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Editorial

Virtual Special Issue: Polymeric Membranes for Advanced Separations

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Membrane technology has been playing an increasingly important role in addressing the global challenges related to water, the environment, and energy. The majority of membranes used in industry are produced by using polymers. Membranes hosting nano-sized or even angstrom-sized pathways, that are fixed or dynamic, regulate the transport of fine particulates, molecules, or ions based on the mechanism of size discrimination, electrostatic interactions, or sorption and diffusion. Advances in polymer science have helped to develop better membranes, and in turn the ever-increasing demands for highly efficacious membrane separations drive further progress in fundamental polymer science. That is, polymer science is essential to the development of polymeric membranes with high performance (Figure 1). *Macromolecules* has long been an important platform for publishing highly relevant and impactful studies regarding polymeric membranes. This Virtual Issue highlights some membrane studies recently published in *Macromolecules*, mainly focusing on membranes for ultrafiltration (UF), gas separations, and fuel cell separators.

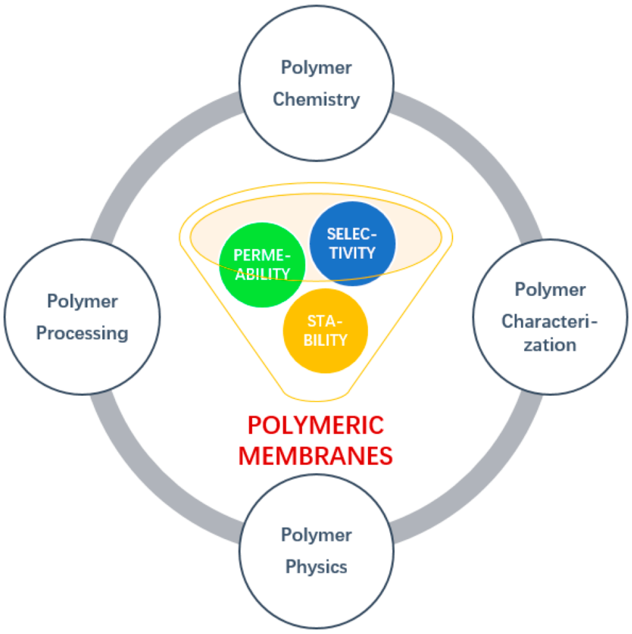

Figure 1. Polymer science eventually determines the performances of polymeric membranes.

UF is enabled by membranes with sizes in the range of ∼2−100 nm. UF membranes are typically prepared by phase inversion and have been widely used in the purification and concentration of, for example, colloids, polymers, and proteins. Unfortunately, typical UF membranes suffer from a wide pore size distribution which is intrinsic to the process of phase inversion, and consequently a trade-off between permeability and selectivity occurs. Self-assembly of block polymers is recognized to be one solution of this bottleneck of UF membranes by forming membranes with nearly monodispersed pores.[1] Such membranes are prepared either by etching away the dispersed cylindrical phases in the perpendicularly aligned block polymers or by performing nonsolvent-induced phase separation of block polymer micellar solutions. Alternatively, well-defined porosities can be generated in self-assembled block polymers by the strategy of selective swelling, which can be finished within 30 s with the assistance of microwave energy.[2] Interestingly, simulation reveals that vesicles of amphiphilic ABA triblock copolymers can be spontaneously perforated driven by the orientation entropy of the semirigid B-blocks, which may inspire efforts to experimentally realize such perforated BCP membranes with ON/OFF switchable pores.[3]

Gas separation relies on much smaller pores, down to the angstrom scale if we consider the free volume in polymers as dynamic pores. Chemical functionalization has been performed to tune the free volume and consequently the gas-separation performance of engineering plastics, and fluorination of polyimide is a representative example.[4] Industrially used membranes for gas separation are usually prepared from glassy polymers with low free volumes and typically exhibit moderate selectivity and low permeability. To solve this issue, significant efforts have been devoted to explore highly permeable polymers, and polymers of intrinsic microscopy (PIMs) are identified as a very promising candidate in this regard. Because of their rigid and contorted backbone structures and consequently severely hindered segmental mobility, PIMs are characterized by remarkably high free volumes, thus greatly facilitating gas permeability.

PIM-1, the most extensively studied PIM polymer, is generally synthesized from the step-growth polymerization of

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two tetrasubstituted monomers via double nucleophilic aromatic substitution. The microstructures of the synthesized PIM-1 and consequently its gas separation properties are sensitive to the applied polymerization conditions. It was revealed that cyclic or other nonlinear topologies identified in the polymerized products of PIM-1 contributed to the increase of the surface areas of PIM-1, and higher contents of branching and network topologies improved the gas pair selectivity of PIM-1.[5] The gas transport behaviors of PIMs can be tuned by postfunctionalization of PIMs. Of particular interest is to convert the nitrile groups in PIM-1 to carboxylic acids because thus-functionalized PIMs show enhanced CO_2 sorption and diffusion selectivity because of strong interaction between CO_2 and carboxylic acid groups. An optimized acid hydrolysis strategy was recently reported to functionalize PIM-1, and >89% conversion was obtained within 48 h while previous methods required 360 h. Thus-synthesized PIM-COOH exhibited smaller free-volume entities and showed significantly improved selectivities for CO_2-based gas pairs.[6] In another work, the nitrile group in PIM-1 was first converted to tetrazole, which was subsequently reacted with amines, thus incorporating ionic-liquid-like side groups to PIM-1. Thus-functionalized PIM-1 exhibited increased gas selectivities for both O_2/N_2 and CO_2/N_2 at the expense of reduced pure-gas permeabilities. This side-group modification strategy is expected to bring a variety of functional groups to PIMs because tetrazoles are versatile in composing a library of different ionic liquids.[7]

Investigations on gas transport behaviors of PIMs are generally performed on PIM bulk films with thicknesses on the scale of 10 μm. However, thus-obtained transport properties cannot be directly used to predict the performances of PIM thin films with thickness down to the submicrometer scale required by industrial applications of gas separations. A recent work used *in situ* interference-enhanced spectroscopic ellipsometry to investigate dilation and sorption of pure and mixed gases in PIMs films.[8] It was found that film thinning promoted the collapse of the frozen-in free volume, and lower gas uptakes were observed in thinner films. Importantly, the mixture effect also occurred in thin PIM films as they dilated to a smaller degree in gas mixtures than in a pure gas. These observations are helpful in predicting the performances of PIM thin films and in designing of PIM membranes in the form of thin-film composites for real-world applications.

Studies on anion exchange membranes (AEMs) are bursting nowadays mainly because AEM-enabled fuel cells have the potential to use cheap electrocatalysts under alkaline conditions, thus overcoming the cost barriers of the mainstream proton exchange membranes. Ion exchange membranes require to be suitably hydrated to maximize performance; therefore, it is essential to understand the hydration behavior and water mobility of these membranes.[9,10] Dekel et al. performed a systematic investigation on the equilibrium state and kinetics of water uptake (WU) in water vapor of different types of AEMs, demonstrating the potentials of the equilibrium WUs and WU kinetics in evaluating AEMs.[11] Kumar et al. investigated the effect of hydration on the transport properties of sulfonated polystyrene-based cationic exchange membranes (CEMs) and found that the water volume fraction underpinned an intrinsic trade-off between permselectivity and ion conductivity.[12] That is, an increase in water content will lead to enhanced ion conductivity but reduced permselectivity because of decreasing charge density. This is also applicable to AEMs. Freeman et al. developed a new and simple method to determine cation and anion diffusion coefficients in ion exchange membranes based on the Nernst−Planck equation and found that counterion diffusion coefficients were greater than co-ion diffusion coefficients after considering the contribution of differences in ion size.[13]

Polymer chemistry is playing a crucial role in developing robust, high-performance AEMs. Poly(arylene ether)s (PAEs) are the most widely used polymers for AEMs. Unfortunately, the aryl ether bonds in PAEs are weak points and are prone to undergo chain scission in alkaline conditions, leading to progressive degradation of the AEMs. A few solutions have been developed to enhance the alkaline stability of PAEs. Bae et al. synthesized quaternized multiblock poly(phenylene-*co*-arylene ether)s from a "pre-aminated" monomer and a series of chloro-terminated oligo(arylene ether)s.[14] These copolymers exhibited enhanced fuel cell performances and alkaline durability because of the well-defined microphase separation of the hydrophilic and the hydrophilic domains and the presence of the phenylene-based structures in the hydrophilic domains. In contrast, He et al. converted the electron-withdrawing C═O groups in the conventional poly(aryl ether ketone) (PEAK) backbone into the electron-donating $C-NH_2$ groups through the Leuckart reaction, thus alleviating the nucleophilic attack of OH^- to the ether-connected phenyl−C in the elevated electron cloud density environment.[15] Alternatively, polymers containing no ether bonds in the backbones, for example, polystyrene, have been successfully explored to develop alkaline-robust AEMs.[16,17] Using Ziegler−Natta polymerization, Hickner et al. synthesized bromoalkyl-functionalized poly(olefin)s with 4-(4-methylphenyl)-1-butene and 11-bromo-1-undecene as the monomers.[18] The synthesized polyolefins were converted to anion-conductive copolymers by reacting the pendant bromoalkyl group with a custom-synthesized tertiary amine containing pendant quaternary ammonium moieties. Thus-prepared polyolefin-based AEMs carried three cations per side chain and showed good chemical and dimensional stability and considerably higher hydroxide conductivities likely due to phase separation in the triple-cation structure. It was also found that AEMs with longer pendant alkyl chains exhibited better alkaline stability because the steric and hydrophobic effects of the alkylene groups in the side chains mitigate the attack by the hydroxide ions to the ammonium groups.[19] Importantly, new approaches such as PIM-based polymers,[20] oppositely charged block copolymer mosaics,[21] and chemical vapor deposition methods[22] have found interesting applications in AEMs and other ion-conductive membranes.

As the pores or "free volume" entities in membranes for desalination and ion exchanges are very small down to a few angstroms and polymeric structures of these membranes are hydrated, it is extremely important to use advanced characterization techniques to reveal the structures and dynamics of these membranes. Neutron scattering is emerging as a powerful tool to *in situ* probe the water and chain dynamics of these membranes because it can resolve motions of hydrogenous species on the length scale of several nanometers and the time scale on the order of nano- to picoseconds. Soles et al. employed neutron scattering to investigate a polyamide desalination membrane and an AEM.[23] It is revealed that on the nanometer length scale water diffuses through the desalination membrane at a rate similar to bulk water, while water diffuses through the AEM 2 times slower than bulk

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water. In another work, neutron reflectometry (NR) was used to distinguish the support and separation layers of membranes composed of polyelectrolyte multilayers.[24] NR reveals that the membranes have an asymmetric structure with distinct bottom and top multilayers in either the dried or hydrated state. It has also been demonstrated that reduced hydration leads to denser and consequently more selective separation layers.

Digesting the works highlighted in this virtual issue, there is a strong impression that the development of a highly effective polymeric membrane relies on the adequate characterization and understanding of the transport behaviors inside the polymer as well as the rational design, synthesis, and processing of the polymer. Clearly, polymer science is playing a pivotal role in the research of polymeric membranes. As a leading journal in polymer science, *Macromolecules* will continue to serve the membrane community by publishing in-depth studies in this fast-growing field.

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Notes

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