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A comparative structure–property study of methylphenylated and fluoromethylphenylated poly(aryl ethers) and their gas permeabilities and permselectivities☆

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Abstract

Two novel poly(aryl ether)s, dimethylphenylated poly(ether nitrile) (6H-PEN) and dimethylphenylated poly(ether ether ketone) (6H-PEEK), derived from (3,5-dimethylphenyl)hydroquinone monomer, were synthesized via aromatic nucleophilic substitution polycondensation. They showed high glass transition temperatures and were soluble in common solvents. A comparison of gas permeabilities and permselectivities among methylphenylated (3H-PEEK and 3H-PEN), trifluoromethylphenylated (3F-PEEK and 3F-PEN), dimethylphenylated (6H-PEEK and 6H-PEN) and 3,5-ditrifluoromethylphenylated (6F-PEEK and 6F-PEN) poly(aryl ether)s were studied. Compared with the methylated polymers, the corresponding fluoromethylated polymers had generally higher permeabilities. The 3F and 6F polymers had combined permeabilities and permselectivity properties attractive for O_2/N_2 separation. 6F-PEN exhibited the best gas separation properties for the O_2/N_2 pair, and $P(O_2)$, and $P(O_2)/P(N_2)$ values were 6.6 and 5.9, respectively.

Keywords: Gas permeability; Poly(ether ketone)s; Fluoropolymers

1. Introduction

Polymer membrane gas separation is one of the fastest growing branches of separation technology [1,2]. The application of high performance polymers such as polyimides and poly(aryl ethers) as gas separation membrane materials is of great interest because of their excellent thermal, chemical and mechanical properties [3–8].

Much effort has been devoted to the design and preparation of membranes that exhibit both higher permeability and higher selectivity than the membranes available at present [9,10]. According to the widely accepted model for gas separation, the incorporation of rigid bulky groups either into the backbone or as pendant groups affect the packing density and segmental motion, and have the potential to improve gas permeability and permselectivity simultaneously. Bulky groups in the main chain generally lead to increased free volume and hence permeability coefficients. They may also lead to high chain stiffness with restricted segmental mobility, which may increase permselectivity in gas separation applications [11–13].

The work of Koros et al. [14,15] and Tanaka et al. [16] on the fluorinated polyimides containing $-C(CF_3)_2-$ moieties as gas separation membranes showed that the polyimides containing hexafluoroisopropylidene linkages in the main chains displayed high permeability and higher permselectivity simultaneously for N_2, H_2 and CO_2, relative to CH_4.

Despite their excellent overall properties, a thorough study the structure–property relationships of fluoropolymers used as gas separation membranes has been somewhat limited by the difficulty in preparing fluorinated polymers and related monomers.

Poly(aryl ether)s, such as poly(aryl ether ketone)s (e.g. PEEK), and poly(aryl ether nitrile) (PEN) are classes of high-performance polymers that have gained significant commercial interest, and their structures are shown in Scheme 1. However, one difficulty for utilizing conventional PEEK and PEN as thin films and coating materials is because of their poor solubility. In

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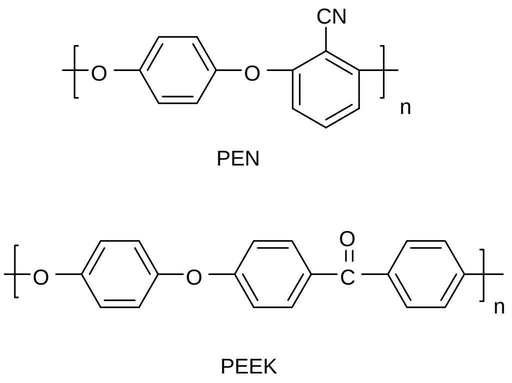


Scheme 1. The structures of PEN and PEEK.

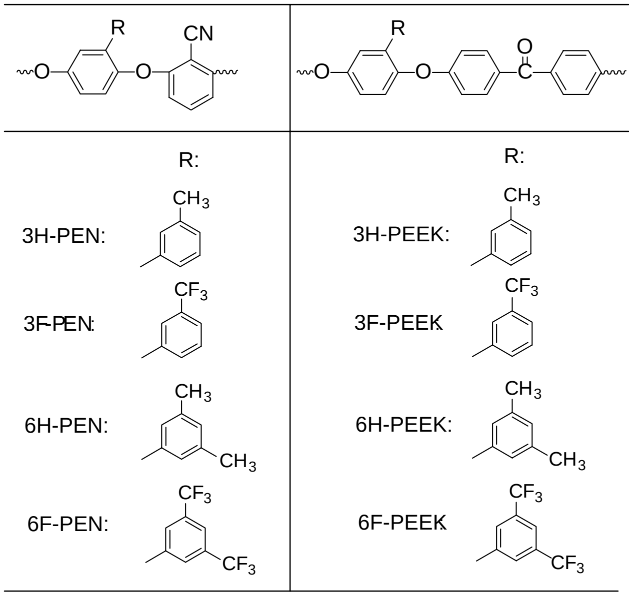
addition, their poor solubility requires that the polymerization conditions are rigorous and exacting. To widen the application fields, considerable effort has been directed to design and develop these two families of high performance polymers with the desired solubility, processability and other properties [17–19].

In a previous study, we reported a series of fluorinated poly(aryl ether)s with some excellent properties, such as high T_gs and thermal stability, good solubility, low dielectric constant, low water absorption, and good processability [20–22]. In a continuation of this study, two novel poly(aryl ethers), dimethylphenylated poly(ether ether ketone) (6H-PEEK) and dimethylphenylated poly(ether nitrile) (6H-PEN), which possess comparable structures with the previous series, were synthesized in order to provide a complete polymer series. The present study is concerned with further elucidating the structure–property relationships of the specific types of incrementally-structured pendant groups of this family of polymers for gas separation properties of methyl/trifluoromethyl and dimethyl/ditrifluoromethyl phenylated poly(aryl ether)s.

2. Experimental

2.1. Chemicals and materials

(3,5-Dimethyl)aniline (Sigma-Aldrich Ltd), 1,4-benzoquinine (Anachemia Chemicals), hydrochloric acid (EMD Chemicals), sodium nitrite (Sigma-Aldrich Ltd), sodium bicarbonate (EMD Chemicals), zinc powder (BDH Chemicals) and 2,6-difluorobenzonitrile (Sigma-Aldrich Ltd) were used as received. 4,4′-Difluorobenzophenone was obtained from Sigma-Aldrich Ltd, and sublimated before use. All other chemicals were obtained from commercial sources, and used without further purification.



Scheme 2. The structures and acronyms of the polymers utilized for gas separation membranes.

3H-PEEK, 3F-PEEK, 6F-PEEK, 3H-PEN, 3F-PEN, and 6F-PEN were synthesized according to previously reported procedures [20–22]. Their structures are illustrated in Scheme 2. The synthetic routes for the preparation of (3,5-dimethyl)phenylhydroquinone (6H-PH) monomer and 6H-PEEK and 6H-PEN polymers are illustrated in Schemes 3 and 4, respectively.

2.2. Synthesis of 6H-PH monomer

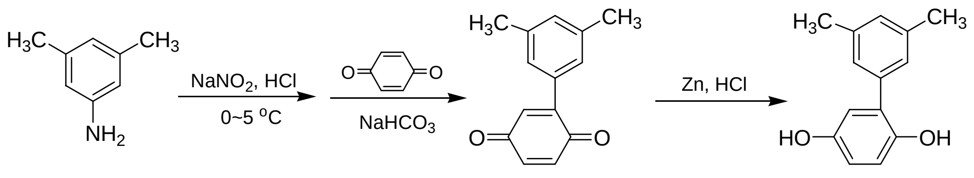
2.2.1. Synthesis of (3,5-dimethyl)phenylquinone (6H-PQ)

Into a 1 L beaker equipped with a magnetic stirrer, 34 mL of hydrochloric acid, 12.1 g (0.1 mol) of (3,5-dimethyl)aniline, and 100 mL of water were added. The mixture was heated and stirred until a homogeneous transparent aqueous solution was formed. The solution was cooled to 0–5 °C by adding ice into the solution. An aqueous solution of sodium nitrite (6.9 g, 0.1 mol) was added dropwise within 1 h to the mixture at 0–5 °C, and then the reaction mixture was stirred for another 1 h to yield a (3,5-dimethyl)phenyldiazonium chloride solution. After stirring at room temperature for 2 h, the resulting mixture was filtered, and filtrate was added dropwise to a stirred mixture of 1,4-benzoquinone (10 g, 0.092 mol), sodium bicarbonate (25.2 g, 0.3 mol), and water (100 mL) at 8–12 °C within 1.2–2 h. The yellow precipitate was collected, washed thoroughly with cold water, and dried at 60 °C in a vacuum oven. The product was recrystallized from butanol to give yellow crystals. Yield: 80%. Mp: 101 °C (DSC). Elem. Anal. Calcd for $C_{14}H_{12}O_2$ (212.24 g/mol): C, 79.22%; H, 5.70%. Found: C, 79.18%; H, 5.67% (Scheme 5).

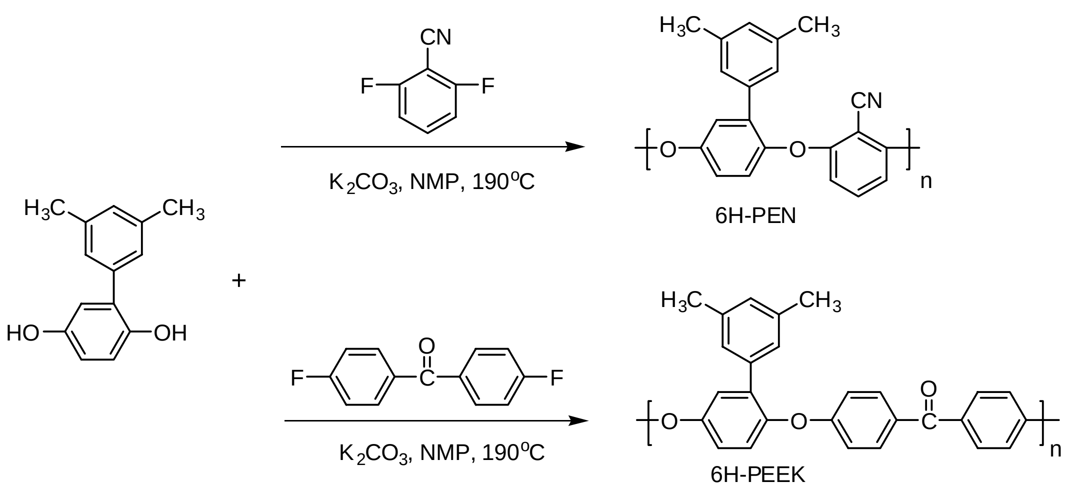
FT-IR (powder, cm^{-1}): 1656 (C=O). ^{1}H NMR (DMSO-d_6, δ, ppm): 7.10 (m, 3H), 6.96 and 6.94 (s, 1H), 6.92 and 6.89 (d, $J=2.5$ Hz, 1H), 6.87 (d, $J=2.5$ Hz, 1H), 2.30 (s, 6H). ^{13}C NMR (DMSO-d_6, δ, ppm): 187.68, 186.61, 145.33, 137.22, 137.21, 135.94, 132.67, 132.00, 131.07, 126.98, 20.77.

2.2.2. Synthesis of 6H-PH

Zinc powder (26.1 g, 0.4 mol), 6H-PQ (21.2 g, 0.01 mol) and water (200 mL) were placed into a 1000-mL three-necked flask equipped with a magnetic stirrer, a dropping funnel and a



Scheme 3. Synthesis route of 6H-PH monomer.



Scheme 4. Synthesis of 6H-PEN and 6H-PEEK.

condenser. Hydrochloric acid (34 mL) was added dropwise into the stirred mixture at reflux with 4 h. The reaction system was allowed to reflux for another 2 h at reflux. The zinc powder was removed after filtrating. The solid in the filtrate was washed with cold water several times and then dried in a vacuum oven. White crystals were obtained after recrystallisation from the toluene. Yield: 80%. Mp: 104 °C (DSC). Elem. Anal. Calcd for $C_{14}H_{14}O_2$ (214.26 g/mol): C, 78.48%; H, 6.59%. Found: C, 78.45%; H, 6.56%.

FT-IR (powder, cm^{-1}): 3380 (–OH). ^1H NMR (DMSO-d_6, δ, ppm): 8.73 (s, 1H), 8.66 (s, 1H), 7.10 (s, 2H), 6.90 (s, 1H), 6.73 (d, $J=8.4$ Hz, 1H), 6.63 (d, $J=2.8$ Hz, 1H), 6.56 (dd, $J=$ 8.4, 2.8 Hz, 1H), 2.29 (s, 6H). ^{13}C NMR (DMSO-d_6, δ, ppm): 149.88, 146.62, 138.65, 136.51, 128.33, 127.76, 126.73, 116.60, 116.41, 114.61, 20.97.

2.3. Synthesis of polymers

The syntheses of the following polymers were accomplished by nucleophilic aromatic substitution polycondensation [23–25].

2.3.1. Synthesis of (6H-PEEK)

To a 100 mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a Dean-Stark trap with a condenser, were added 6H-PH (2.140 g, 10 mmol), 4,4′-difluorobenzophenone (2.180 g, 10 mmol), anhydrous K_2CO_3 (1.794 g, 13 mmol), NMP (22 mL) and toluene (15 mL). The system was allowed to reflux for 3 h, and then the toluene was removed. The reaction mixture was heated to 190 °C. After 10 h, another 10 mL of NMP was added into the viscous reaction mixture. The polymerization was complete after another 2 h. The viscous solution was then poured into 250 mL of ethanol. The polymer was refluxed in deionized water for several times to remove the salts and solvents, and dried at 120 °C for 24 h. FT-IR (film, cm^{-1}): 1656 (C=O), 1224 (Ar–O–Ar). ^1H NMR ($CDCl_3$, δ, ppm): 7.82 (d, $J=8.4$ Hz, 1H), 7.77 (d, $J=8.4$ Hz, 1H), 7.73 (d, $J=8.4$ Hz, 1H), 7.67 (d, $J=8.4$ Hz, 1H), 7.21 (m, 1H), 7.00–7.18 (m, 6H), 7.00–6.80 (m, 3H), 2.26 (s, 6H). ^{13}C NMR ($CDCl_3$, δ, ppm): 194.13, 161.74, 161.65, 161.34, 161.24, 152.50, 148.50, 137.75, 136.54, 136.24, 132.52–131.75, 129.51, 126.72, 123.10, 122.70, 120.10, 117.10, 116.32, 21.27.

2.3.2. Synthesis of 6H-PEN

6H-PEN was synthesized by the polymerization of 2, 6-difluorobenzonitrile with 6H-PH using a procedure similar to that of 6H-PEEK. FT-IR (film, cm^{-1}): 2230 (–CN), 1243 (Ar–O–Ar). ^1H NMR ($CDCl_3$, δ, ppm): 7.45–6.95 (m, 6H), 6.92 and 6.89 (s, 1H), 6.70–6.10 (m, 2H), 2.31 (s, 6H).

2.4. Characterization and measurements

2.4.1. FT-IR, NMR and elemental analysis

FT-IR spectra were measured on a Nicolet 520 Fourier transform spectrometer. Thin films for polymer samples and powder for monomer and precursors were used. The structure of the polymeric materials was fully characterized using high field nuclear magnetic resonance (NMR) spectroscopy. NMR analyses were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz for ^1H and 100.579 MHz for ^{13}C. ^1H NMR spectra (1D, homonuclear decoupling and 2D-COSY) were obtained from samples dissolved in $CDCl_3$ or DMSO-d_6 using a 5 mm pulsed field gradient indirect detection probe. The solvent signals ($CHCl_3$ ^1H 7.25 ppm, ^{13}C 77.00 ppm; DMSO-d_6 ^1H 2.50 ppm, ^{13}C 39.43 ppm) were used as the chemical shift reference. ^1H–^{13}C heteronuclear 2D experiments (HSQC, HMBC) were also obtained from the same indirect detection probe. The elemental analysis was carried out with a Thermoquest CHNS-O elemental analyzer.

2.4.2. DSC and TGA

Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments 2920 DSC at a heating rate of 10 °C/min under nitrogen. Thermogravimetric analysis (TGA) was performed on a TA Instruments Hi-Res TGA 2950 thermal analyzer system at a heating rate of 10 °C/min under nitrogen. All the samples were kept in the furnace at 150 °C for 60 min in N_2 atmosphere to remove residual water and solvent before measurement.

2.4.3. Viscosity and membrane density

Inherent viscosities of the polymer series were measured in DMAc (0.5 g/dL) at 30 °C using an Ubbelohde viscometer.

Polymer density was determined by the displacement method using a Mettler Toledo density kit with anhydrous ethanol at 23 ± 0.1 °C.

2.4.4. Wide angle X-ray diffraction (WAXD)

The wide-angle X-ray diffractometer (WAXD) patterns were measured on a MacScience model M18XHF22 with Cu K_α radiation of wavelength (λ) 1.54 Å and the scanning speed was 5 °/min.

2.5. Preparation of the membranes

Dense polymer films for gas permeability measurements were made from 5 wt% polymer solutions in anhydrous DMAc that were filtered through 1 μm poly(tetrafluoroethylene) filters, and then poured into flat-glass dishes and dried under a nitrogen atmosphere at 50 °C. The detached films were further dried for 24 h in a vacuum oven at 100 °C to remove the residual solvent and then annealed at 130 °C for 4 h. Optically clear films were obtained with a thickness of about 40–60 μm in all cases. The absence of residual solvent in the films was confirmed by observing T_g derived from DSC.

3. Results and discussion

3.1. Synthesis of the monomers and polymers

Bisphenol monomer 6H-PH was synthesized by a three-step synthetic process involving a diazotization reaction of (3,5-dimethyl)aniline and coupling reaction with benzoquinone, followed by a reduction with Zn/HCl. The structures of 6H-PH and precursor 6H-PQ were confirmed by FT-IR and NMR spectroscopy. In the IR spectra, 6H-PQ showed a strong absorption band around 1656 cm^{-1} due to the carbonyl groups. After the reduction reaction, the characteristic band of the hydroxyl groups appeared at around 3280 cm^{-1}, while the absorption around 1656 cm^{-1} disappeared. Fig. 1 shows the simple ^1H NMR spectrum of the pure 6H-PH monomer dissolved in DMSO-d_6. The 3-spin system H-3,5,6 is easily recognizable by its three and four bond couplings ($J = 8$, 2 Hz).

In order to obtain a complete series of non-fluorinated and partially fluorinated polymers with directly comparable structures, two novel poly(aryl ether)s, 6H-PEN and 6H-PEEK, were synthesized in addition to polymers reported previously. Generally, two polymerization routes, aromatic nucleophilic substitution and electrophilic substitution, are often used to obtain poly(aryl ethers). In this work, high molecular weight poly(aryl ethers) were obtained by the reaction of 6H-PH monomer with either benzonitrile or diphenylketone monomers bearing activated fluorine atoms via aromatic nucleophilic polycondensation. It is well known that vigorous reaction conditions, such as high temperature (above 300 °C), have to been used for the polymerization of

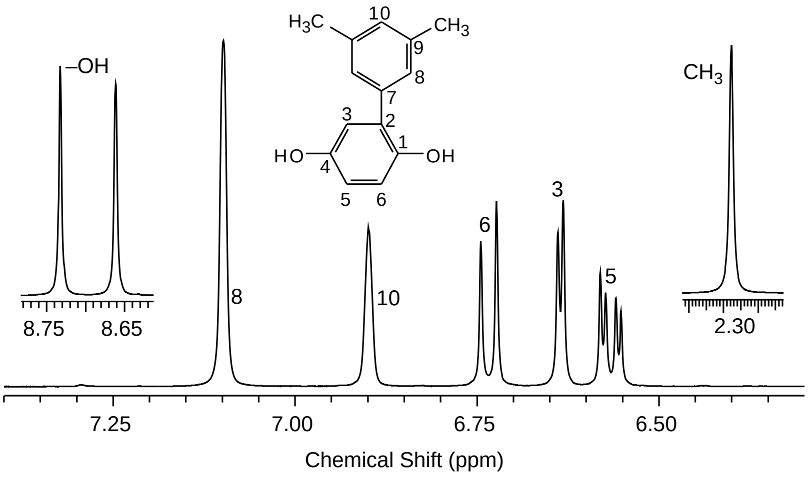


Fig. 1. ^1H NMR spectrum of 6H-PH in DMSO-d_6.

conventional PEEK. Its poor solubility arises from partial crystallinity, which leads to precipitation of the growing polymer chain during polymerization. In the present study, high molecular weight polymers were readily obtained at 190 °C under relatively mild conditions, since the bulky 3,5-dimethylphenyl pendant group imparts solubility to the growing polymer chain. The inherent viscosities of 6H-PEEK and 6H-PEN were 0.68 and 0.71 dL/g in DMAc, respectively.

FT-IR and NMR spectral data were in good agreement with the expected molecular structures of the polymers. Characteristic carbonyl absorption bands at around 1656 cm^{-1}, and nitrile absorption bands at around 2230 cm^{-1} were observed for 6H-PEEK and 6H-PEN, respectively. ^{1}H NMR and ^{13}C NMR spectra of 6H-PEEK in $CDCl_3$ are displayed in Fig. 2 as an example. The introduction of the 3,5-dimethylphenyl group on the hydroquinone monomer results in a more complex ^{1}H spectrum due to its unsymmetrical nature. All the proton and carbon signals for 6H-PEEK were assigned using 1D and 2D NMR sequences. Reduced mobility around the carbonyl group due to conjugation results in multiple signals for H-9,9′ and H-11,11′. The same phenomenon causes C-9,10 and 11 to also appear as multiple signals in the carbon spectrum. Furthermore, the unsymmetrical nature of the hydroquinone monomer causes H-8,12 to appear as multiple signals since they can either be in close proximity or distant from the pendant phenyl group. Also in Fig. 2 is displayed a ^{1}H spectrum of 6H-PEN. The benzonitrile protons H-8,10 appear at low frequencies due to the combined electron shielding effect of the two ether groups. The unsymmetrical hydroquinone monomer causes the H-8,10 to once again appear as multiple signals as explained in a previous publication [26]. The ratio of integral values for the chemical shift regions 6.0–6.7 and 6.7–7.5 is exactly as expected: 2H:7H. The ^{13}C NMR spectrum of 6H-PEN is not represented in Fig. 2 due to its complexity as a result of factors explained above.

3.2. Thermal properties and solubility

Table 1 compares the thermal properties of the two polymer series, which had high T_gs in the range of 134–185 °C. It is readily apparent that the PEN series had higher T_g values than that of PEEK series, which is due to the presence of strong

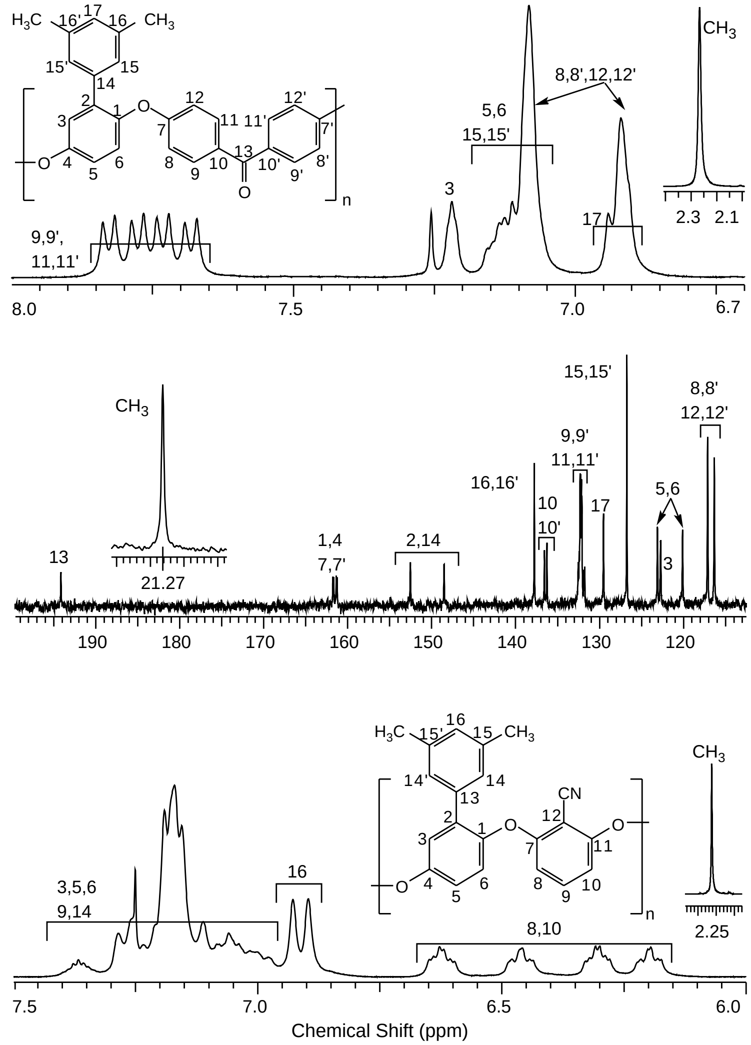


Fig. 2. NMR spectra of 6H-PEEK (^{1}H top, ^{13}C middle) and 6H-PEN (^{1}H bottom).

Table 1
Viscosities and thermal properties of the polymers

Polymer	$[\eta]$ (dL/g)[a]	T_g (°C)[b]	T_d (°C)[c]	T_{d10} (°C)[d]	RW (%)[e]
3H-PEEK	0.70	147	453	481	63.68
3F-PEEK	0.53	134	525	546	58.74
6H-PEEK	0.68	162	438	460	53.87
6F-PEEK	0.48	146	534	546	48.75
3H-PEN	1.40	168	449	466	60.41
3F-PEN	0.82	151	482	494	48.21
6H-PEN	0.71	185	417	438	59.91
6F-PEN	1.02	171	484	501	41.60

[a] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.
[b] Glass transition temperature from the second heating cycle of DSC.
[c] Onset temperature of decomposition.
[d] Ten percent weight loss temperature measured by TGA.
[e] Residue weight at 700 °C in N_2.

polar nitrile (–CN) groups that affect the intermolecular interactions. The partially fluorinated polymers exhibited lower T_g values in comparison with methylated polymers [20]. The T_gs of disubstituted polymers were higher than those of the corresponding mono-substituted polymers, due to the bulky steric effect of the substituent. All the polymers had excellent thermal stability, and no obvious decomposition was observed below 380 °C in the TGA curves. A TGA comparison of fluorinated and nonfluorinated polymers is shown in Fig. 3, where it is noted that the fluorinated polymers possessed higher decomposition temperatures than those of methylated polymers. This result is attributed to the stronger C–F bonds compared with C–H bonds.

The crystallinity of the polymers was evaluated by wide-angle X-ray diffraction (WAXD). All the polymers exhibited amorphous patterns. The amorphous behavior of the polymers was mainly due to the existence of the bulky substituents, which disrupted the regularity of the molecular chains and inhibited their close packing.

All the polymers in this study could be readily dissolved in polar aprotic solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), and less polar solvents, such as chloroform and THF at room temperature. All the polymers could be readily processed by solution casting and thermal compression molding.

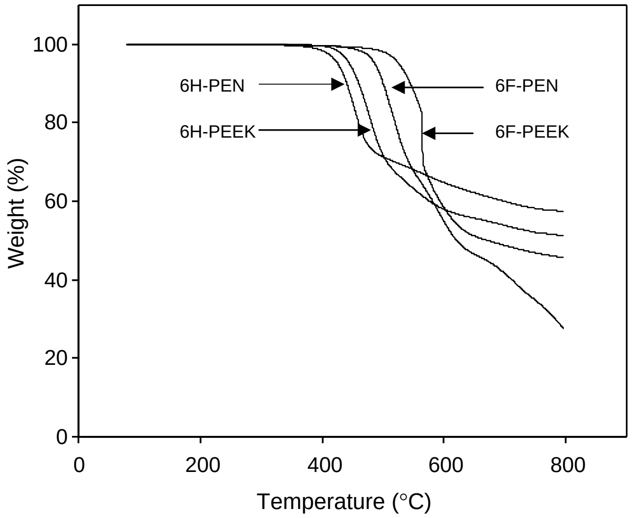


Fig. 3. A TGA comparison of 6H polymers and 6F-polymers.

3.3. Gas separation properties

Fractional free volume (FFV) and the packing density (PD) is also an indicator of chain packing. FFV was calculated using the following relationship [27]:

$$V_f = (V_{sp} - 1.3V_w)$$

$$\text{FFV} = \frac{V_f}{V_{sp}}$$

where V_f is the free volume, V_{sp} is the specific volume and V_w is the specific van der Waals volume, calculated using the group contribution method of Bondi [28,29]. PD was calculated using [30]:

$$\text{PD} = \frac{V_{sp}}{(V_{sp} - V_w)}$$

PD and FFV data are listed in Table 2. PEN derivatives have larger FFV and PD than PEEK directives. It is apparent that the trifluoromethyl group is effective in disrupting chain packing, which is directly correlated with gas permeability.

A trade-off relationship is usually observed between P and α for common gases in glassy or rubbery polymers. That is, higher permeability is gained at the cost of permselectivity and vice versa. A guiding principle for overcoming this trade-off behaviour so as to achieve simultaneously higher permeability and permselectivity is that the polymer chain stiffness should be maintained while increasing with the interchain separation. On this basis, trifluoromethyl groups were introduced onto the polymer chains.

Permeability coefficients (P) of the pure gases H_2, CO_2, O_2, N_2 and CH_4 were measured by the constant volume method at 35 °C with an upstream pressure of 4000 Torr. The experimental gas permeability data for these gases are presented in Table 3 and presented graphically in Fig. 4 for the O_2/N_2 gas pair. The dashed and solid lines in the figures represent the upper bound lines of Robeson [31] and Park et al. [32], respectively. The distance (δ) from the permeability point (P_i,

Table 2
Physical properties of the polymers

Polymer	ρ (g/cm^3)	V_{sp} (cm^3/g)	M^a (g/mol)	V_w (cm^3/mol)	V_f (cm^3/g)	PD	FFV
3H-PEEK	1.22	0.82	378.4	207.1	0.108	3.01	0.132
6H-PEEK	1.19	0.84	392.5	218.2	0.118	2.95	0.140
3F-PEEK	1.30	0.77	432.4	214.7	0.124	2.82	0.162
6F-PEEK	1.34	0.75	500.4	233.5	0.140	2.67	0.187
3H-PEN	1.20	0.83	299.3	164.3	0.120	2.93	0.144
6H-PEN	1.17	0.86	313.4	175.4	0.127	2.90	0.149
3F-PEN	1.31	0.76	353.3	171.9	0.131	2.76	0.171
6F-PEN	1.36	0.73	421.3	190.7	0.146	2.61	0.199

[a] Molecular weight of repeat unit.

Table 3
Gas permeabilities of the polymers

Polymers	P (barrer)[a]					α[b]		$\delta\times10^3$	
	H_2	CO_2	O_2	N_2	CH_4	H_2/CH_4	O_2/N_2	H_2/CH_4	O_2/N_2
PSf	14.0	6.7	1.4	0.25	0.28	56	5.6	787	213
3H-PEEK	3.8	1.0	0.2	0.029	0.024	158	6.7	834	287
6H-PEEK	4.6	1.6	0.33	0.053	0.05	92	6.2	953	284
3F-PEEK	4.1	1.5	0.38	0.051	0.041	100	7.4	960	198
6F-PEEK	21	8.7	3.3	0.54	0.38	55	6.1	673	110
3H-PEN	6.8	1.9	0.45	0.07	0.05	136	6.4	713	242
6H-PEN	9.6	3.5	0.94	0.17	0.06	160	5.5	560	252
3F-PEN	9.3	3.7	0.87	0.15	0.09	103	5.8	710	235
6F-PEN	35	19	6.6	1.12	0.83	42	5.9	610	72

[a] Permeability coefficients measured at 35 °C and 1 atm pressure. 1 Barrer = 10^{-10} [cm^3 (STP) cm]/(cm^2 s cmHg).
[b] Ideal permselectivity $\alpha=(P_a)/(P_b)$.

vs. α_{ij}, where ideal permselectivity $\alpha_{ij}=P_i/P_j$) to the upper bound line was calculated by the method developed previously [7]. Table 3 compares P, α and δ values for the complete PEEK and PEN polymer series. The gas permeability coefficients decrease in the following order: $H_2>CO_2>O_2>N_2>CH_4$, which is also the order of increasing kinetic diameters of the gases.

The gas permeability coefficients increase in the following order for two polymer series, except 3F-PEN: 3H < 6H < 3F < 6F, which is also the order of increasing FFV and PD of the polymers. When comparing polymers with –CF_3 groups to the analogous –CH_3 derivatives, –CF_3 groups lead to a significant increase in $P(O_2)$ with a little decrease in $\alpha(O_2/N_2)$. The only exception is 6F-PEN, which while showing a large increase in $P(O_2)$ with a concurrent increase in $\alpha(O_2/N_2)$ compared with 3F-PEN. For the O_2/N_2 gas pair, the lowest δ value of 0.072 was obtained for 6F-PEN, indicating the importance of 6F in inhibiting chain packing. The incorporation of 6F groups onto the pendant phenyl of these particular polymers is clearly effective in improving the permeabilities to gases without an upper-bound coupled reduction in permselectivities, especially for the O_2/N_2 gas pair. The polymers in this study, from which flexible films could be cast, all fall below the upper bound line, although some polymers lie close to it. The polymers with the most desirable combination of permeability and selectivity (i.e. those closest to the upper bound line for the gas pair) are 6F-PEEK and 6F-PEN.

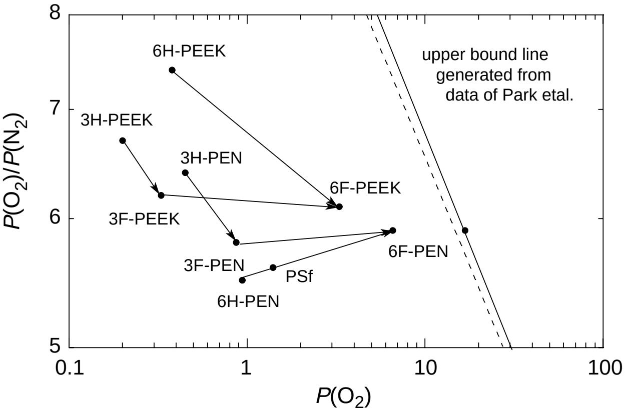


Fig. 4. Gas separation properties of the polymers for O_2/N_2 pair relative to the upper bound line.

The FFV is closely connected to the diffusion coefficients in a strict sense according the free volume theory. However, it has been experimentally found that the permeability can also be similarly correlated with FFV as follows [33]:

$$P = A\exp\left(\frac{-B}{\mathrm{FFV}}\right)$$

where A and B are parameters. Fig. 5 shows that a fairly linear relationship between $\log(P)$ vs. 1/FFV exists for the trifluoromethyl-modified PEN polymers for all five gases. The exception for the unmodified polymers could be due to the solubility difference between modified and unmodified polymers because the linear relationship between $\log(P)$ and (1/FFV) is based on the identical solubility coefficients [31,27]. This suggests that the increased permeability appears to be

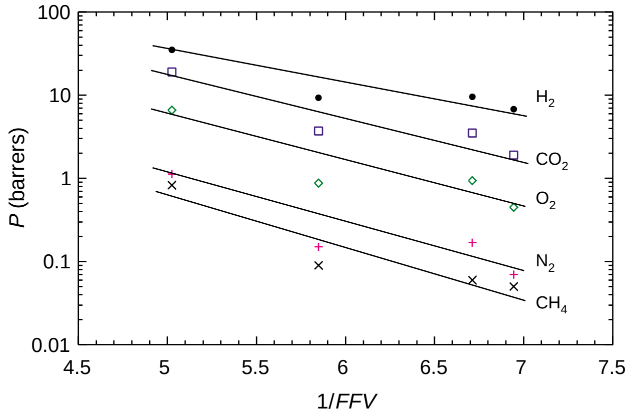


Fig. 5. Log P as a function of reciprocal FFV at 35 °C and 1 atm upstream pressure.

closely correlated with an increase in the diffusion coefficient, which is associated with high free volume or low packing density due to ditrifluoromethyl substitution.

3.4. Molecular modeling

Conformational analysis of 6F-PEEK/PEEK and 6F-PEN/PEN with 10 repeating unit chain lengths was performed to study the effect of ditrifluoromethylphenyl substitution (6FP) and distribution of 6FP on chain geometry and steric interaction. The calculation results of geometry optimization with minimum energy using AMBER method gave a visual indication of major conformational changes in the polymers containing 6FP moieties, as shown in Fig. 6. The chains of both PEEK and PEN without pendant groups shown for comparison are relatively linear and regular coils, which would lead to their close chain packing, in agreement with their semi-crystalline morphology. Compared with PEEK, 6F-PEEK showed a similarly unperturbed coil conformation. This could be due to the rigid phenyl-*CO*-phenyl linkage, which would lead to relatively difficult movement of molecular backbones [34,35]. According to a reported result [35], the calculated configuration of PEN is a rather random coil-like structure. The conformation of 6F-PEN exhibited a kinked coil structure in spite of polar nitrile groups. The free rotation of the sterically bulky 6FP group is limited because it is directly connected with benzene ring of the polymer main chain (the torsional angle between the two benzene rings was around 40°). The carbons of both $–CF_3$ groups were coplanar with their adjacent benzene rings, and they had undistorted bonding angles of 120°. These results suggest that the rigid and bulky 6FP groups affect the packing density and segmental motion of 6F-PEEK and 6F-PEN, and therefore improve their gas permeability and

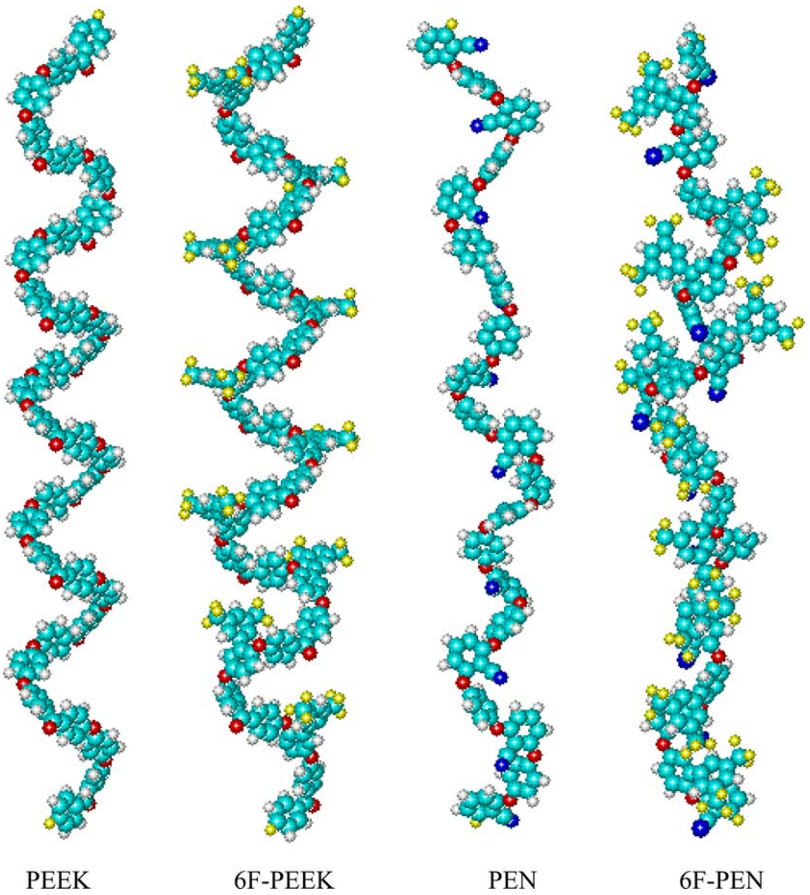


Fig. 6. Chain conformation of 6F-PEN/PEN and 6F-PEEK/PEEK (10 repeat units).

permselectivity. The higher relative content of bulky 6FP side groups in 6F-PEN compared with 6F-PEEK demonstrated that the 6F-PEN had superior gas separation properties.

4. Conclusion

To investigate the incremental structural effect of fluorinated and nonfluorinated pendant groups on gas separation properties, two novel dimethyl phenylated poly(aryl ethers), 6H-PEN and 6H-PEEK, and six previously reported poly(aryl ethers), including methylated 3H-PEN and 3H-PEEK, trifluoromethylated 3F-PEN and 3F-PEEK, and 3,5-ditrifluoromethylated 6F-PEN and 6F-PEEK, were prepared. All the polymers had improved solubility in common solvents, such as DMAc, DMF, NMP, chloroform and THF in comparing PEEK and PEN. Compared with the methylated polymers, the corresponding fluoromethylated polymers showed lower T_gs and higher thermal stability. PEN directives have larger FFV and PD and higher permeabilities than PEEK directives. Both the permeabilities and ideal permselectivities of 3F and 6F polymers were better than those of the corresponding 3H and 6H polymers. It is apparent that the 6FP group is effective in disrupting chain packing and segmental motion, which is directly correlated with gas permeability $P(O_2)$, and $P(O_2)/P(N_2)$ values of 6F-PEN were 6.6 and 5.9, respectively. The conformational analysis of 6F-PEEK/PEEK and 6F-PEN/PEN was in agreement with the gas separation properties and these two polymers exhibited the best overall performance. The development of other polymers containing bulky rigid 6FP groups that could effectively improve gas separation properties will be continued.

Acknowledgements

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