

ND ENERGY STUDENT RESEARCH FELLOWSHIP FINAL REPORT

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REPORT PERIOD:	Dec. 2018 – Aug. 2019
PROJECT TITLE:	Toward a better understanding of iptycene-based polyimide membranes: structure microporosity and gas separation performance
CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY):	<input checked="" type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS:

List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

MAJOR RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Synthesis and characterization of diamine and dianhydride monomers	The designed iptycene-based diamines and dianhydrides were synthesized successfully.	100%
Synthesis of triptycene-based polyimides with high molecular weight (MW) for membrane fabrication	Four comparable polyimides and polyamides (two triptycene-based and two non-triptycene) were synthesized with high MW. Robust films without defects were fabricated for characterization and gas permeation test.	100%
Membrane characterization and gas permeation test	The triptycene-based polyimide (TP-6FDA-d) showed extremely high permeability due to the highly rigid structure. The CO ₂ /CH ₄ separation performance is close to Robeson upper bound even in the presence of sour gas.	100%

RESEARCH OUTPUT:

Please provide detailed information below regarding any output resulting from your research project.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount)
EXTERNAL AWARDS	(Sponsor, Project Title, PIs, Award Date, Award Amount)
JOURNAL ARTICLES	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
BOOKS AND CHAPTERS	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
PUBLIC PRESENTATIONS, SEMINARS, LECTURES	(Event, Presentation Title, Presentation Date, Location)
AWARDS, PRIZES, RECOGNITIONS	(Purpose, Title, Date Received)
INTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation)
EXTERNAL COLLABORATIONS FOSTERED	(Collaborator Name, Organization, Purpose of Affiliation) Dr. Ben Sundell, Aramco, binary mixed gas and sour gas permeation test at various pressures.

WEBSITE(S) FEATURING RESEARCH PROJECT	(URL)
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	(Please describe each item in detail)

MAJOR GOALS AND ACCOMPLISHMENTS (Additional Details, Technical Results, Charts and Graphics)

Part I:

Triptycene-diamine-direct (TPDA_m-d) was prepared according to previously reported procedure by our group. The purity was further improved by recrystallization in ethanol. Triptycene-based dianhydride (TPDA_n) and diacid chloride (TPDC) were also synthesized. Pure white crystals were ready for use after drying in vacuum oven at 160 °C overnight.

A modified method for the preparation of triptycene-based dianhydride (TPDA_n) was applied. A triptycene-based tetranitrile compound was first synthesized. Then, 6.14 g of the tetranitrile compound (11.4 mmol) and 26 g KOH were added to a two-neck flask with a nitrogen inlet and a condenser. A mixture of DMSO and water (250 ml, 1:1) was added into the flask and the reaction was heated to 130 °C. The suspension turned to greenish color and NH₃ gas started releasing. After 3 days, a two-layered clear solution was formed when stopped stirring. The upper layer was collected and acidized by adding 4 M HCl solution until pH = 2. The white tetracarboxylic compound was filtered out and dried at 100 °C overnight. Triptycene-based dianhydride was synthesized by refluxing the tetracarboxylic compound (6 g, 9.7 mmol) in 46 ml of 1:1 mixture of acetic anhydride and acetic acid for 6 h with nitrogen protection. The white final product was collected by filtration, washed with petroleum ether and dried at 180 °C for 24 h under vacuum.

The structures of synthesized monomers were confirmed by ¹H NMR.

Part II:

Two polyimides (TP-6FDA-d and TP-TPDA_n-d) were obtained by chemical imidization method to convert poly (amic acid) to polyimide. Reaction conditions were carefully optimized to achieve favorable molecular weight that are high enough to cast films but not too high to dissolve.

For TP-6FDA-d, TPDA_md and half of prepared anhydrous NMP were added to a three-neck flask equipped with mechanical stirrer and a N₂ inlet. After fully dissolved, the flask was immersed in ice bath and the same molar amount of 6FDA as the dianhydride was added with rest of the anhydrous NMP to give a 15 w/v% solution. A highly viscous poly (amic acid) solution was obtained after stirring overnight. Chemical imidization method was applied by adding acetic anhydride and pyridine with ice bath accompanied with stirring. After 24 h, the solution was pour into methanol to form fibrous product. The product was collected by vacuum filtration and dried at 180 °C under vacuum.

For TP-TPDA_n-d, the same procedure was applied to synthesize highly viscous poly (amic acid) solution from TPDA_md and TPDA_n. Then, the reaction solution was diluted to 6 w/v% to avoid gelling in the next step. Imidization agent amounts were doubled and added into the reaction. The reason for using low concentration is the remarkably high reactivity of TPDA_md monomer, which easily lead to over high molecular weight polymers that decreased the solution-processability for membrane fabrication. Also, due to the high content of three-dimensional triptycene units in TP-TPDA_n-d, the strong pi-pi interaction between benzene rings and the interlocking phenomenon between hook-like structures reduced the solubility significantly during imidization. The final product was obtained by precipitating the polyimide solution into methanol, filtered and dried in vacuo at 180 °C.

Two comparable polyamides (TP-6FDC-d and TP-TPDC-d) were also synthesized using typical polycondensation reactions. The polymer structures are shown in Figure 1. The structures were confirmed by proton NMR according to Figure 2.

Film were prepared using the solution casting method. 0.3 g polyimide or polyamide fibers were dissolved in 4.3 ml NMP solvent (7 w/v%) and stirred overnight to obtain a fully dissolved solution. The clear solution was filtered through a PTFE syringe filter with pore size of 0.45 μm and poured onto a clear glass plate under IR lamp. The solvent was allowed to evaporate slowly at around 65 °C in air to form a free-standing film. The robust film was put into methanol for 24 h, followed by vacuum oven drying at 180 °C for 24 h to remove any residual solvent.

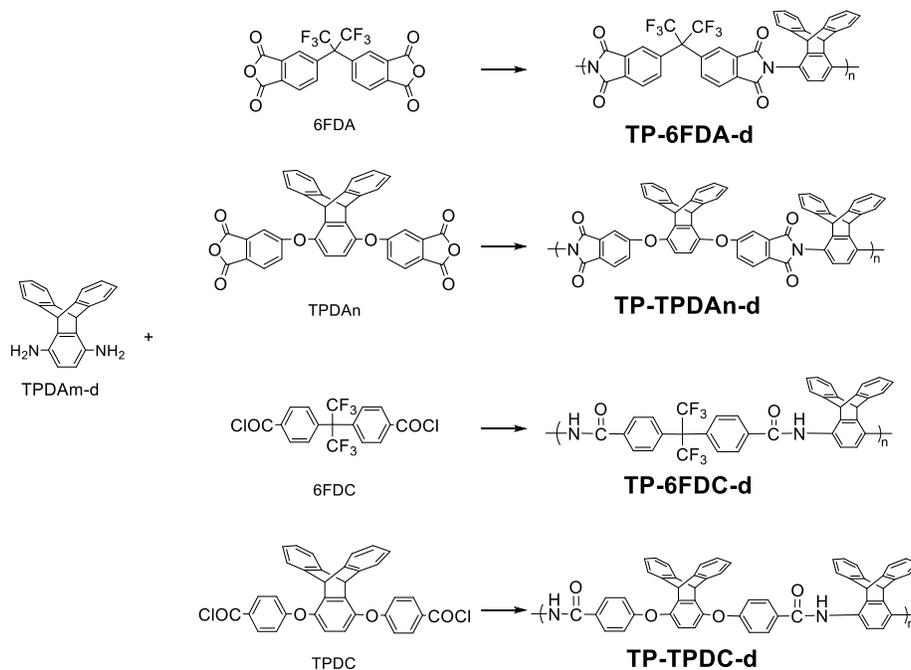


Figure 1. The structure of the triptycene-direct-diamine containing polyimides and polyamides in this work.

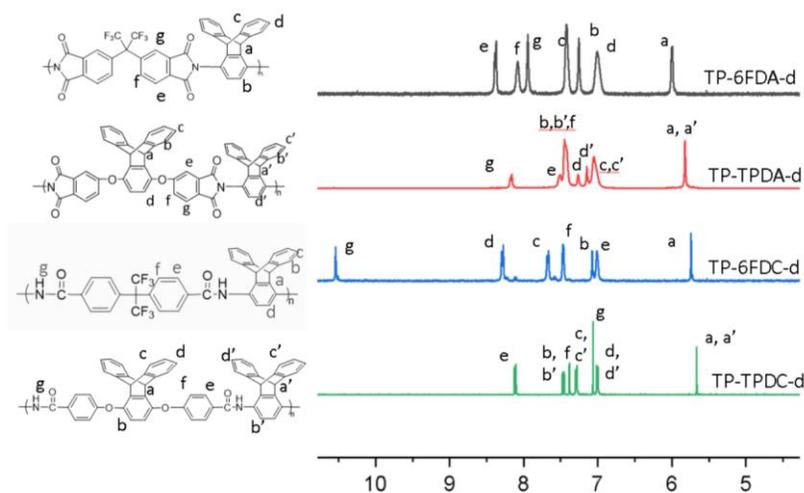


Figure 2. $^1\text{H NMR}$ spectra of the four triptycene-containing polymers in DMSO-d_6 .

Part III: Membrane characterization and gas permeation test

Table 1. Physical properties and calculated fractional free volume (FFV) of the membranes in this study. The glass transition temperature (T_g) was obtained from DSC measurement. Thermal stability was characterized using TGA to study the decomposition temperature at 5% weight loss ($T_{d,5\%}$). The densities were measured using an analytical balance with a density kit, with water as buoyancy liquid. FFVs were calculated according to the measured densities and van der Waals volumes of the polymer repeating unit.

	Polymer	T_g (°C)	$T_{d,5\%}$ (°C)	density (g/cm ³)	FFV%
PI	TP-6FDA-d	376	498	1.266	23.3
	TP-TPDAn-d	Not visible	303	1.292	13.3
PA	TP-6FDC-d	339	464	1.322	20.2
	TP-TPDC-d	313	414	1.250	16.0

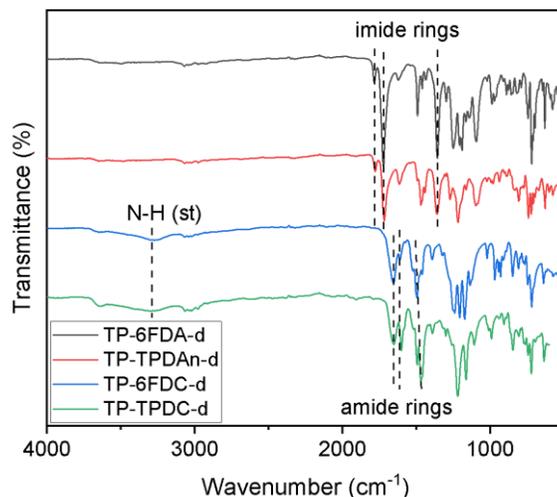


Figure 3. The FTIR spectra of the TP-6FDA-d, TP-TPDAn-d, TP-6FDC-d and TP-TPDC-d. The characteristic peaks for imide structures can be observed at 1783 cm^{-1} (C=O st), 1722 cm^{-1} (C=O st) and 1357 cm^{-1} (C-N st). The spectra indicate the polymer structures were fully imidized. For the polyamides, the peaks at wavenumber 1655 cm^{-1} and 1597 are representative of C=O st and in plane N-H deformation from amide groups. The peaks at about 3300 cm^{-1} can be attributed to the N-H st

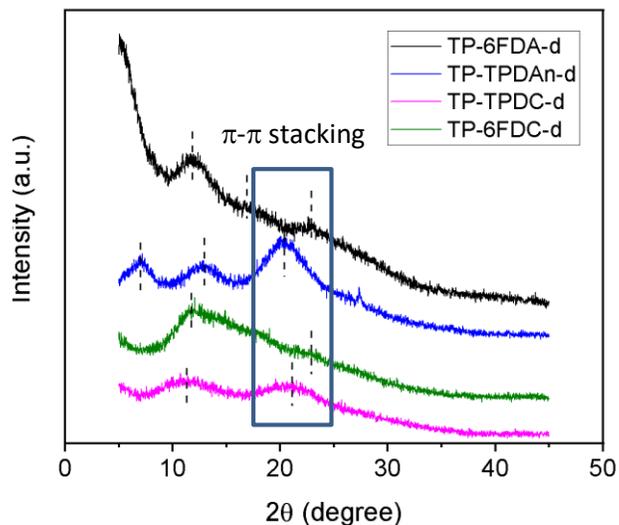


Figure 4. WAXD of the four membranes in this study. The polymers with high triptycene contents (TP-TPDAn-d and TP-TPDC-d) showed strong π - π stacking interaction between triptycene benzene rings.

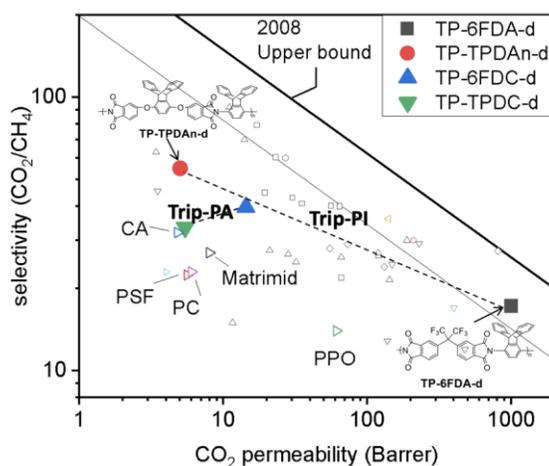


Figure 5. CO_2/CH_4 upper bound plot for our membranes and some representative commercial relevant polymers. Gas permeation was tested using a custom-built gas cell at 35 °C, with feed pressures ranging from 3.0 atm – 9.8 atm (data obtained at 9.8 atm shown in the figure).

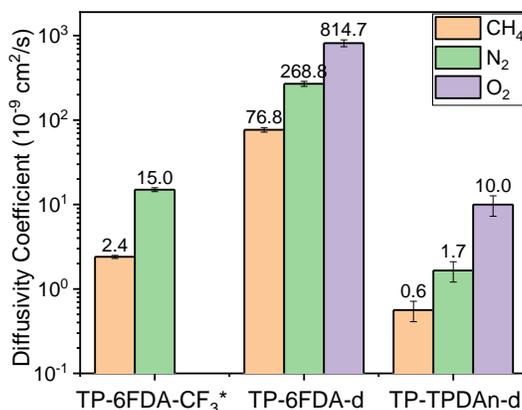


Figure 6. Comparison of diffusivity coefficients in different polyimide membranes. Diffusivity coefficients were calculated based on time-lag methods. The permeation was controlled by diffusion behavior, and the high permeability in TP-6FDA-d came from the high FFV due to loosely packed polymer backbones.

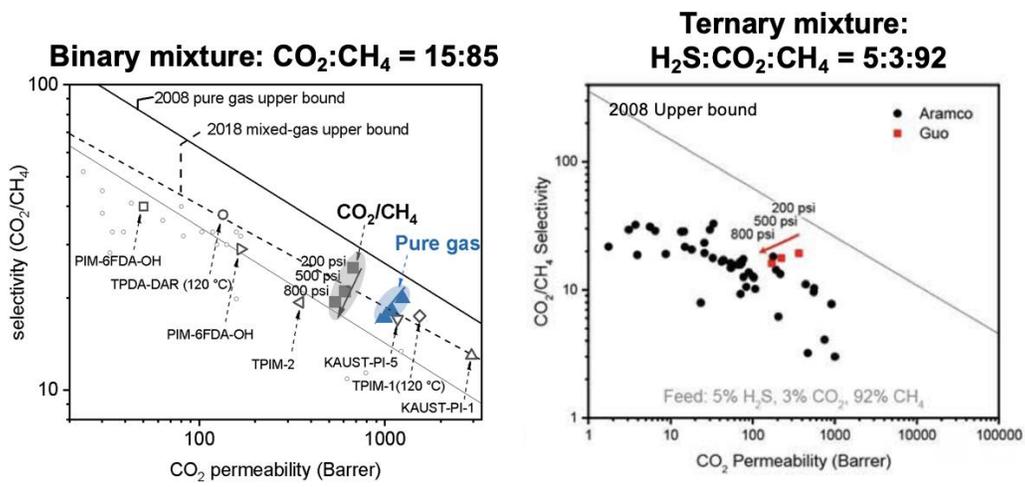


Figure 7. The membranes were measured with (left) binary mixed gas CO₂/CH₄ and (right) ternary sour gas, which are close to the more aggressive industrial operation conditions. The performance of our TP-6FDA-d membrane is located on the 2018 upper bound for mixed-gas. It is one of the best performed membrane for CO₂/CH₄ separation in the presence of H₂S tested by Aramco.