

Microporous Polymer Membranes for the Separation of Hydrocarbon Mixtures

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Abstract Crude oil has long been the "black gold" of the global economy, and its fractionation relies on thermal distillation, a highly energy-intensive process. In contrast, crude oil fractionation via membrane separation can operate under mild conditions, avoiding phase transitions, and thereby substantially reducing the energy consumption associated with thermal separation processes. Numerous microporous polymer membranes have been developed to target the fractionation of oil mixtures through precise molecular design and structural modulation for the selective separation of hydrocarbon compounds. However, the intrinsic trade-off between permeance and selectivity remains a core bottleneck limiting their advancement. Herein, we summarize the synthetic strategies for microporous polymer membranes, focusing on tailored pore structures, anti-swelling capabilities, and selective transport of hydrocarbon compounds across these membranes. The performance of representative materials for practical crude oil fractionation was also highlighted. We also outline critical unresolved challenges, including cost-efficient large-scale fabrication, long-term stability under harsh crude oil environments, and further optimization of the permeance-selectivity balance, issues that must be addressed to promote the deployment of microporous polymer membranes.

Keywords Microporous polymer; Membrane separation; Trade-off; Hydrocarbon separation; Crude oil separation

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1 INTRODUCTION

Hydrocarbons in crude oil serve as the primary feedstock for the production of fuels, plastics, and polymers, and play an indispensable role in the global economy.^[1–4] Global oil refineries process approximately 100 million barrels of crude oil daily, relying on distillation, an extremely energy-intensive process that

accounts for approximately 1% of the world's annual energy consumption and contributes to 6% of global greenhouse gas emissions.^[5–7] The development of alternative technologies will play a crucial role in the decarbonization of the petroleum refining sector while securing the supply of fuels and feedstocks.^[8–11] However, developing alternative energy-saving technologies for crude oil fractionation is particularly challenging, largely because of the complex chemical composition of crude oil.^[12,13] Targeting the fractionation of crude oil, membrane-based organic solvent reverse osmosis (OSRO) has recently emerged as an extremely promising substitute for the thermal distillation of crude oil. The OSRO process can separate liquid molecular mixtures by exploiting differences in molecular size and affinity.^[14–18] Notably, it delivers remarkable environmental and energy advantages: the energy consumption of membrane separation amounts to only one-tenth that of traditional thermal distillation, accompanied by a reduction in carbon emissions of more than 90%.^[19–22] Beyond this, it offers operational flexibility and easy scale-up, further solidifying its potential as a transformative technology for the industry.^[23–26]

A highly permeable and selective membrane is the core component of OSRO, and the exploration of advanced polymeric membrane materials stands at the forefront of this research frontier. Notably, polymers of intrinsic microporosity (PIMs) serve as highly promising candidates for OSRO applications.^[27–30] Recent studies have focused on the development of microporous polymer membranes and their applications in

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crude oil fractionation.^[21,22,31] However, there are few summaries of this emerging field, and there appears to be a pronounced trade-off between permeance and separation factor for most membranes,^[22,32] although no clear boundary can be found. Thus, establishing a correlation between the membrane chemical structure and OSRO performance, understanding, and fighting the permeation and selectivity trade-off is critical for the efficient separation of hydrocarbon mixtures.^[33]

Given the potential merits of microporous polymer membranes for selective hydrocarbon separation, there is a pressing need to summarize the advances in this rapidly evolving field and discuss the associated challenges. In this review, we outline the synthetic strategies for microporous polymer membranes, discuss their microporous structures and swelling behavior in hydrocarbon mixtures, summarize their OSRO performance in hydrocarbon separation, and exemplify the practical application of OSRO to crude oil fractionation using representative microporous polymer membranes. Finally, we offer insight into the design of high-performance microporous polymer membranes.

2 SYNTHESSES OF MICROPOROUS POLYMERS

Microporous polymer membranes allow small solutes to pass through intrinsic micropores.^[34–37] The micropores within these polymer membranes arise from the inefficient packing of highly rigid or nonplanar polymer chains.^[38–41] Based on the topological structure of polymers, we classified microporous polymers into seven categories: dibenzodioxane-based microporous polymers, microporous polyamines, microporous polytriazoles, microporous polyamides, microporous polyimines, microporous polyimides, and microporous polyureas.

2.1 Dibenzodioxane-based Microporous Polymers

Dibenzodioxane-based microporous polymers, also known as polymers of intrinsic microporosity (PIMs), consist of linear or ladder chains with contorted rigid structures.^[40,41] These materials dissolve in organic solvents, enabling the fabrication of free-standing membranes by solution casting. PIM-1, the first of this type, was first reported by McKeown *et al.* in 2004. PIM-1 was synthesized by the polycondensation of 5,5',6,6'-tetrahydroxy-3,3',3'-tetramethyl-1,1'-spirobisindane with tetrafluoroterephthalonitrile (Fig. 1, top panel).^[42,43] Polymers with similar

dibenzodioxane linkages were later synthesized, which represent a well-established category of PIMs, and were developed for gas separation applications.^[44]

Livingston *et al.* first explored the use of PIM-1 membranes in organic solvent separation systems, demonstrating a typical molecular weight cutoff (MWCO) of 500–800 g·mol⁻¹.^[45] Finn *et al.* introduced spirobifluorene-based polymers of intrinsic microporosity (PIM-SBF) membranes (Fig. 1, bottom panel) for this application.^[32,46] Compared with PIM-1, PIM-SBF membranes exhibited higher toluene permeance and toluene/1,3,5-triisopropylbenzene (TIPB) selectivity.

2.2 Microporous Polyamine Polymers

PIM-1 experiences severe swelling in organic solvents, leading to irreversible changes in the pore size and a significant reduction in the separation factor.^[19,21,45] To address this issue, Lively *et al.* exploited the classic Buchwald-Hartwig amination reaction to polymerize spirobifluorene dibromide with a series of aromatic amines, yielding four distinct microporous spirocyclic polymers (SBADs-1-4, Fig. 2).^[19] The spirobifluorene moieties within these polymers exhibit high rigidity and π - π stacking interactions to form non-interconnected micropores, which help suppress membrane swelling during the separation of organic mixtures. Meanwhile, the incorporation of aromatic amines and C–N bonds imparts partial flexibility to the polymer segments, enhancing the guest flux and improving the affinity toward certain organic compounds, thereby improving the separation performance of the membranes. Later, the polymer series was expanded by modifying the diamine monomers and N-alkylation of SBAD polymers (SBADs-1, SBADs-5-7, and SBiADs; Fig. 2) to investigate the impact of bond rotational rigidity and the electronic properties of amine components on membrane separation performance.^[32] The results suggested that, although no enhancement in solute rejection was achieved for SBAD-1, the permeance of SBAD materials derived from spirobifluorene monomers was improved by the introduction of bulky N-substituents.

More recently, Guo *et al.* incorporated fluorine-enriched side chains into the rigid backbones of poly(arylene amine) materials to enhance chemical robustness, mitigate solvent-induced swelling, and thereby improve membrane separation performance.^[21] Linear polymer membranes with low fluorine loading experience considerable solvent-induced swelling, resulting in the loss of separation capabilities,

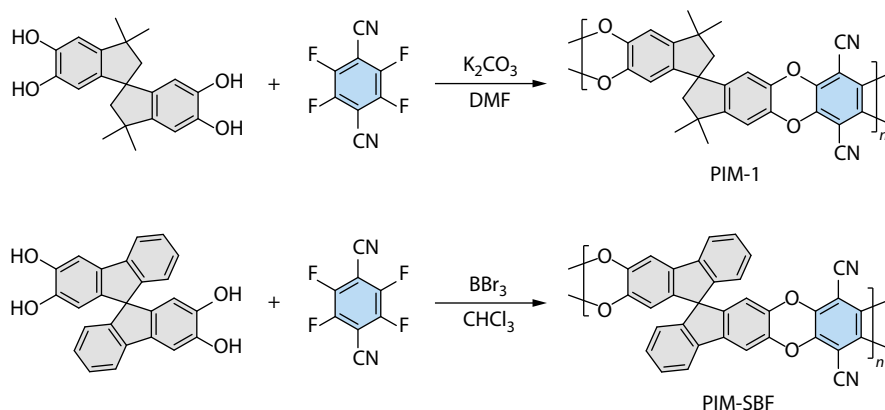


Fig. 1 The synthesis of dibenzodioxane-based PIMs, exemplified by PIM-1 (top) and PIM-SBF (bottom). SBF represents spirobifluorene.

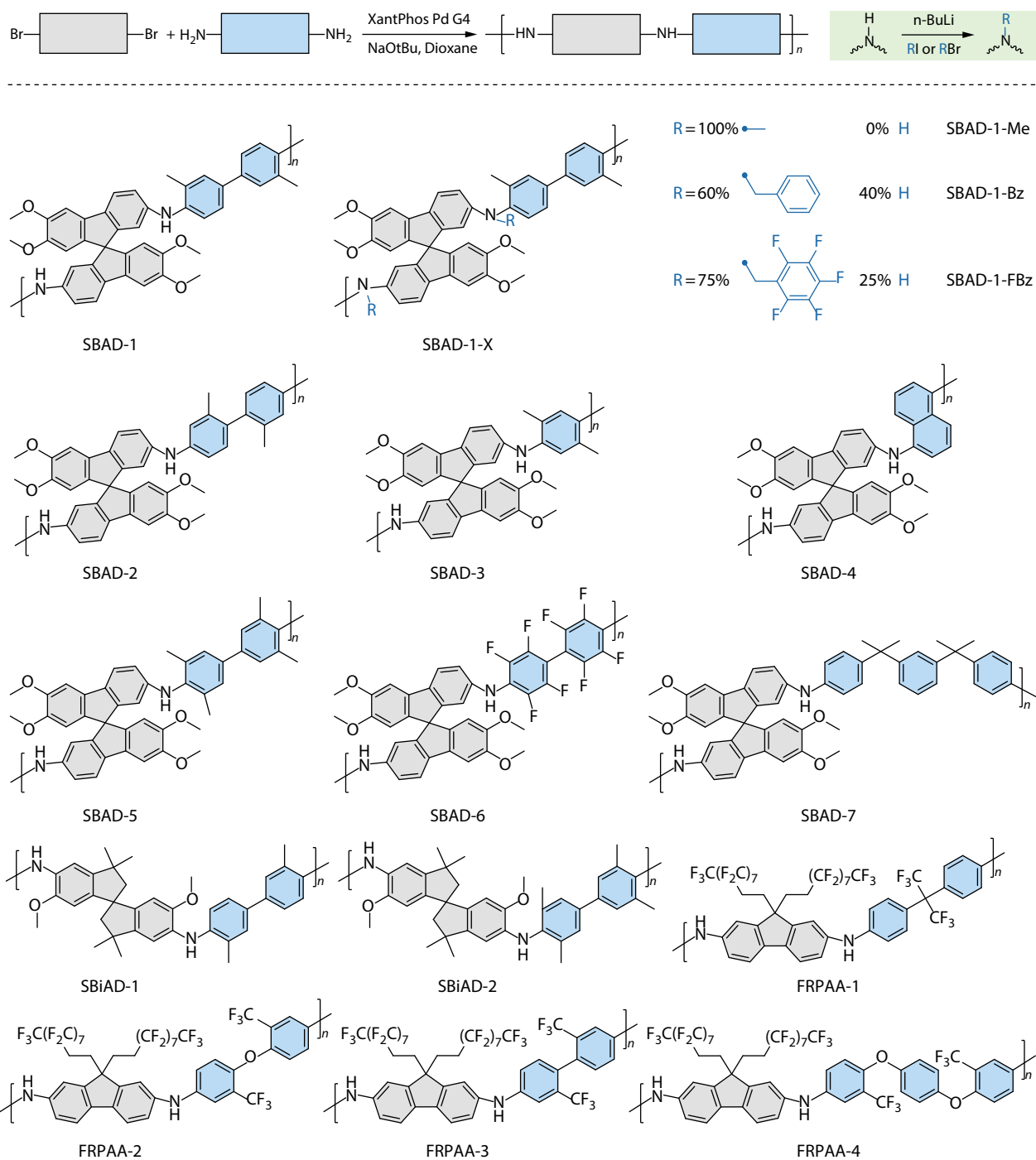


Fig. 2 The synthetic route for polyamine polymers (top panel) and chemical structures of representative SBAD, SBIAD, and FRPAA polymers (bottom panel). SBAD and SBIAD stand for spirobifluorene aryl diamine and spirobisindane aryl diamine, respectively, while FRPAA represents fluorine-rich poly(arylene amine).

whereas elevated fluorine content is apt to reinforce resilience against solvent-driven dilation and, more importantly, membrane separation selectivity. However, fully perfluorinated polymers (e.g., Teflon with 76% F content) display inferior solution processability in conventional solvents,^[47] necessitating specialized fluorosolvents, alongside low permeation fluxes attributed to minimal swelling in hydrocarbon-based solvents.^[48] By adjusting the fluorine concentration, re-

searchers addressed the trade-off between membrane selectivity and permeability while preserving processability with traditional solvents. Eventually, fluorine-rich poly(arylene amine) (FRPAA) polymer materials were obtained to separate low-molecular-weight aliphatic compounds (Fig. 2). For the C₆–C₂₂ Fischer-Tropsch (FT) hydrocarbon mixture, the FRPAA series membranes enabled efficient short-chain/long-chain hydrocarbon separation. Through single-stage membrane

separation, a mixture containing 74 wt% light hydrocarbon components can be enriched to 95 wt% in the permeate, with a rejection rate of over 90% for long-chain hydrocarbons ($C > 20$).

2.3 Microporous Polytriazole Polymers

Finn *et al.* established a simple strategy for fabricating polytriazole polymers (DUCKYs) tailored for Arabian light crude oil sep-

aration (Fig. 3).^[49] This strategy entails step-growth polymerization of spirocyclic bis(alkynes) derived from 3,3,3',3'-tetramethyl-1,1'-spirobisindane-6,6'-diol and diazides, with a copper(I) phosphine complex serving as the catalyst. Similar to polymers of intrinsic microporosity (PIMs), these polymers employ spirocyclic building blocks, but without rigid ladder-type linkages. The DUCKY polymers had abundant micropores but were not inter-

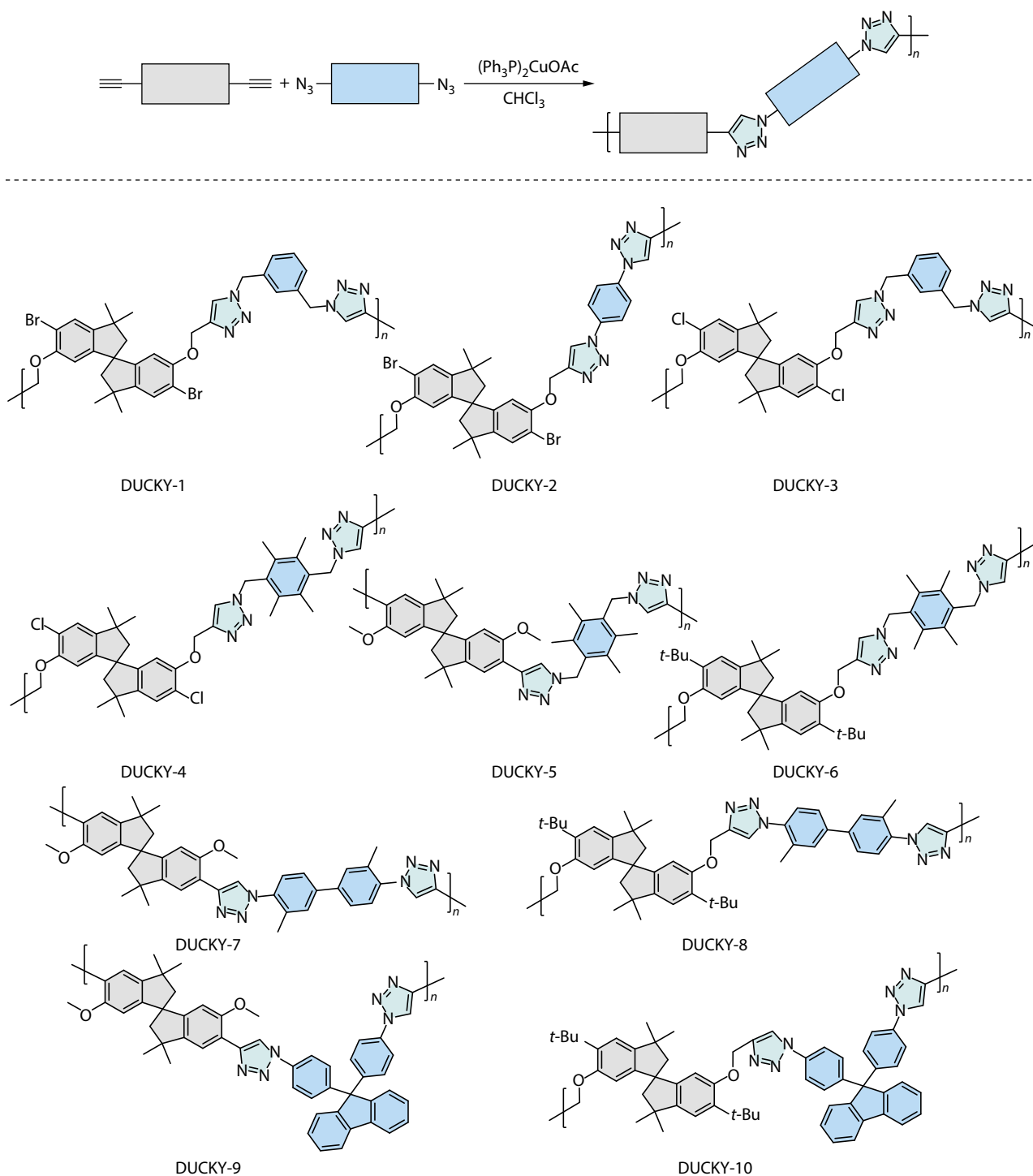


Fig. 3 The synthetic route for polytriazole polymers (top panel) and chemical structures of DUCKY polymers (bottom panel). DUCKY stands for a nickname derived from the pronunciation of "CuAAC" (copper-catalyzed azide–alkyne cycloaddition), the key reaction for polymer synthesis.

connected. They exhibit adequate chain flexibility to enable the dynamic connection of large microporous voids, thereby increasing the membrane permeability. Notably, chain flexibility does not cause extensive swelling, which undermines the selectivity of the membrane. The DUCKY-9 membrane is capable of isolating transparent permeate from black, molasses-like feedstock (Arabian light crude oil), demonstrating the complete elimination of colored bodies and high-molecular-weight species. Additionally, it exhibited a distinct cutoff at C20 ($282 \text{ g} \cdot \text{mol}^{-1}$), accompanied by minimal leakage of long-chain paraffinic waxes.

2.4 Microporous Polyamide Polymers

Matsuyama *et al.* fabricated MPD-TMC and FAFPA-1 membranes *via* interfacial polymerization of amines and acid chlorides (Fig. 4).^[50] Compared to the MPD-TMC membranes, the fluorine-containing FAFPA-1 membrane demonstrated a rejection rate of up to 93.9% toward TIPB and could operate stably for over 20 days. Smith *et al.* used *m*-phenylenediamine (MPD), *p*-phenylenediamine (PPD), piperazine (PIP), Tröger's base diamine (TBD), tetracid-chloride spirobifluorene (SBF), and trimesoyl chloride (TMC) as the diamine and acid chloride monomers to prepare MPD/PPD/PIP/TBD-SBF/TMC membranes (Fig. 4).^[51] Polyamide membranes featuring high specific surface areas and superior solvent permeabilities were successfully developed by incorporating two rigid molecular building blocks (TBD and SBF). Notably, the methanol permeance of the TBD-SBF membrane (578 LMH/MPa) significantly outperforms that of previously reported thin-film composite (TFC) membranes with a thinner selective layer ($<20 \text{ nm}$) fabricated *via* interfacial polymerization. This finding underscores the critical role of ultrahigh microporosity of TBD-SBF in enabling ultrafast molecular transport. For MPD/PPD/PIP-based polyamides, SBF-containing derivatives exhibited higher toluene/1,3,5-triisopropylbenzene (TIPB) separation factors than their TMC-based counterparts. This observation highlights the ability of the SBF moiety to modulate nanoscale pore size and porosity, which are key attributes for organic solvent reverse osmosis (OSRO) applications. Furthermore, the PPD-SBF membrane demonstrated a remarkable 500% enhancement in toluene permeance (25 LMH/MPa) relative to the PPD-TMC membrane. They also used triaminotriptycene (Trip) as the amine monomer, with TMC and SBF as acid chloride monomers, to fabricate Trip-TMC and Trip-SBF membranes (Fig. 4).^[22] The integration of rigid, three-dimensional, shape-persistent triptycene moieties markedly enhanced the microporosity of the as-prepared membranes. Notably, both the toluene permeance and toluene/TIPB separation factor of Trip-SBF were nearly twice those of Trip-TMC. To establish a clear structure-activity relationship between fluorination modification and separation performance, Xu *et al.* fabricated a series of fully aromatic fluorinated polyamides (FAFPA) and their corresponding control polyamide (PA) samples.^[12] It was found by the team that fluorinated groups, serving as gating motifs, play a dominant role in activating and reconstructing the chemical environment and spatial structure of subnanometer channels within FAFPAs. Gating-stimulating molecules (*e.g.*, acetone) interact strongly with the FAFPA network, which can reversibly regulate and restructure the connectivity and chemical properties of subnanometer channels. This process, in turn, facilitates the rapid transport of hydrocarbon liquids and achieves an efficient and stable crude oil separation. In contrast, when traditional polyamide (PA) membranes are ex-

posed to gating-stimulating molecules, they exhibit minimal alterations in channel structure and properties, failing to trigger effective gating effects.

2.5 Microporous Polyimine Polymers

Smith *et al.* substituted the relatively polar amide bond ($-\text{CONH}-$) with an imine bond ($-\text{C}=\text{N}-$), which is smaller in size and less polar, to synthesize microporous polyimine polymers.^[22] The replacement of the carbonyl oxygen moiety not only reduces the dipole-dipole interactions between the polymer matrix and hydrocarbon permeates, but also releases a portion of the fractional free volume (FFV) to facilitate mass transport. Specifically, MPD and Trip were used as amine monomers, with triformylbenzene (TFB) and tetraformylspirobifluorene (TFS) as aldehyde monomers, which were copolymerized to yield MPD/Trip-TFB/TFS (Fig. 5). For MPD/Trip-based polymers, TFS-containing derivatives showed higher toluene permeance than their TFB-based counterparts, attributed to TFS's more rigid three-dimensional shape-persistent structure of TFS, optimizing microporous channels and membrane-solvent interactions while lowering toluene transport resistance. Using a model crude oil (naphtha-, kerosene-, diesel-grade fractions) as a practical feed, Trip-TFS was validated to enrich $\text{C} < 12$ hydrocarbons in the permeate with a moderate permeance ($8.2 \text{ LMH} \cdot \text{MPa}^{-1}$).

2.6 Microporous Polyimide Polymers

Among the numerous polymer materials, polyimides have garnered considerable interest owing to their outstanding processability, adjustable structural properties, and superior chemical stability.^[16,52–54] Notably, as a category of versatile engineering plastics, polyimides have been industrially produced on a large scale, with applications spanning various fields. Through reasonable structural modifications, polyimides are anticipated to provide a more feasible application potential for membrane-enabled liquid hydrocarbon separation. Zhu *et al.* used 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 3,5-diaminobenzoic acid (DABA), and 2,4,6-trimethyl-1,3-diaminobenzene (DAM) as comonomers to synthesize a series of microporous polyimide copolymers.^[31] 6FDA-DABA/DAM membranes (AXMYs) were successfully fabricated using a hybrid non-solvent-induced phase separation (NIPS) method (Fig. 6). The torsional energy barrier of the 6FDA-DABA segment was significantly lower than that of the 6FDA-DAM segment, enabling segmental adjustment and dense stacking. As the DABA ratio decreased and the DAM ratio increased, the specific surface area and pore connectivity of the 6FDA-DABA/DAM polymers gradually improved and the pore size distribution shifted toward larger pores. Thus, A1M3-M displayed the highest toluene permeance, whereas A4M0-M exhibited the highest toluene/TIPB selectivity. Therefore, the A4M0-M and A1M3-M membranes were employed to mimic the multistage membrane fractionation of complex hydrocarbon mixtures using a toluene feed consisting of 5 wt% kerosene and 5 wt% liquid paraffin. The results showed that A1M3-M effectively eliminated high-molecular-weight components during the first-stage filtration; subsequently, A4M0-M selectively filtered out paraffin components (*e.g.*, heptadecane) in the second stage while preserving kerosene fractions such as undecane and dodecane. Following two-stage separation, the relative kerosene proportion of the solution was enriched from 50% to 93%. Jin *et al.* devised and prepared a series of microporous polyimide membranes (*p*-PDA,

tm-PDA, and TBDA), followed by coordination crosslinking using copper ions for membrane-enabled crude oil fractionation.^[55] Specifically, the synthesized Cu-p-PDA membranes displayed a maximum toluene permeance of $2.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{MPa}^{-1}$ and a rejection efficiency of more than 80% for liquid hydrocarbons with a molecular weight exceeding 170 Da. Using a two-step membrane separation process, the gasoline

content from an actual gasoline-diesel blend was successfully concentrated from 54.5% to 96.8%.

2.7 Microporous Polyurea Polymers

Xu *et al.* prepared FANFPU membranes with low-polarity channel chemistry and a highly rigid channel architecture through the interfacial polymerization of 1,3,5-tris(4-aminophenyl) ben-

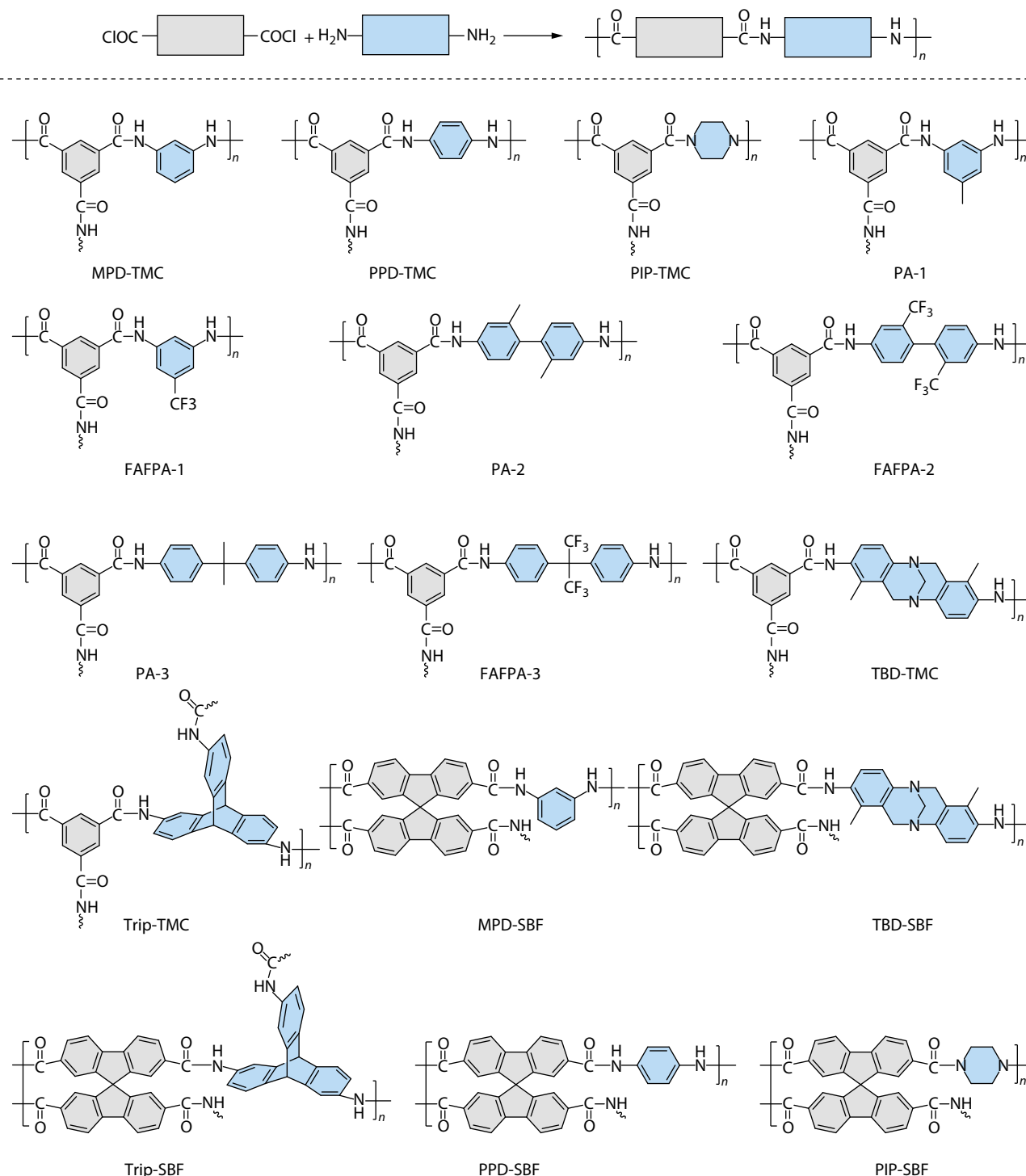


Fig. 4 The synthetic route for polyamide membranes (top panel) and chemical structures of MPD/PPD/PIP/Trip/TBD-TMC/SBF, PAs, and FAPAs polymers (bottom panel). The abbreviations of polymers are based on the monomers utilized for the polymerization reaction.

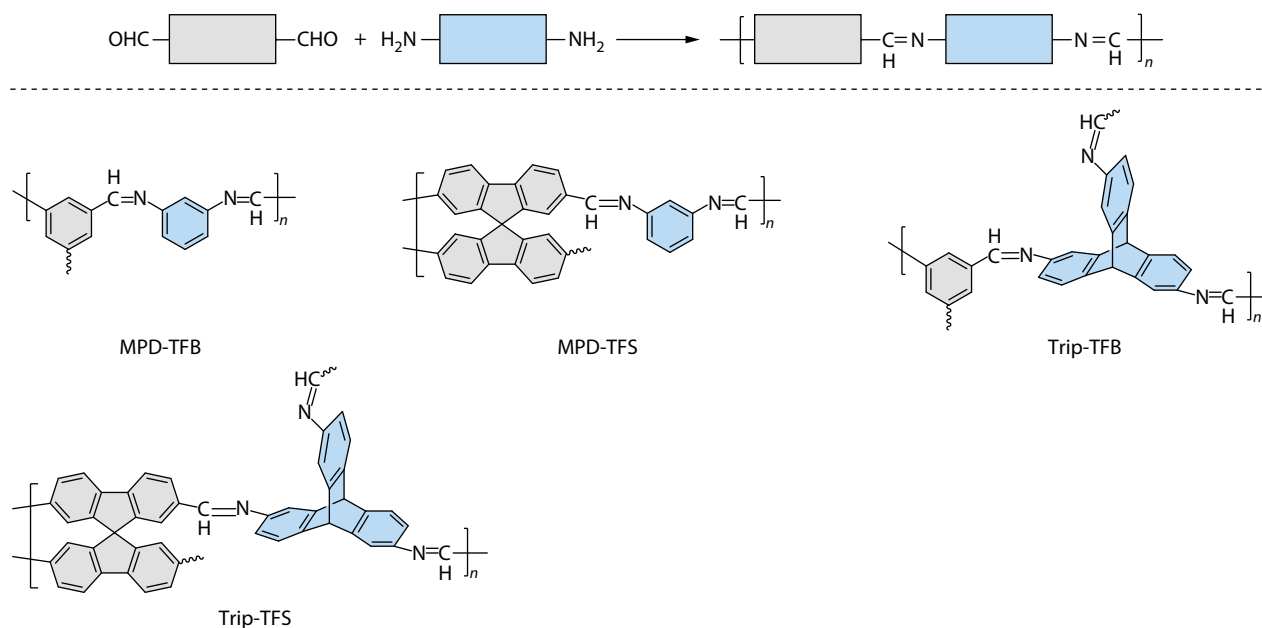


Fig. 5 The synthetic route for polyimine membranes (top panel) and chemical structures of MPD/Trip-TFB/TFS polymers (bottom panel).

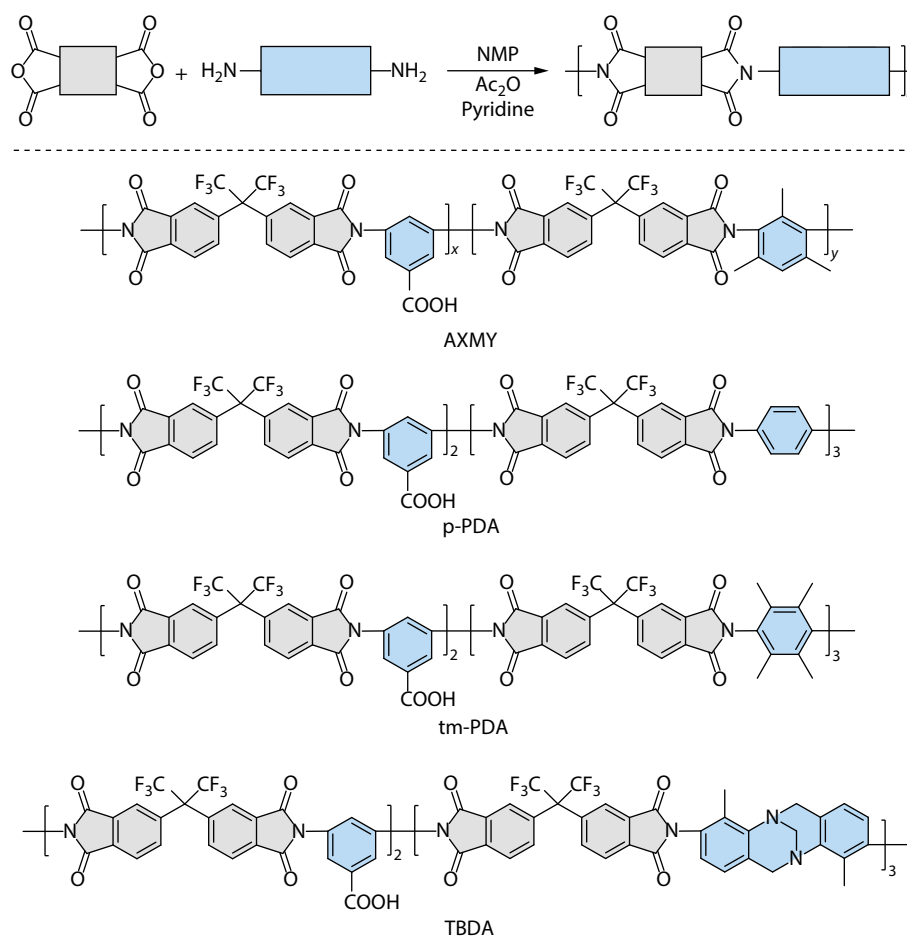


Fig. 6 The synthetic route for polyimide membranes (top panel) and chemical structures of AXMYs, *p*-PDA, *tm*-PDA, and TBDA polymers (bottom panel). AXMY stands for 6FDA-based polyimide with diamine monomers 3,5-diaminobenzoic acid (A) and 2,4,6-trimethyl-1,3-diaminobenzene (M) at a molar ratio of X:Y.

zene and toluene diisocyanate (Fig. 7).^[56] In the preparation process, an ionic liquid-water binary solvent was used to regulate the diffusion behavior of the monomers, thus achieving an optimized microporous structure. Specifically, the FANFPU40 membrane demonstrated a maximum toluene permeance of $22 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{MPa}^{-1}$ and could also effectively concentrate the light components in diluted crude oil blends at both room temperature and temperatures as high as 80°C . This study offers meaningful perspectives for the advancement of non-fluorinated membranes for crude oil fractionation in the petrochemical industry.

3 PORE STRUCTURE OF MICROPOROUS POLYMERS

Microporous polymers have abundant microporosity due to their highly rigid and contorted molecular structures.^[57–60] Diverse characterization approaches are utilized to determine the size and size distribution of free volume elements (FVEs) within microporous polymers. Such approaches include positron annihilation lifetime spectroscopy (PALS), inverse gas chromatography (IGC), cryogenic physisorption (N_2 sorption), ^{129}Xe -NMR spectroscopy, molecular simulation, and scattering techniques (e.g., small-angle X-ray scattering (SAXS) and X-ray diffraction (XRD)). Each of these methods is elaborated on in detail below.

PALS capitalizes on lifetime fluctuations of positronium (P_s), where the lifetimes of triplet-state o-P_s (1.5–4.0 ns) are correlated with FVE size; it can identify pores as small as $1.06 \text{ \AA}$, delivers data on size distribution and environmental responsiveness, but necessitates an inert environment to preclude oxygen-induced interference and often exhibits bimodal distribution characteristics.^[61–64] IGC employs volatile probe molecules to establish a connection between solute mixing enthalpy (ΔH_m) and average FVE size ($>5 \text{ \AA}$), with results aligning with those from PALS—yet it carries the potential to induce polymer swelling and thus overestimate the size of larger pores.^[65–67] Physisorption, predominantly utilizing N_2 (-196°C , detection limit $\geq 4.5 \text{ \AA}$) and CO_2 (0°C , suitable for ultramicropores $<0.7 \text{ nm}$), relies on HK/NLDFT or GCMC models for pore distribution analysis; CO_2 is more effective at probing narrower pores compared to N_2 , though both methods are based on the assumption of a slit-pore model.^[44,68–71]

^{129}Xe -NMR spectroscopy exploits the sensitivity of ^{129}Xe chemical shifts to FVE dimensions (detection range: $3.2\text{--}4.6 \text{ \AA}$), enabling the capture of temperature-dependent behavior while being susceptible to paramagnetic particles and relying on zeolite-based calibration standards.^[72,73] Molecular modeling, centered on molecular dynamics (MD) simulations of models containing 2000–10000 atoms, facilitates the visualization of FVE connectivity and dynamic fluctuations; it strikes a balance between computational efficiency (united atom approach) and precision (all-atom approach) to complement experimental data.^[74–76] Scattering techniques (SAXS/WAXS/XRD) apply Bragg's law to calculate d-spacings with a detection limit of $\geq 0.5 \text{ \AA}$. These d-spacings correlate with interchain distances and FVE sizes, enabling analysis of temperature and pressure effects, but require intricate interpretation when applied to amorphous polymers such as PIMs, which are characterized by distinct broad WAXS peaks.^[77,78]

Physisorption is one of the most mature and widely used characterization methods for determining key physicochemical properties of microporous polymer materials, such as specific surface area, pore diameter, and pore size distribution. CO_2 adsorption at 0°C and N_2 adsorption at -196°C are among the most commonly employed pore characterization methods. PIM-1 exhibits a CO_2 sorption capacity of $51.5\text{--}57.8 \text{ cm}^3\cdot\text{g}^{-1}$ and a N_2 sorption capacity of $271.1\text{--}325.5 \text{ cm}^3\cdot\text{g}^{-1}$ (Figs. 8a, 8b and Table 1).^[19,22] SBADs, DUCKYs, polyamide, polyimine, polyimide, and polyurea polymers exhibit relatively lower CO_2 and N_2 sorption capacities than those of PIM-1 (Figs. 8a and 8b and Table 1).^[19,22,31,49,51] Notably, Trip-TFS demonstrated CO_2 and N_2 sorption capacities comparable to those of PIM-1, benefiting its cross-linked structure (Figs. 8a and 8b and Table 1).^[22] Besides gas adsorption isotherms, molecular simulation is also utilized to evaluate pore structure and connectivity of microporous polymers. PIM-1 exhibits a high proportion of interconnected micropores regions, that is a greater number of accessible pores (Fig. 8c, left panel).^[19] In contrast, the relatively flexible SBAD polymers feature more isolated pores (Fig. 8c, right panel).^[19]

Microporous polymer materials may swell in organic solvents (Fig. 8d and Table 2).^[19,21,31,49] For instance, PIM-1 exhibited a high toluene uptake of about 125%, and the resultant

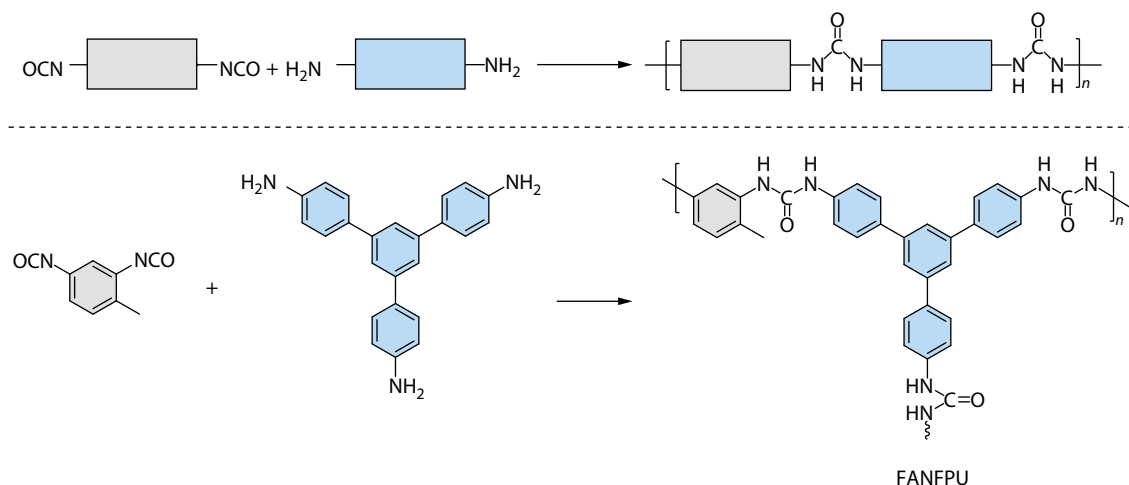


Fig. 7 The synthetic route for polyurea membranes (top panel) and FANFPU (bottom panel).

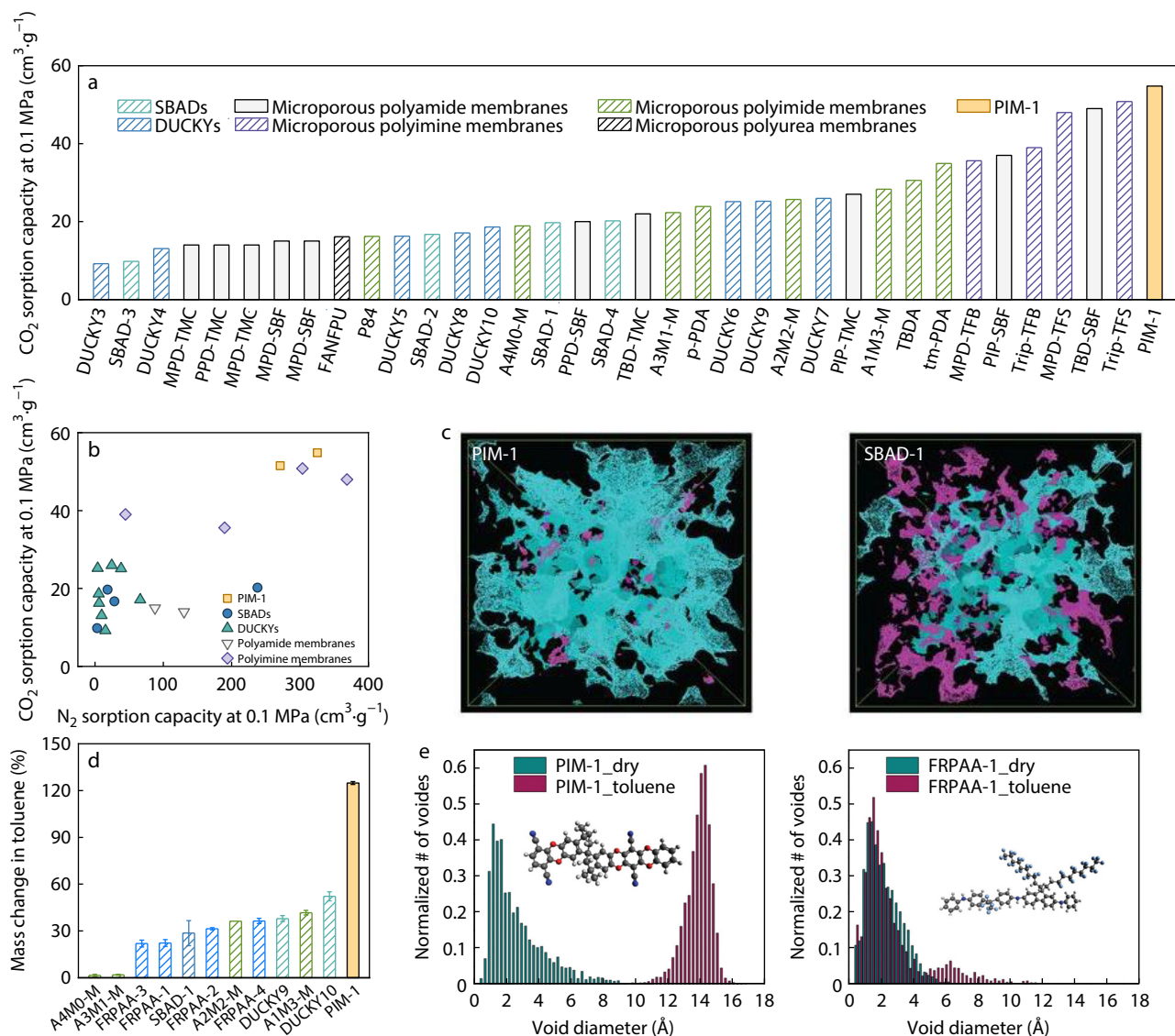


Fig. 8 (a) CO₂ sorption capacities at 0.1 MPa for representative microporous polymers; (b) CO₂ sorption capacity plotted against N₂ sorption capacity at 0.1 MPa for microporous polymers. Detailed values are provided in Table 1; (c) Simulated micropore surfaces of PIM-1 (left panel) and SBAD-1 (right panel) with a probe of 2.2 Å in diameter. Teal denotes the accessible (interconnected) surface area, while magenta indicates the isolated micropores (Reproduced with permission from Ref. [19]; Copyright (2020), the American Association for the Advancement of Science). (d) Liquid toluene uptake by microporous polymers. Detailed values are provided in Table 2; (e) Pore size distributions of PIM-1 (left panel) and FRPAA-1 (right panel) in both the dry and toluene-solvated states through molecular dynamics (MD) simulations (Reproduced with permission from Ref. [19]; Copyright (2020), the American Association for the Advancement of Science; Reproduced with permission from Ref. [21]; Copyright (2025), the American Association for the Advancement of Science).

large pores were insufficient for separation (Figs. 8d and 8e).^[21] Based on this, numerous studies have focused on strategies such as introducing rigid units (*e.g.*, SBF, Trip, *etc.*), fluorination, and crosslinked networks to inhibit segmental motion, thereby forming non-interconnected pores and reducing the organic solvent uptake of the membrane. The toluene uptakes of SBAD-1, DUCKY-9, DUCKY-10, A1M3-M, A2M2-M, and FRPAAs ranged from 22% to 55% (Fig. 8d and Table 2) and these membranes demonstrated moderate selectivity. In contrast, a lower toluene uptake indicates an anti-swelling capability and a robust micropore structure, which could enhance the selectivity in the separation of hydrocarbon mixtures. For instance, A3M1-M and A4M0-M exhibited

ultralow toluene uptake (<2%), and their high toluene/TIPB selectivities were four and two times that of A1M3-M (with a toluene uptake of 41.7%), respectively.

FRPAA-1 retains a rigid porous architecture in the wet state and delivers a higher selectivity than PIM-1 *via* the synergistic chemical structural design of a rigid fully aromatic backbone combined with segregated fluorine-rich side chains. The rigid backbone serves as a structural scaffold through aromatic units and high cross-linking density, counteracting solvent-induced pore collapse, whereas the fluorine-rich side chains boost hydrophobicity to mitigate excessive swelling and constrain polymer chain mobility through steric hindrance and weak intermolecular interactions. This yielded a wet-state

Table 1 Summary of N₂/CO₂ sorption capacities at 0.1 MPa for microporous polymers.

Polymers	N ₂ capacity (cm ³ ·g ⁻¹)	CO ₂ capacity (cm ³ ·g ⁻¹)	Ref.	Polymer	N ₂ capacity (cm ³ ·g ⁻¹)	CO ₂ capacity (cm ³ ·g ⁻¹)	Ref.
PIM-1	325.5	54.8	[22]	PIP-TMC	–	27	[51]
PIM-1	271.1	51.5	[19]	PIP-SBF	–	37	[51]
SBAD-1	18.4	19.7	[19]	TBD-TMC	–	22	[51]
SBAD-2	28.6	16.7	[19]	TBD-SBF	–	49	[51]
SBAD-3	3.2	9.8	[19]	A1M3-M	–	28.3	[31]
SBAD-4	237.8	20.2	[19]	A2M2-M	–	25.7	[31]
DUCKY3	15.3	9.2	[49]	A3M1-M	–	22.3	[31]
DUCKY4	9.8	13	[49]	A4M0-M	–	18.9	[31]
DUCKY5	6.1	16.2	[49]	tm-PDA	–	34.9	[55]
DUCKY6	38.4	25.1	[49]	TBDA	–	30.6	[55]
DUCKY7	24.5	25.9	[49]	p-PDA	–	23.9	[55]
DUCKY8	66.2	17.1	[49]	FANFPU	–	16.1	[56]
DUCKY9	4	25.2	[49]	MPD-TMC	130.3	14	[22]
DUCKY10	5.5	18.6	[49]	MPD-SBF	87.9	15	[22]
MPD-TMC	–	14	[51]	MPD-TFB	189.6	35.6	[22]
MPD-SBF	–	15	[51]	MPD-TFS	368.7	48	[22]
PPD-TMC	–	14	[51]	Trip-TFB	44.6	39	[22]
PPD-SBF	–	20	[51]	Trip-TFS	303.4	50.8	[22]

Table 2 Summary of toluene uptake for microporous polymers.

Polymer	Mass change (%) in toluene	Ref.	Polymer	Mass change (%) in toluene	Ref.
SBAD-1	28.6±8	[19]	A3M1-M	1.9±0.3	[31]
PIM-1	124.8±0.9	[19]	A4M0-M	1.5±0.7	[31]
DUCKY9	37.9±1.9	[49]	FRPAA-1	22.3±2.2	[21]
DUCKY10	52.2±2.9	[49]	FRPAA-2	31.4±0.7	[21]
A1M3-M	41.7±1.5	[31]	FRPAA-3	21.9±2.2	[21]
A2M2-M	36.3	[31]	FRPAA-4	36.4±1.7	[21]

pore size distribution largely consistent with its dry-state counterpart, with only a minor portion of pores undergoing a slight shift to 6–10 Å (Fig. 8e). In contrast, PIM-1 depends exclusively on its rigid ladder-type backbone for free volume formation and lacks the regulatory function of the fluorine-rich side chains. Solvent sorption in the wet state triggers substantial pore deformation and elevated chain mobility, precluding precise sieving of small molecules. FRPAA's dual-structure mechanism of FRPAA not only balances controlled swelling with pore rigidity but also sustains molecular sieving capability by suppressing chain relaxation, thereby achieving enhanced selectivity.^[21]

4 FABRICATION OF MICROPOROUS POLYMER MEMBRANES

Microporous polymers can be processed into membranes using two distinct strategies (Fig. 9).^[19,21,22,49] For linear microporous polymer membranes, the polymers were first dissolved in organic solvents (e.g., chloroform). Each solution was then blade-coated onto a pre-prepared flat substrate (e.g., crosslinked polyetherimide) using a bar applicator. After solvent evaporation at room temperature, the membranes were carefully peeled off once the solvent was completely removed. Branched microporous polymer membranes were fabricated *via* interfacial polymerization of aqueous- and organic-phase monomers. Specifically, the substrate was fixed on a glass plate and an aqueous phase solution (e.g., diamine) was applied to the support. After removing the aqueous phase solution, the residual water droplets were wiped off using a bar applicator. An organ-

ic-phase solution (e.g., dialdehyde and diacyl chloride) was then poured onto the diamine-impregnated substrate to initiate polymerization at room temperature. After the reaction, the excess organic-phase solution was rinsed with an organic solvent (e.g., hexane), and the resulting branched microporous polymer membranes were collected after thorough washing with pure water. The membrane thickness was tailored by regulating the concentration of the casting solution or the monomers.

5 HYDROCARBON SEPARATION PERFORMANCE

To fully assess and compare the separation performance of these microporous polymer membranes, we collected the performance data of representative membranes for toluene/TIPB mixture separation (Fig. 10a and Table 3).^[19,21,22,31,32,49–51] The permeance-selectivity trade-off, a core challenge in membrane separation, is clearly demonstrated in Fig. 10(a): an obvious inverse relationship exists between the toluene/TIPB separation factor and toluene permeance for most microporous polymer membranes.

For example, PIM-1, which features abundant large micropores, adopts a strategy oriented toward high throughput and demonstrates an ultra-high toluene permeance of 35 L·m⁻²·h⁻¹·MPa⁻¹, but is positioned in the low-selectivity region of the trade-off curve with a separation factor of only 1.1. The SBF-based polyamide (PPD-SBF) membrane, located at the middle section of the trade-off curve, exhibits a balanced performance with a toluene permeance of 24.9 L·m⁻²·h⁻¹·MPa⁻¹ and a moderate separation factor of 3.83.^[51] The polyimide (AXMYS-M) membranes further verify the

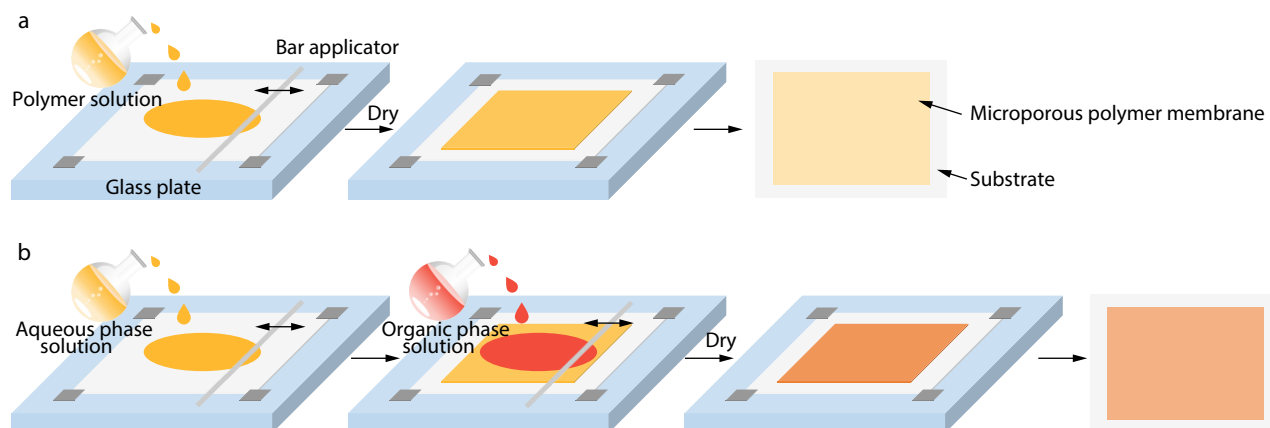


Fig. 9 Fabrication of microporous polymer membranes. (a) Schematic illustration for the preparation of linear microporous polymer membranes (e.g., SBADs, DUCKYs, FRPAAs); (b) Schematic illustration for the preparation of branched microporous polymer membranes (e.g., polyamide, polyimide, polyurea).

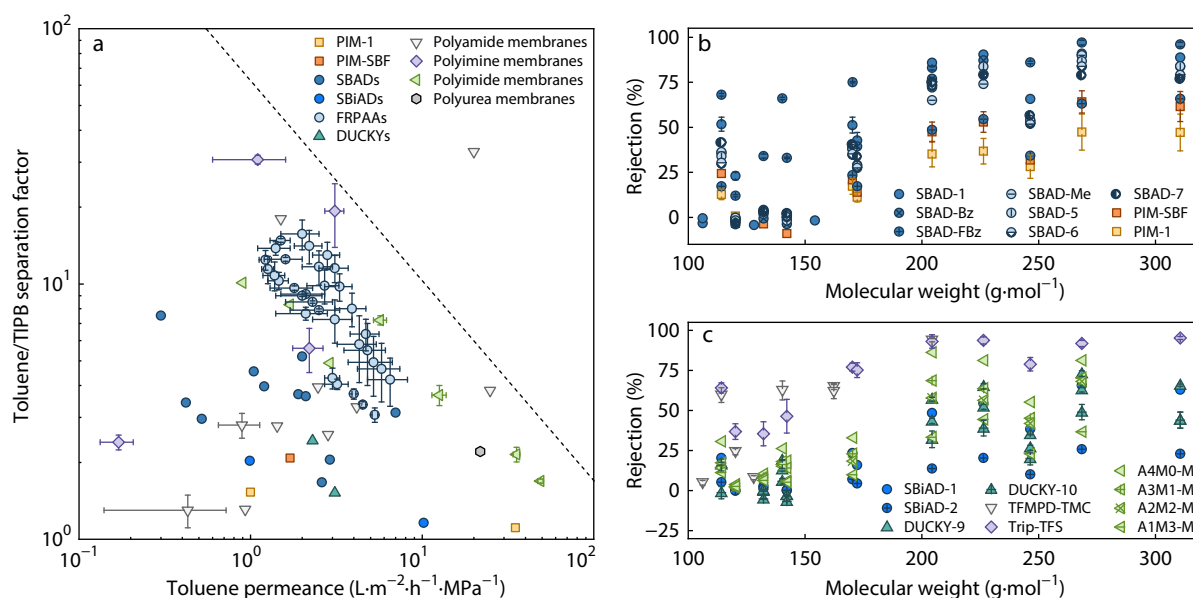


Fig. 10 (a) Toluene/TIPB separation factor versus toluene permeance for microporous polymer membranes. Detailed values are provided in Table 3. Dashed lines and shades are visual guides. (b, c) Rejection rates of different hydrocarbons by microporous membranes plotted against hydrocarbon molecular weight. Detailed values are provided in Table 4.

trade-off: their toluene permeance ranges from 5.7 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{MPa}^{-1}$ to 49 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{MPa}^{-1}$, while the separation factor decreases sharply from 7.21 to 1.69, shifting along the trade-off curve from the high-selectivity to high-permeance region as micropore connectivity increases.^[31]

In contrast, the Trip-based polyimines (Trip-TFB and Trip-TFS) employ a strategy favoring high selectivity *via* the triptycene unit's rigid molecular structure. Trip-TFB achieves a high separation factor of 30.7, and Trip-TFS a factor of 19.3, with both anchored in the high-selectivity region of the trade-off curve.^[22] Notably, fluorine-rich microporous polymer membranes (FRPAAs) adopt a strategy aiming to balance permeance and selectivity through fluorine substitution, maintaining a separation factor of 3.07–15.7 and a permeance of 1.2–6.5 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{MPa}^{-1}$, thus distributed in the balanced region of the trade-off curve.^[21]

Crucially, the FAFPA-2 membrane breaks through the long-

standing permeance-selectivity trade-off that limits most previously reported materials, exhibiting a toluene permeance of 20 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{MPa}^{-1}$ and exceptional separation factor of 33.^[12] This breakthrough is attributed to its synergistic structural design: the rigid fully aromatic backbone and highly cross-linked structure ensure pore size stability for molecular sieving, whereas fluorinated groups form specific interactions with α -hydrogen-containing polar molecules to activate a molecular gating effect. This effect reconstructs sub-nanometer channel connectivity and reduces mass transport resistance without enlarging the pore sizes, ultimately realizing the synergy of high permeability and high selectivity. This strategy transcends the boundary of the existing trade-off, and such performance makes FAFPA-2 highly promising for crude oil fractionation.

In summary, Trip-TFS, Trip-TFB, PPD-SBF, AXMYs-M, and FRPAAs are all positioned on the existing trade-off curve, with

Table 3 Summary of toluene permeance and toluene/TIPB separation factor for microporous polymer membranes.

Membrane	Toluene permeance (L·m ⁻² ·h ⁻¹ ·MPa ⁻¹)	Toluene/TIPB separation factor	Applied pressure (MPa)	TIPB concentration (mol%)	Ref.
PIM-1	35	1.11	1.5	1	[19]
SBAD-1	2	5.2	1.5	1	[19]
SBAD-2	1.9	3.7	1.5	1	[19]
SBAD-3	7	3.13	1.5	1	[19]
SBAD-4	2.6	1.67	1.5	1	[19]
TFMPD-TMC	1.5	18	3	5	[50]
PIM-1	1	1.53	1	1	[32]
PIM-SBF	1.7	2.08	1	1	[32]
SBAD-1	0.3	7.52	1	1	[32]
SBAD-1-Me	0.52	2.96	1	1	[32]
SBAD-1-Bz	1	4.54	1	1	[32]
SBAD-1-FBz	2.9	2.05	1	1	[32]
SBAD-5	2.1	3.63	1	1	[32]
SBAD-6	1.2	3.97	1	1	[32]
SBAD-7	0.42	3.43	1	1	[32]
SbAD-1	0.99	2.03	1	1	[32]
SbAD-2	10.2	1.16	1	1	[32]
DUCKY-9	2.3	2.43	3	1	[49]
DUCKY-10	3.1	1.52	3	1	[49]
MPD-TMC	0.93	1.31	5	2	[51]
MPD-SBF	2.47	3.95	5	2	[51]
PPD-TMC	4.15	3.3	5	2	[51]
PPD-SBF	24.9	3.83	5	2	[51]
PIP-TMC	2.83	2.57	5	2	[51]
PIP-SBF	1.43	2.78	5	2	[51]
A4M0-M	5.7±0.5	7.21±0.30	0.8	1	[31]
A3M1-M	12.6±1.2	3.67±0.33	0.8	1	[31]
A2M2-M	35.5±1.6	2.15±0.14	0.8	1	[31]
A1M3-M	49±1.8	1.69±0.03	0.8	1	[31]
FRPAA-1 269 nm	2.1±0.7	7.66±0.45	3	1	[21]
	1.8±0.5	9.64±0.19	4	1	[21]
	1.6±0.4	12.49±0.21	5	1	[21]
	1.4±0.3	13.79±0.84	6	1	[21]
	1.5±0.2	14.8±0.24	7	1	[21]
FRPAA-1 166 nm	4.7±0.9	6.37±0.9	3	1	[21]
	3.9±0.8	8.00±1.2	4	1	[21]
	3.3±0.6	9.76±1.2	5	1	[21]
	3.1±0.6	11.53±1.4	6	1	[21]
	2.8±0.5	12.97±1.6	7	1	[21]
	3.1±0.8	7.26±1.4	3	5	[21]
	2.7±0.57	9.85±1.5	4	5	[21]
	2.5±0.5	11.69±1.8	5	5	[21]
	2.2±0.4	14.19±2.1	6	5	[21]
	2±0.5	15.71±2.1	7	5	[21]
FRPAA-2 253 nm	2.5±0.8	7.9±0.09	4	1	[21]
	2.3±0.7	8.5±0.09	5	1	[21]
	2.1±0.6	9.13±0.08	6	1	[21]
	2±0.6	9.00±0.07	7	1	[21]
	1.46±0.2	10.3±0.8	4	5	[21]
	1.38±0.2	10.8±1.4	5	5	[21]
	1.26±0.1	11.43±1.4	6	5	[21]
	1.22±0.1	12.43±1.1	7	5	[21]
FRPAA-3 233 nm	5.3±0.2	3.07±0.20	3	1	[21]
	4.5±0.2	3.37±0.09	4	1	[21]
	4±0.1	3.71±0.17	5	1	[21]
	3.2±0.5	4.05±0.19	6	1	[21]
	3±0.3	4.28±0.40	7	1	[21]
FRPAA-4 246 nm	6.5±1.7	4.22±0.9	3	1	[21]
	5.8±1.6	4.65±1.2	4	1	[21]
	5.2±1.5	4.93±1.3	5	1	[21]
	4.8±1.3	5.50±1.5	6	1	[21]
	4.3±1.1	5.81±1.7	7	1	[21]

Table 3 Continued.

Membrane	Toluene permeance (L·m ⁻² ·h ⁻¹ ·MPa ⁻¹)	Toluene/TIPB separation factor	Applied pressure (MPa)	TIPB concentration (mol%)	Ref.
MPD-TMC	0.43±0.29	1.3±0.19	5	2	[22]
MPD-SBF	0.89±0.24	2.8±0.31	5	2	[22]
MPD-TFB	0.17±0.037	2.4±0.16	5	2	[22]
MPD-TFS	2.2±0.44	5.6±1.1	5	2	[22]
Trip-TFB	1.1±0.50	30.7±1.2	5	2	[22]
Trip-TFS	3.1±0.39	19.3±5.4	5	2	[22]
FAFPA-2	20	33	not given	not given	[12]
Cu-p-PDA	0.9	10.1	3	1	[55]
Cu-TBDA	1.7	8.3	3	1	[55]
Cu-tm-PDA	2.9	4.9	3	1	[55]
FANFPU	21.8	2.208	0.3	0.01	[56]

their strategies tilting toward high selectivity, balanced performance, or high throughput. By contrast, FAFPA-2 is the only material identified here that breaks through the trade-off boundary *via* a synergistic structural regulation strategy. Further optimization of microporous structures (*e.g.*, pore size distribution, surface chemistry, and channel connectivity) to replicate or surpass FAFPA-2 performance remains a key challenge in advancing membrane separation for crude oil processing.

To align with the practical application of crude oil separation, we summarize the reported microporous polymer membranes tested in more complex mixture systems, all evaluated with a dilute feed solution comprising various aromatic and aliphatic hydrocarbons (Figs. 10b and 10c and Table 4).^[19,22,31,32,49,50] Although multicomponent separation involves size sieving, competitive adsorption, and diffusion dif-

ferences, membranes demonstrating high toluene/TIPB separation factors in single-component separation tend to exhibit lower molecular weight cut-offs (MWCO) in multi-component separation. For example, SBAD-1 (with a high toluene/TIPB separation factor of 5.2) and Trip-TFS (with a high toluene/TIPB separation factor of 30.7) tended to exhibit significantly sharper rejection profiles than the other membranes (Figs. 10b and 10c and Table 4) and the molecular weight cut-offs of SBAD-1 and Trip-TFS were 253 and 252 g·mol⁻¹, respectively. DUCKY-9 (with a low toluene/TIPB separation factor of 2.43) exhibited a high molecular weight cut-off of 415 g·mol⁻¹ in a 12-component mixture in toluene. DUCKY-9 can serve as an excellent complement to SBAD-1 (253 g·mol⁻¹) or Trip-TFS (252 g·mol⁻¹), both with lower MWCOs, and can be applied to enrich crude oil through fractional filtration.

Table 4 Summary of hydrocarbon rejection for microporous polymer membranes.

Membrane	Solute	MW (g·mol ⁻¹)	Rejection (%)	Solute	MW (g·mol ⁻¹)	Rejection (%)	Ref.
SBAD-1	<i>p</i> -Xylene	106.17	−3.3	Tetralin	132.2	34±1.1	[19]
	<i>o</i> -Xylene	106.17	−0.6	<i>n</i> -Butylcyclohexane	140.27	66±0.6	
	Mesitylene	120.19	12±0.6	1-Methylnaphthalene	142.2	33±0.4	
	Naphthalene	128.17	−4.3	Dodecane	170.33	75±0.4	
	Biphenyl	154.21	−1.8	Dodecylbenzene	246.43	86±0.7	
	TIPB	204.36	83±1.1	Pristane	268.51	97±1.3	
	Isooctane	114.22	68±0.7	<i>n</i> -Docosane	310.6	96±1.2	
DUCKY-9	Toluene	92.14	−4.2±0.09	Isooctane	114.22	16±3.7	[49]
	Isooctane	114.22	16.8±0.88	Tetralin	132.21	0.25±0.56	
	Butylcyclohexane	140.27	13.0±0.82	<i>n</i> -Butylcyclohexane	140.27	19±0.29	
	Tetralin	132.21	−0.4±0.16	1-Methylnaphthalene	142.2	−3.1±0.57	
	Methylnaphthalene	142.2	−3.0±0.12	Pyrene	202.26	2.5±0.19	
	Isocetane	226.45	52.2±1.55	TIPB	204.36	57±1.2	
	TIPB	204.36	43.4±1.74	Isocetane	226.45	65±1.7	
	Pristane	268.53	62.9±1.4	<i>n</i> -Dodecylbenzene	246.44	35±0.26	
	Dodecylbenzene	246.44	26.7±1.63	Pristane	268.53	73±1.8	
	Docosane	310.61	65.8±0.67	Docosane	310.61	44±5	
DUCKY-10	Squalane	422.83	87.7±1.06	Squalane	422.83	93±4.5	[19]
	Isooctane	114.22	−1.3±3.8	Isocetane	226.45	39±4.9	
	Tetralin	132.21	−5.2±0.26	<i>n</i> -Dodecylbenzene	246.44	20±4.0	
	<i>n</i> -Butylcyclohexane	140.27	5.8±1.7	Pristane	268.53	49±4.8	
	1-Methylnaphthalene	142.2	−6.7±0.079	Docosane	310.61	44±5	
	Pyrene	202.26	0.49±1.6	Squalane	422.83	79±2.0	
TFMPD-TMC	TIPB	204.36	32±5.2				[50]
	Methylcyclohexane	98.2	39.3±4.14	<i>n</i> -Butylcyclohexane	140.3	62.5±5.95	
	<i>p</i> -Xylene	106.2	4.90±1.51	1,3-diisopropylbenzene	162.3	64.9±1.79	
	Isooctane	114.2	59.6±4.64	1,4-diisopropylbenzene	162.3	61.8±4.37	
	IsoPropylbenzene	120.2	24.3±1.90	TIPB	204.4	93.9±1.02	
	Naphthalene	128	8.10±1.26				

Table 4 Continued.

Membrane	Solute	MW (g·mol ⁻¹)	Rejection (%)	Solute	MW (g·mol ⁻¹)	Rejection (%)	Ref.
PIM-1	Isooctane	114.2	12.7±2.9	TIPB	204.35	35.1±7.1	[32]
	Propylbenzene	120.2	0.7	Isocetane	226.35	36.7±7.1	
	Tetralin	132.2	2.9	Dodecylbenzene	246.4	28.1±6.4	
	1-Methylnaphthalene	142.2	0.6	Pristane	268.5	47.3±10	
	Dodecane	170.3	17.2±4.4	Docosane	310.6	47.1±10.2	
	<i>n</i> -Butylcyclohexane	172.3	11.2±2.7				
PIM-SBF	Isooctane	114.2	24.3	TIPB	204.35	47.4±5.5	[32]
	Propylbenzene	120.2	-3.4	Isocetane	226.35	52.9±5.7	
	Tetralin	132.2	-3.7	Dodecylbenzene	246.4	31.8	
	1-Methylnaphthalene	142.2	-9	Pristane	268.5	64.1±6.2	
	Dodecane	170.3	20.8	Docosane	310.6	61.5±8.3	
	<i>n</i> -Butylcyclohexane	172.3	13.9				
SBAD-1	Isooctane	114.2	51.7±3.9	TIPB	204.35	85.8	[32]
	Propylbenzene	120.2	-2.4	Isocetane	226.35	90.4	
	Tetralin	132.2	3.7	Dodecylbenzene	246.4	65.7	
	1-Methylnaphthalene	142.2	1.9	Pristane	268.5	90.9	
	Dodecane	170.3	51.2±4.4	Docosane	310.6	88.7	
	<i>n</i> -Butylcyclohexane	172.3	42.7±4.4				
SBAD-1-Bz	Isooctane	114.2	35.8	TIPB	204.35	76.9	[32]
	Propylbenzene	120.2	-3.9	Isocetane	226.35	87.1	
	Tetralin	132.2	-0.7	Dodecylbenzene	246.4	53.3	
	1-Methylnaphthalene	142.2	-3.8	Pristane	268.5	89.7	
	Dodecane	170.3	37.9	Docosane	310.6	83.7	
	<i>n</i> -Butylcyclohexane	172.3	39.3				
SBAD-1-FBz	Isooctane	114.2	17.2	TIPB	204.35	48.5	[32]
	Propylbenzene	120.2	-0.4	Isocetane	226.35	54.5	
	Tetralin	132.2	3.3	Dodecylbenzene	246.4	34.2	
	1-Methylnaphthalene	142.2	1.9	Pristane	268.5	63.1	
	Dodecane	170.3	23.4	Docosane	310.6	65.8	
	<i>n</i> -Butylcyclohexane	172.3	17.2				
SBAD-1-Me	Isooctane	114.2	36.2	TIPB	204.35	65	[32]
	Propylbenzene	120.2	-0.3	Isocetane	226.35	74	
	Tetralin	132.2	4.1	Dodecylbenzene	246.4	53	
	1-Methylnaphthalene	142.2	-0.5	Pristane	268.5	90	
	Dodecane	170.3	39.1	Docosane	310.6	77.6	
	<i>n</i> -Butylcyclohexane	172.3	29				
SBAD-5	Isooctane	114.2	33.9	TIPB	204.35	72.1	[32]
	Propylbenzene	120.2	-2.5	Isocetane	226.35	83.7	
	Tetralin	132.2	1.9	Dodecylbenzene	246.4	54.1	
	1-Methylnaphthalene	142.2	-1.8	Pristane	268.5	86.7	
	Dodecane	170.3	37.9	Docosane	310.6	83.9	
SBAD-6	Isooctane	114.2	30.7	TIPB	204.35	73.7	[32]
	Propylbenzene	120.2	-1.4	Isocetane	226.35	79.8	
	Tetralin	132.2	3.6	Dodecylbenzene	246.4	52.2	
	1-Methylnaphthalene	142.2	0.5	Pristane	268.5	84.2	
	Dodecane	170.3	35.6	Docosane	310.6	79.4	
	<i>n</i> -Butylcyclohexane	172.3	27.8				
SBAD-7	Isooctane	114.2	41.6	TIPB	204.35	75.1	[32]
	Propylbenzene	120.2	-3.1	Isocetane	226.35	78.9	
	Tetralin	132.2	3.7	Dodecylbenzene	246.4	56.6	
	1-Methylnaphthalene	142.2	2.3	Pristane	268.5	78.9	
	Dodecane	170.3	40.6	Docosane	310.6	76.9	
	<i>n</i> -Butylcyclohexane	172.3	33.8				
SBiAD-1	Isooctane	114.2	20.3	TIPB	204.35	48.4	[32]
	Propylbenzene	120.2	-0.11	Isocetane	226.35	54.4	
	Tetralin	132.2	2.7	Dodecylbenzene	246.4	38.4	
	1-Methylnaphthalene	142.2	0.1	Pristane	268.5	65.7	
	Dodecane	170.3	23.4	Docosane	310.6	63	
	<i>n</i> -Butylcyclohexane	172.3	15.9				
SBiAD-2	Isooctane	114.2	5.2	TIPB	204.35	13.8	[32]
	Propylbenzene	120.2	0.1	Isocetane	226.35	20.3	
	Tetralin	132.2	1.1	Dodecylbenzene	246.4	10.1	
	1-Methylnaphthalene	142.2	0.2	Pristane	268.5	25.8	
	Dodecane	170.3	7	Docosane	310.6	23	
	<i>n</i> -Butylcyclohexane	172.3	4.4				

Table 4 Continued.

Membrane	Solute	MW (g·mol ⁻¹)	Rejection (%)	Solute	MW (g·mol ⁻¹)	Rejection (%)	Ref.
A4M0-M	Isooctane	114.22	30.7	Dodecane	170.33	32.9	[31]
	Propylbenzene	120.2	3.9	TIPB	204.36	86.2	
	Tetralin	132.2	10.5	<i>i</i> -Hexadecane	226.44	81.3	
	<i>n</i> -Butylcyclohexane	140.27	26.3	Dodecylbenzene	246.43	55.2	
	1-Methylnaphthalene	142.2	18.6	Pristane	268.51	81.2	
A3M1-M	Isooctane	114.22	17.4	Dodecane	170.33	23	[31]
	Propylbenzene	120.2	2.7	TIPB	204.36	68.6	
	Tetralin	132.2	8.3	<i>i</i> -hexadecane	226.44	63.8	
	<i>n</i> -Butylcyclohexane	140.27	18.2	Dodecylbenzene	246.43	45.2	
	1-Methylnaphthalene	142.2	14.1	Pristane	268.51	70.4	
A2M2-M	Isooctane	114.22	14.2	Dodecane	170.33	18.4	[31]
	Propylbenzene	120.2	1.8	TIPB	204.36	57.8	
	Tetralin	132.2	7.6	<i>i</i> -Hexadecane	226.44	56.4	
	<i>n</i> -Butylcyclohexane	140.27	15.2	Dodecylbenzene	246.43	41.9	
	1-Methylnaphthalene	142.2	6	Pristane	268.51	68.2	
A1M3-M	Isooctane	114.22	11.3	Dodecane	170.33	9.9	[31]
	Propylbenzene	120.2	2.6	TIPB	204.36	33.3	
	Tetralin	132.2	6.4	<i>i</i> -Hexadecane	226.44	44.4	
	<i>n</i> -Butylcyclohexane	140.27	16.3	Dodecylbenzene	246.43	23.1	
	1-Methylnaphthalene	142.2	5.2	Pristane	268.51	36.7	
Trip-TFS	Isooctane	114.2	64.1±3.2	TIPB	204.4	93.1±4.2	[22]
	Propylbenzene	120.2	36.8±4.9	Isocetane	226.4	93.7±2.2	
	Tetralin	132.2	35.4±7.5	Dodecylbenzene	246.4	78.9±4.2	
	1-Methylnaphthalene	142.2	46.4±10.5	Pristane	268.5	91.8±1.9	
	Dodecane	170.3	77.1±2.5	Docosane	310.6	95.2±0.9	
Cu-p-PDA	<i>p</i> -Xylene	106.17	17.6	1-Methylnaphthalene	142.20	48.1	[55]
	<i>o</i> -xylene	106.17	25.5	TIPB	204.36	87.9	
	Isooctane	114.22	59.0	Pristane	268.51	87.6	
	Mesitylene	120.19	32.4	<i>n</i> -Docosane	310.60	85.2	
Cu-tm-PDA	<i>p</i> -Xylene	106.17	14.7	1-Methylnaphthalene	142.20	31.3	[55]
	<i>o</i> -Xylene	106.17	21.38	TIPB	204.36	78.3	
	Isooctane	114.22	45.8	Pristane	268.51	81.4	
	Mesitylene	120.19	26.3	<i>n</i> -Docosane	310.60	80.4	
Cu-TBDA	<i>p</i> -Xylene	106.17	12.2	1-Methylnaphthalene	142.20	39.0	[55]
	<i>o</i> -Xylene	106.17	15.3	TIPB	204.36	81.6	
	Isooctane	114.22	56.6	Pristane	268.51	82.4	
	Mesitylene	120.19	28.7	<i>n</i> -Docosane	310.60	83.1	

6 DEMONSTRATION OF SEPARATION PERFORMANCE FOR ACTUAL CRUDE OIL

Finn *et al.* applied a microporous polymer membrane (SBAD-1) for the fractionation of light shale crude oil, demonstrating the potential of membrane separation as an alternative for crude oil fractionation.^[19] This process can separate crude oil into low- and high-molecular-weight fractions, enabling the direct production of carbon-number-classified products (*e.g.*, gasoline: C5–C12 alkanes/cycloalkanes; jet fuel: C10–C18 alkanes/aromatics). Fig. 11(a) plots the permeate/retentate concentration ratio against the component molecular weights, and both low- and high-molecular-weight fractions were present in the retentate with varied enrichments. Fig. 11(b) shows the molecular distribution as a function of the boiling point of the molecules in the feed, permeate, and retentate. Approximately 38% of the feed components boiled below 200 °C, this fraction was markedly enriched in light molecules after separation with the SBAD-1 thin-film composite membranes, with 60% of its components boiling below 200 °C. Fig. 11(c) presents photographs of the crude oil feed and the lightly colored permeate. Fig. 11(d) depicts the discrepancies in GC×GC-FID (flame ionization detec-

tion) chromatography between the feed and the permeate, and the results (Fig. 11e) confirm the enrichment of molecules with a carbon number <12 (or about 170 Da) in the permeate. However, the membrane permeance needs to be further improved. Crude oil separation experiments confirmed that SBAD-1 effectively retained C>12 hydrocarbons (boiling point >200 °C) in crude oil, with a total rejection rate of >60%. C>12 hydrocarbons can be further concentrated for jet fuel, and C<12 fractions for light gasoline. Overall, the SBAD-1 membrane was selective toward low-molecular-weight and saturated hydrocarbon molecules in the naphtha and early kerosene boiling ranges, with very limited permeation of high-molecular-weight linear paraffins.

In a subsequent study by this group, Arabian light crude oil, which is heavier than shale-based light crude oil, was employed as the feed to assess the performance of the DUCKY-9 membrane.^[19,49] At low-stage cuts, a marked enrichment of light hydrocarbons was noted (Fig. 12a), although the membrane permeance remained relatively low. Among all the feed components, 26% had boiling points below 200 °C, and this fraction was concentrated to 80% in the permeate at a 1% stage cut and 69% at a 2% stage cut. For feed components

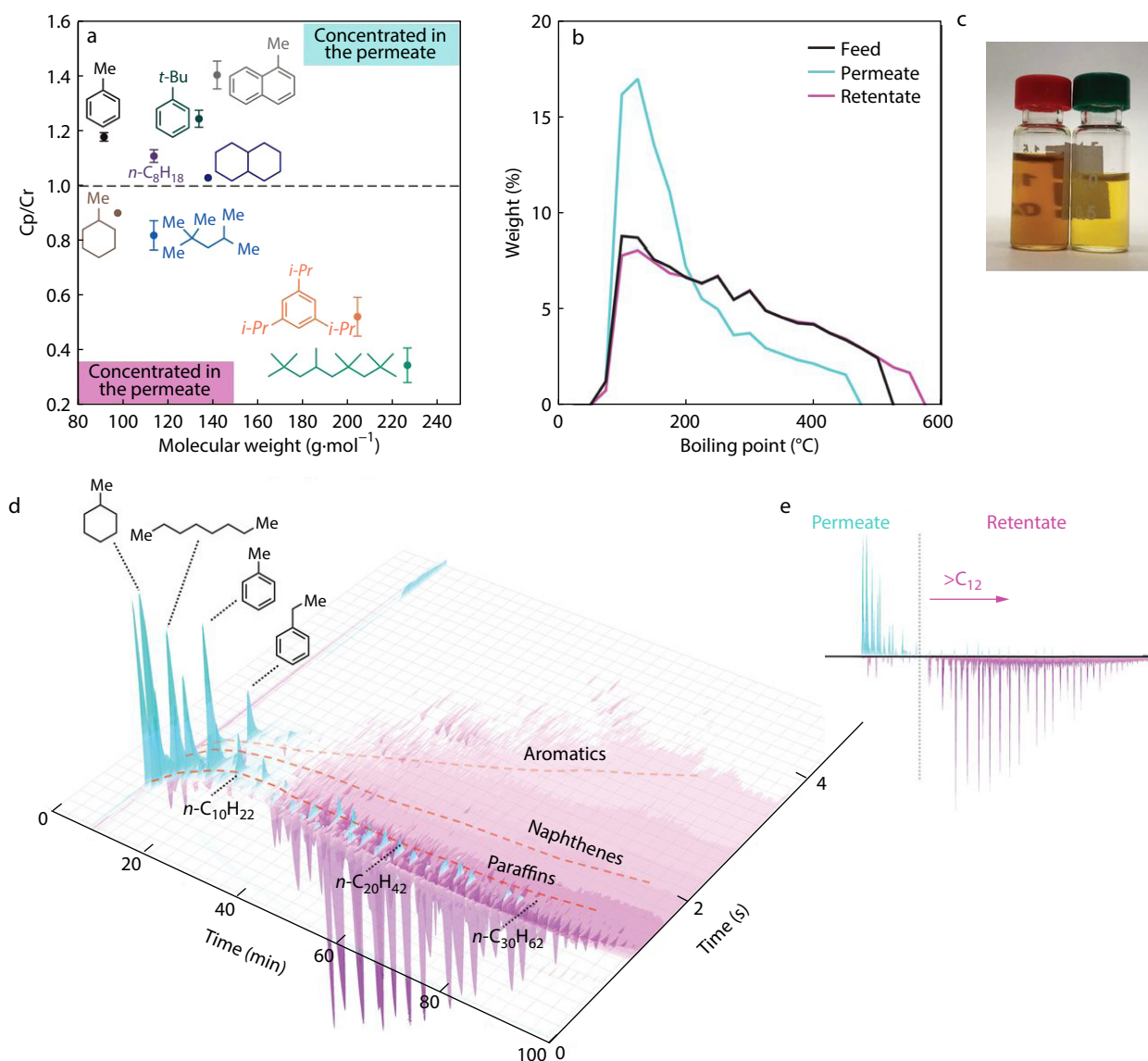


Fig. 11 SBAD-1 membrane for crude oil separation. (a) Permeate (C_p)/retentate (C_r) concentration ratio of complex model crude oil components separated by SBAD-1; (b) Weight distribution of feed, permeate, and retentate as a function of boiling point during the separation of shale-derived crude oil with SBAD-1 TFC membrane; (c) Photos of feed (left panel) and permeate (right panel); (d) GCxGC-FID traces for shale-derived crude oil separation with the SBAD-1 TFC membrane. Teal peaks: permeate-enriched; magenta peaks: retentate-concentrated. (e) GCxGC-FID side view from d: carbon number distribution. (Reproduced with permission from Ref. [19]; Copyright (2020), the American Association for the Advancement of Science.)

with boiling points below 260°C , which account for 37% of the total feed, the enrichment levels reached 94% and 90% in the permeate at the 1% and 2% stage cuts, respectively. This highlights the material's outstanding selectivity for molecules that fall within the upper limit of the diesel boiling range. The isolation of a transparent permeate from the black molasses-like feed further verified the removal of high-molecular-weight colorants. The GCxGC chromatogram (Fig. 12b) shows the differences between the feed and permeate based on the boiling point and polarity. This revealed a distinct separation cutoff at carbon number 20 (C_{20} , $282\text{ g}\cdot\text{mol}^{-1}$).

Smith *et al.* utilized a microporous polymer membrane (Trip-TFS) for the fractionation of model crude oil.^[22] Tests on

a concentrated nine-component feed blend (simulated light shale oil) demonstrated that Trip-TFS can enrich small molecules ($<6.5\text{ \AA}$) on the permeate side and retain large molecules ($>6.5\text{ \AA}$) on the retentate side (Fig. 13a). Notably, the molecular sieving performance of Trip-TFS is more prominent than that of Puramem and SBAD-1, which endows Trip-TFS with an excellent separation factor for multiple solvent pairs classified by molecular size and type (Fig. 13b). They further adopted a model crude oil consisting of naphtha-, kerosene-, and diesel-grade fuels as a realistic feed to verify the actual separation performance of the Trip-TFS membrane. Gas chromatography-mass spectrometry (GC/MS) analysis identified the composition of the feed, which contained aro-

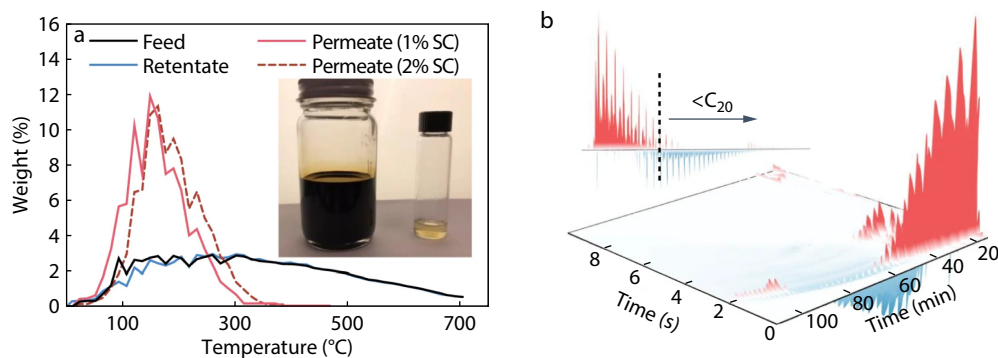


Fig. 12 DUCKY-9 membrane for crude oil separation. (a) Boiling point distribution of feed, permeate, and retentate from DUCKY-9 separated Arabian light crude oil. Inset: Arabian light feed and 2% stage cut (SC) sample (left to right). (b) GCxGC-FID analysis of Arabian light crude oil. Red peaks: permeate-enriched; blue peaks: retentate-concentrated. Inset: Carbon number partition of the crude oil. (Reproduced with permission from Ref. [49]; Copyright (2023), Springer Nature.)

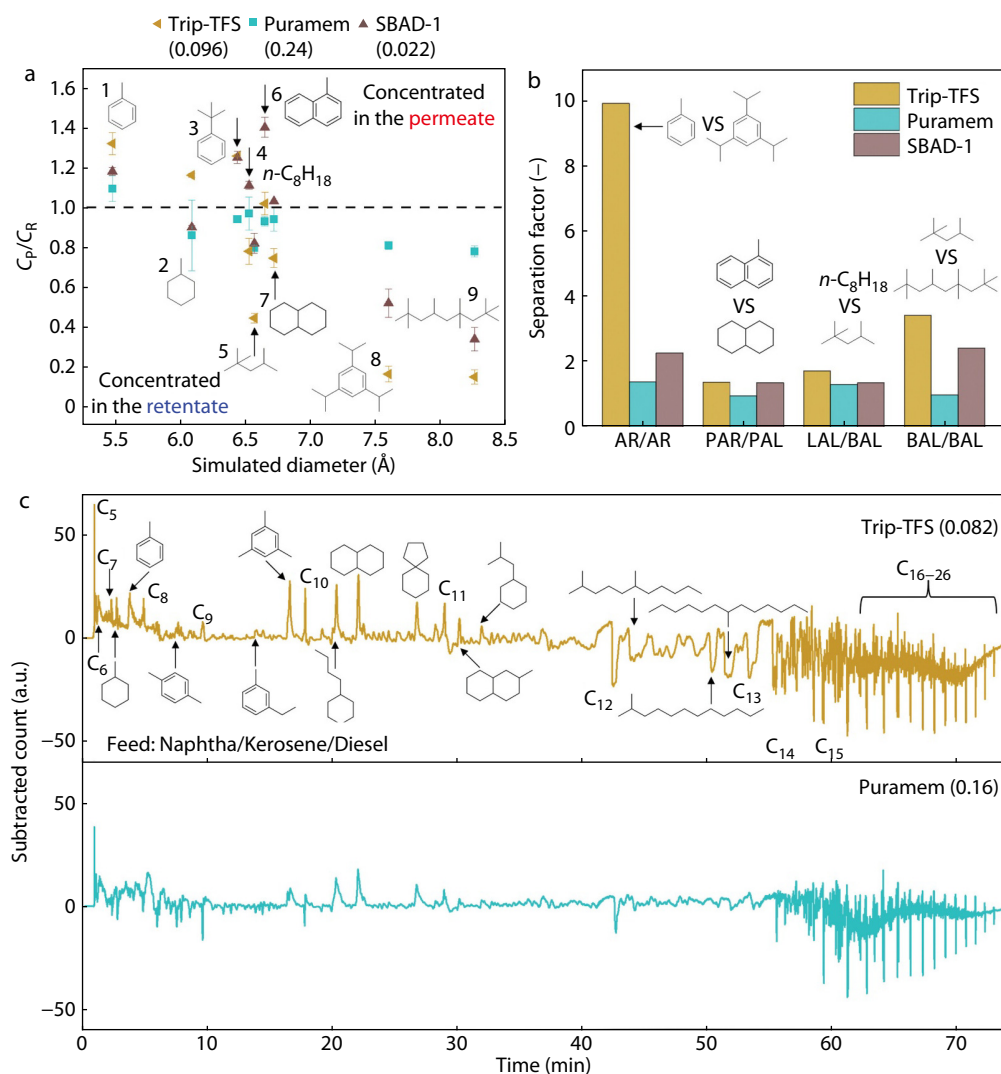


Fig. 13 Trip-TFS membrane for crude oil separation. (a) C_p/C_R of complex model crude oil components separated by Trip-TFS, SBAD-1, and Puramem; (b) Corresponding separation factors for various molecular pairs, *i.e.*, aromatic/aromatic, polyaliphatic/polyaromatic, linear aliphatic/branched aliphatic, and branched aliphatic/branched aliphatic; (c) GC/MS analysis of the fractionated model crude oil (naphtha, kerosene, diesel) after treatment with the Trip-TFS membrane and Puramem. (Reproduced with permission from Ref. [22]; Copyright (2025), the American Association for the Advancement of Science.)

matic hydrocarbons, cycloalkanes, and linear alkanes, with carbon numbers ranging from 5 to 26. Significantly, Trip-TFS effectively enriched hydrocarbon molecules with less than 12 carbon atoms in the permeate from the complex feed system and exhibited a moderate permeance of $0.82 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{MPa}^{-1}$ (Fig. 13c).

Xu *et al.* used a microporous polymer membrane (FAFPA-2) for crude oil separation.^[12] Tests on synthetic crude oil (nine nonpolar hydrocarbons) showed varying enrichment or reduction of filtrate components versus initial feed levels (Fig. 14a). Specifically, the filtrate methylnaphthalene and 1,3,5-triisopropylbenzene were 160% higher and 50% lower than the retentate levels, respectively, confirming the excellent synthetic crude fractionation performance. Viscous black crude oil containing heavy complex hydrocarbons was used. After membrane separation (Fig. 14b), it became a transparent light-brown filtrate with a boiling temperature of 380°C (initial temperature: 550°C). GC×GC and FT-ICR MS analyses verified that the gating-on FAFPA membranes selectively sepa-

rated high-value fractions ($<400 \text{ Da}$). Rigid fully aromatic backbones and high cross-linking density endow FAFPA membranes with excellent thermal stability for thermally enhanced fractionation. Elevated temperatures reduce the crude viscosity, accelerate hydrocarbon mass transfer, and increase permeance. At $25\text{--}80^\circ\text{C}$, the permeance increased about 32-fold with a nearly unchanged separation performance (Fig. 14c). Long-term testing at 80°C showed stable performance over 132 h (Fig. 14d); the performance was restored via simple gating-on regeneration. This thermally enhanced performance provides new insights for improving the viscous crude fractionation efficiency.

7 SUMMARY AND OUTLOOK

Microporous polymer membranes that deliver both high permeability and selectivity have garnered growing interest in recent years.^[79–83] A variety of such materials have been developed, including polymers of intrinsic microporosity (PIMs),

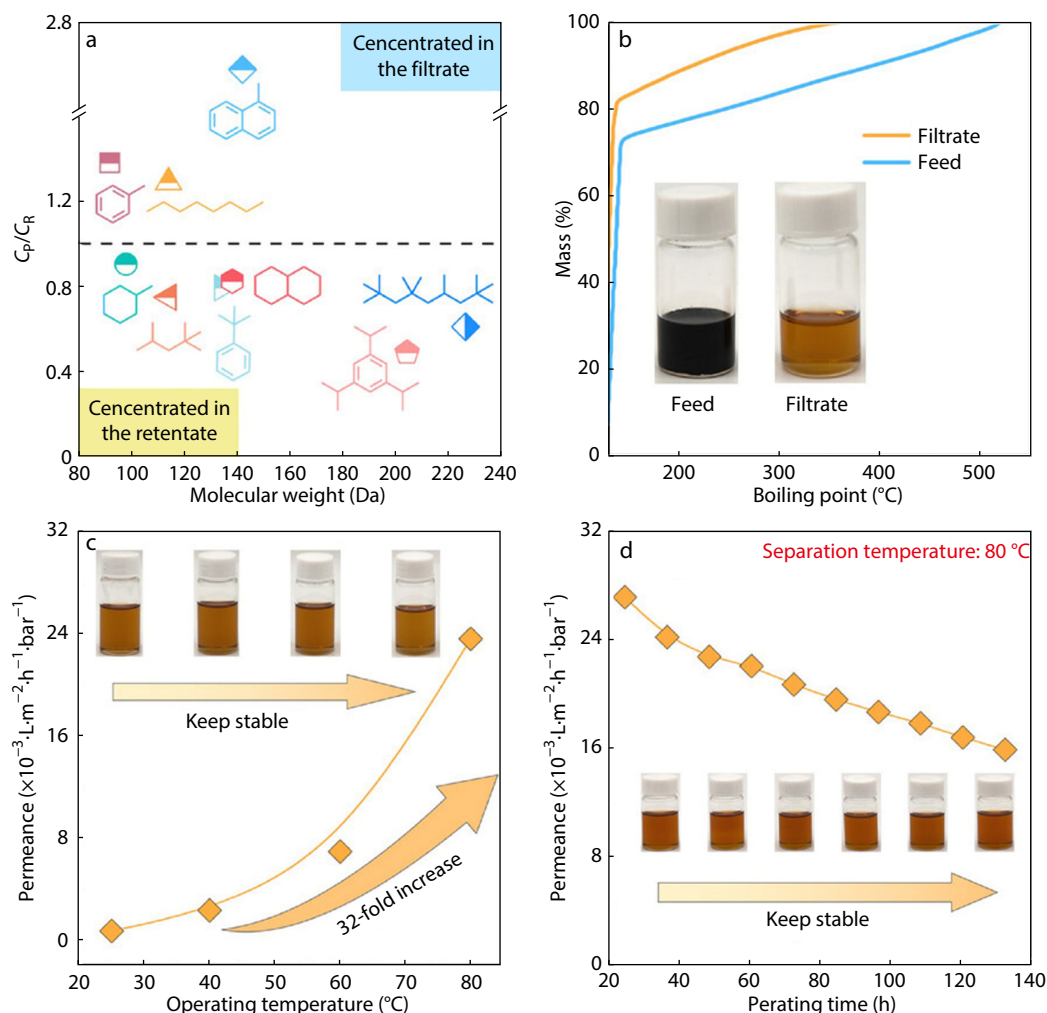


Fig. 14 FAFPA-2 membrane for crude oil separation. (a) C_P/C_R of complex model crude oil components separated by FAFPA-2; (b) Boiling-point distribution of the feed and filtrate of black crude oil post-fractionation with gating-enabled FAFPA-2 membrane. Inset digital images show the feed (left) and filtrate (right) solutions. (c) Permeation performance of gating-enabled FAFPA-2 for crude oil fractionation at varying temperatures. Inset digital images present the filtrate of the fractionated crude oil; (d) Long-term stability of gating-enabled FAFPA-2 for crude oil fractionation at 80°C . Inset digital images display the filtrate of the fractionated crude oil, verifying thermally enhanced and stable fractionation capabilities. (Reproduced with permission from Ref. [12]; Copyright (2026), Wiley.)

whose synthetic strategies are summarized in Section 2. Membranes derived from these materials have been tested for practical crude oil fractionation to isolate products with different carbon numbers. However, several challenges persist.

The synthesis of these membranes should prioritize cost efficiency and precision. Most microporous polymer membranes are currently synthesized using cumbersome processes, noble-metal catalysts, and harsh reaction conditions (e.g., Pd catalysts for SBADs and FRPAAs). Process simplicity and cost efficiency must be prioritized for large-scale production. Additionally, strategies that enable facile regulation of pore chemistry and structure merit further research. Expanding the diversity of membrane materials with tailored pore structures could facilitate function-driven design of advanced microporous polymer membranes.

Most microporous membranes rely on size-sieving effects for high selectivity. It is critical to determine the optimal pore structures and chemical compositions of high-performance membranes. By combining machine learning predictions with the comprehensive performance database summarized in this review, the rational design of advanced microporous polymer membranes can be significantly accelerated, which provides an efficient pathway for the targeted design and synthesis of novel polymer monomers. It should be noted that most PIMs with linear backbones are prone to physical aging or solvent swelling during long-term operations. This issue can be effectively alleviated by optimizing the pore microenvironment (e.g., regulating the affinity between the polymer chains and organic solvents) and enhancing intermolecular interactions (such as π - π sieving). Furthermore, guided by the concept of multilevel membrane separation, the rational design of membrane modules in series or parallel to construct continuous separation systems represents another promising direction, which is expected to realize the precise and fractional separation of complex crude oil with multicomponent mixtures.

Accordingly, we summarize the key design principles for high-performance microporous membranes for crude oil separation as follows: first, pore-size engineering should be prioritized, as precise tuning to match the kinetic diameter of target hydrocarbons (e.g., toluene, TIPB, and alkanes with different carbon numbers) enables efficient size-sieving separation. Second, rigid, contorted building blocks (e.g., triptycene and spirobifluorene) and covalent cross-linking (e.g., imine linkages) enhance the stability and suppress aging/swelling while preserving the intrinsic microporosity. Third, the surface chemistry should be tailored to boost selective hydrocarbon affinity and reduce fouling. Fourth, hierarchical membrane assembly (series/parallel) allows for the continuous, precise fractionation of complex crude oil. Fifth, machine-learning-assisted data-driven design, combined with the performance database in this work, accelerates the rational screening and design of new monomers and structures. These principles provide clear guidance for the development of next-generation high-performance microporous membranes for the separation of industrial crude oil.

Compared with other membrane materials, PIM membranes exhibit intrinsic microporosity, excellent permeability-selectivity balance, and synthetic modifiability, but are plagued by poor anti-aging/anti-swelling performance and

potentially high synthesis costs.^[19,49] In contrast, traditional polyamide membranes have mature preparation processes but weak anti-plasticization capabilities.^[51,55] Covalent organic framework (COF) membranes exhibit tunable pore structures but poor processability.^[84,85] Commercial membranes (e.g., Puramem) ensure stability but lack high separation efficiency.^[22] In the authors' view, modified PIM-based membranes (e.g., imine-linked polymers incorporating triptycene or spirobifluorene units, such as Trip-TFS) represent the most promising materials for future development. They not only retain the high mass transfer efficiency inherent to PIMs but also address stability challenges through structural optimization, rendering them highly suitable for crude oil separation requirements.

Focus should be placed on understanding hydrocarbon transport in size-confined micropore channels. This fundamental understanding is critical for membrane design. Hydrocarbon transport under micropore confinement is a highly complex process, involving various interactions between hydrocarbon components and the membrane materials. To elucidate these transport and separation mechanisms, advanced characterization methods (e.g., pulsed-field gradient NMR (PFG-NMR),^[86–89] 2D exchange spectroscopy NMR,^[90–93] quasi-elastic neutron scattering^[94–97]) coupled with all-atomistic molecular dynamics simulations merit further investigation.^[98–101]

As we dedicate unremitting and concerted efforts to addressing these challenges in the future, we anticipate that practical crude oil separation applications of microporous polymer membranes will soon be realized.

BIOGRAPHY

Zheng-Jin Yang is a professor at the University of Science and Technology of China (USTC). He received his Ph.D. from the Tsinghua University in 2014. Afterward, he joined the research groups of Prof. Tongwen Xu at USTC and Prof. Michael J. Aziz at Harvard University for postdoctoral research. In 2019, he was enlisted in the Excellent Young Scientists Fund Program of the National Natural Science Foundation of China. His research interests include aqueous organic redox flow batteries, water electrolysis, polymers of intrinsic microporosity, and membranes for advanced separations.

Conflict of Interests

The authors declare no interest conflict.

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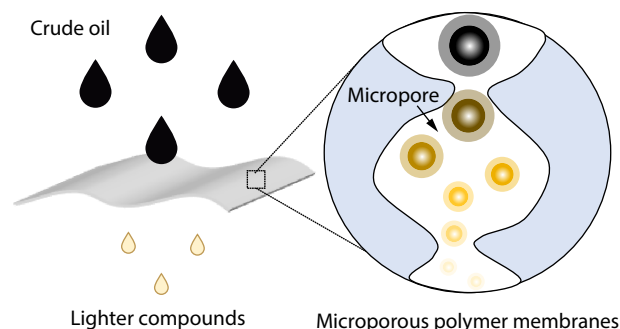
Graphical Abstract

Microporous Polymer Membranes for the Separation of Hydrocarbon Mixtures

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and Tong-Wen Xu

University of Science and Technology of China

Crude oil separation via micropores in microporous polymer membranes is illustrated: selective acquisition of lighter compounds from actual crude oil.



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