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Polyarylate Based Thin Film Composite (TFC) Membranes: Effects of Coating Parameters, Gutter Layer, and Intrinsic Material Properties

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Investigations in thin film composite (TFC) membrane formation with polyacrylonitrile ultrafiltration membrane as a support and three polyarylates with sequentially increased polarity are reported. Effects of TFC membrane preparation parameters viz., concentration of the coating solution, dip time, presence of solvent in pores of UF membrane support, and presence of the gutter layer were examined towards the formation of the selective skin layer, which was assessed by gas permeation analysis. TFC membranes prepared using dimethyl bisphenol-A based polyarylate exhibited ~3 orders of magnitude higher permeability and comparable selectivity as that of its dense membrane.

Keywords gas permeation; gutter layer; polarity; polyarylates; TFC membrane

INTRODUCTION

High permeation and selectivity towards the desired component are the primary criteria for a membrane material to be applicable for separation of gas mixtures. In addition, the ability to form an ultra-thin selective layer is also crucial in order to maintain the membrane integrity. Thin film composite (TFC) membrane is one of the most common forms being widely used in the membrane based separations (1). Acceptable fluxes can be obtained by lowering the membrane thickness and by increasing operational pressure, though the intrinsic permeability of the membrane material is low (2,3). In order to reduce the thickness of the top selective layer, a gutter layer having high permeability and low selectivity is usually introduced. This middle layer helps in the formation of a defect free thin layer by providing a smooth surface (3,4). Organo-polysiloxane was used as a gutter layer and ultra-thin 6FDA-type polyimide as a selective layer on the top of polyacrylonitrile (PAN) porous membrane as the structural support (4). Polydimethyl siloxane (PDMS) was used as a gutter layer for the preparation of composite poly(phenylene oxide) (PPO) based membranes on a polysulfone UF support (5). A thin layer of amphiphilic chitosan, which has an affinity for both, hydrophobic PSF-substrates and hydrophilic poly(amidoamine) dendrimers (selective layer) was employed as a gutter layer. This membrane exhibited excellent selectivity towards CO_2 (6,7).

During the preparation of TFC membrane with the gutter layer, certain crucial parameters such as coating material compatibility, support layer porosity, coating solution properties, etc. need to be considered. The porous support layer (usually UF membrane) should also retain its morphology during the coating of the gutter layer and selective layer. Present work investigated the effects of some of these properties on gas permeance and selectivity of TFC membranes prepared using PAN based UF membrane as a structural support and polyarylates as a selective layer. The potential of polyarylate as gas separation membrane materials is well demonstrated. This family of polymers has a good combination of physical and permeation properties (8–13). Three promising polyarylates with varying properties (chemical structure variations affecting gas permeation properties) were selected to prepare TFC membranes. PDMS was used as the gutter layer. Effects of different parameters for making TFC membranes (viz., presence of solvent in the pores of UF support, dip time, concentration of the coating solution, and the nature of polymer used as top selective layer) were evaluated by analyzing pure gas permeance and selectivity of different gas pairs of the formed TFC membranes.

EXPERIMENTAL

Materials

Dimethylbisphenol-A (DMBisA), tetramethylbisphenol-A (TMBisA), terephthalic acid, isophthalic acid and nitroterephthalic acid were procured from Aldrich Chemicals, USA. PDMS (RTV-615, part A and B) was procured from GE Silicones, USA. Polyacrylonitrile (PAN,

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viscosity-averaged molecular weight of 24,800) was gifted by IPCL, India. The nonwoven polyester fabric (Viledon H-1006) was obtained from Frudenberg, Germany. Solvents and reagents used, viz., thionyl chloride, *1,1,2,2*-tetrachloroethane (TCE), methanol, *N,N*-dimethyl formamide (DMF), hexane, chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), toluene, isopropanol (IPA) were of AR grade and were procured from S. D. Fine Chemicals, India. Pure gases used (He, N_2, O_2 and CO_2) were obtained from Inox (India) with minimum purity of 99.9%. DMBisA and TMBisA were purified by recrystallization in acetic acid: water mixture (3:1), while all other chemicals were used as received.

Synthesis of Monomers and Polyarylates

Dibromodimethylbisphenol-A (DBrDMBisA) was synthesized by bromination of the DMBisA as described earlier (10). Acid chlorides were prepared by refluxing respective acid with 4-molar equivalents of thionyl chloride and few drops of DMF as the catalyst. After completion of the reaction, excess of thionyl chloride was distilled off. Isophthaloyl (I) and terephthaloyl (T) chloride were recrystallized from hexane. Traces of thionyl chloride from nitroterephthaloyl (NO_2T) chloride were removed by addition of dry toluene, followed by distillation.

Polyarylates using three bisphenols, viz., DMBisA, TMBisA, and DBrDMBisA were synthesized by interfacial polycondensation (9,10) and purified by dissolution in $CHCl_3$, precipitation in methanol and subsequent drying in a vacuum oven at 60°C for 48 hrs. The structures of monomers and abbreviations used for formed polyarylates are given in Table 1.

Polymer Characterization

Intrinsic viscosity (η) of polyarylates was determined by graphical method using TCE as the solvent at 35°C. Physical properties for PAr_1 and PAr_3 were determined as given below, while that of PAr_2 are taken from our earlier report (9). These are reproduced in Table 2 for comparison. The density of polymers (ρ) in film form was determined at 40°C by the floatation method using aqueous K_2CO_3 or $ZnCl_2$ solutions. Reproducibility of the density measurements was $\pm 0.005\,g/cm^3$ (10). Using measured density, fractional free volume (v_f) and solubility parameter (δ) were estimated by the group contribution method (14). Wide angle X-ray diffraction (WAXD) spectra of polyarylates in film form were performed using Rigaku X-ray diffractometer (D-max 2500) with Cu-K_α radiation in 2θ range of 4–40°. Average d-spacing (d_{sp}) for amorphous peak maxima was calculated using Bragg's equation ($n\lambda = 2d.\sin\theta$). The glass transition temperature (T_g) was determined by differential scanning calorimeter (DSC) on Perkin-Elmer DSC-7 with a heating rate of 20°C/min. Scanning electron microscope (SEM) images

TABLE 1
Chemical structures of monomers used for polyarylate synthesis

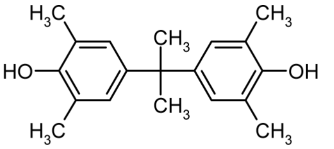
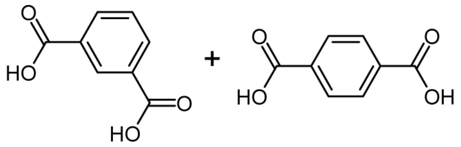
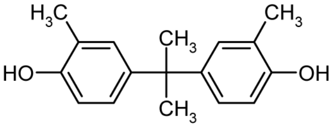
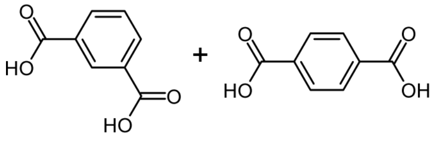
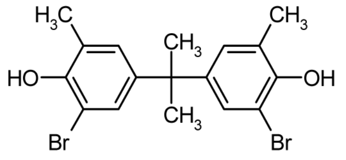
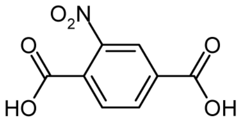
Monomers		
Bisphenol	Diacid	Polymer abbreviation
 Tetramethyl bisphenol-A	 Isophthalic + terephthalic acid (2:8)	(PAr_1)
 Dimethyl bisphenol-A	 Isophthalic + terephthalic acid (1:1)	(PAr_2)
 Dibromodimethyl bisphenol-A	 Nitroterephthalic acid	(PAr_3)

TABLE 2
Physical properties, intrinsic permeability (P)[a] and selectivity (α)[b] of polyarylates

Property	PAr_1	PAr_2	PAr_3
[η] (dl/g)	0.57	0.62	0.539
ρ (g/cm)	1.103	1.174	1.484
d_{sp} (Å)	6.06	5.28	4.26
Ester group density (MW_{ester}/MW_{RU})	0.213	0.228	0.150
T_g (°C)	240	161	213
δ $(cal/cm^3)^{1/2}$	9.23	9.74	10.12
v_f (cm^3/cm^3)	0.364	0.351	0.365
P(He)	43.7	13.6	19.5
$P(N_2)$	1.21	0.13	0.17
$P(O_2)$	5.4	0.73	1.2
$P(CO_2)$	26.5	3.8	4.6
$\alpha(O_2/N_2)$	4.5	5.6	7.0
$\alpha(He/N_2)$	36.1	105	115
$\alpha(CO_2/N_2)$	22	30	27

[a] Permeability expressed in Barrer (1 Barrer $= 10^{-10} cm^3 (STP) \cdot cm/cm^2 \cdot sec \cdot cm\ Hg$).

[b] Ratio of pure gas permeability.

of UF and TFC membranes were obtained using Leica SEM (Model Stereoscan 440).

Preparation of Dense Membranes and Gas Permeation

A 3% (w/v) polymer solution of PAr_1 and PAr_3 was prepared in $CHCl_3$ individually and was poured onto a flat-bottomed glass surface under dry atmosphere. The solvent was allowed to evaporate at ambient, and the formed film was peeled off and dried under vacuum at 60–65°C for a week. Complete removal of the solvent was confirmed by DSC. Thickness of formed films was $40 \pm 3\,\mu m$. Intrinsic permeability of PAr_1 and PAr_3 for He, N_2, O_2, and CO_2 (in the same sequence) were determined by standard variable volume method (15) at 35°C and at $10\,Kg/cm^2$ upstream pressure while maintaining permeate side at ambient pressure. The permeability determination for each polyarylate membrane was repeated with three different samples prepared under identical conditions and the data averaged as given in Table 2 (variation ± 5–12% for different gases).

Preparation of Ultrafiltration (UF) Membrane

The support used for TFC membrane preparation, a PAN based UF membrane was prepared by phase inversion process using pilot scale membrane casting facility. The dope solution was prepared by dissolving 32 g of $ZnCl_2$ and 200 g of PAN in 786 g of DMF while stirring at ambient for 36 hrs. The degassed and centrifuged (3000 rpm) dope solution was casted on to a running nonwoven polyester fabric (Viledon – H1006) with air-dry time of 8 sec, before it entered into the gelation bath containing water as the nonsolvent at 27°C. Formed UF membrane of $\sim 250\,\mu m$ thickness was left in running water for 16 hrs to ensure complete removal of the solvent and then stored at 4°C. The water flux, the bubble point, and the rejection properties of this UF membrane were determined as described earlier (16).

UF Membrane Stability Towards Solvents

UF membrane stability towards different solvents viz., $CHCl_3$, CCl_4, hexane, and toluene was determined to assess the applicability of these solvents during TFC membrane preparation. Initially, water flux (J_w) of the UF membrane samples of $11\,cm^2$ active area was measured in a stirred cell at $1.02\,Kg/cm^2$. These membranes were then dipped in IPA for 16 hrs and subsequently in individual solvent for defined time (1, 3, or 12 hrs). After this period, membranes were again dipped in IPA for 16 hrs to exchange the solvent, and then in water for 16 hrs to exchange the IPA. Water flux (J'_w) of such solvent treated membrane samples was again measured at $1.02\,Kg/cm^2$ upstream pressure. At least six membrane samples were analyzed for a particular solvent, while comparing J_w and J'_w of membranes before and after the solvent treatment.

Preparation of TFC Membranes

UF membranes of $15 \times 8\,cm^2$ size were used for the TFC membrane preparation by dip coating method. In this method, the support UF membrane of $15 \times 8\,cm^2$ was initially mounted on a glass plate with all four sides taped with a scotch tape. This plate was then dipped into a tray of $18 \times 10 \times 4\,cm^3$ size filled with coating solution. This way, only the top side of the support UF membrane is allowed to expose to the coating solution.

Two types of TFC membranes were prepared,

i. without gutter layer and
ii. with PDMS as the gutter layer.

TFC membranes without the gutter layer were prepared with either IPA or a solvent (that was used for coating solution preparation) present in pores of the support UF membrane (Table 3). The solvents used for the preparation of the coating solution were hexane for PDMS, toluene for PAr_1 and PAr_2 and $CHCl_3$ for PAr_3. After dip coating, the formed TFC membranes were air dried for 2 min and then in an oven at 70°C for 15 min. In another type, PDMS coated TFC membranes (prepared as per the conditions given in Table 3) were used for coating of polyarylate solutions of varying concentration. The dip time was varied from 30 to 120 sec; 2 min was kept as air-dry time and then oven dried at 70°C for 15 min. Minimum six TFC membranes were prepared under identical set of conditions and analyzed for gas permeance by a variable volume

TABLE 3
TFC membrane preparation conditions (without gutter layer)

Coating polymer	Solvent	Air dry time before dipping (min)	Dip time (sec)
PDMS	Hexane	4, when hexane in pores/10, when IPA in pores	30
PAr_1	Toluene	4 – 12, when toluene in pore/10, when IPA in pore	10–120
PAr_2	Toluene	4	30–120
PAr_3	Chloroform	4	30–120

method at upstream pressure of 1.4 to 4.9 Kg/cm^2, while keeping permeate side at the ambient pressure. He, N_2, O_2, and CO_2 were used in the same sequence. Variation in permeance (expressed in GPU) for different membrane samples of the same TFC membrane composition was upto ±20%, depending on the gas analyzed.

RESULT AND DISCUSSION

Dense Membrane Properties

Selection of polyarylates for making TFC membranes was based on their structural aspects and physical properties governing gas permeation properties. PAr_1 having symmetric tetramethyl substitution on its bisphenol moiety exhibited a good combination of high permeability and selectivity (Table 2) for various gas pairs. PAr_2 containing asymmetric dimethyl substitution on bisphenol moiety showed lower permeability but higher selectivity than that of PAr_1. The polyarylate, PAr_2, also exhibited higher solubility parameter than that of PAr_1 owing to its higher ester group density per repeat unit (a ratio of molecular weight of ester groups and monomer repeat unit, Table 2). The d_{sp} of PAr_3 was lowest in the series, though its v_f was similar to that of PAr_1. Both these properties are considered as parameters representing chain packing in the polymer matrix. It is known that they may not necessarily follow the same trend (17). The bisphenol moiety in PAr_3 is tetra-substituted with two bromine and two methyl groups situated in an asymmetric manner (phenyl ring carrying different substituents). The acid moiety of this polyarylate is substituted with the polar $–NO_2$ group. Combination of these substitution types (asymmetric and polar) resulted in the lower permeability but higher selectivity for PAr_3, in comparison to respective properties of PAr_1 (Table 2). The $–NO_2$ group is known to impart polarity to the resulting polymer and leads to improved selectivity in different families of polymers like polyarylates (11), poly(phenylene oxide) (18), polysulfone (19), etc. Selectivity of PAr_3 was comparable with that of PAr_2, but gas permeability of the earlier was higher. Both of these polymers have asymmetric substitution on their bisphenol moiety. It is known that in comparison to unsubstituted bisphenol-A (BisA) based polyarylate, TMBisA based polyarylates exhibited higher permeability and comparable selectivity (9); DMBisA based polyarylate exhibited higher selectivity but lower permeability (9); while DBrDMBisA based polyarylate exhibited an excellent combination of high selectivity and permeability (11). Increased polarity by nitro and bromine substituents present on the acid and bisphenol moiety, respectively, could be combinely responsible for higher selectivity of PAr_3; while the tetra-substitution on bisphenol (by –Br and $–CH_3$) led to the higher permeability.

UF Membrane Properties

PAN based UF membrane exhibited average water flux of 37 $l/m^2 \cdot hr$, bubble point of 4.6 Kg/cm^2 (air–water) and >93% rejection for ovalbumin (MW = 43 kDa). SEM image of this membrane (Fig. 1a) showed typical pore morphology of UF membranes. Solvent stability of this membrane was determined as described in the Experimental Section. It was observed that there was no change in water flux after the IPA, hexane, or toluene treatment for 12 hrs. Water flux remained unchanged after $CHCl_3$ and CCl_4 treatment for 1 hr. A longer treatment duration of 3 and 12 hrs increased water flux by 8 and 50%, respectively. It is reported that PAN is highly resistant to chlorinated hydrocarbons and almost all other low-boiling and moderate solvents such as acetone, hexane, heptane, tetrahydrofuran, methyl ethyl ketone, IPA and methylene chloride (4). The damage to membrane morphology after a long-time treatment by $CHCl_3$ or CCl_4 could be ascribed to the partial dissolution of oligomers or re-alignment of polymer chains in the presence of these solvents, leading to a change in the pore size. It is known that the morphology of PAN based UF membranes can be considerably disturbed even by hot water treatment as assessed by the change in water flux (20). Since the dip time for TFC membrane preparation used in the present case was maximum upto 2 min, solvents stability investigations permitted the use of not only IPA and toluene, but also of $CHCl_3$ and CCl_4 for making polyarylate solutions (to be used for coating on the PAN based UF membrane). Toluene was used as a solvent for making PAr_1 and PAr_2 solutions, while $CHCl_3$ was used as a solvent for making PAr_3 solution. Hexane was used as a solvent for PDMS.

TFC Membrane Formation

PAN based UF membrane was prepared by phase inversion method with water as the non-solvent. Water present in

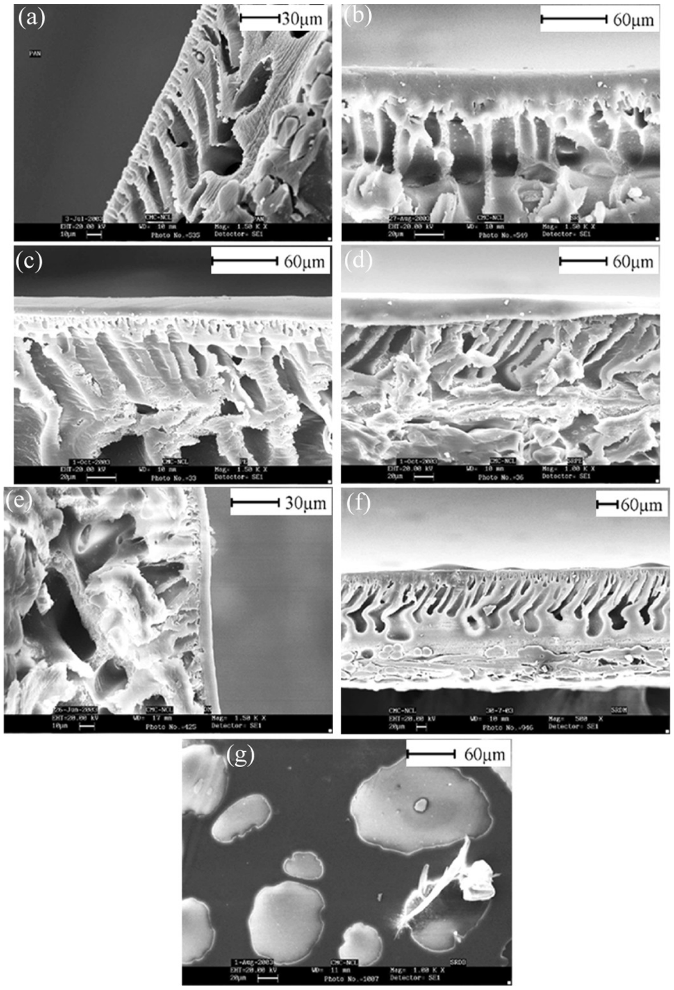


FIG. 1. SEM images of (a) PAN based UF support membrane, (b) PDMS based TFC membrane, (c) PAr_1 based TFC membrane without gutter layer, (d) PAr_1 based TFC membrane with gutter layer, (e) PAr_2 based TFC membrane without gutter layer, (f) PAr_2 based TFC membrane with gutter layer, (all cross section) and (g) surface image of PAr_3 based TFC membrane with gutter layer.

pores of thus formed UF membrane needs to be replaced in view of hydrophobicity of PDMS and polyarylate solutions to be coated on the top of UF membrane surface. The drying of UF membrane support did not lead to the selective TFC membrane formation, as described in individual cases below. Hence the presence of the appropriate solvent in UF membrane pores was thought to be beneficial.

It would facilitate

i. formation of a continuous layer of coating solution on the top surface owing to solution miscibility with the solvent already present and
ii. intrusion of the coating solution into the pores of UF-support upto some depth to provide better anchoring, leading to better stability of the formed TFC membrane.

Though the second phenomenon would result into an increased effective skin layer thickness, by appropriate manipulation of TFC membrane preparation parameters (such as dip time and concentration of coating solution), the intrusion depth could be controlled (21,22).

TFC Membranes Based on PDMS

PDMS (RTV-615, 10:1 proportion of A and B components, as specified by the supplier) based TFC membranes were prepared while either IPA or hexane was present in pores of the UF support (Table 3). These solvents were introduced in pores by the solvent exchange method as described in the Experimental Section. This presence of the solvent was necessitated due to inability of formation of the selective TFC membrane when the pre-dried (60°C) PAN-UF support was used. TFC membrane prepared with 3% PDMS (w/v) solution concentration and hexane present in pores exhibited better selectivity of a particular gas pair than the TFC membrane prepared with IPA in pores (Table 4). This is attributable to the better miscibility of PDMS solution with hexane than with IPA. As a result, the estimated skin layer thickness of the formed TFC membrane [estimated by taking a ratio of the intrinsic permeability of dense membrane and the permeance of TFC membranes (22)] as given in Table 4 was lower in case of IPA present in the pores than when hexane in the pores. The thickness based on SEM image (Fig. 1b) may appear different than the one estimated from the permeability measurements, since PDMS penetrated into the pores of UF support membrane is evident in SEM image. The change of concentration from 3 to 6% of PDMS reduced the permeance by 40–50% for different gases, without a large variation in selectivity of different gas pairs. Thus, a 3% PDMS concentration, 30 sec dip time and hexane being present in pores of UF membrane

TABLE 4
Permeance $(P_r)^a$ and selectivity $(\alpha')^b$ of PDMS (3% w/v) based TFC membranes (dip time = 30 sec) prepared with either IPA or hexane in the pores of UF support

Property	Solvent in pores	
	IPA	Hexane
$P_r(N_2)$	130	87
$P_r(O_2)$	190	160
$P_r(CO_2)$	460	500
$\alpha'(O_2/N_2)$	1.5	1.8
$\alpha'(CO_2/N_2)$	3.5	5.8
Average thickness (μm)	4.7	5.3

[a] Permeance expressed in GPU (1 GPU = 10^{-6} cm^3 (STP)/$cm^2 \cdot sec \cdot cm$ Hg).

[b] Ratio of pure gas permeance.

support were opted as preferred conditions for making PDMS coated TFC membranes. The SEM of this TFC membrane is given in Fig. 1b, wherein a continuous film formation on the top of the UF membrane with some penetration of coating material into pores could be seen.

TFC Membranes Based on PAr_1

TFC membrane preparation with pre-dried UF support did not offer selective membranes in this case also. Thus, TFC membranes were prepared with either IPA or toluene present in pores of the support UF membrane. The coating solution concentration needed was 6%, as the lower concentration led to membranes with poor selectivity for different gas pairs. The dip time was maintained as 30 sec. Permeation analysis of these membranes is given in Table 5. The TFC membrane prepared with toluene in pores offered better selectivity than the membrane prepared with IPA in pores. Similar observation on the presence of solvent in pores was noted with PDMS based TFC membranes and was attributed to the better miscibility of coating solution, when the same solvent (as that used for coating solution preparation) is present in pores. Isopropyl alcohol (IPA) is a non-solvent for PAr_1. IPA treated support membrane showed low selectivity. This could be attributable to the precipitation of PAr_1 from coating solution, leading to defect formation in the skin layer. This is further supported by the fact that the estimated skin layer thickness (Table 5) of the TFC membrane prepared when IPA present in the pores was higher than for the case of toluene, but its selectivity was still lower. It was thus decided that further TFC membrane formations (with PAr_2 and PAr_3) need to be done with UF support pretreated with the same solvent as that was used for the preparation of the coating solution. The effect of the air-dry time between membrane taken out from the solvent (toluene) bath and dipped into the coating solution was also investigated. Gas permeation analysis did not show appreciable variation when this air-dry time was varied from 4 min to 12 min. Hence, 4 min as the air-dry time at ambient temperature was continued for further TFC membrane preparations.

Effect of the coating solution concentration was investigated while varying concentration from 2 to 6%, toluene present in the pores and the dip time of 30 sec in PAr_1 bath. The permeation performance of resulting membranes (without gutter layer) is plotted in Fig. 2. Though O_2/N_2 selectivity of 4.1 for TFC membrane prepared with 2% coating solution concentration could be reasonable, He/N_2 selectivity of 23.3 was rather low. This could be ascribed to insufficient coating at the lower coating solution concentration. It was improved to 42.7, only when the coating solution concentration was 6%. Thus, in absence of the gutter layer, a defect free TFC membrane (Fig. 1c) could be obtained only when the coating solution concentration was 6%. In case of TFC membranes prepared with gutter layer, the concentration was varied from 1 to 3% while maintaining dip time as 30 sec. As could be seen from Fig. 3, though an increase in concentration led to decrease in the permeance as expected, in view of the glassy nature of this polymer, variation in selectivity was rather unusual. At 1% coating solution concentration, the selectivity for CO_2/N_2 (8.9) was higher than that of He/N_2 (4.6), a behavior, which is reverse than that observed for intrinsic selectivity of PAr_1 (Table 2). The same behavior was continued for 2% coating solution concentration and was reversed at 3% concentration. When compared with the results of the TFC membrane prepared without the gutter layer, it was noted that He/N_2 selectivity (18.7) at 3% coating solution concentration with the gutter layer membrane was lower

TABLE 5
Permeance $(P_r)^a$ and selectivity $(\alpha')^b$ PAr_1 (6% w/v) based TFC membranes (dip time = 30 sec) prepared with either IPA or toluene in the pores of UF support

	Solvent in pores	
Property	IPA	Toluene
$P_r(He)$	2.9	6.4
$P_r(N_2)$	0.07	0.15
$P_r(O_2)$	0.26	0.7
$P_r(CO_2)$	0.59	3.9
$\alpha'(O_2/N_2)$	3.7	4.7
$\alpha'(He/N_2)$	41.4	42.7
$\alpha'(CO_2/N_2)$	8.4	26
Average thickness (μm)	17.7	7.4

[a] Permeance expressed in GPU.

[b] Ratio of pure gas permeance.

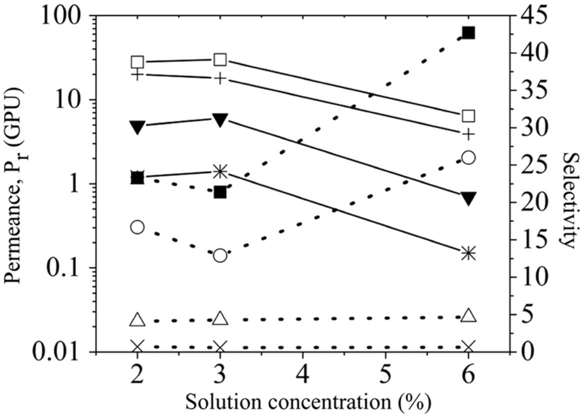


FIG. 2. Variation in permeance (—) and selectivity (···) for PAr_1 based TFC membranes (without gutter layer) with variation in coating solution concentration; [□: He, +: CO_2, ▼: O_2, ∗: N_2, ■: $\alpha'(He/N_2)$, Δ: $\alpha'(O_2/N_2)$, ○: $\alpha'(CO_2/N_2)$, ×: $\alpha'(CO_2/He)$].

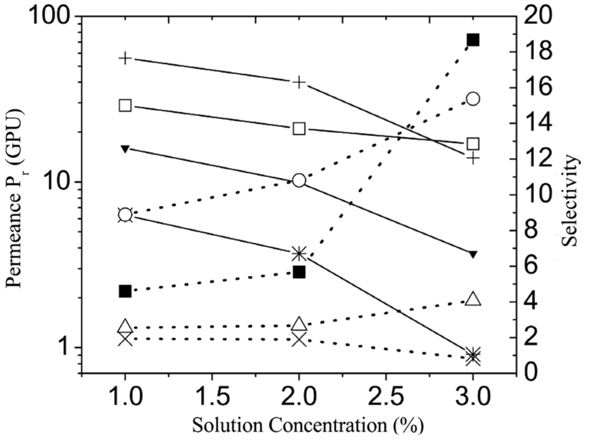


FIG. 3. Variation in permeance (—) and selectivity (···) for PAr_1 based TFC membranes (with gutter layer) with variation in coating solution concentration; [□: He, +: CO_2, ▼: O_2, ∗: N_2, ■: $\alpha'(He/N_2)$, Δ: $\alpha'(O_2/N_2)$, ○: $\alpha'(CO_2/N_2)$, ×: $\alpha'(CO_2/He)$].

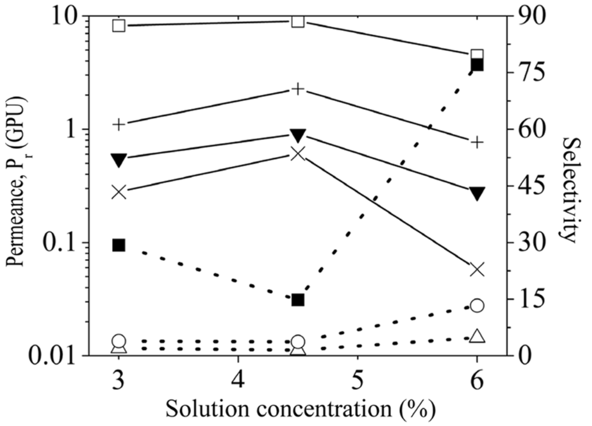


FIG. 4. Variation in permeance (—) and selectivity (···) with coating solution concentration for PAr_2 based TFC membranes (without gutter layer); [□: He, +: CO_2, ▼: O_2, ∗: N2, ■: $\alpha'(He/N_2)$, Δ: $\alpha'(O_2/N_2)$, ○: $\alpha'(CO_2/N_2)$].

than the He/N_2 selectivity (21.4) of membrane prepared with same concentration, but without gutter layer. Similarly, for the TFC membrane with gutter layer and 3% coating solution concentration, $\alpha'(CO_2/N_2)$ was 15.4; while for the membrane prepared without the gutter layer, it was 12.9. Moreover, due to gutter layer incorporation, the permeance of CO_2 approached nearer to the permeance of He and the selectivity $\alpha'(CO_2/He)$ decreased with increase in the coating solution concentration (Fig. 3). This indicated that during coating, the solvent used (toluene) made the PDMS layer to swell to such an extent that the PAr_1 chains got intermixed with the PDMS matrix. As a result, PAr_1 lost its identity as an individual layer and the permeance behavior is actually a result of such PDMS-PAr_1 composite layer (Fig. 1d). Thus, the formed layer offered intermediate gas permeation characteristics than that of PDMS and PAr_1. Higher permeation of CO_2 is an inherent property of PDMS polymer (23), which led to initial higher CO_2/N_2 selectivity than that of He/N_2. Though this effect was masked at 3% concentration of PAr_1, the observed selectivity [esp. $\alpha'(He/N_2)$] being lower than that of the membranes prepared without the gutter layer at the same concentration, higher concentrations of PAr_1 were not tried.

TFC Membranes Based on PAr_2

In case of PAr_2, the TFC membrane preparation without gutter layer was investigated with 30 sec dip time while varying coating solution concentration from 3% to 6%. Gas permeance and selectivity of these membranes are plotted in Fig. 4. With an increase in coating solution concentration from 3% to 4.5%, the permeance was slightly increased for all gases and then decreased at 6% concentration. As an effect of this, the selectivity for different gas pairs decreased from 3% to 4.5% coating solution concentration. This can be attributed to the combined effect of the solution viscosity and increased polymer polarity (higher ester group density and solubility parameter, Table 2). Increased solution viscosity from 3% to 4.5% would create some hindrance to the diffusion of solution into pores of support membrane. Such an observation of increase in permeance, combined with decrease in selectivity with increase in coating solution concentration was previously noted during TFC membrane formation based on aminated silicone rubber (22). As could be seen from the selectivity values in Fig. 4, both these concentrations led to defective TFC membrane formation. When the solution concentration was further raised to 6%, formed TFC membrane showed appreciable selectivity as a result of continuous skin layer formation, as observed by SEM analysis (Fig. 1e). Increase in polarity of the polymer would be predominant especially at lower concentrations, which allow solution agglomeration due to the lower viscosity of this solution. On the other hand, at higher concentration of 6%, increased viscosity would be more significant to form a continuous layer. This behavior was more evident in the case of TFC membrane formation with gutter layer, as discussed below.

As could be seen from Table 6, appreciable selectivity in case of TFC membrane formed with gutter layer could be obtained only when the coating solution concentration was 4.5% and the dip time was 120 sec. At this solution concentration, the selectivity of various gas pairs (O_2/N_2, He/N_2 and CO_2/N_2) were nearer to that of intrinsic selectivity of PAr_2 (Table 2). By the incorporation of gutter layer in this TFC membrane, permeation of different gases was similar to the permeation of respective gas in membrane without the gutter layer. At 6% coating solution

TABLE 6
Permeance $(P_r)^a$ and selectivity $(\alpha')^b$ of PAr_2 based TFC membranes; prepared with gutter layer and different coating solution concentration

	Solution concentration (%)	
Permeation property	3	4.5
$P_r(He)$	9.8	3.8
$P_r(N_2)$	0.31	0.048
$P_r(O_2)$	1.2	0.23
$P_r(CO_2)$	4.8	1.2
$\alpha'(O_2/N_2)$	3.8	4.9
$\alpha'(He/N_2)$	31.6	79.2
$\alpha'(CO_2/N_2)$	15.5	25
$\alpha'(CO_2/He)$	0.5	0.3

[a] Permeance expressed in GPU.
[b] Ratio of pure gas permeance.

concentration, only a small improvement in the selectivity was observed. Thus, by introduction of the gutter layer, there was an advantage that the coating solution concentration needed was lower.

PAr_2 based gutter layer incorporated TFC membrane preparation needed 120 sec as the dip time (below which, selective membranes could not be obtained), as against 30 sec dip time required for membrane formation without the gutter layer. Inability of continuous layer formation at lower dip time could be due to the increased polarity of PAr_2, which makes it incompatible with the PDMS layer. As dip time was increased to 120 sec, formation of a selective layer could take place due to sufficient swelling of the PDMS layer, and anchoring of PAr_2 into such swollen layer, as also observed in the case of PAr_1. The SEM image (Fig. 1f) showed some humps on the surface, as against continuous film formation when PDMS layer was absent (Fig. 1e). This could be related to the coating material incompatibility (nonpolar PDMS versus polar PAr_2). As the time of coating (dip time) increased, intrusion of PAr_2 chains into the swollen PDMS layer provided a base for coating of PAr_2. The effect of polarity was more prominently observed in the case of PAr_3, as discussed below.

TFC Membranes Based on PAr_3

PAr_3 based TFC membrane formation was investigated until 4.5% coating solution concentration for both cases, with and without the gutter layer. Both these types of membranes possessed low selectivity, unexpectedly. Maximum selectivity of $\alpha'(O_2/N_2)$ was just 1.4 and 1.9 and $\alpha'(CO_2/N_2)$ were 2.1 and 5.8, for membrane prepared without and with gutter layer, respectively. Rather than a continuous film, the SEM image (Fig. 1g) showed globule formation on top of the membrane surface. This behavior could be ascribed to the incompatibility of PAr_3 with the UF support. Higher polarity of PAr_3 as evidenced from its higher solubility parameter, δ (Table 2) stems from a polar bromine substitution on its bisphenol moiety and the nitro group substitution on its acid moiety. Though the intrinsic permeation property (Table 2) of PAr_3 shows that the polar group substitution led to increased selectivity than for the similarly tetra-methyl substituted PAr_1, its increased polarity led to failure in obtaining continuous coating on the UF support.

CONCLUSIONS

PDMS and PAr_1 based TFC membranes offered better permeation characteristics when the solvent present in pores of UF membrane support was the same as the one used for coating solution preparation. Though PAr_1 and PAr_2 based TFC membrane prepared without gutter layer offered appreciable selectivity at relatively high coating solution concentration (6%), incorporation of the gutter layer showed different behaviors. PAr_1 based TFC membrane incorporating gutter layer could not reach selectivity as that of TFC membranes prepared without gutter layer. This was attributed to the intermixing of PAr_1 with PDMS gutter layer. Though such intermixing could be possible in case of PAr_2 possessing higher polarity than that of PAr_1, the cross-sectional SEM image of its TFC membrane showed some agglomeration in the top skin layer. In spite of such agglomeration, continuous skin formation was possible, which resulted in appreciable selectivity. When polarity was further increased in the case of PAr_3 by incorporating polar bromine and nitro group in polymer backbone, both types of TFC membranes (with and without gutter layer) could not be prepared due to coating polymer incompatibility with the UF-support. Permeance and selectivity of TFC membranes prepared using these three polyarylates showed that not only TFC membrane preparation parameters, but also the inherent material properties are crucial in preparing selective TFC membranes successfully.

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