Understanding the Role of Free Volume in Microporous Polymers for Membrane-based Gas Separations

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Microporous polymers exhibit high free volume (V_f) within their matrix due to their rigid and contorted backbone structures and/or bulky monomer units, which hinder efficient packing. As a result, these membranes demonstrate exceptionally high gas flux with decent diffusion selectivity. However, despite significant advancements in these materials, membrane-based gas separation technology has yet to achieve the performance and stability required to compete with conventional thermal separation methods such as cryogenic distillation and absorption. Thus, it is crucial to develop scalable microporous polymers and investigate their long-term stability under industrial conditions.

The gas permeability and selectivity of these membranes are highly dependent on their packing structure and the resulting free volume elements. Understanding how to design microporous polymers by controlling V_f, as well as how V_f evolves over time and under external influences, is essential. One effective strategy involves incorporating V_f-promoting groups into the polymer backbone, such as highly rigid triptycene units that create intrinsic size-sieving V_f, and stereo-contorted spirobifluorene groups within a highly stable poly(arylene ether) (PAE) matrix. This approach has led to polymeric membranes with 1–2 orders of magnitude higher gas flux than commercial alternatives while maintaining appreciable selectivity. Notably, this methodology is scalable and versatile, allowing for the incorporation of functional groups and branched linkers through monomer selection to fine-tune gas separation properties for specific applications.

Alternatively, backbone contortions can be introduced to induce polymer packing inefficiencies, significantly enhancing V_f. This approach is exemplified in rigid hydrocarbon ladder polymers with contorted backbones synthesized via catalytic arene-norbornene annulation (CANAL) polymerization, which results in some of the highest microporosity observed in polymers. However, the absence of flexible linkages, such as the ether bonds present in PAEs, poses a challenge: these highly glassy polymers undergo physical aging, where they densify over time even in the absence of external stress due to their substantial departure from thermodynamic equilibrium.

A comprehensive analysis of transport properties—via permeation and sorption experiments—combined with V_f characterization has shown that, if controlled properly, physical aging can significantly enhance size-selectivity without compromising fast gas permeability, leading to an optimal separation regime. Additional strategies, such as reducing membrane thickness and introducing single-bond defects to enhance backbone flexibility, were explored to further regulate aging behavior. Lastly, various physical aging models were evaluated to provide predictive insights into membrane property evolution over time, guiding polymer design and optimizing aging conditions for long-term industrial applications.

This thesis primarily focuses on establishing structure–property–performance relationships in microporous polymers, particularly regarding the role of V_f and physical aging. The insights gained offer strategic directions for the development and maintenance of high-performance microporous membranes for gas separation applications.

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