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Spiro[fluorene-9,9'-xanthene]-containing copolymers of intrinsic microporosity: synthesis, characterization and gas permeation properties



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ABSTRACT

In the present study, a new bis(catechol) containing spiro[fluorene-9,9'-xanthene], namely, 4,4'-(spiro[fluorene-9,9'-xanthene]-2',7'-diyl)bis(benzene-1,2-diol) (THSFX) was designed and synthesized. Polycondensation reactions of THSFX and varying compositions of THSFX and 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI) were carried out with 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN) to obtain a homopolymer and copolymers, respectively. The organo-soluble polymers exhibited reasonably high molecular weights (23300–34,100 g/mol) and could be cast into self-standing films from their chloroform solutions. X-Ray diffraction studies indicated that PIMs were amorphous in nature. These polymers exhibited high thermal stability ($T_{10} = 490-510$ °C) and possessed intrinsic microporosity with high BET surface area (360–796 m²/g). The gas permeation properties of SFX-PIM-25 and SFX-PIM-33 were evaluated and they exhibited high gas permeability ($CO_2 = 3595-4034$ Barrer). The gas permeability data of SFX-PIM-25 and SFX-PIM-33 was located close to 1991 Robson upper bound for CO_2/N_2 , CO_2/CH_4 and O_2/N_2 gas pairs.

1. Introduction

Over the last two decades, polymers of intrinsic microporosity (PIMs) have gained significant attention for various applications such as gas separation [1-4], gas storage [5,6], sensors [7,8], catalysis [9] and so on due their high BET surface area, solution processability and excellent thermo-chemical stability. Polymeric membranes exhibiting high permeability and selectivity for gas separation applications are desirable in order to decrease the capital area and to increase the gas purity. However, polymeric membranes generally suffer from trade-off relationship between gas permeability and selectivity, wherein improvement in permeability characteristics is attained at the cost of selectivity and vice-versa [10,11]. It has been demonstrated that the incorporation of rigid and contorted spirocyclic units into polymers offers advantages in terms of improving both gas permeability and selectivity [3,12,13]. In 2004, an interesting approach was introduced to obtain improved gas permeability characteristics by incorporation of microporosity into polymers. PIM-1 is the first example of this class of polymers which is a ladder-type solution processable polymer with high free volume [14]. By virtue of its high internal free volume and high BET surface area, PIM-1 exhibited 100-fold enhancement in permeability compared to commercial polymers such as Matrimid [15] and polysulfone [16]. The microporosity in PIMs is intrinsic and is attributed to their characteristic features such as twisted and extended structure. Since the invention of PIM-1, considerable research efforts have been devoted to improve the understanding of structure-property relationships by structural tuning.¹¹ Motivated by this approach to induce intrinsic microporosity into polymers, various research groups reported synthesis and structure-property relationships of polymers of intrinsic microporosity (PIMs) possessing units such as spirobisindane [17], spirobifluorene [18], Trögers base [19], tetraphenylethylene [20], binaphthalene [21,22], adamantane [23], hexaphenylbenzene [24], tribenzotriquinacene [25], spirobischromane [26], triptycene [27,28], etc.

Spiro[fluorene-9,9'-xanthene] (SFX) is a spirocyclic unit containing oxygen in the spiro-skeleton in which fluorene and xanthene moieties are connected through a quaternary carbon atom [29]. Recently, SFX unit containing polymers have been used for various applications such as solar cells [30], OLEDs [31], hydrogen uptake [32], and gas separation [33] due to their excellent thermo-chemical and physical properties. To the best of our knowledge, PIMs-containing SFX units have not yet been synthesized and studied for gas separation applications.

The present work reports the synthesis, characterization and gas permeation properties of new PIMs containing spiro[fluorene-9,9'xanthene] units. Towards this end, a new bis(catechol) containing SFX

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https://doi.org/10.1016/j.reactfunctpolym.2018.10.008 Received 12 August 2018; Accepted 22 October 2018 Available online 30 October 2018 1381-5148/ © 2018 Published by Elsevier B.V. unit, namely, 4,4'-(spiro[fluorene-9,9'-xanthene]-2',7'-diyl)bis(benzene-1,2-diol) (THSFX) was designed and synthesized. Homopolymer was synthesized by polycondensation of THSFX with 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN) *via* double aromatic nucleophilic substitution reaction. In addition, copolymers with intrinsic microporosity were synthesized by polycondenstaion of varying compositions of THSFX and 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI) with TFTPN. Polymers were characterized by IR, ¹H and ¹³C NMR spectroscopy, GPC, XRD, TGA, and N₂ adsorption and desorption. Furthermore, the gas permeation properties of soluble PIMs were evaluated and the influence of SFX units on physical and gas permeation properties was investigated.

2. Experimental part

2.1. Materials

4-Bromophenol (Aldrich), 9-fluorenone (Aldrich), methanesulfonic acid (Aldrich), 3,4-dimethoxyphenylboronic acid, tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄), potassium carbonate (Aldrich), BBr₃ in dichloromethane (Aldrich) and 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN, Aldrich) were used as received. 2',7'-Dibromospiro[fluorene-9,9'-xanthene] (DBSFX) was synthesized according to the reported procedure [34]. 3,3,3',3',-Tetramethylspirobisindane-5,5',6,6'-tetraol (TTSBI) was purified by recrystallization from a mixture of methanol and dichloromethane (DCM). Toluene, DCM, chloroform (CHCl₃), tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc) were purchased from Merck India and were purified standard procedures before use.

2.2. Characterization

Melting points were measured using electrothermal MEL-TEMP apparatus. Infrared spectra were recorded in the range 4000-600 cm⁻¹ using Bruker a-T spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ or DMSO-d₆ using Bruker-AV 200 MHz spectrometer. Chemical shifts were recorded in parts per million (ppm) using tetramethylsilane as a reference. High resolution mass spectroscopy (HRMS) analysis data were obtained on Thermo scientific Q-exacative instrument. Molecular weights and dispersity values of PIMs were determined by gel permeation chromatography (GPC) equipped with spectra series UV 100 and spectra system RI 150 detectors using chloroform as an eluent and polystyrene as a standard. X-Ray diffractograms of powder samples were recorded by a Rigaku Dmax 2500 using Cu K α radiation with scan rate of 2° min⁻¹. Thermo gravimetric analysis (TGA) was performed at a heating rate of 10 °C min⁻¹ under N₂ in the range from 30 to 800 °C using Perkin-Elmer TGA-7 system. Differential scanning calorimetry (DSC) was performed on DSC Q10 system in the range from 30 to 390 °C at a heating rate of 10 °C min⁻¹ under N2. Nitrogen adsorption/desorption measurements of PIM powders were made using Micrometrics ASAP 2020 at 77 K. Samples were degassed at 120 °C under high vacuum before analysis.

2.3. Synthesis

2.3.1. Synthesis of 2',7'-dibromospiro[fluorene-9,9'-xanthene] (DBSFX)

Into a two-necked round-bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were charged 4-bromophenol (17.3 g, 100 mmol), 9-fluorenone (3.38 g, 10 mmol) and methanesulfonic acid (2.6 mL, 3.84 g, 40 mmol). The reaction mixture was heated at 150 °C for 12 h, cooled and precipitated into methanol. The crude product was then extracted with ethyl acetate, washed with brine and was concentrated on a rotary evaporator. The crude product was purified by column chromatography on silica gel using pet ether and ethyl acetate (98: 2, ν/ν) as eluent to obtain DBSFX as a white solid.

Yield: 14.8 g, 30%; Melting Point: 218 °C; IR: 1260 (C-O-C) and 1095 (Ar-Br); ¹H NMR (200 MHz, DMSO- d_{6_3}), δ (ppm): 8.0 (d, J = 10 Hz, 2H, Ar-H), 7.45–7.41 (m, 4H, Ar-H), 7.30–7.27 (m, 4H, Ar-H), 7.13 (d, 2H, Ar-H), 6.23 (s, 2H, Ar-H).); ¹³C-NMR (50 MHz, DMSO- d_6 , δ /ppm): 153.3, 149.7, 138.9, 131.7, 129.1, 129.0, 128.8, 126.4, 125.2, 120.9, 119.4, 115.1, 53.2; HRMS: calcd. for C₂₅H₁₄Br₂O: 487.9406, found: 487.9397.

2.3.2. Synthesis of tetramethoxyxanthene2',7'-bis(3,4-dimethoxyphenyl) spiro[fluorene-9,9'-xanthene] (TMSFX)

Into a Schlenk tube were charged DBSFX (5 g, 10.2 mmol), 2,4-dimethoxyphenylboronic acid (4.08 g, 22.4), potassium carbonate (8.28 g) and toluene (40 mL) and the reaction mixture was degassed for 30 min. Tetrakis(triphenylphosphine)palladium (0) (0.58 g, 0.5 mmol) was added and the reaction mixture was degassed for 10 min. The reaction mixture was heated at 100 °C for 20 h. After completion of reaction (monitored by TLC), the reaction mixture was cooled to room temperature and extracted with ethyl acetate. The ethyl acetate solution was washed with brine and was evaporated on a rotary evaporator. The crude product was purified by column chromatography on silica gel using pet ether: ethyl acetate (70:30, ν/ν) as eluent to obtain TMSFX as a white solid.

Yield: 4.1 g, 66%; Melting Point: 254 °C; IR: 1248 (C-O-C); ¹H NMR (200 MHz, DMSO- d_6 , δ /ppm): 7.81 (d, 2H, Ar-H), 7.41–7.38 (m, 4H, Ar-H), 7.31 (d, 2H, Ar-H), 7.27 (d, 2H, Ar-H), 7.25 (d, 2H, Ar-H), 6.76 (d, 6H, Ar-H), 6.59 (d, 2H, Ar-H), 6.57 (dd, 2H, Ar-H), 3.84 (s, 6H, -CH₃), 3.81 (s, 6H, -CH₃); ¹³C-NMR (50 MHz, CDCl₃, δ /ppm): 154.5, 150.7, 148.9, 148.2, 139.7, 136.2, 133.4, 128.3, 127.8, 126.6, 126.0, 125.6, 125.3, 120.0, 118.9, 117.0, 111.2, 110.2, 55.9, 55.8, 54.8.; HRMS: calcd. for C₄₁H₃₂O₅: 604.2244, found: 604.2239.

2.3.3. Synthesis of tetrahydroxyxanthene4,4'-(spiro[fluorene-9,9'-xanthene]-2',7'-diyl)bis (benzene-1,2-diol) (THSFX)

Into a two necked round bottom flask equipped with a magnetic stirrer bar, a nitrogen inlet and an addition funnel were charged TMSFX (4 g, 6.6 mml) and dichloromethane (150 mL). To the reaction mixture, BBr₃ in dichloromethane (10.2 mL, 26.4 mmol) was added dropwise over a period of 15 min at 0 °C and then stirred at room temperature for 12 h. The reaction mixture was quenched by addition of water and was extracted with ethyl acetate. The ethyl acetate solution was washed with brine and was evaporated on a rotary evaporator. The crude product was purified by column chromatography on silica gel using pet ether: ethyl acetate (50:50, ν/ν) as eluent to obtain THSFX as a colourless solid.

Yield: 3.2 g, 88%; Melting Point: 264 °C; IR: 3428 and 3260 cm⁻¹ (-OH); ¹H NMR (200 MHz, DMSO- d_6 , δ /ppm): 8.96 (s, 2H, Ar-H), 8.94 (s, 2H), 8.04 (d, 2H, Ar-H), 7.48–7.43 (t, 2H, Ar-H), 7.41 (dd, 2H, Ar-H), 7.34 (d, 2H, Ar-H), 7.29 (t, 2H, Ar-H), 7.18 (d, 2H, Ar-H), 6.65 (d, 2H, Ar-H). 6.53 (d, 2H, Ar-H), 6.49 (dd, 2H, Ar-H), 6.34 (d, 2H, Ar-H); ¹³C-NMR (50 MHz, CDCl₃, δ /ppm): 154.4, 149.6, 145.4, 144.9, 139.1, 135.8, 130.4, 128.7, 128.3, 126.3, 125.2, 124.6, 124.2, 120.6, 117.2, 117.0, 116.0, 113.1, 53.9.; HRMS: calcd. for C₃₇H₂₅O₅: 549.1697, found: 549.1686.

2.3.4. Polymerization

Into a 100 mL three-necked round-bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were charged THSFX (1.5 g, 4.25 mmol), TFTPN (0.85 g, 4.25 mmol) and DMAc (15 mL). The reaction mixture was heated at 120 °C for 5 min and then potassium carbonate (3.5 g, 25.53 mmol) was added in one portion (color changed from orange-red to orange- yellow). The reaction mixture was heated at 150 °C for 5 min; 2 mL toluene was added and stirred at same temperature until the solution became viscous (10–20 min). The resulting viscous solution was precipitated into methanol; yellow powder was collected by filtration, washed with hot water and methanol and dried at 100 °C for four days.

Copolymers were synthesized by polycondensation of varying compositions of THSFX and TTSBI with TFTPN using the similar procedure. PIMs were designated as SFX-PIM-25, SFX-PIM-33, SFX-PIM-40 and SFX-PIM-50 wherein the content of THSFX was 25, 33, 40 and 50 mol%, respectively.

2.4. Preparation of dense membranes

Dense polymer films for gas permeability measurements were prepared from $\sim 5\,wt\%$ polymer solutions in chloroform by solution casting method. Polymer solution was cast onto a clean levelled petridish and solvent was evaporated slowly at room temperature. The thickness of membrane was in the range 75 \pm 5 μm as measured by digital micrometer.

2.5. Gas permeability measurements

Variable-volume method was used to evaluate gas permeability and selectivity. The order of gases for permeability measurement was He, H₂, N₂, O₂, CH₄, and CO₂. For permeability measurements, three membrane samples for each polymer were prepared under similar conditions and the permeability was averaged. The membrane area was 4.9 cm^2 . Depending on the gas analysed, the variation in the permeability measurement from the average was in the range 1–6% (1–5% for He, 2–6% for H₂, 1–4% for N₂, 1–4% for O₂, 4–5% for CH₄, and 3–6% for CO₂). The permeability of all gases was measured at 2 bar using the following equation

$$P = \frac{J.\,l}{p_1 - p_2}$$

wherein, P is the permeability and is expressed in Barrer (1Barrer = 10^{-10} [cm³ (STP) cm]/[cm² s cmHg]), N is the steady-state penetrate flux (cm³ cm⁻² s), l is the membrane thickness (cm), and p₁ and p₂ are the feed and permeate side pressures (cmHg), respectively.

3. Results and discussion

3.1. Synthesis and characterization of monomer

The synthesis of a new bis(catechol) containing spiro[fluorene-9,9'xanthene] viz., 4,4'-(spiro[fluorene-9,9'-xanthene]-2',7'-diyl)bis(benzene-1,2-diol) (THSFX) was carried out in three steps as shown in Scheme 1. First, the condensation of 9-fluorenone with 4-bromophenol was carried out in the presence of methanesulfonic acid to obtain 2',7'dibromospiro[fluorene-9,9'-xanthene] (DBSFX) using the reported procedure [34]. The second step is the Suzuki coupling reaction of DBSFX with 3,4-dimethoxyphenylboronic acid, which was performed using tetrakis(triphenylphosphine)palladium(0) as the catalyst to afford 2',7'-bis(3,4-dimethoxyphenyl)spiro[fluorene-9,9'-xanthene] (TMSFX). Finally, demethylation of TMSFX was carried out using BBr₃ to afford THSFX. The chemical structure of THSFX was confirmed by IR, ¹H and ¹³C NMR spectroscopy and HR-MS.

In IR spectrum of THSFX (Fig. S5), the bands were observed at 3428 and 3260 cm⁻¹ which could be attributed to phenolic -OH group. ¹H NMR spectrum of THSFX along with assignments is shown in Fig. 1. The peaks due to phenolic hydroxyl protons appeared at $\delta = 8.96$ and 8.94 ppm and aromatic protons appeared in the range $\delta = 8.05-6.34$ ppm. ¹³C NMR spectrum (Fig. S6) and HR-MS analysis were used to support the chemical structure of THSFX.

3.2. Synthesis and characterization of polymers

Spiro[fluorene-9,9'-xanthene]-containing polymer of intrinsic microporosity (SFX-PIMs) were synthesized by polycondensation of THSFX with TFTPN *via* double aromatic nucleophilic substitution polymerization reaction to form dibenzodioxine ring as shown in Scheme 2. Polycondensation reactions were performed in DMAc at 150 °C in the presence of potassium carbonate.

In addition, copolymers were prepared by the similar procedure using various feed ratios of THSFX and 5,5,6',6'-tetrahydroxy-3,3,3',3'tetramethylspirobisindane (TTSBI). The content of THSFX was varied such as 25, 33, 40 and 50 mol% and the corresponding copolymers are designated as SFX-PIM-25, SFX-PIM-33, SFX-PIM-40 and SFX-PIM-50, respectively. PIM-1 was synthesized as a reference polymer under similar reaction conditions by polycondensation of equimolar quantities of TTSBI with TFTPN.

The solubility tests of PIMs were carried out room temperature (Table S1) in various organic solvents. SFX-PIM-40, SFX-PIM-50 and SFX-PIM were found to be insoluble or partially soluble in organic solvents such as CHCl₃, THF and DMF which impeded their solutionbased characterization such as GPC, NMR spectroscopy and film-fabrication. SFX-PIM-33 and SFX-PIM-25 were found to be soluble in chloroform which permitted their characterization by GPC and NMR spectroscopy. The chemical structure of PIM-1, SFX-PIM-25 and SFX-PIM-33 was elucidated by IR and ¹H NMR spectroscopy. IR spectrum (Fig. S7) of SFX-PIM-33 showed characteristic bands of -CN and Ar-O-Ar at 2240 and 1260 cm⁻¹, respectively. The stacked ¹H NMR spectra of PIMs are shown in Fig. 2. The copolymer composition was determined from integrated intensity ratio of protons (labeled as 13) of spirobisindane unit with aromatic protons (labeled as 10) of SFX unit and there was good agreement between observed and feed compositions.



Scheme 1. Synthesis of 4,4'-(spiro[fluorene-9,9'-xanthene]-2',7'-diyl)bis(benzene-1,2-diol) (THSFX).



Fig. 1. ¹H NMR spectrum (in DMSO-d₆) of 4,4'-(spiro[fluorene-9,9'-xanthene]-2',7'-diyl)bis(benzene-1,2-diol) (THSFX).



m/n = 1/3 (SFX-PIM-25); 1/2 (SFX-PIM-33); 2/3 (SFX-PIM-40); 1/1 (SFX-PIM-50); 0/1 (PIM-1)

Scheme 2. Synthesis of SFX-PIMs and PIM-1.

Molecular weights (M_n) and dispersity values of synthesized organo soluble PIMs, as determined by GPC, were in the range 34,100–23,300 mol / g and 2.1–2.8, respectively, (Table 1). The selfstanding films of SFX-PIM-25 SFX-PIM-33 and PIM-1 could be cast from their chloroform solution using solution-casting method (Fig. S11).

The broad halo around $2\theta = 10-25^{\circ}$ in X-ray diffraction patterns indicated amorphous nature of SFX-PIMs (Fig. S8). The inter-segmental distance (*d*-spacing) is considered as the distance between polymer chains and was calculated by Bragg's equation from the peak maxima of XRD patterns (Table 2). The *d*-spacing of PIMs were in the range 7.96–6.65 Å. The high *d*-spacing of PIMs is due to poor chain packing efficiency attributed to the incorporation of SFX and TTSBI units in polymer backbone. The order of *d*-spacing is as: PIM-1 > SFX-PIM-25 > SFX-PIM-33 > SFX-PIM-40 > SFX-PIM-50 > SFX-PIM. The data on density and fractional free volume (FFV) of films of SFX-PIM-

25, SFX-PIM-33 and PIM-1 are given in Table 2. The density of PIMs films was calculated by density bottle method and was in the range $1.12-1.20 \text{ g cm}^{-3}$. The density of SFX-PIMs was higher than that of PIM-1 which indicated relatively closer chain packing in the former systems. The FFV values of SFX-PIM-25, SFX-PIM-33 and PIM-1 were calculated using Bondi's method and the values were in the range 18–22%. The FFV values of SFX-PIM-25 and SFX-PIM-33 were lower than that of PIM-1. The data concerning *d*-Spacing, density and FFV indicated that SFX unit is less effective for disturbing polymer chain packing than spirobisindane unit.

The thermal stability of PIMs was determined by TGA measurements under nitrogen. SFX-PIMs showed 10% weight loss in the temperature range 480–512 °C (Fig. S9 and Table 2) indicating their excellent thermal stability. No transition corresponding to T_g of PIMs was detected in DSC measurements carried out up to 390 °C. Similar



Table 1 Synthesis and Properties of SFX-PIMs and PIM-1.

Sr. No.	Polymer	THSFX (mol %)	TTSBI (mol %)	TFTPN (mol %)	M _n (g∕ mol) ^a	M _w (g∕ mol) ^a	Dispersity ^b
1	SFX-PIM	100	0	100	ns	ns	ns
2	SFX-PIM-50	50	50	100	ns	ns	ns
3	SFX-PIM-40	40	60	100	ns	ns	ns
4	SFX-PIM-33	33	67	100	23,300	65,200	2.8
5	SFX-PIM-25	25	75	100	28,900	83,000	2.8
6	PIM-1	0	100	100	34,100	71,100	2.1

^a Molecular weights were obtained from GPC in chloroform (polystyrene standard).

^b Dispersity = Mw/Mn. ns: GPC measurements could not be made due to insolubility of PIMs in CHCl₃, THF and DMF.

observations have been reported for PIMs in the literature [24].

Microporosity of PIMs was evaluated by nitrogen adsorption/desorption method at 77 K. Adsorption/desorption isotherms (Fig. S10) of PIMs demonstrated high nitrogen uptake at low pressure and showed characteristics loops for microporosity (Type I). This indicated that

spirocyclic units such as SFX and spirobisindane units. The N2 adsorp-
tion isotherms provided high BET surface area and the values were in
the range 366–796 m^2/g (Table 2). The order of BET surface area is as:
PIM-1 > SFX-PIM-25 > SFX-PIM-33 > SFX-PIM-40 > SFX-PIM-
50 > SFX-PIM. These results are in accordance with the trends ob-
served in <i>d</i> -spacing and FFV values.

PIMs possessed intrinsic microporosity due to the presence of ladder

as:

4. Gas permeability

The pure gas permeability of films of SFX-PIM-25, SFX-PIM-33 and PIM-1 was determined using variable-volume method for He, H₂, N₂, O₂, CH₄ and CO₂ gases with feed pressure in 28–32 psi. The order of gas permeability for SFX-PIM-25, SFX-PIM-33 and PIM-1 is as: $PN_2 < PCH_4 < PO_2 < PHe < PH_2 < PCO_2$. Similar trends were observed for PIMs in the literature [24]. The gas permeability and selectivity data of methanol-treated films of SFX-PIM-25, SFX-PIM-33 and PIM-1 are presented in Table 3. The gas permeation properties of previously reported PIM-1, SBF-PIM and SFX-based polymers are also included in Table 3 for comparison.

SFX-PIM-25 and SFX-PIM-33 exhibited high permeability and

Table 2	
Physical properties	of SFX-PIMs and PIM-1.

Sr. No.	Polymer	<i>d</i> -Spacing ^b	$S_{BET} (m^2/g)^c$	Pore Volume ^d	Density ^d (g cm ⁻³)	FFV ^e (%)	T _{10%} ^a (°C)	
1	SFX-PIM	6.65	366	0.37	-	-	480	
2	SFX-PIM-50	7.07	596	0.45	-	-	505	
3	SFX-PIM-40	7.55	661	0.47	-	-	504	
4	SFX-PIM-33	7.62	682	0.50	1.20	18	508	
5	SFX-PIM-25	7.82	731	0.56	1.15	19	512	
6	PIM-1	7.96	796	0.62	1.12	22	490	

^a Temperature at which 10 wt% loss was observed.

^b *d*-Spacing was calculated from Bragg's equation.

^c BET surface area was obtained from N₂ adsorption and desorption method.

^d Density was calculated by specific gravity bottle method.

^e Fractional free volume (FFV = $V-V_o/V$).

Table 3

Gas permeability and selectivity of SFX-PIMs and PIM-1.

Sr. No.	Polymer	Permeabi	Permeability (Barrer) ^a					Selectivity $(\alpha)^b$			
		Не	H ₂	N_2	O ₂	CH_4	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2	CO ₂ /CH ₄
1	SFX-PIM-33 ^c	626	1284	153	489	413	3595	8.4	3.2	23.5	8.7
2	SFX-PIM-33 ^d	318	749	60	289	155	1848	12.5	4.8	30.8	11.9
3	SFX-PIM-25 ^c	793	1522	208	606	500	4034	7.3	2.9	19.4	8.0
5	SFX-PIM-25 ^d	496	1018	105	411	200	2120	9.7	3.9	20.2	10.6
5	PIM-1 ^c	992	2152	316	822	618	4644	6.8	2.6	14.7	7.5
6	PIM-1 ^d	590	1432	154	510	308	2526	9.3	3.3	16.4	8.2
7	SBF-PIM [18]	2200	6320	786	2640	1100	13,900	8.04	3.35	17.7	12.63
8	PIM-1[18]	1950	5010	823	2270	1360	13,600	6.08	2.8	16.6	10
9	PA S1 [33]	-	-	1.88	14	1.5	48	-	7.45	25.53	32
10	PA S2 [33]	-	-	1.50	11	1.27	45	-	7.80	30	35.43

^a Units of permeability (P): 1 Barrer = 10^{-10} cm³ (STP)cm /cm² s cm Hg.

^b Selectivity (α) = P₁/P₂.

^c Gas permeability after methanol treatment.

^d Gas permeability after 130 days of physical aging.



Fig. 3. Robeson plots for (a) H₂/N₂; (b) O₂/N₂; (c) CO₂/N₂; and (d) CO₂/CH₄ gas pairs. 1) PIM-1, 2) SFX-PIM-25, 3) SFX-PIM-33, 4) SBF-PIM, 5) PA S1 and 6) PA S2.

appreciable selectivity of one gas over other. Under the similar conditions of measurements, SFX-PIMs are more selective for all gas pairs and less permeable as compared to PIM-1. For instance, methanol-treated film of SFX-PIM-33 exhibited CO_2 permeability of 3595 Barrer with selectivity for CO_2/N_2 gas pair was 23.5 whereas methanol-treated film of PIM-1 exhibited CO_2 permeability of 4644 Barrer with selectivity for CO_2/N_2 gas pair was 14.7. These results implied that SFX unit disturbed polymer chain packing less effectively as compared to spirobisindane unit. This trend is also consistent with *d*-spacing, BET surface area and FFV (Table 3).

Physical aging is a process in which polymer chains undergo relaxation resulting into decrease in permeability over time due to reduction of free volume [35]. The gas permeability and selectivity data of SFX-PIM-25, SFX-PIM-33 and PIM-1 for the methanol-treated films which were physically aged over 130 days at room temperature are shown in Table 3. It was observed that there was decrease in permeability with increase in selectivity for all gases. For instance, the CO_2 permeability of SFM-PIM-33 decreased from 3595 to 1848 Barrer with increase in selectivity for CO_2/N_2 and CO_2/CH_4 gas pairs from 23.5 to 30.8 and from 8.7 to 11.9, respectively. Thus, films of SFX-PIMs after aging demonstrated further enhancement in gas selectivity.

In order to understand efficacy of SFX-PIM-25 and SFX-PIM-33, it is worth to compare the gas permeability data of SFX-PIMs with reported PIMs and SFX-based polymers. It is interesting to note that the present SFX-PIMs showed higher permeability than SFX-based polymers and higher selectivity than SFX-PIMs containing spirobisindane and spirobifluorene units [18]. In the Robeson plots (Fig. 3), the present SFX-PIMs films followed the usual trade-off relationship between permeability and selectivity and the gas permeability data of SFX-PIM-25 and SFX-PIM-33 for CO_2/N_2 , CO_2/CH_4 , H_2/N_2 and O_2/N_2 was located close to 1991 Robeson upper bound.

5. Conclusions

In this work, a new bis(catechol) containing spiro[fluorene-9,9'xanthene] unit, namely, 4,4'-(spiro[fluorene-9,9'-xanthene]-2',7'-diyl) bis (benzene-1,2-diol) (THSFX) was designed and synthesized in three steps. Polycondensation of THSFX and varying compositions of THSFX and TTSBI with TFTPN was carried out to afford homo and copolymers with intrinsic microporosity. The organo-soluble PIMs showed reasonably high molecular weights and could be cast into self-standing thin films. PIMs exhibited excellent thermal stability ($T_{10} = 490-510$ °C), amorphous nature and high FFV (18-22%). These PIMs possessed intrinsic microporosity as indicated by N₂ adsorption method and showed high BET surface area in the range $360-796 \text{ m}^2/\text{g}$. Gas permeability analysis showed that methanol-treated films of SFX-PIM-25 and SFX-PIM-33 are highly permeable with appreciable selectivity. The gas permeability of methanol-treated films of SFX-PIMs for CO₂/N₂ and O₂/ N₂ gas pairs was close to 1991 Robeson upper bound. Overall, the results indicated that SFX unit is an attractive moiety to induce intrinsic microporosity and SFX-containing PIMs exhibited improved gas permeability characteristics.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.reactfunctpolym.2018.10.008.

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