting group [Scheme 5 (C)].[19] Hexaalkylguanidinium hydroxide is a stronger base than quaternary ammonium hydroxide.[111,112] The high alkalinity yields a high concentration of mobile hydroxide ions, which is useful for hydroxide conductivity. The cardo PES shows a hydroxide conductivity that is much higher than that of the quaternized ammonium HEMs with similar structures. The membranes with pendant quaternized guanidinium groups exhibit a moderate water uptake and swelling ratio, and better thermal stability and alkaline stability than quaternized ammonium PES.

Membranes for Water Purification
Advanced technologies for water purification are needed to satisfy requirements for water. Membrane separation techniques have potential for water purification.[113,114] Separation membranes for water purification can be divided into several categories according to their pore size. Membranes with pore sizes of 5000 nm or greater are particulate filters. Microfiltration membranes have pore sizes in the range of 100–5000 nm and are capable of removing suspended particles like blood cells and latex emulsions. Ultrafiltration membranes have pore sizes in the range of 2–100 nm and can remove large molecules like albumin or pepsin. Nanofiltration membranes have a pore size of less than 10 Å and can separate small molecules like divalent salts, dissociated acids and sugar. Reverse osmosis membranes separate chemicals like sodium and chloride on the molecular level and have pore sizes in the range of a few angstroms.[114–116]

Nanofiltration is important for water purification and both high water flux and high solute rejection are needed. To obtain both high water permeability and high solute rejection, nanofiltration membranes require materials with high hydrophilicity.[117] As hydrophilic polymers take up water and swell in aqueous media, the membranes lose their mechanical integrity if they are too hydrophilic—a balance could be found by adjusting the hydrophilicity–hydrophobicity ratio. Blanco et al. studied hydrophilization of three kinds of PESs, including polysulfone Udel® (PSU), poly(ether sulfone) Victrex® and PES-C, by sulfonating them using concentrated sulfuric acid.[118,119] They carefully
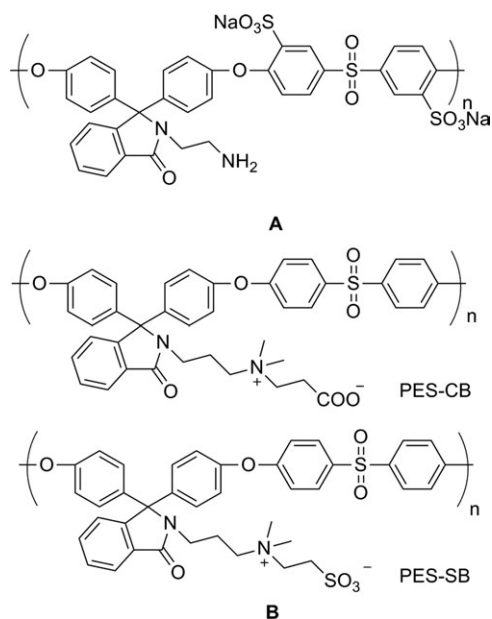
Scheme 6. Structures of zwitterionic cardo PESs.

studied the sulfonation conditions and the degradation mechanism during the sulfonation process. Of the three polymers, PES-C is the best candidate, because the DS can be easily controlled by adjusting the time and temperature of the sulfonation reaction. PES-C, a type of phenolphthalein-based PES, appears to be most resistant to chain scission under controlled sulfonation conditions. Thus, it is convenient to prepare an asymmetric membrane with hydrophilic SPES-C by a simple phase inversion method with water as the precipitation medium. Such membranes can also be used as hydrophilic membranes for ultrafiltration or nanofiltration.

To improve the performance of reverse osmosis, it is necessary to increase hydrophilicity.[120] We synthesized a sulfonated cardo PES with amine side groups SPES-NH$_2$ [Scheme 6 (A)] and added it to the interfacial polymerization amine solution partly substitute of m-phenylenediamine (MPDA).[22] The salt rejection of membrane prepared from SPES-NH$_2$ (97.5%) is slightly lower than that of membrane prepared from MPDA (99%). However, the water permeability of the former (51.2 L/m^2 h) is more than that of the latter (37.4 L/m^2 h). Higher water permeability of the membrane prepared from SPES-NH$_2$ arises from the hydrophilic sulfonic acid groups in the SPES-NH$_2$. The high rejection rate is contributed to the chain stiffness of the cardo PES copolymer and the high degree of cross-linking.

High performance ultrafiltration (UF) membranes made from poly(arylene ether sulfone)s are easily fouled by many solutes, including proteins, polysaccharides, and humic substances.[121,122] Fouling deteriorates the performance of UF membranes, due to longer filtration times and shorter membrane life. In recent years, zwitterionic substances have been reported as a class of materials with excellent antifouling properties.[123,124] We designed an easy way to attach zwitterionic groups onto poly (arylene ether sulfone).[17] Using the cardo PES with tertiary amine side groups prepared earlier, sodium bromoacetate or

sodium 2-bromoethanesulfonate were used to react with the tertiary group and zwitterionic groups were introduced into the polymer [Scheme 6 (B)]. Next, flat sheet ultrafiltration membranes were made by a phase inversion method using the prepared polymer. Under a pressure gradient driven filtration process, the carboxybetaine poly(arylene ether sulfone) (PES-CB) ultrafiltration membrane shows a 95% pure water flux recovery ratio after three cycles of lysozyme solution filtration, while only about 25% flux is recovered for the PES-C ultrafiltration membrane. This demonstrates that ultrafiltration membranes made of cardo PES with zwitterionic groups exhibit excellent antifouling properties.

Most commercially available nanofiltration composite membranes have a negatively charged separation layer. Because of the Donnan effect, the rejection of multivalent anions is higher than monovalent anions, which means membrane charge has a significant influence on solute rejection in the NF process.[125,126] In addition, positively charged NF membranes should exhibit enhanced rejection of multivalent cations and positively charged organic components, but few such membranes have been reported due to the difficulty in their preparation. Since tertiary amine groups can accept protons and carry a positive charge when in contact with water, we prepared a kind of positively charged NF in a facile way with tertiary amine containing cardo PES that may become positively charged in an aqueous environment.[14] The prepared membrane exhibits rejection of salts in the order of FeCl$_3$ > MgCl$_2$ > NaCl and high rejection to basic dyes (>98%), which is a typical performance of a positively charged NF. Meanwhile, these membranes exhibit excellent chlorine tolerance which is an important property needed for applications of NF membranes. This membrane could efficiently purify or concentrate basic dyes, and purify wastewater containing positively charged components.

From the examples above, we can see that Cardo PES possesses numerous advantages as water purification membrane materials: excellent chemical stability, which makes it easy to hydrophilization by sulfonation without degradation; easy chemical modification, which makes it possible to introduce various functional groups to improve the performance of the membranes; bulky and stiff structure, which results in good mechanical properties of the membranes. Cardo PES is a potential candidate material for high performance water purification membranes, including ultrafiltration, nanofiltration, and reverse osmosis (Table II).

Gas Separation Membranes

Separation of gases using membranes is a dynamic and rapidly growing field. Membranes separate gases from their mixtures because of the differences in permeabilities of different gases through the membranes. Since 1980, gas separation membranes have been commercialized. Gas separation membranes are used in industry for separation of CO$_2$ and H$_2$O from natural gas, production of oxygen-enriched air, purification of H$_2$, and dehydration of compressed air.[127] Membranes for gas separation must have both high permeability and selectivity, be thin but robust, and low cost, to be made into high-surface-area modules.[128] On the basis of their permeability and selectivity, membranes can be classified broadly into three categories: porous,

Table II. Properties of Cardo PES Separation Membranes

Ref.	Polymer	IEC	Mechanical properties (MPa)	Swelling ratio (%)	Conductivity (S/cm)	Methanol permeability ($\times 10^{-6}$ cm^{2}s^{-1})
				Ion exchange membranes		
25	SPES-C (Scheme 2 (A))				4.12×10^{-3} (82% DS, RT), 0.011(80°C 70% DS), 0.0338 (110°C 70% DS)	0.21 (85% DS, RT)
24	PWA(40 wt%)/SPES-C (70%DS)				4.14×10^{-3} (RT), 4.5×10^{-2} (90°C), 6.7×10^{-2} (110°C)	
21	SPEEK/SPES-C			29.7 (80°C, 61.7% DS SPEEK/40 wt% SPES-C)	0.16 (110°C/30 wt % SPES-C)	
15	SPES-C-100 (Scheme 2 (B))	1.41	41.7, 432, 17[a]	5.8 (20°C), 6.6 (80°C)	0.056 (RT)	1.38 (RT)
16	SPES-3 (Scheme 2 (C)) FSPES-3	1.53 1.45	23.5, 420, 67 25.6, 564, 50	7.5 (20°C), 10.1 (100°C) 6.3 (20°C), 9.1 (100°C)	0.056 (20°C), 0.13 (100°C) 0.080 (20°C), 0.152 (100°C)	0.57 (RT) 0.41 (RT)
12	PES-DS-60 (Scheme 3)	0.91	60.3, 1910, 16.8	3.9 (20°C), 4.3 (80°C)	0.013 (20°C), 0.041 (80°C)	
20	PPHO-BPS100 5K-5K (Scheme 4)	1.73			0.154 (30°C)	
26	QPES-C (Scheme 5(A))	1.25			0.0524(4M NaOH, RT)	0.057 (RT)
18	PES-P-OH (Scheme 5(B))	1.50	31.9, 540, 31.7	4.2 (20°C), 5.4 (60°C)	0.021 (20°C) 0.031 (60°C)	
19	PES-G-OH (Scheme 5(C))	1.39	58.3, 830, 30.7	10.6 (20°C), 15.2 (60°C)	0.037 (50°C), 0.042 (60°C)	

Ref.	membrane	Type	Operation condition	Flux	Rejection (%)
			Membranes for water purification		
118	SPES-C	NF	$\geq$P = 12 bar, T = 25°C, [CaCl$_2$] feed = 10^{-3} M	450 (L/m^2 days)	66 (CaCl$_2$)
22	TMC/MPDA/SPES-NH$_2$(2/1) (Scheme 7 (A))	RO	2.0 MPa, 2000 ppm NaCl solution, RT	51.2 L/m^2 h	97.3 (NaCl)
17	PES-CB (Scheme 7 (B))	UF	1.0 mg/mL lysozyme, 0.1 MPa	410 L/m^2 h (pure water) 95% recovery	98.2 (lysozyme)
14	PES-TA (Scheme 6 (B))	NF	1000 ppm for NaCl, MgCl$_2$ or FeCl$_3$ 100 ppm for methyl green (MG), 0.5 MPa,	30.2	36.6 (NaCl), 63.3 (MgCl$_2$), 70.2(FeCl$_3$), 99.9 (MG)

Table II. (Continued)

Gas separation membranes

Ref.	Polymers	P (barrers)					α			
		H$_2$	O$_2$	CO$_2$	N$_2$	CH$_4$	H$_2$/N$_2$	O$_2$/N$_2$	CO$_2$/CH$_4$	H$_2$O/N$_2$
133	PES-C	12.1	0.949	5.74	0.167	0.143	72.6	5.68	40.1	1.3×10^4
133	DMPES-C	10.8	0.868	3.12	0.110	0.0727	98.1	7.62	42.9	
133	TMPES-C	16.9	1.55	7.69	0.201	0.225	84.1	8.46	34.2	
133	IMPES-C	30.6	4.85	19.4	0.669	0.928	43.8	5.49	20.9	
132	SPES-C									2×10^5
23	2a	5.59	0.35	2.30	0.051	0.086	109.61	6.86	26.74	
23	2b	7.11	0.52	2.61	0.093	0.088	76.45	5.59	29.66	
23	2c	8.08	0.56	3.18	0.098	0.098	5.71	82.44	32.45	
23	2d	23.43	1.78	13.80	0.42	0.48	4.24	55.79	28.75	

^{a}The three values stand for tensile strength, Young's modulus, elongation at break, respectively.

nonporous, and asymmetric membranes. Porous membranes for gas separation can provide very high flux but low selectivity. Nonporous or dense membranes possess high selectivity of different gases but low flux. Asymmetric membranes consist of two layers with different functions. One layer is a porous matrix that can provide physical support for the upper layer, which is a thin, dense selective layer.[129–131]

From the industrial point of view, membrane should work under high temperatures so that the gas separation process can be done directly without cooling, and no additional heating is needed to reuse the separated gas. Because of the excellent properties of phenolphthalein-based cardo PES-C, especially its high glass transition temperatures (260°C) and high thermal stability (T_d 460°C), PES-C is a potential candidate material for high temperature gas separation.[54] Liu et al. tested permeability and selectivity of eight gases. The PES-C membrane exhibits high permeability for CO$_2$ (9.3×10^{-10} at 100°C, 1.2×10^{-9} at 160°C), and high permeability ratios of CO$_2$/N$_2$ (35 at 100°C and 8.2 at 160°C) and of CO$_2$/CH$_4$ (29 and 9, respectively), which means that PES-C can be used to separate CO$_2$ from waste gases or from lower hydrocarbons. The membrane materials would also be useful for separating hydrogen from carbon monoxide and nitrogen, because the permeability for H$_2$ is high and the permeability ratios of H$_2$/CO or H$_2$/N$_2$ are good.

Jia et al. used sulfonated PES-C (SPES-C) to separate water vapor and N$_2$.[132] The permeability for water vapor through SPES-C increases linearly with increases in the DS while the permeability for N$_2$ decreased, thus leading to increased selectivity for water vapor/N$_2$. Thus, SPES-C is a potential candidate membrane material for air and natural gas dehydration.

Chemical structures of polymers determine their physical properties, such as packing density and segmental motion of the polymer chains, which affect the gas permeation behavior in polymer membranes. Wang et al. synthesized a series of cardo PESs and systematically studied the influence of different chemical structures on their gas separation properties.[133] The permeability coefficients and permselectivity coefficients vary with structural changes, which makes it possible to choose some of them for specific uses. These include hydrogen purification, oxygen enrichment, removal of CO$_2$ from natural gas, and air dehumidification.[134] We also found that introduction of bulky phthalimide moieties to the polymer chain could increase the free volume of the membrane, resulting in higher gas permeability.[23]

Cardo PESs have pendant cardo structures in the repeating units, which twist the phenylene moieties of the main chain out of a planar conformation, thereby increasing the free volume of the polymer. And the bulky side groups can restrict the rotational motion and intersegmental packing of the molecular chains, which are effective to improve the performance of gas separation membranes. In addition, bulky side groups in cardo PESs disrupt crystallization and improve their solubility, which is another important requirement for gas separation membrane materials. Asymmetric membranes are usually made by the phase inversion method, where 15% or more concentration of polymer solution is required. All of these characteristics make

cardo PES suitable candidates for gas separation applications (Table II).[135]

CONCLUSIONS

Poly(arylene ether sulfone)s with cardo groups, especially phenolphthalein-based cardo PESs, possess good solubilities, excellent mechanical toughness, thermal stability, and easy functionalization, and they would attract more and more attentions in the future. Besides the applications of separation membranes, including ion exchange, water purification, and gas separation membranes, more application fields could be found for cardo PESs, which may be lithium batteries, electrochemical sensors, dielectric materials, coatings, glass-reinforced plastics, and so on.

There are still problems with cardo PES that must be resolved in the future. For example, there are lactone or lactam groups in phenolphthalein-based cardo PES. It is not known if the cardo ring would be opened in specific situation or in long-term use, and cause degradation of the polymers or not. And because of the large molecular weight of the phenolphthalein-based cardo structures, the IECs of the ion-functionalized cardo PES, especially the side-chain type polymers, are relatively low, while high IECs polymers could be needed and have better performance in some situation. Introduction of multifunctional groups to the cardo PES or copolymerization with monomers of small molecular weight are possible ways to solve the problem.

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