

ORIGINAL ARTICLE

Structure and properties of new highly soluble aromatic poly(etherimide)s containing isopropylidene groups

Aleksandra Wolinska-Grabczyk¹, Ewa Schab-Balcerzak¹, Eugenia Grabiec¹, Andrzej Jankowski¹, Marek Matlengiewicz², Urszula Szeluga¹ and Piotr Kubica¹

A series of amorphous poly(etherimide)s (PEIs) was synthesized from 4,4'-(4,4'-isopropylidene-diphenoxy)bis(phthalic anhydride) and different diamines or from 4,4'-(4,4'-isopropylidene-diphenyl-1,1'-diyldioxy)dianiline and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride. The structures of the obtained PEIs were confirmed by Fourier transform infrared spectroscopy (FTIR), ¹H and ¹³C nuclear magnetic resonance spectroscopies (¹H and ¹³C NMR) and by elemental analysis. These polymers show excellent solubility in a broad range of solvents and produce strong and flexible films. The films were examined using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD) and mechanical testing, and were characterized by gas transport measurements. The obtained films exhibit thermal stability up to 500 °C, good mechanical properties and a CO₂ permeability of 7.85 Barrer with a CO₂/N₂ selectivity of 21.2 for the polymer that contains hexafluoroisopropylidene moieties. The effects of the chemical structures on the physical and gas permeation properties were studied. The introduction of bulky cardo or hexafluoroisopropylidene moieties into the polymer chain increases the glass transition temperature (*T*_g) and fractional free volume (FFV), while the incorporation of additional ether linkages produces the opposite effect. Using an existing free volume approach, we found that the permeabilities of the studied PEIs are well correlated with their FFVs.

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INTRODUCTION

Aromatic polyimides (PIs) were first produced in 1908; since then, interest in this type of polymers has been growing because of their exceptional properties, such as excellent thermal, thermo-oxidative and dimensional stability; high radiation and solvent resistance; low dielectric constant; and unusually good mechanical properties.^{1–3} This unique combination of properties makes PIs ideal for a variety of applications, for example, in microelectronics, microelectro-mechanical systems, aerospace and photoelectronics or as gas separation membranes, materials for memory devices, alignment layers in liquid crystal displays, and redox-active, electrochromic polymers.^{3–6} Although many excellent polyimides are known and commercially available, new polyimides are emerging as research continues on the chemical structure-property correlations and on the search for new compounds with unique combinations of properties for special applications. Recently, particular attention has been paid to new materials and technologies for gas separation applications because of environmental concerns and economic interests. Polymeric gas separation membranes exhibit good mechanical properties, often

very good productivity (flux and ability to separate various gas mixtures), and offer simple and low energy cost operations.⁷ Many polymers have been investigated as potential membrane materials, and several of them have found industrial application. It should be noted that polyimides are among these materials.⁸ Of the polymers that contain imide rings, poly(etherimide)s (PEIs) are of particular interest because they combine both high stiffness and heat resistance owing to their aromatic imide units, and improved processability owing to the presence of flexible ether linkages.⁹ One commercialized PEI, which is obtained from 4,4'-(4,4'-isopropylidene-diphenoxy) bis(phthalic anhydride) (IPDA) and 1,3-phenylene diamine, is known under the trade name Ultem 1000. This polymer has already been used in many applications, including membrane separation techniques.^{9–13} However, to the best of our knowledge, the application of IPDA-based PEIs, except for Ultem, to gas separation has only been described in five articles.^{10,14–17} Eastmond *et al.*¹⁴ described the permeability and diffusion coefficients for oxygen, carbon dioxide, nitrogen and argon in a membrane that was made from a PEI obtained from IPDA and 4,4'-bis(4''-aminophenoxy)

¹Centre of Polymer and Carbon Materials, Polish Academy of Sciences, Zabrze, Poland and ²Institute of Chemistry, Faculty of Mathematics, Physics and Chemistry, University of Silesia, Katowice, Poland

Correspondence: Professor A Wolinska-Grabczyk, Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M Curie-Sklodowska Street, 41-819 Zabrze, Poland.
E-mail: aleksandra.wolinska@cmpw-pan.edu.pl

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biphenyl. Xia *et al.*¹⁰ reported the gas permeability of a PEI that was synthesized from IPDA and diamino-diphenyl sulfone and compared it with those of polysulfone and Ultem. Lazareva *et al.*¹⁵ estimated the permeability and diffusion coefficients of H₂, CO, CO₂ and CH₄ in two PEIs that were prepared from IPDA, 4,4'-(4,4'-isopropylidene-diphenyl-1,1'-diyldioxy)dianiline, and 4,4'-(hexafluoroisopropylidene)bis(p-phenyleneoxy)diamine. Additionally, Ronova *et al.*¹⁶ described a correlation between the conformational rigidity of these PEIs and their gas permeabilities. Bruma *et al.*¹⁷ reported the physical properties and gas permeabilities (He, H₂, O₂ and CO₂) of a polymer that was synthesized from IPDA and 4,4'-(hexafluoroisopropylidene)dianiline.

In this paper, we report the synthesis and thermal (differential scanning calorimetry, DSC; thermogravimetric analysis, TGA), thermomechanical (dynamic mechanical analysis, DMA), mechanical, structural (X-ray diffraction), and gas transport characterization of a set of new PEIs with isopropylidene moieties in the main chain. Additionally, to verify the results of the characterization, the commercial PEI Ultem, which contains the same isopropylidene units, was also studied. The Ultem properties were measured using the same procedures and compared with the data that were provided by the manufacturer or found in the literature.^{9–14} This work is a continuation of our earlier research¹⁸ and was performed to find a correlation between the polyimide structure and its physical properties. Although much information has been gathered on polyimides, the development of new methodologies for PI chemical modification, which could enhance the application potential of PIs, is still required.

EXPERIMENTAL PROCEDURE

Measurements

¹H nuclear magnetic resonance (NMR) and ¹³C NMR spectra were recorded on an Avance II UltraShield Plus Bruker MT 600 MHz spectrometer (Bruker, Rheinstetten, Germany) using chloroform (CDCl₃) as a solvent and TMS as the internal standard. Infrared measurements were performed on a FTS 40 A Fourier transform infrared spectrometer (Bio-Rad, Digilab Division, Cambridge, MA, USA). The Fourier transform infrared spectroscopy (FTIR) spectra were acquired between 4000–400 cm⁻¹ with a resolution of 2 cm⁻¹ for 32 accumulated scans. The samples were analyzed as KBr pressed pellets or as films cast onto KBr wafers. Elemental analysis data were obtained using a Vario EL III apparatus (Elementar, Hanan, Germany). The molar masses and dispersities (M_w/M_n) of the polymers were determined using gel permeation chromatography measurements conducted at 80 °C with DMF as an eluent at a flow rate of 1 ml min⁻¹. A Knauer apparatus with MIXED-DPL gel columns (Knauer, Bad Hamburg, Germany) and polystyrene standards were used. The X-ray diffraction patterns of the film samples were recorded using CuK α radiation (wavelength $\lambda = 1.54051 \text{ \AA}$) on a wide-angle HZG-4 diffractometer (Carl Zeiss, Jena, Germany) in the typical Bragg geometry. The X-ray diffraction angle, θ , at which a maximum of a broad peak appeared on the WAXD profile and the following Bragg's expression:

$$\lambda = 2d \cdot \sin\theta \quad (1)$$

were used to calculate the average interchain distance, that is, the d -spacing. DSC experiments were performed with a TA-DSC 2010 apparatus (TA Instruments, Newcastle, DE, USA) under nitrogen using a heating/cooling rate of 20 °C min⁻¹. The glass transition temperature, T_g , was taken as the midpoint of the heat capacity step change that was observed in the second run. TGA was performed with a Mettler Toledo TGA/DSC STARE system over the temperature range from 25–800 °C at a heating rate of 10 °C min⁻¹ under a constant nitrogen flow of 60 ml min⁻¹. DMA was performed using a TA Instruments DMA 2980 apparatus. The measurements were made for film samples 0.07–0.1 mm thick, 6–7 mm wide and 10–11 mm long. The samples were oscillated at a single frequency of 1 Hz with an oscillation amplitude of

10 μm . A tensioning clamp, a static force of 0.01 N, and an autostrain of 150% were applied. Mechanical spectra were obtained using a temperature scan rate of 3 °C min⁻¹ starting from room temperature and ending just above the glass transition temperature of the samples. Changes in the storage modulus (E'), loss modulus (E''), and loss factor ($\tan \delta$) were recorded as a function of temperature. The glass transition temperature (T_g) was taken as the temperature at the maximum of the $\tan \delta$ peak. The mechanical properties of the investigated materials were determined using an Instron Model 4204 tensile tester. Strips 8 mm wide and 50 mm long were cut from the films. Tensile stress tests were conducted at room temperature with a 20-mm min⁻¹ tensile speed. The results were taken as the average of three uniform samples. The density of the polymer films (ρ) was determined using a buoyancy method by weighing the sample in water (m_L) and in air (m_A). The density was then calculated as follows:

$$\rho = \frac{m_A}{m_A - m_L} \rho_0 \quad (2)$$

where ρ_0 was the density of water. The results were taken as the average of several measurements. The fractional free volume (FFV) was calculated using the following equation:

$$\text{FFV} = \frac{V - V_0}{V} \quad (3)$$

where V is the specific volume at temperature T , that is, the reciprocal of the measured density, and V_0 is the molar volume that is occupied by a macromolecule at 0 K. The value of V_0 can be estimated from the van der Waals volume (V_w) using the following relation:¹⁹

$$V_0 = 1.3V_w \quad (4)$$

In this work, the V_w of a polymer repeating unit was obtained in two ways: (i) using the group contributions to V_w that were collected by Bondi²⁰ and the method of van Krevelen¹ and (ii) using the HyperChem computer program, version 8.0.²¹ Permeation measurements were performed at an applied gas pressure of 7 bar and 30 °C using a constant-pressure/variable-volume apparatus.²² For the permeation experiments, pure helium, oxygen, nitrogen and carbon dioxide were used, and these gases were measured in the given sequence. The gas permeability, P , expressed in Barrer units was determined from the following expression:

$$P = \frac{q \cdot l}{(p_1 - p_2)A \cdot t} \quad (5)$$

where q is the quantity of permeant (cm³(STP)) passing through the membrane in time t (s), A is the effective membrane area (cm²), l is the membrane thickness (cm), and p_1 and p_2 are the upstream and downstream pressures (cm Hg), respectively. The permeability coefficient error that was associated with this system was in the range of 10–15%, and the error was larger for a lower gas permeability. The ideal selectivity (α) for gases A and B was calculated from single gas permeation experiments using the following equation:

$$\alpha = \frac{P_A}{P_B} \quad (6)$$

Materials

4,4'-(4,4'-Isopropylidene-diphenyl-1,1'-diyldioxy)dianiline, 4,4'-(9-fluorenylidene)dianiline, 2,4-diaminotoluene, 2,7-diaminofluorene, 4,4'-(hexafluoroisopropylidene)dianiline, IPDA, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, *N*-methyl-2-pyrrolidinone (NMP), and other necessary chemicals were purchased from Aldrich Chemical Co. (Poznan, Poland) and were used as received, except for 4,4'-(9-fluorenylidene)dianiline, which was crystallized from methanol in the presence of decolorizing charcoal. The commercial polyimide film Ultem was kindly supplied by CS Hyde. Helium, nitrogen and carbon dioxide with purities of 99.998%, and oxygen with a purity of 99.95% were purchased from Air Products Sp. z o. o., Siewierz, Poland and were used as received.

Synthesis of PEIs

Polymers were prepared by the polycondensation reaction of equimolar amounts of IPDA with various diamines, that is, 4,4'-(4,4'-isopropylidene-

diphenyl-1,1'-diylidiox)dianiline, 4,4'-(9-fluorenylidene)dianiline, 2,4-diaminotoluene, 2,7-diaminofluorene and 4,4'-(hexafluoroisopropylidene)dianiline, which resulted in PEI-1, PEI-2, PEI-3, PEI-4 and PEI-5, respectively. The polycondensation reaction of equimolar amounts of 4, 4'-(hexafluoroisopropylidene)diphthalic anhydride and 4,4'-(4,4'-isopropylidene-diphenyl-1, 1'-diylidiox)dianiline produced PEI-6. The polymerization was conducted using NMP as a solvent (20% of the total monomer concentration). The reaction was performed in two steps. In the first step, the reaction mixture was stirred for 18 h at room temperature under an argon atmosphere to produce a viscous poly(amic acid) (PAA) solution. Then, toluene was added as a low boiling azeotropic agent to the PAA solution, and azeotropic distillation was performed at 160–185 °C for 5 h. Afterwards, the polymer solution was cooled to room temperature and precipitated in methanol. The precipitate was collected by filtration, washed with hot methanol to remove any residual solvent, and dried at 100 °C under vacuum for at least 24 h. PEIs were obtained with a yield above 80%.

Membrane preparation

Membranes for gas permeability, as well as for thermal (DMA, DSC) and mechanical measurements, were prepared from polymer solutions (0.3 g of the PEIs in 4 ml of DMF, except for PEI-4), filtered through a 0.5- μm filter, and cast onto a Teflon plate that was mounted in a metal mold. In the case of PEI-4, 0.3 g of the polymer were dissolved in 5 ml of NMP and heated until the whole polymer was completely dissolved. The membranes were soft dried in an oven at 50–70 °C for 2 days and then heated at 70–80 °C for another 2 days. Afterwards, the membranes were removed from the Teflon plates and dried in a vacuum oven at 150 °C for 20 h. The temperature was then increased to 200 °C, and drying was continued for additional 3 h. The thicknesses of the membranes, which were calculated as the average of several thickness measurements, were in the range of 40–100 μm .

RESULTS AND DISCUSSION

Synthesis and characterization of PEIs

In this work, the ring-opening polyaddition of diamines with aromatic dianhydrides was conducted in NMP at room temperature and yielded a PAA solution. Thermal imidization in the presence of a low boiling azeotropic agent was used to form polyimides without isolating the intermediate PAA. The chemical structures of the synthesized PEIs are presented in Figure 1.

The polymers from PEI-2 to PEI-4 are new, whereas PEI-1, PEI-5 and PEI-6 have already been described in the literature.^{15–17,23,24} The

chemical structures of the obtained PEIs were studied using FTIR, ¹H NMR, ¹³C NMR and elemental analysis techniques. The detailed spectral and elemental analysis data for all the polymers are presented in the Supplementary Information. The results that were obtained from these studies confirm that the PEI structures were in accordance with the assumed ones.

In Figure 2, an exemplary FTIR spectrum of PEI-3 is presented.

The FTIR spectra of all the polymers show characteristic absorption bands from the asymmetric and symmetric stretching vibration of the carbonyl group in the imide ring at 1776–1784 and 1720–1730 cm^{-1} , respectively. The lack of absorption bands at 1650 and 3350 cm^{-1} , which are typical for amide and carboxyl groups, respectively, indicates a virtually complete conversion of the PAA precursor into a polyimide.

The assumed chemical structures of the obtained polymers are well confirmed by their NMR spectra. The ¹H and ¹³C NMR spectra of the exemplary PEI-2 are presented in Figure 3, while the spectra of the others PEIs are shown in Supplementary Figure 1S in the Supplementary Information.

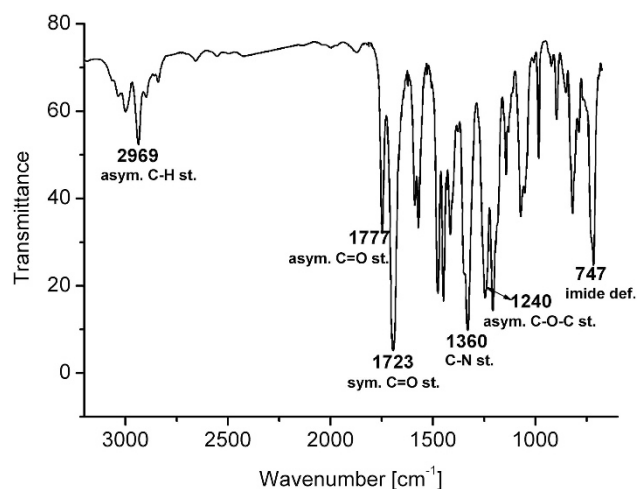


Figure 2 Fourier transform infrared spectroscopy (FTIR) spectrum of poly(etherimide)-3 (PEI-3).

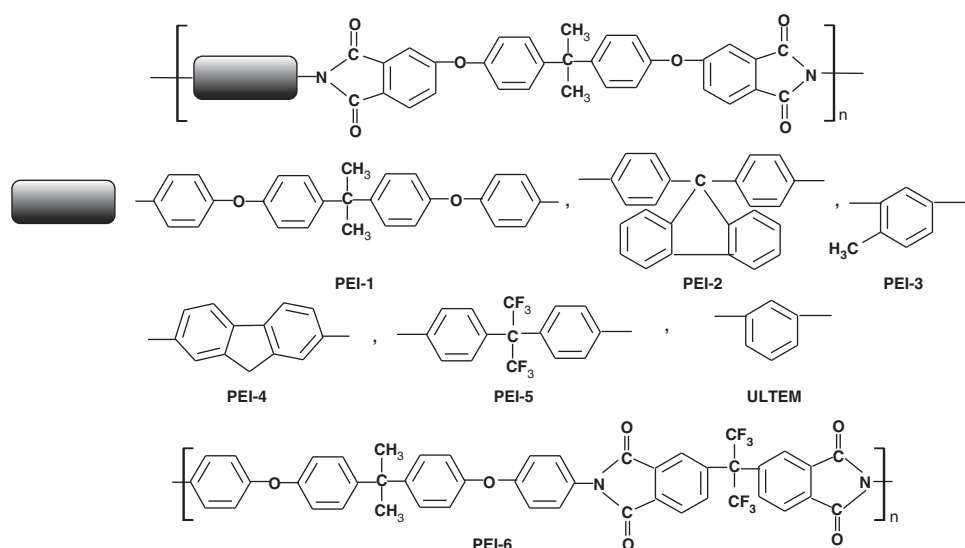


Figure 1 Chemical structures of the poly(etherimide)s (PEIs).

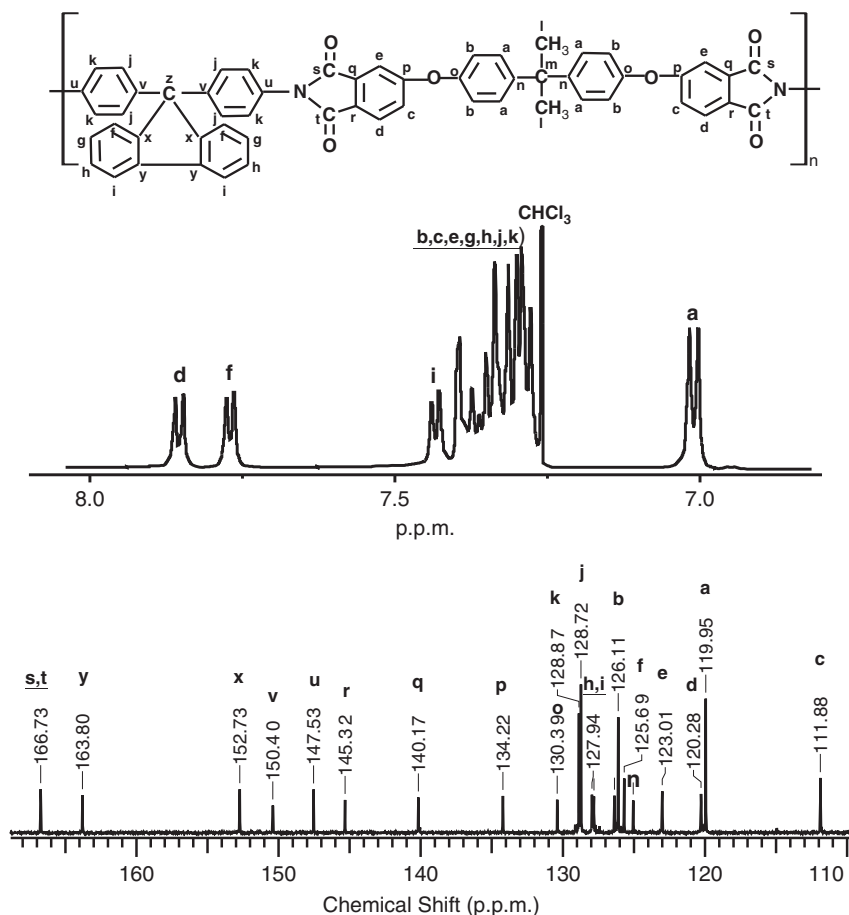


Figure 3 Aromatic regions of the ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra of poly(etherimide)-2 (PEI-2).

All of the ^1H NMR spectra consist of a clear methyl signal at ~ 1.7 p.p.m. in the aliphatic part and a characteristic group of signals in the aromatic part. The regions of the aromatic protons illustrate very well the differences between the particular structures (see the detailed discussion in the Supplementary Information). In the PEI-2 spectrum, despite the high magnetic field applied, most of the signals are superimposed in the region of 7.25–7.91 p.p.m., except for the four clear doublets at 7.01, 7.43, 7.77 and 7.85 p.p.m. due to the protons *a*, *i*, *f* and *d*, respectively. However, the chemical shifts of the signals, their relative intensities, which were obtained from the integration of the separated regions, and the spin couplings agree well with the chemical structure of the polymer repeating unit. The aliphatic region of the ^{13}C NMR spectrum of PEI-2 consists of three lines at 31.00, 42.55 and 65.02 p.p.m. owing to three carbons denoted *l*, *m* and *z*, respectively. The aromatic part is more complicated, and a detailed attribution of some of the lines may be equivocal; nevertheless, their number, relative intensities, and chemical shifts reflect very well the structure that is presented for PEI-2. As the standard carbon spectra that were recorded here with a short repeating time, $D1 = 2$ s, are not exactly quantitative, the non-protonated carbons exhibit visibly smaller intensities than the protonated ones. Therefore, in the aromatic part of the spectrum, the protonated and non-protonated carbons can be distinguished. Two close peaks at 166.71 and 166.73 p.p.m. can be readily attributed to the carbonyl carbons *s* and *t*, confirming that these two carbonyls are not magnetically identical. If we look at the structure of the PEI-2 polymer, we notice that, besides the carbonyls, the repeating unit of the macromolecular

chain consists of 18 non-protonated carbons, which can be grouped into 9 bands due to the symmetry of the structure. All of these 11 signals with comparable intensities for carbons *n* to *y* (including the carbonyl carbons *s* and *t* that were mentioned above) represent two carbons each and can be found in the spectrum at 125.0, 130.39, 134.22, 140.17, 145.32, 147.53, 150.40, 152.73 and 163.80 p.p.m. On the same basis of symmetry, the protonated carbons can be grouped into 11 bands; however, the relative intensities of these lines due to one carbon are approximately one-third higher. Four of these bands represent four carbons each, while the rest of the bands represent two carbons. Due to the symmetry of the structure, the four lines of the doubled intensities at 119.95, 126.11, 128.72 and 128.87 p.p.m. can be attributed to the *a*, *b*, *j* and *k* carbons. The remaining seven lines for carbons *c* to *i* can be found at 111.88, 120.28, 123.01, 125.69, 126.38, 127.82 and 127.94 p.p.m. The presence of 20 aromatic and 3 aliphatic lines in the ^{13}C NMR spectrum, as well as the lines relative intensities and chemical shifts, confirm well the chemical structure of the PEI-2 polymer.

The molar masses of the poly(ether-imide)s were measured by gel permeation chromatography using polystyrene standards, and the data are presented in Table 1.

The synthesized PEIs exhibited M_w and dispersities (M_w/M_n) in the range of $11.06\text{--}15.58 \times 10^4$ and $1.8\text{--}2.4 \text{ g mol}^{-1}$, respectively, indicating that polymers were obtained that can form tough films. However, in the case of PEI-5, despite the film-forming ability of this polymer, the prepared films were too brittle to test as membranes for gas separation. Therefore, the examination of PEI-5 was limited in this work.

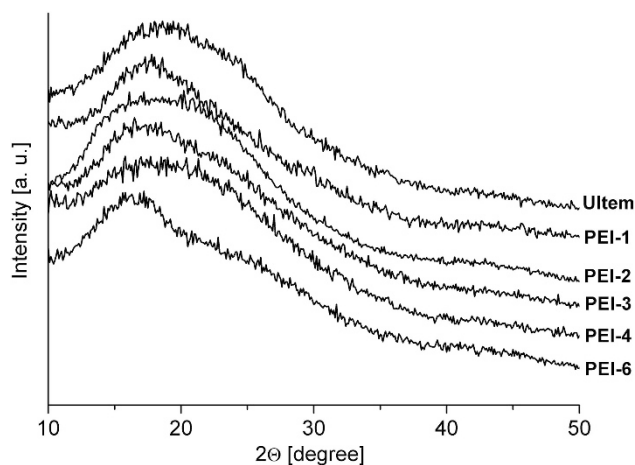
Table 1 GPC characteristics of the PEIs

Code	GPC data ^a		
	$M_n(\times 10^4)$ ($g\ mol^{-1}$)	$M_w(\times 10^4)$ ($g\ mol^{-1}$)	M_w/M_n
Ultem	3.60	6.99	1.9
PEI-1	7.30	12.89	1.8
PEI-2	5.51 ^s	13.41	2.4
PEI-3	5.22	11.06	2.1
PEI-4	— ^b	— ^b	— ^b
PEI-5	5.24	12.40	2.4
PEI-6	8.23	15.58	1.9

Abbreviations: GPC, gel permeation chromatography; PEI, poly(etherimide).

^aRelative to polystyrene standard, using DMF as the eluent.

^bInsoluble in DMF.

**Figure 4** Wide-angle X-ray diffractograms of the poly(etherimide) (PEI) films.

The supermolecular structures of the PEIs were evaluated by WAXD measurements of the film samples.

As shown in Figure 4, the synthesized PEIs exhibited a similar diffraction pattern that is typical for fully amorphous materials. This pattern is characterized by a broad diffraction peak with a maximum in the range of 16–18° (2θ). The d -spacing values, which express the mean distance between neighboring segments, were calculated from the WAXD data and are listed in Table 2.

These values do not show any significant differences, except for PEI-6. The highest d -spacing value, which was obtained for this polymer, is an effect of the bulky CF_3 groups that were introduced into the main chain linkage. The presence of fluorine atoms in PEI-6 is why this polymer exhibits also the highest density of the studied PEI films, despite the loose packing structure that was demonstrated by the WAXD data. On the other hand, the lowest density value, which was found for PEI-2, indicates that the bulky cardo moieties effectively reduce the packing density. To analyze the molecular packing property associated with the polyimide molecular unit, the FFV values were determined for the PEI series. The observed differences in the FFV results that are listed in Table 2 may be because HyperChem takes into account the chemical environment when estimating the van der Waals volume, whereas the Bondi method does not. Although the FFV values that were obtained by both methods differ from one another, they exhibit the same trend, enabling the PEIs to be ranked in the following order: PEI-6 > PEI-2 > PEI-3 > Ultem > PEI-4 > PEI-1. The highest FFV values were

Table 2 Physical properties of the PEI films

Code	ρ ($g\ cm^{-3}$)	d -spacing (\AA)	FFV ^a (%)	FFV ^b (%)
Ultem	1.270	4.72	15.3	13.1
PEI-1	1.256	5.01	14.0	11.6
PEI-2	1.204	4.95	18.1	15.7
PEI-3	1.238	5.21	16.4	14.6
PEI-4	1.266	5.00	15.1	13.0
PEI-6	1.304	5.37	18.9	17.8

Abbreviations: FFV, fractional free volume; PEI, poly(etherimide).

^aBondi method.

^bHyperChem 8.0.

Table 3 Solubilities of the PEIs

Code	Solvents				
	$CHCl_3$	THF	DMF	NMP	DMSO
Ultem	++	+	±	++	±
PEI-1	++	++	+	++	±
PEI-2	++	++	++	++	+
PEI-3	++	++	++	++	+
PEI-4	±	–	±	+	–
PEI-5	++	++	++	++	++
PEI-6	++	++	++	++	++

Abbreviations: $CHCl_3$, chloroform; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; NMP, *N*-methyl-2-pyrrolidinone; THF, tetrahydrofuran.

++, soluble at room temperature; +, soluble on heating; ±, partially soluble on heating; –, insoluble on heating.

found for the polymers with bulky CF_3 and cardo moieties, whereas the lowest value was found for PEI-1. The reason for the relatively low FFV of PEI-1 may be its high packing owing to the presence of an additional amount of flexible ether linkages. It can also be seen that the addition of a methyl substituent to the phenyl ring in the Ultem macromolecules remarkably increases the FFV value of the resulting PEI-3. This phenomenon can be attributed to the reduced chain packing that is caused by the steric hindrance of the methyl substituent.

Solubility of PEIs

The solubilities of the synthesized polyimides were qualitatively determined by the dissolution of 2.5 mg of the solid in 1 ml of an organic solvent at room temperature or upon heating. The obtained results are summarized in Table 3 and indicate that all of the PEIs, except for PEI-4 and Ultem, were soluble in low boiling organic solvents, such as chloroform and tetrahydrofuran, even at room temperature.

The reduced solubility of PEI-4 may be due to the fluorene moieties that were incorporated into the polymer main chain. PEI-5 and PEI-6 exhibited the best solubilities due to the presence of fluorine atoms, which can lower the cohesive energy and reduce the molecular interaction between polymer chains. The improved solubility of the studied polymers compared with that of traditional polyimides can be explained by the presence of flexible ether bridges in the polymer chains.

Thermal properties of PEIs

The thermal behavior of the PEIs was evaluated by TGA in a nitrogen atmosphere, DSC and DMA, and the data are presented in Tables 4 and 5.

Table 4 Thermal characteristics of the PEI films

Code	T_{10}^a (°C)	T_{max}^b (°C)	Char yield ^c (%)	LOI ^d (%)	T_g^e (°C)
Ultem	524	532	52	38	220
PEI-1	519	530	45	36	192
PEI-2	537	546	64	43	275
PEI-3	510	526	56	40	234
PEI-4	510	595	65	44	242
PEI-5 ^f	537	548	51	—	240
PEI-6	520	524	57	—	247

Abbreviations: LOI, limited oxygen index; PEI, poly(etherimide).

^a T_{10} : temperatures at 10% weight loss.^bTemperature of maximum decomposition rate.^cResidual weight when heated at 800 °C in nitrogen.^dCalculated limited oxygen index.^e T_g estimated by DSC, II run.^fData for a powder sample.**Table 5** Dynamic mechanical properties of the PEI films

Code	T_g^a (°C)	$\tan \delta$	T_g^b (°C)	E'_{max} (MPa)	E'_{30} (MPa)	I (°C)	$\Delta E'$ (MPa)
Ultem	232	1.793	227	233	958	225	780
PEI-1	208	1.519	198	198	1078	199	859
PEI-2	300	1.628	290	119	2157	270	1107
PEI-3	239	1.533	215	124	1224	216	1022
PEI-4	257	1.228	232	125	1549	233	1099
PEI-6	265	1.731	256	233	2064	255	1141

Abbreviation: PEI, poly(etherimide).

 T_g^a : temperature of loss factor peak; $\tan \delta$: loss factor maximum value; T_g^b : temperature of loss modulus peak; E'_{max} : loss modulus maximum value; E'_{30} : storage modulus value at 30 °C; I : inflection point of storage modulus drop; $\Delta E'$: change of storage modulus at glass transition region.

All of the polymers showed a similar TGA pattern, in which the decomposition proceeded through one step (Supplementary Figure 2S in the Supplementary Information).

Taking into account the results of the TGA analysis, it can be found that the obtained PEIs demonstrated excellent thermal stability without significant weight loss <480 °C, which was the observed onset of decomposition. The 10% weight loss temperature (T_{10}), which is usually considered a criterion for determining the thermal stability of high temperature polymers, was in the range of 510–537 °C (Table 4). Slightly higher T_{10} values were observed for the polymers that contained cardo units (PEI-2) or hexafluoroisopropylidene moieties (PEI-5). On the other hand, the presence of one methyl group as a substituent in the phenyl ring (PEI-3 vs Ultem) reduced T_{10} by 14 °C. The polymers that were investigated in this work exhibited very high residual weight at 800 °C, in the range of 45–65%. This value may indicate their good flame-retardant properties.²⁵ The limited oxygen index values, which were calculated using a linear relation with the char residue, limited oxygen index = 17.5 + 0.4 char residue,^{26,27} were in the range of 36–44%. Therefore, such polymers can also be classified as self-extinguishing polymers.²⁸ The PEI glass transition temperature, T_g , which is the key parameter during polyimide processing, was determined from the DSC and DMA measurements. All of the PEIs that were studied here had similar DSC profiles with no melting endotherms and with a clear T_g transition, confirming their amorphous nature. The T_g values that were determined from the DSC scans were in the range of 192–275 °C (Table 4). The highest T_g value was detected for the polymer with cardo moieties (PEI-2). Relatively high values of T_g were also observed for the PEIs with fluorene (PEI-4) moieties and

Table 6 Mechanical properties of the PEI films

Code	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
Ultem	111.4	131.3	2.4
PEI-2	88.6	17.5	1.0
PEI-3	93.0	16.0	1.1
PEI-4	21.0	11.0	2.3
PEI-6	90.9	78.1	1.7

Abbreviation: PEI, poly(etherimide).

with fluorine atoms (PEI-6 and PEI-5). On the other hand, the lowest T_g was found for PEI-1. The T_g value that was measured for PEI-1 was the same as that reported in the literature.¹⁶ Generally, T_g tends to increase with decreasing polymer backbone flexibility. Thus, based on the T_g values, PEI-2 can be regarded as the most rigid due to the most hindered main chain motion. On the other hand, PEI-1 has the main chain with the least restricted rotation mobility due to an additional amount of flexible ether linkages. Looking at the T_g values for Ultem and PEI-3, it appears that the introduction of a methyl group as an asymmetric substituent into the phenyl ring increased the barriers to main chain motion, consequently increasing the T_g of PEI-3. Similarly, the presence of bulky CF_3 substituents in PEI-5 and 6 restricts the main chain mobility, leading to a more rigid polymer backbone.

The glass transition temperature, which was determined from the results of the DMA measurements in the three varied ways,²⁹ as a temperature of the loss factor peak (T_g^a) and of the loss modulus peak (T_g^b), and as an inflection point of the storage modulus drop (I) ranges from 198–300 °C (Table 5).

These values are comparable to those that were obtained from the DSC runs with differences ranging from 5–25 °C, thus giving the following order of decreasing T_g for the film samples: PEI-2 > PEI-6 > PEI-4 > PEI-3 > Ultem > PEI-1. A discussion concerning the T_g values that were obtained from different measurements is presented in the Supplementary Information. The DMA measurements not only reveal the glass transition of the polymers but also reflect their mechanical properties.³⁰ The storage modulus, loss modulus and $\tan \delta$ profiles can be discussed in close relation to the polymer chemical structure. From the results in Table 5, it appears that the PEIs exhibited a storage modulus at 30 °C, E'_{30} , in the range of 958–2157 MPa. The highest E'_{30} values were detected for PEI-2 with cardo units and for PEI-6 with hexafluoroisopropylidene moieties, whereas the lowest values were detected for Ultem and PEI-1. Taking into account the loss modulus, E'' , PEI-2 exhibited the lowest value. Assuming that the storage modulus reflects the total mobility of a polymer and that it should decrease when the motion of the segments is enhanced, the obtained results are in agreement with the polymer structure. However, some discrepancies can be observed when the loss modulus and $\tan \delta$ are considered. The examined polymers maintained their mechanical properties up to their T_g . Afterwards, these polymers exhibited a significant decrease in the storage modulus of approximately three orders of magnitude when the materials passed from the glassy to the rubbery state.

Mechanical properties of PEIs

The mechanical properties of the membranes that were prepared from the selected PEIs and from Ultem were investigated, and the results are given in Table 6.

Table 7 Gas transport properties of the PEI membranes at 30 °C

Code	Permeability P (Barrer)				Selectivity α	
	He	O ₂	N ₂	CO ₂	O ₂ /N ₂	CO ₂ /N ₂
Ultem	6.11	0.34	0.05	1.16	6.8	23.2
PEI-1	4.07	0.23	0.05	0.86	4.6	17.2
PEI-2	9.59	0.63	0.10	1.82	6.3	18.2
PEI-3	9.31	0.51	0.08	1.37	6.4	17.1
PEI-4	4.26	0.28	0.04	0.70	7.0	17.5
PEI-6	19.16	1.65	0.30	6.36	5.5	21.2

Abbreviation: PEI, poly(etherimide).

According to the analyses conducted by the manufacturer, the respective values for Ultem are as follows: 113.8 MPa, 80%, and 3.3 GPa. These values are similar to those that were measured here, except for the elongation at break. A somewhat surprisingly high value of this parameter may be explained by the lower applied tensile speed (20 mm min⁻¹ vs 50 mm min⁻¹). The tensile stress parameters of the PEIs (see the discussion in the Supplementary Information) indicate that these PEIs are strong and tough polymeric materials.

Gas transport properties

The gas permeability and ideal selectivity values for the different gas pairs through the PEI-based membranes are summarized in Table 7.

The measured gas transport properties of the Ultem membrane are in agreement with those that are found in the literature.^{10,31,32} For the CO₂ permeability, the following data have been reported: 1.33 at 10 bar and 35 °C,¹⁰ 1.45 at 3.5 bar and 35 °C,³¹ and 1.55 at 1 bar and 30 °C.³² The CO₂ permeability value of 0.762 that has been reported for PEI-1^{15,16} is in accordance with the data obtained here. The observed permeability order for the tested gases was as follows: $P(\text{He}) > P(\text{CO}_2) > P(\text{O}_2) > P(\text{N}_2)$, which is in the same order as the kinetic diameters of the gases (Å): 2.6 for He, 3.3 for CO₂, 3.46 for O₂ and 3.64 for N₂. The presented permeability and selectivity ranges are rather low relative to, for instance, those of the best performing polyimides that have been reported in the literature.^{8,33} However, the obtained results can be used as a probe of the polyimide morphology, and as a basis for further tailor-made modifications. As seen from the data in Table 7, PEI-6 exhibits the highest gas permeability, which is accompanied by a reasonably high selectivity. The polymer PEI-1 exhibits the lowest permeability of all the studied PIs.

Generally, the permeation properties depend on the average interchain spacing between the backbones of the amorphous polymer matrix (d -spacing), on the FFV, and on the chain stiffness. The latter property can be characterized by the onset temperature for large-scale rotational motions (T_g). Considering the interchain distance, which is assumed to provide a relative measure of the diffusion resistance, it was expected that the d -spacing in the series of the studied PEIs would increase in the same order as the permeability. However, the observed permeability data (Table 7) did not correlate to the d -spacing values that are given in Table 2. A similar lack of correlation was observed by Hirayama *et al.*,³⁴ who suggested that the diffusion of gases through PI membranes is most likely not reflected by d -spacing data alone. Additionally, the same conclusion was drawn by these authors concerning the correlation between the diffusivity and the chain flexibility. The lack of a correlation between both parameters as noted by these authors is consistent with the results of our studies. The data that are shown in Tables 7 and 4 indicate that the permeability does not correspond with the T_g behavior either.

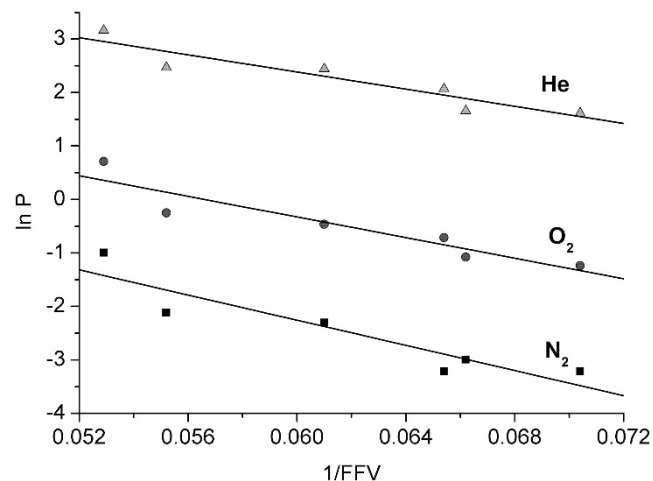


Figure 5 Relationship between the permeability and fractional free volume (FFV) as determined by HyperChem 8.0.

However, it was found that the order of permeability for a given gas in the studied PEIs is in accordance with their FFVs. Such correlations between the permeability and FFV were not observed by Hirayama *et al.*³⁴

The free volume concept is widely used to describe diffusion in gas separation membranes.³⁵ By applying the equation of Fujita,³⁶ the relation between the diffusion coefficient, D , and FFV can be expressed as:

$$D = A \cdot \exp(-B/\text{FFV}) \quad (7)$$

where A is a pre-exponential factor and B is a constant that is related to the penetrant size. On the basis of a solution-diffusion model, the expression:

$$P = S \cdot D \quad (8)$$

where S is a solubility coefficient, can be combined with equation 7 to obtain the following equation:

$$P = A \cdot S \cdot \exp(-B/\text{FFV}) \quad (9)$$

Assuming a small solubility of light gases, such as He, O₂ and N₂, in polymers, the changes in S can be neglected, and equation 9 can therefore be used to fit the results of the experimental permeability coefficients for these gases. As illustrated by the plots in Figure 5, the obtained data appear to be represented by a linear relation between the reciprocal of FFV and the logarithm of P with a correlation coefficient in the range of 0.88–0.90.

The slope, B , of the straight lines increases in the order He, O₂ and N₂, thus following the increasing kinetic diameter order of the gases. This result is consistent with the theoretical basis for the exponential nature of equation 9 that was established by Cohen and Turnbull.³⁷ The presented relations clearly indicate that FFV is a major parameter that enables the prediction of gas permeability through PEI-based membranes. Thus, because the FFV of PEI-2 is lower, this material exhibits a lower permeability than PEI-6 despite its more rigid structure, which was documented by its significantly higher T_g values.

CONCLUSION

A series of new PEIs containing isopropylidene groups was synthesized and characterized. The incorporation of $-\text{C}(\text{CH}_3)_2-$, $-\text{O}-$ and/or $-\text{C}(\text{CF}_3)_2-$ groups into the polymer backbone enabled a decrease in the intermolecular forces and looser chain packing. The obtained polymers were amorphous in nature, as confirmed by the results from

X-ray and DSC analyses, and exhibited excellent solubility in common organic solvents (except for the polymer with fluorene units). These polymers displayed high resistance against thermal decomposition up to 480 °C, which is an advantage for a wide variety of applications. Moreover, a large interval between T_g and the decomposition temperature (above 200 °C) observed for the obtained PEIs, could be beneficial for processing using the thermoforming technique. The limited oxygen index values suggest that these materials can be used as self-extinguishing polymers. Preliminary mechanical testing also indicates that these materials are strong and tough polymeric materials. The gas separation properties of this group of materials were found to be moderate compared with those of the best performing polyimides that have been reported in the literature. The highest gas permeability and CO₂/N₂ selectivity was exhibited by the polymer that contained a hexafluoroisopropylidene unit in the backbone. The influence of the chemical structure on the physical and gas permeation properties was studied. The introduction of bulky cardo or hexafluoroisopropylidene moieties into the polymer main chain increased T_g and FFV, while the incorporation of additional ether linkages produced the opposite effect. Using an existing free volume approach, it was found that the permeabilities of the studied PEIs were well correlated with their FFVs. However, for a comprehensive description of the structure-properties correlations, a systematic accumulation of sufficient data is needed, which will be the aim of future studies.

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