Properties of Gas Transport and Molecular Dynamics Simulations of Cardo Moiety Semifluorinated Poly(ether amide)s

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Abstract

Researches on polymer membranes are of great technological interest for a range of molecular separations due to its technical advantages. The advancement of the membrane-based separation technology depends on the availability of the superior membrane materials with high gas permeability and gas selectivity. Here, processable reported polyamide (PA) membranes were prepared by bis(phenylphenyl)fluorene containing cardo diamine monomer with commercially available diacids via conventional polycondensation method. The permeability of four different gases CH_4, N_2, O_2 and CO_2 through these PA membranes was investigated at 35 °C under a defined applied upstream pressure. PAs showed high gas permeability (P_{CO2} up to 142 and P_{O2} up to 18 barrer) and high permselectivity (P_{CO2}/P_{CH4} up to 60 and P_{O2}/P_{N2} up to 7.6). The gas transport properties have been correlated with the polymer structures with respect to their experimental and simulated molecular modelling, fractional free volume (FFV) and trajectories of gas diffusion in polymer membranes. The results from our molecular dynamics (MD) simulations were integrated with experimental findings already reported in the literature, yielding insightful indications.

Index Terms - Poly(ether amide)s, trifluoromethyl groups, Gas permeability, Cardo moiety and Molecular dynamics simulation..

1. Introduction:

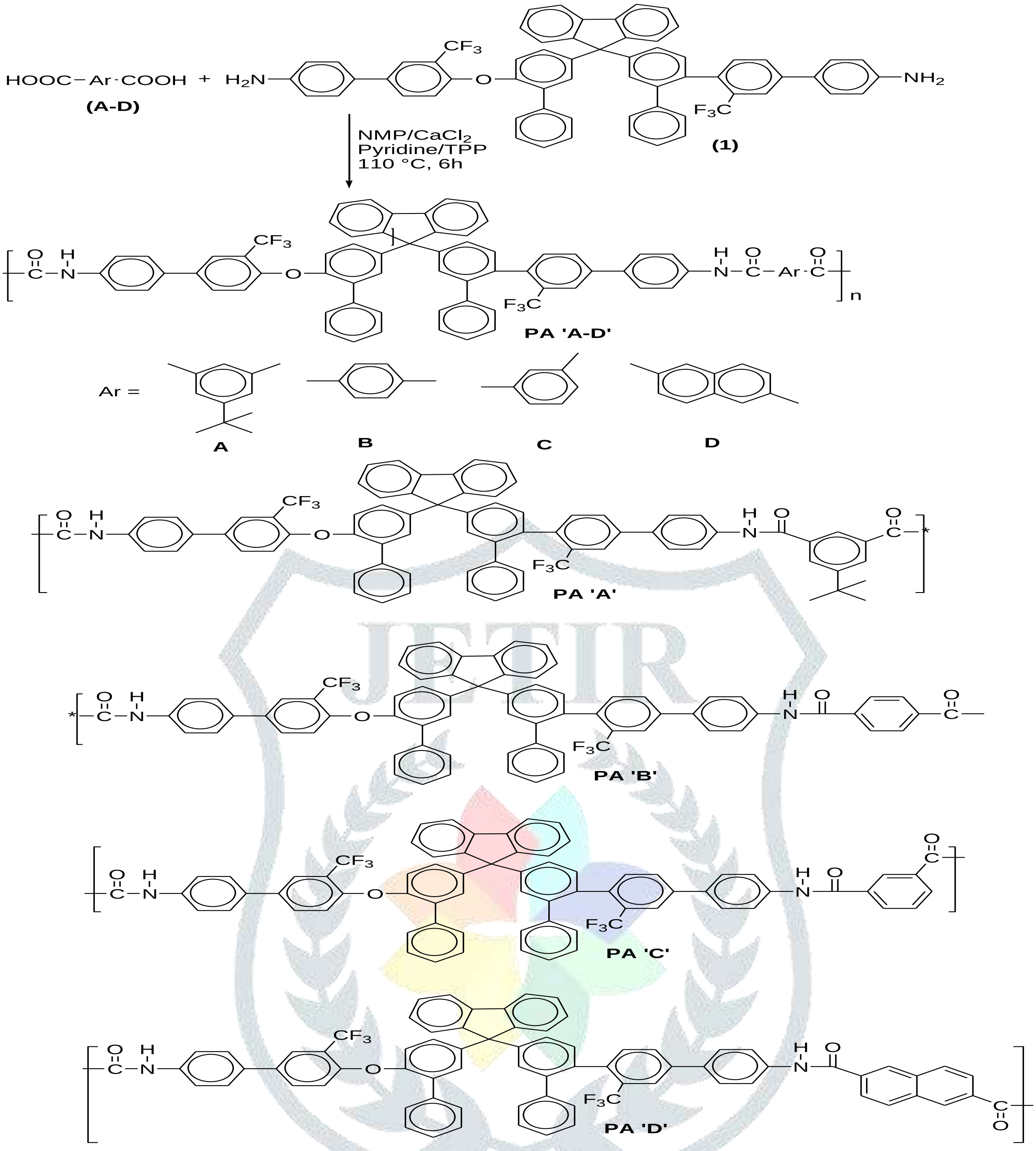
In recent decades, gas separation by polymeric membranes has attracted considerable interest due to their energy efficiency, non-environmental emission, compact, and modular procedure. Polymeric membranes are used in various areas of industry such as separation of carbon dioxide in natural gas purification, production of oxygen and nitrogen enriched stream from air, and food packaging. Amorphous polymers with high glass transition temperature (T_g), such as Polyamides (PAs) are known as super engineering plastics and are used in membrane-based gas separation industries.[1] It is observed that the structural changes that lead to increase in permeability generally decrease the selectivity and vice versa, which was shown in Robeson upper-bound relationships.[2] It is commonly known that gas permeability of amorphous PAs depends on their fractional free volume (FFV). Structural modifications by introducing cardo group, bulky pendant groups into the polymer main chain increases FFV and reduces the rotational mobility around the flexible linkages and that can improve both permeability and permselectivity. Semifluorinated polymers containing trifluoromethyl (-CF_3) groups in the polymer main chain improve gas permeability and permselectivity values simultaneously. The bis(phenyl)fluorene-based cardo polymers have a structure in which a bulky fluorene moiety projects vertically from the polymer main chain.[1] In recent years, molecular dynamics (MD) simulations have progressed to such a level to predict the structural and transport properties of membranes, but few studies have been done on structure–property relationship of Cardo Fluorene based Polyamides from molecular simulation viewpoints.

Therefore, we would like to report the gas transport properties and molecular dynamics (MD) simulations study of four reported PAs prepared from a diamine monomer 9,9-bis-[3-phenyl-4-{2'-trifluoromethyl-4'-(4"-aminophenyl) phenoxy}phenyl]fluorene.[1] The polymer properties have been correlated with their FFV. MD simulations were carried out to examine the effect of Cardo Fluorene on the fractional free volume and gas separation properties. An attempt has been made to understand the structure property correlationship of the PAs.

2. Experimental

2.1. Polymerization and membrane preparation

The diamine monomer (1) was reacted with four different aromatic diacids (2-5) in molar ratio of 1:1 using NMP (N-methyl-2-pyrrolidone) as solvent and in the presence of triphenyl phosphite (TPP), $CaCl_2$ and pyridine as shown in **Scheme 1.** A representative polymerization reaction (PA 'D') is as follows: a mixture of diamine, 9,9-bis-[3-phenyl-4-{2'-trifluoromethyl-4'-(4"-aminophenyl) phenoxy}phenyl]fluorene (0.493 g, 7.71 mmol), 5-tert-butyl-isophthalic acid (0.534 g, 7.71 mmol), calcium chloride (0.36 g), NMP (5 mL), pyridine (1.4 mL) and TPP (1.4 mL, 5.34 mmol) were taken in a 50 mL round bottom flask equipped with reflux condenser. The mixture was heated with continuous stirring (using magnetic stirrer) at 110 °C for 6 h under nitrogen atmosphere. The reaction mixture became highly viscous during this period. The mixture was poured in methanol (500 mL) with constant stirring and obtained fibrous polymer. The off-white fibrous polymer was dried overnight at 80 °C under vacuum.[1] The analogous three PAs were prepared from the diamine monomer on reaction with three different aromatic dicarboxylic acids by similar phosphorylation reaction.



Scheme 1. Synthesis of the poly(ether amide)s (PA‘A’-‘D’).[1]

The analogous three PAs were prepared from this previously reported diamine monomer and three other diacids monomer namely, isophthalic acid, terephthalic acid and naphthalene-2,6-dicarboxylic acid. The polymeric membranes were prepared by casting 10-15% (w/v) homogeneous polymer solutions in DMAc solvent onto clean glass Petri dishes. The Petri dishes were placed in an oven heated at 80 °C overnight, followed by slow heating to 150 °C and then kept for 6h. Free standing flexible membranes were obtained for all the polymers varying thickness from 60-80 µm. The physical properties of the membranes are summarized in **Table 1.** The density values (ρ) of the polymers were used to determine the fractional free volume (FFV) of the polymers by using the following Eq. $FFV = (V-1.3V_w)/V_W$ where V is the specific volume ($V = 1/\rho$). The vander Waals volume (V_w) was estimated using the Hyperchem computer program, version 8.0.

Table 1 Physical properties of the polyamide membranes

Polymer	η_{inh} (dL g^{-1})^{a}	Density (g cm^{-3})^{b}	V_w (cm^3 mol^{-1})^{c}	T_{d10} (°C)^{d}	T.S. (MPa)^{e}	FFV^{EXP}	FFV^{SIM}
PA ‘A’	0.52	1.388	345.611	410	82.0	0.123	0.116
PA ‘B’	0.61	1.295	445.437	425	95.0	0.146	0.132
PA ‘C’	0.73	1.258	793.681	418	81.0	0.176	0.153
PA ‘D’	0.62	1.168	647.309	425	85.0	0.241	0.228

$^{a}\eta_{inh}$ = inherent viscosity at 30 °C. ^{b}Density (g cm^{-3}) measured at 30 °C. $^{c}V_w$ = Vander Waals volume, ^{d}10% degradation temperature measured by TGA. ^{e}Tensile strength. EXP =Experimental, SIM = Simulation.

3. Results and discussion

3.1. Polymer synthesis and their properties

Polyamides were prepared by the typical phosphorylation polycondensation of the reported diamine monomer (1) with four different diacid monomers (A-D) (**Scheme 1**).

Polymer repeat units structures were confirmed by elemental analyses, FTIR-ATR and NMR spectroscopic methods. These poly(ether amide)s showed characteristic absorption bands for amide group in the range of 3338-3291 cm^{-1} (N-H stretching) and 1653-1661 cm^{-1} (carbonyl group stretching) in the FTIR-ATR spectra. The absence of absorption peak due to the diamine above 3400 cm^{-1} supported high conversion of diamines to polyamides. The polymer repeat unit structures were also in good agreement with their ^{1}H-NMR spectra. Representative ^{1}H-NMR spectrum of PA ‘D’ in pyridine-d_5**.** The singlet above 11.36 ppm (corresponds to the amide proton for all the PAs). The results are matches with the reported data.

Transparent and flexible membranes were obtained from these PAs from their solution in DMAc. The membranes showed tensile strength values of 81-95 MPa **(Table 1)**. The highest tensile strength and modulus of PA ‘B’ was due to presence of the symmetrical structure. The PA ‘C’ showed lowest elongation at break in comparison to the other PAs due to the presence of unsymmetrical moiety.

The TGA thermograms of the polymers are done under air. TGA thermograms indicated that all the PAs have high thermal stability in air with 10% decomposition temperatures were in the range of 410-425 °C.

3.2. Gas transport properties

3.2.1. Effect of chemical structures on gas transport properties

The mean gas permeability coefficients and ideal permselectivity values for four different gases (CO_2, O_2, N_2 and CH_4) of the PAs are tabulated in the **Table 2.** The gas permeability of four different gases through these PAs membranes follow the order of P (CO_2) > P (O_2) > P (N_2) > P (CH_4); which is essentially the reverse order of their kinetic diameter, CO_2 (3.3 Å) < O_2 (3.46 Å) < N_2 (3.64 Å) < CH_4 (3.8 Å).[3] The order of gas permeability of the PAs was PA ‘D’ > PA ‘C’ > PA ‘B’ > PA ‘A’ which was in accordance to the decreasing order of fractional free volume of the polymers (**Table 1**). The highest gas permeability values for PA ‘D’ was due to the highest FFV value of this polymer and the lowest gas permeability values of polymer PA ‘A’ was due to its lowest FFV.

Table 2 Gas permeability coefficients (P) measured at 35 °C (3.5 bar) and permselectivities (α) values of the synthesized poly(ether amide)s and their comparison with other reported polymers.

Polymer	$P(CO_2)$	$P(O_2)$	$P(N_2)$	$P(CH_4)$	$\alpha(CO_2/CH_4)$	$\alpha(O_2/N_2)$	Ref
PA ‘A’	9.00	2.40	0.45	0.35	26.00	5.30	This study
PA ‘B’	15.00	4.30	0.85	0.70	21.50	5.00	do
PA ‘C’	40.00	11.00	1.60	1.20	33.50	6.90	do
PA ‘D’	81.00	20.00	3.00	1.70	47.50	6.70	do
Matrimid®	8.70	1.90	0.27	0.24	36.00	7 .00	[3]
Ultem®	1.33	0.41	0.05	0.03	36.90	8.00	[3]
Extem®	3.28	0.81	0.13	0.13	25.20	6.20	[3]
P3[a]	37.40	9.80	1.70	1.50	24.93	5.76	[3]
3g[b]	35.30	7.35	1.36	0.91	39.00	5.40	[3]
3h[b]	31.20	7.23	1.30	0.90	35 .00	5.50	[3]

[a] *Gas permeability coefficient (P) values taken from ref. [3]. P = gas permeability coefficient in barrer. 1 barrer* $=10^{-10}$ cm^3 *(STP)* $cm\ cm^{-2}\ s^{-1}\ cm^{-1}\ Hg^{-1}$.

3.2.2. Molecular dynamics simulation of the polymer structure vs. gas transport properties and correlation with the experimental results.

Over the last few years, MD simulations have been used for understanding the structure and transport behavior of amorphous polymer membrane. In the present study, MD simulations of PAs were performed to investigate the effect of various moity on the structural properties of the polymers for understanding the role of polymer packing on the gas transport properties at a molecular level.[4] The FFV of bulky PAs, calculated from simulations (FFV^{SIM}) was varied from 0.116 to 0.238. However, the trend was similar in both experiments and simulations, PA ‘D’> PA ‘C’ > PA ‘B’ > PA ‘A’. It has been reported that the FFV^{EXP} methods barely present the total free volume and only suggestion average size of the free volume element, these methods do not provide any information regarding their connectivity or distribution. MD simulations, on the other hand, provide additional information regarding the size distribution (FVD) and the spatial arrangement of the free volume elements, which are known to heavily influence the gas permeability and permselectivity of the polymer membrane.

The free volume morphologies of the PA membranes, as shown in **Fig. 1**, were analysed using the free volume size, shape and connectivity. The gray regions indicate the void spaces in the membrane matrix.[5] The bulk groups in the PA membranes are mainly responsible for large elongated microcavities within the matrix. The number and connectivity of the void spaces monotonically decreases from PA 'D' to PA 'A' with PA 'A' containing smaller and discontinuous cavities because of the tight packing of the polymer chains. The free volume morphology can thus be qualitatively correlated with the permeability of the membranes. PA 'D' with higher free volume and well-connected network of void spaces exhibited the highest permeability, whereas PA 'A' with the lowest free volume and discontinuous cavities exhibited the least permeability.

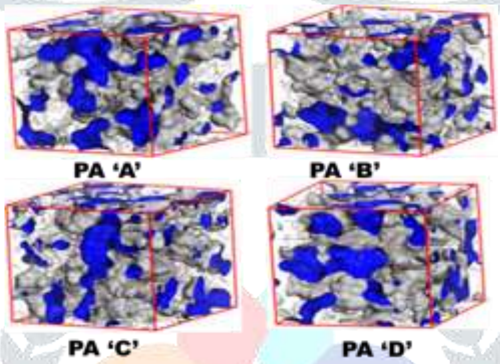


Fig. 1. Free volume morphologies of the polymer membrane matrix estimated for a probe radius of 0.5 Angstrom. Gray regions are the membrane voids network.

Trajectories of gas particles diffusing in PA 'D' membrane during 500 ps NVT MD simulation run are shown in Fig. 2 which indicates that the gas molecule oscillates in a particular void and when a proper pathway is created by the polymer chains, it occasionally jumps into a neighbouring void. These patterns of trajectories confirm the common hopping mechanism of diffusion of molecules in polymer. It also indicates that CO_2 and O_2 jump more than other molecules.[5]

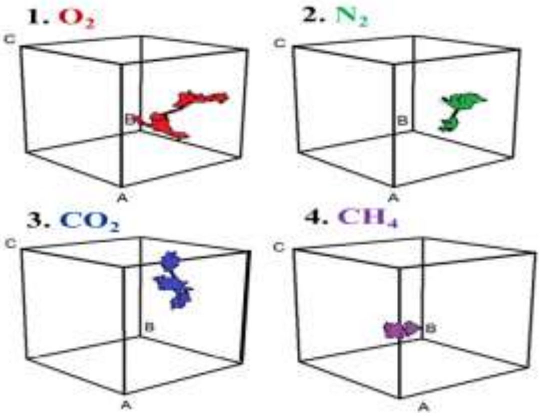


Fig. 2. Trajectories of gas diffusion: (1) O_2 (2) N_2 (3) CO_2 (4) CH_4 in PA 'D'.

3.2.3. Comparison of gas permeabilities with structurally related polymer membranes

The gas permeability and permselectivity values of bis(phenylphenyl)fluorene containing cardo group based fluorinated PAs (PA ‘A’-‘D’) was compared with other commercially available polymers (e.g., Matrimid®, Extem® and Ultem®) and some previously reported polymer (3g, 3h and P3) [3]. A better comparison of the CO_2/CH_4 permselectivity vs. CO_2 gas permeability (**Fig. 3**) have been obtained in terms of the Robeson plots. In general, these PAs showed good permeability with comparable or higher selectivity than the previously reported polyamides. PA ‘D’ shows very good permeability of CO_2 gases with an improvement in permselectivity than other structurally analogous PAs. The good permselectivity values of PA ‘A’-‘D’ for CO_2/CH_4 gas pairs were credited to their higher diffusivity selectivity values. The present PAs showed good improvements in gas-separation performance as proved by their trade off points close to the Robeson's upper bound.

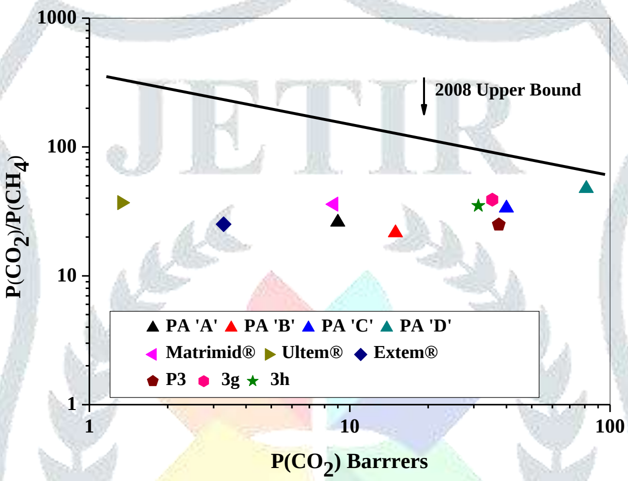


Fig. 3. Robeson plot for a comparison of CO_2/CH_4 selectivity vs. CO_2 permeability coefficients of the PAs under this investigation and some other reported polymers.

4. Conclusion

Four polymeric membranes considered in this study are prepared from reported literature. Physical properties are studied to characterize the membranes and exactly matches with reported literature. Molecular simulation has been adopted to investigate the effect of bis(phenylphenyl)fluorene containing cardo group on gas separation properties of four polymer membranes. Transport behaviors of polymeric membranes are strongly related to the amount and morphology of the free volume. The gas transport studies showed that the incorporation of the bulky tert-butyl groups (PA ‘D’) improved both the gas permeability and permselectivity of these polymer membrane. The simulated free volume morphologies and size distribution curve of the PAs were well corelated with the experimental FFV approach and gas transport properties. Simulated free volume morphologies is in good agreement with experimental tendencies. This study shows that molecular simulation techniques are reliable tools for predicting the gas separation properties of the polymeric membranes and may provide a guideline for designing membrane with desirable properties.

5. Acknowledgment

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6. Reference

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