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Physicochemical and thermal effects of pendant groups, spatial linkages and bridging groups on the formation and processing of polyimides

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Abstract

Aromatic polyimides are known for their remarkable thermal and chemical properties which are greatly influenced by their precursors. In this study, we report synthesis and characterization of four different aromatic polyimides. The four different dianhydrides (ODPA, BTDA, BPDA and PMDA) were reacted with a diamine (BisAPAF) via azeotropic imidization under same conditions. FTIR analysis confirmed the formation of aromatic polyimides and all but one polyimide (HPI-BPDA) were found to be completely soluble in common solvents. The obtained molecular weights were between 16,000-32,000 Da, glass transition temperatures were between 250-275°C, degradation temperatures were above 550°C and the *d*-spacing values were around 5Å. These properties are promising and can be beneficial for various applications such as thin films and membranes.

Keywords: Aromatic polyimides, Azeotropic imidization, Solubility, Glass transition temperature, Molecular weight

1. Introduction

Aromatic polyimides are well known for their good thermal stability, chemical resistance and outstanding mechanical properties.^[1] These properties are mainly attributed to the strong intermolecular forces between the polymer chains such as the polar interactions, aromatic stacking and charge transfer complexation.^[1, 2] Hence, aromatic polyimides are available in a variety of commercial forms and used in a wide range of demanding applications such as high performance

fibers, films, thermosetting or thermoplastic resins, heat-resistant adhesives and coatings as well as foamed plastics.^[1,2]

Aromatic polyimides are prepared from aromatic diamines via a two-step synthesis process: (1) poly(amic-acids) synthesis then (2) poly(amic-acids) to polyimides conversion.^[1, 3] The poly(amic-acid) is mainly prepared by the condensation reaction of a diamine and a dianhydride in an appropriate solvent at relatively low temperatures because the reaction is exothermic. This step aims to prepare a *soluble* poly(amic acid) which is crucial because fully aromatic polyimides have low solubilities due to their high chain rigidity and strong interchain interactions, causing applicability limitations due to poor processability.^[4] The poly(amic acid) is then converted into polyimide through the imidization reaction which could be performed via three routes: azeotropic (*Az*), thermal (*T*) or chemical (*Ch*) imidization.^[4-9] It is worth mentioning that for the three aforementioned imidization routes, the sequence of adding the diamine first followed by the dianhydride is important due to the moisture sensitivity of the dianhydride.^[10, 11] An undesired side reaction between the dianhydride and any trace amounts of moisture could, most likely, lead to incomplete imidization.^[10, 11] Despite the imidization route chosen, the final synthesized polyimide must have identical chemical structures. Nevertheless, the route choice has an impact on the physical properties of the synthesized polyimides.^[10, 11] Among the three imidization routes, the most commonly used imidization route seems to be the azeotropic imidization mainly due to its simplicity and the efficient dehydration of the water formed from the condensation reaction.

The aim of this study is to synthesize four different aromatic polyimides using four different dianhydride precursors and investigate the potential variation in their chemical and physical properties. One aromatic diamine (BisAPAF) is reacted with four aromatic dianhydride (ODPA, BPDA, BTDA and PMDA) via an azeotropic imidization route to form aromatic

polyimides. These aromatic precursors were chosen based upon three primary factors: type of pendant group, type of spatial linkages and type of bridging groups. These factors have a direct effect on several physiochemical and thermal properties of the polyimide.

Pendant groups are groups of molecules attached to the backbone chain of a polymer; they have a major impact on the mobility of the polymer chains.^[12-14] For instance, a precursor with high rigidity, bulkiness or polarity mainly result in high packing efficiency which is attributed to the stiffness of the chains which restrict their rotational freedom.^[12-14] Moreover, having a high packing efficiency results in elevated T_g .^[15, 16] Furthermore, the introduction of bulky pendant side groups, or bridging groups, to a polymer backbone chain constrains crystallinity which causes the molecular weight of the polymer to increase.^[15] Additionally, the inhibition of crystallinity could result in soluble polyimides.^[15]

Spatial linkage groups are those that link and space the pendant group. They, like the pendant groups, also play a role in determining the T_g .^[12, 17] *Para*-substitutions usually have high T_g and thus high packing efficiency because this position inhibits chain mobility.^[12] On the other hand, spatial linkages with *ortho*-positions are usually expected to be flexible because the chains tend to have more freedom resulting in low T_g . However, that is not the case with polyimides because spatial linkages with *ortho*-positions result in high T_g , which is substantially due to the strong dipolar attractions between the imide linkages and the diamine.^[12] *Meta*-spatial linkages, like *para*-spatial linkages, also tend to have high packing efficiency due to the increased rigidity it imparts on the chains^[18, 19] and consequently result in high T_g . It is worth mentioning that, beside the presence of spatial linkages, the number of benzene rings in the precursors have a significant effect on the T_g as well.^[12, 20]

Bridging groups have major influence on electrophilicity of the dianhydrides which is usually evaluated in terms of electron affinity (E_a) of the molecules.^[12] In other words, bridging groups govern the reactivity of the precursors which also impacts T_g . Among the four considered dianhydrides, PMDA has the highest E_a (1.90 eV) followed by BTDA (1.55 eV), BPDA (1.38 eV) and ODPa (1.30 eV).^[21] Moreover, the presence of any bridging groups in the dianhydrides have a strong impact on the glass transition because the bridging groups change the E_a which possibly promotes the formation of charge transfer complex.^[12] Nonetheless, as the bridging group in the dianhydride becomes longer, the T_g becomes insensitive to E_a .^[12] Generally, diamines with bridging groups that enhances crystallinity mainly causes the packing density to decrease which consequently reduces T_g .^[12, 22] The properties of the precursors used in this study are summarized in Table. 1.

Table 1. Physical properties of used precursors ^[10]

Precursor	Rigid	Flexible	Bulky	Unbulky
BisAPAF	✓	-	✓	-
ODPA	-	✓	-	✓
BTDA	✓	-	-	✓
PMDA	✓	-	-	✓
BPDA	✓	-	-	✓

2. Experimental section

2.1 Materials

Diamine: 2,2-Bis(3-amino-4-hydroxyphenyl)-hexafluoro-propane (bisAPAF-98%) was purchased from Matrix Scientific (USA). Dianhydrides: 4,4'-oxydiphthalic anhydride (ODPA-97%), 3,3',4,4'- benzophenone tetracarboxylic dianhydride (BTDA-96%), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA-97%), and benzene-1,2,4,5-tetracarboxylic dianhydride, also known as pyromellitic dianhydride (PMDA-97%) were purchased from Sigma Aldrich Co. LLC (USA). N-methyl-2-pyrrolidinone ReagentPlus (NMP-99%), o-xylene (>98%) reagent grade,

diethylene glycol anhydrous (DEG-99.5%), dimethylformamide anhydrous (DMF-99.8%), methanol histological grade, acetone histological grade and tetrahydrofuran, HPLC grade (THF->99.9%) were also purchased from Sigma Aldrich Co. LLC (USA). Mineral oil and anti-bumping granules were bought from Sigma Aldrich Co. LLC (USA). All diamines and dianhydrides were dried in a vacuum oven for 24 hours at 60°C temperature before use. All the glassware was dried for 24 hours in an oven at 80°C and then purged with Nitrogen for one hour before being used. All the reagents were used as received without further purification. The chemical structures of the used monomers are presented in Figure. 1.

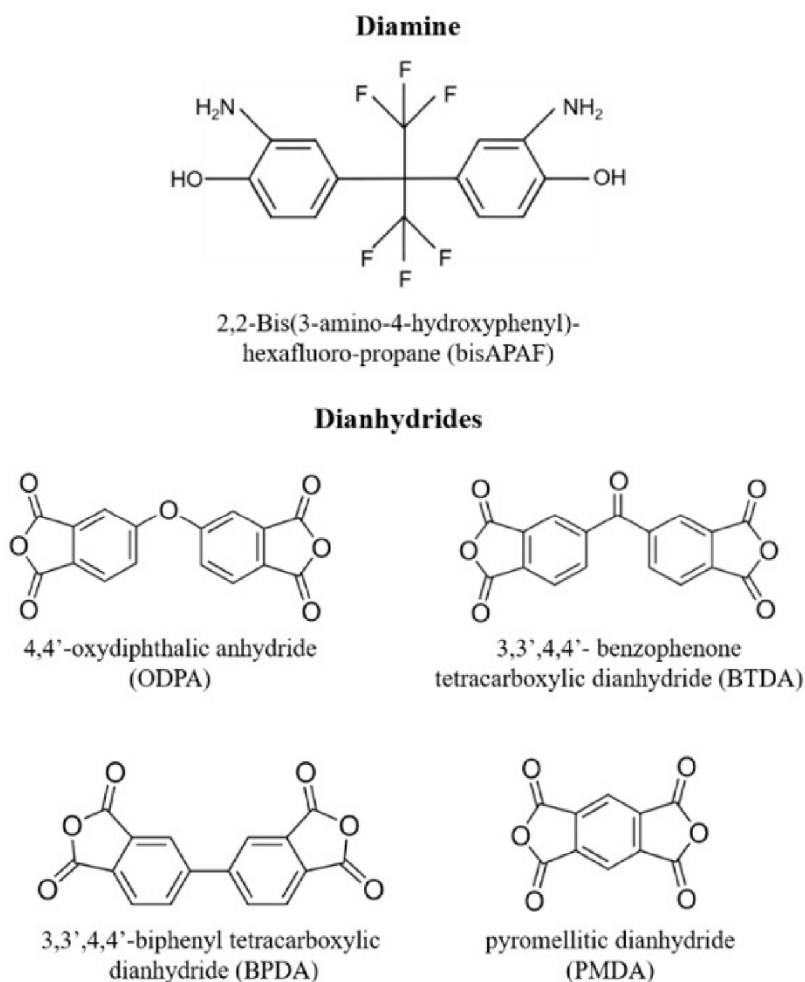


Figure 1. Chemical structures of the monomers used to synthesize the hydroxyl-polyimides (HPIs)

2.2 Polymer synthesis

2.2.1 Hydroxyl polyamic acid (HPAA) synthesis

The polymers were synthesized using an azeotropic imidization method previously describes by several articles.^[23, 24] 10 mmol of APAF was inserted into a 500 ml round bottom flask which was purged with dry nitrogen for 1 hour prior to the reaction. The final monomer solution concentration is 20 wt%; hence, half of the total amount of the solvent (NMP) was added to the AFAP and was allowed to dissolve completely using a magnet stirrer for 1 hour under a nitrogen atmosphere. The diamine solution was then cooled to below 10°C in an ice bath. Next, 10 mmol of the dianhydride was gradually added in three batches each 2-3 minutes apart and then the remaining NMP was added for an overall 20 wt% monomer solution. The diamine and dianhydride were allowed to react below 10°C for 48 hours resulting in the formation of a viscous yellow HPAA solution. This procedure was repeated for each of the dianhydrides.

2.2.2 Hydroxyl polyimide (HPI) synthesis

In this stage, the water resulting from the condensation reaction was distilled off continuously under o-xylene reflux in the form of a water/o-xylene azeotropic mixture. First, an equivalent volumetric amount of o-xylene as NMP was added to the HPAA solution. Then, a couple of anti-bumping agent granules were added to the round-bottom flask to sooth the boiling of the solution. After that, a dean-stark trap with a circulated condenser was equipped on top of the round-bottom flask containing the HPAA solution and o-xylene. The solution was then placed in a 700 mL mineral oil bath which was heated to a temperature between 160-180°C for around 6 hours. This resulted in an orange to brown solution that was then cooled to room temperature. This solution was then precipitated in an 800 mL beaker filled with 3:1 water:methanol solution (600 mL and 200 mL respectively) that was cooled to around 13°C. A vortex was then created in the

water:methanol solution using a stirrer and the orange to brown solution was slowly poured into the solution. This resulted in a precipitant that floated at the top of the beaker and was left for 12 hours at a temperature of around 13°C. Afterwards, the precipitant was filtered and soaked again in deionized water for another 12 hours. Finally, the precipitant was filtered using a vacuum filter and dried in a vacuum oven for 24 hours at around 70°C.

2.3 Characterizations

2.3.1 Solubility

About 100 mg of each HPI was put in contact with 3 mL of various solvents under continuous mixing for 48 hours, or until completely dissolved, at room temperature. Polymer solubility was determined to be either soluble, partially soluble, or insoluble. This was determined visually, where completely soluble polymers were completely dissolved before 48 hours, partial solubility refers to a noticeable dissolution, but undissolved polymer remaining after 48 hours, and insolubility refers to no visible dissolution after 48 hours. The solubility parameters were calculated according to equations (1) to (4):

$$\delta_d = \frac{\sum F_{di}}{V} \quad (1)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \quad (2)$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{V}} \quad (3)$$

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (4)$$

Where δ_d , δ_p , δ_h are the dispersive, polar, and hydrogen bonding solubility parameters respectively. F, E and V are polar attractive constant, cohesive energy and molar volume respectively. Also, δ_t is the total solubility parameter.

2.3.2 Fourier transform infrared spectroscopy (FTIR)

The chemical compositions of the HPIs were investigated using the Thermo Scientific Nicolet NEXUS 460 FTIR equipped with a ZnSe crystal and DTGS detector. The samples were tested in attenuated total reflection mode with a resolution of 2 cm^{-1} and 16 scans per sample.

2.3.3 Differential scanning calorimetry (DSC) & thermogravimetric analysis (TGA)

The glass transition temperatures (T_g) of the HPIs were initially investigated using PerkinElmer DSC. The DSC method consisted of three cycles each started at 25°C and ramped up to 300°C at a rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ and the temperature was held for 2 minutes at 300°C . The obtained temperatures were then confirmed and corrected using TA Instruments SDT Q 600 TGA from room temperature to 900°C at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere with flow rates of $100\text{ mL}\cdot\text{min}^{-1}$ using around 15 mg of HPI powder samples.

2.3.4 Gel permeation chromatography (GPC)

The molecular weight of the HPI powders were evaluated using a Varian Prostar GPC with a TSKTM SuperMultipore HZ-M column and a refractive index detector in THF.

2.3.5 X-ray diffraction (XRD)

The XRD analysis was conducted using a diffractometer with $\text{Cu K}\alpha$ radiation of $\lambda = 1.5406\text{ \AA}$, voltage of 60 kV and current of 30 mA. The samples were scanned in 2θ from 5° to 40° at a rate $1^\circ\cdot\text{min}^{-1}$. The d -spacing values of the HPIs were calculated using the XRD patterns via Bragg's law [25]:

$$n\lambda = 2d\sin\theta \quad (5)$$

Where n is the order of reflection ($n=1$), λ is the X-ray wavelength, d is the d -spacing and θ is the X-ray diffraction angle.

3. Results and discussion

3.1 Solubility


All the HPIs were found to be completely or partially soluble in the organic solvents tested as seen in Table. 2. Their solubility can be attributed to bulky hexafluoroisopropylidene moieties in the diamine monomer as well as the flexibility of the HPI chains.^[21] The solubility is also a result of intermolecular interactions between the main chains of the HPIs and the solvents. Specifically, there are three intermolecular interactions present between the polymers and solvents, dispersion, polarity, and hydrogen bonding forces.




Table 2. Solubility of HPIs in common organic solvents: (+) represents complete solubility and (+/-) represents partial solubility

Solubility in Organic Solvents				
Solvent	ODPA	BPDA	BTDA	PMDA
NMP	+	+/-	+	+
DEG	+	+/-	+	+
DMF	+	+/-	+	+
MeOH	+	+/-	+	+
THF	+	+/-	+	+

To gain insight into the solubility and the level of interaction between HPIs and the solvents selected, the solubility parameters were calculated. The dispersive, polar, and hydrogen bonding solubility parameters were determined by the group contribution approach based on Krevelin.^[26] The functional groups present in the HPIs, their frequency in the polymer monomers, and their energy contribution are recorded in Table. 3.

Table 3. Solubility parameter component group contributions from Hoftyzer-Van Krevelen method^[26]

Material	Functional Group	Frequency	Components		
			F_{di} (MJ ^{1/2} m ^{2/3} mol ⁻¹)	F_{Pi} (MJ ^{1/2} m ^{2/3} mol ⁻¹)	E_{hi} (Jmol ⁻¹)
HPI-ODPA		4	1270	110	0
	Ring	2	190	0	0
	>N-	2	20	800	5000
	-C=O-	4	270	770	2000
	-O-	1	100	400	3000
	-OH	2	210	500	20000

	-F	6	220	0	0
	>C<	1	-70	0	0
		4	1270	110	0
	Ring	2	190	0	0
HPI-BPDA	>N-	2	20	800	5000
	-C=O-	4	270	770	2000
	-OH	2	210	500	20000
	-F	6	220	0	0
	>C<	1	-70	0	0
		4	1270	110	0
	Ring	2	190	0	0
HPI-BTDA	>N-	2	20	800	5000
	-C=O-	5	270	770	2000
	-OH	2	210	500	20000
	-F	6	220	0	0
	>C<	1	-70	0	0
		3	1270	110	0
	Ring	2	190	0	0
HPI-PMDA	>N-	2	20	800	5000
	-C=O-	4	270	770	2000
	-OH	2	210	500	20000
	-F	6	220	0	0
	>C<	1	-70	0	0

The dispersive, polar, and hydrogen bonding solubility parameters, molar attractive constant and cohesive energy used in the solubility calculations were taken from Table. 3, and the molar volumes were calculated by dividing the monomer molecular weight by the density. It is important to note that the molar volumes were determined to be 457.379, 445.950, 465.957, and 391.621 for HPI-ODPA, HPI-BPDA, HPI-BTDA, and HPI-PMDA, respectively. Table.4 shows the calculated parameters for each HPI and solvents.

Table 4. Hoftzyer-Krevelen solubility parameters of HPIs and various solvents

Name	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	δ_t (MPa ^{1/2})	Source
HPI-ODPA	18.256	8.003	11.549	23.037	This work
HPI-BPDA	18.500	8.159	11.404	23.214	This work
HPI-BTDA	18.285	9.250	11.348	23.424	This work
HPI-PMDA	17.823	9.262	12.170	23.485	This work
NMP	15.970	16.281	8.520	24.346	[25]
DEG	15.603	8.455	7.953	19.447	[25]
DMF	14.853	20.277	9.508	26.874	[25]
MeOH	15.2	12.3	22.3	29.7	[26]

THF	16.8	5.7	8.0	19.5	[26]
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The solubility parameters for each HPI are similar to each other, and similar to experimentally determined, and calculated parameters for other polyimides.^[27-29] Interestingly, due to the closeness of the total solubility parameters of each HPI with the solvents, all HPIs are expected to be soluble in each solvent investigated. However, HPI-BTDA was only partially soluble in all solvents, indicating intermolecular interactions were not completely responsible for solubility. The chain rigidity is the probable cause for the partial solubility of the HPI-BTDA as it has a rigid bridging group. Another potential explanation is the extent of cross-linking that takes place at 160-180°C while distilling the water formed during the reaction (prior to precipitation). As the degree of cross-linking increases due to the elevated temperatures, the solubility tends to decrease.^[30] Moreover, considering that the solubility parameters for each HPI are similar to each other, they would be viable options for polymer blends and would interact well in solution together. Due to the partial solubility of HPI-BPDA in THF, GPC analysis was not carried. Also, XRD analysis was not shown due to incompatibilities between the sample and sample preparation requirements.

3.2 FTIR analysis

The chemical structures and the completion of the imidization processes were revealed via the FTIR analysis. Figure.2 represents the IR spectra for HPI-ODPA, HPI-BTDA, HPI-PMDA and HPI- BPDA powders imidized azeotropically. The four dianhydride precursors have very similar structures which resulted in homopolymers with relatively similar structures in terms of characteristic vibrational bands.^[4] Therefore, no significant differences between the HPIs were observed and only some minor differences in composition were detected. For all HPIs, an incomplete cyclization was evident due to the presence of amides at wavelengths of $\sim 1515\text{ cm}^{-1}$.^[4] Moreover, all the HPIs have O-H stretching (~ 3400 to $\sim 2400\text{ cm}^{-1}$) and the C-F stretch (~ 1300 to

$\sim 1000\text{ cm}^{-1}$) which are mainly attributed to the diamine. Additionally, the presence of the C-N stretch in all HPIs ($\sim 1518\text{ cm}^{-1}$) indicate the presence of imide functional groups demonstrating that the polyimide is cured and the more abundant the C-N stretch is, the more fully cured the polyimide is. Also, the presence of C=O stretching ($\sim 1778\text{ cm}^{-1}$ and $\sim 1714\text{ cm}^{-1}$) could indicate the presence of anhydrides and ketones. For instance, in the case of HPI-BTDA, the C=O stretch most likely indicates the presence of ketones due to the presence of the clear aryl ketone in its structure. Whereas, the C=O stretch in the HPI-PMDA most likely indicates an anhydride functional group not a ketone again due to its structure that lacks of a clear ketone functional group. Finally, C-H stretch at $<1000\text{ cm}^{-1}$ corresponds to aromatic functional groups such as benzene. Moreover, somewhere at $\sim 714\text{ cm}^{-1}$ usually corresponds to imide ring deformation. Therefore, the FTIR analysis indicates the formation of polyimides form the different dianhydride precursors and the similarity between the spectra is significant. The minor differences in the HPI-ODPA are mainly due to the presence of the ether functional group in its structure.

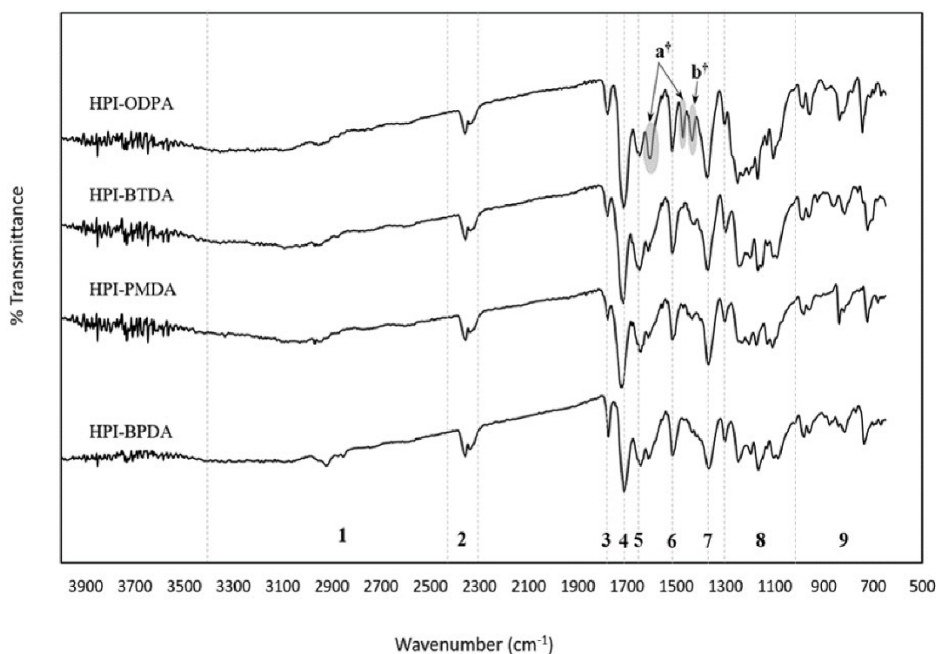


Figure 2. FTIR spectra of HPI-ODPA, HPI-BTDA, HPI-PMDA and HPI-BPDA

Table 5. HPI-ODPA wavelengths and corresponding functional groups and molecular motion

Peak	Wavelength (λ) [cm-1]	Functional Group	Molecular Motion
1	3400-2400	Carboxylic Acids	OH Stretch
2	2352 & 2328	Hydroxyl Group	OH Stretch
3	1778	Anhydride	C=O Stretch
4	1714	Ketone	C=O Stretch
5	1645	Alkenes	C=C Stretch
6	1518	Amides	N-H Bend (1°)
7	1375	Alkenes	C-C In-Plane Bend
8	1300-1000	Halogenated Organic Molecules	C-F Bond
9	<1000	Aromatics (Benzene Rings)	C=C
a†	1608 & 1473	Aromatics	C=C Stretch
b†	1435	Carboxylic Acids	OH Stretch

3.3 GPC, DSC, TGA & XRD analyses

The two main properties of a polymer that significantly affect their performance are molecular weight and glass transition temperature (T_g). For instance, in order for polymers to be used in gas separation membranes, they need to have medium to high molecular weights because higher molecular weights usually correspond to better mechanical properties.^[31] The molecular weights of the HPI powders, displayed in Table. 6, are discussed in terms of M_w . Homopolymers, like the ones synthesized in this study, generally have low M_w of below 50,000 Da.^[23] In this case, this is mainly attributed to the presence of several bulky 6 fluorine (6F) groups that originate from the BisAPAF diamine. These bulky groups restrict the amine group and make it harder for the amine group to react with another dianhydride.^[25] Moreover, it is clearly observed that the M_w of the HPI-ODPA is significantly lower than the others and that is attributed to the flexibility of dianhydride pendant groups. All in all, the obtained M_w are consistent with previously reported values.^[23, 31, 32]

The rigidity of the polymer chains, or flexibility, could be directly measured using T_g . This becomes crucial in the application of HPis when they are fabricated into films or membranes, for example, because the rigidity or flexibility affects the thermal rearrangement kinetics and could consequently affect the gas permeabilities and selectivities.^[23] The glass transition temperatures

presented in Table. 6 are consistent with those in the literature since the average expected T_g of other polyimides is in the range of 230-330°C.^[23, 33] As mentioned earlier, precursors with rigid and bulky groups tend to result in high T_g . Hence, the high T_g could be attributed to the rigidity of the dianhydrides and the presence of several bulky 6F groups that originate from the BisAPAF diamine. Moreover, the synthesized polymers showed fairly high thermal stability where no weight loss was detected before a temperature of around 550°C in nitrogen.^[34] This could be observed from the degradation temperatures (T_d) in Table. 6.

Table 6. Properties of the HPI powders

	GPC	GPC	GPC	DSC	TGA*	TGA	XRD
Polymer	Mn	Mw	PDI	T_g (°C)	T_g (°C)	T_d (°C)	d-spacing (Å)
HPI-ODPA	10,124	16,281	1.6082	230	246	566	4.9734
HPI-BTDA	14,187	30,648	2.1603	226	266	561	5.1394
HPI-PMDA	20,369	32,243	1.5829	233	274	566	5.5764
HPI-BPDA	-	-	-	271	277	557	-

* Based on mass corrected heat flow due to moisture losses.

A broad and undefined peak was observed between 2θ values of 10° and 22° for HPI-ODPA, HPI-BTDA and HPI-PMDA indicating an amorphous structure. The 2θ values at the maximum peaks found from the XRD analysis are expected to be positioned somewhere in the centre with the d -spacing, or average interchain distance, of around 5 Å.^[35] The 2θ values for HPI-ODPA, HPI-BTDA and HPI-PMDA were found to be 17.82°, 17.24° and 15.88° respectively. This corresponds to d -spacing values of 4.9734 Å, 5.1394 Å and 5.5764 Å respectively as shown in table. 6. Among the three HPIs, HPI-PMDA was found to have the highest d -spacing which is a measure of the molecular distance between chains.

4. Conclusions

Four different dianhydride precursors (ODPA, BPDA, BTDA and PMDA) and a diamine (BisAPAF) were used to synthesize four different aromatic HPIs at a 1:1 dianhydride:diamine

molar ratio via two-step method of hydroxyl poly(amic acid) and azeotropic imidization. Three dianhydrides (ODPA, BTDA and PMDA) out of the four were successfully synthesized into *soluble* HPIs. HPI-BPDA was not soluble potentially due to the occurrence of intensive crosslinking during the azeotropic imidization stage. The chemical and physical properties of the three soluble HPIs were investigated intensively. It was found that the chemical composition of the HPIs indicate the formation of polyimides with a likely incomplete cyclization due to the presence of amide functional groups. Moreover, the obtained molecular weights, glass transition temperatures, degradation temperatures and d-spacing values agree with other polyimides. Therefore, this detailed analysis provides sufficient characterization that would facilitate implementing these polyimides for various applications.

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References

- [1] Edward P. Savitski , Fuming Li , Sheng-Hsien Lin , Kevin W. McCreight , William Wu , Elaine Hsieh , Roland F. Rapold , Mark E. Leland , Donald M. McIntyre , Frank W. Harris , Stephen Z. D. Cheng , Simon Chi Man Kwan & Chi Wu. 1997. Investigation of the Solution Behavior of Organosoluble Aromatic Polyimides, *International Journal of Polymer Analysis and Characterization*, 4:2, 153-172.
- [2] Migdalia Alvarado & Issifu I. Harruna. 2005. Characterization of HighPerformance Polyimides Containing the Bicyclo[2.2.2]oct-7-ene Ring System, *International Journal of Polymer Analysis and Characterization*, 10:1-2, 15-26.
- [3] Sroog, C. E. 1976. Polyimides. *J. POLYMER SCI.* 11:161-208.
- [4] Tena, A. Shishatskiy, S. Meis, D. Wind, J. Filiz, V and Abetz, V. 2017. Influence of the composition and imidization route on the chain packing and gas separation properties of fluorinated copolyimides. *Macromolecules*. 50: 5839-5849.
- [5] Bessonov, M. I.; Zubkov, V. A. 1993. *Polyamic Acids and Polyimides: Synthesis, Transformations, and Structure*. New York: Taylor & Francis.
- [6] Okamoto, K.-i.; Fuji, M.; Okamoto, S.; Suzuki, H.; Tanaka, K.; Kita, H. 1995. Gas permeation properties of poly(ether imide) segmented copolymers. *Macromolecules*. 28 (20), 6950–6956.
- [7] Furusho, Y.; Ito, Y.; Kihara, N.; Osakada, K.; Suginome, M.; Takata, T.; Takeuchi, D. 2004. *Polymer Synthesis* Berlin: Springer.
- [8] Tena, A.; Marcos-Fernandez, A.; Lozano, A.; de Abajo, J.; Palacio, L.; Pradanos, P.; Hernández, A. 2013. Influence of the PEO length in gas separation properties of segregating aromatic–aliphatic copoly (ether-imide). *Chem. Eng. Sci.* 104, 574–585.
- [9] Coletta, E.; Toney, M. F.; Frank, C. W. 2015. Influences of liquid electrolyte and polyimide identity on the structure and conductivity of polyimide–poly (ethylene glycol) materials. *J. Appl. Polym. Sci.* 132 (12), 41675.
- [10] Drioli, E., Barbieri, G., and Brunetti, A. 2013. *Membrane Engineering for the Treatment of Gases* volume 1: Gas-Separation Issues with Membranes. 2nd ed., p.276. Croydon: CPI Group (UK) Ltd.
- [11] Wen-ke, Y., Fang-fang, L., Guo-min, L., En-song, Z., Yan-hu, X., Zhi-xin, D., Xue-peng, Q., and Xiang-ling, J. 2016. Comparison of Different Methods for Determining the Imidization Degree of Polyimide Fibers. *Chinese Journal of Polymer Science*. 34(2): 209-220.
- [12] REVIEW Varun Ratta, “POLYIMIDES: chemistry & structure-property relationships – literature review”, chap. 1, Dissertation Thesis, 1999, Faculty of Virginia Polytechnic Institute and State University.
- [13] Tanaka K, Osada Y, Kita H, Okamoto K. Gas permeability and permselectivity of polyimides with large aromatic rings. *Journal of Polymer Science Part B: Polymer Physics*. 1995. 33(13):1907-1915.

- [14] Wook, T. 2016. "Effects of bridging group of dianhydride precursor on resulting thermally rearranged polybenzoxazole for removal of nitrogen from natural gas." Master's thesis, University of North Dakota.
- [15] St. Clair, A.K. and St. Clair, T.L. 1987. *Polymers for High technology*, Ed. Bowden, M.J. and Turner, S.R., Amer. Chem. Soc. Symposium Series, 483.
- [16] Wook. T., Bjorgaard, S. Tande, B., and Alshami, A. 2016. Purification of natural gas using thermally rearranged polybenzoxazole and polyimide membranes- A review: Part 1. *Membrane Technology*. 9: 7-12.
- [17] Wook. T., Bjorgaard, S. Tande, B., and Alshami, A. 2016. Purification of natural gas using thermally rearranged polybenzoxazole and polyimide membranes- A review: Part 2. *Membrane Technology*. 10: 7-12.
- [18] Tanaka K, Kita H, Okano M, Okamoto K. 1992. Permeability and permselectivity of gases in fluorinated and non-fluorinated polyimides. *Polymer*. 33(3):585-592. 140.
- [19] Kawakami H, Anzai J, Nagaoka S. 1995. Gas transport properties of soluble aromatic polyimides with sulfone diamine moieties. *J Appl Polym Sci*. 57(7):789-795.
- [20] Tamai, S., Yamaguchi, A. and Ohta, M. 1996. *Polymer*. 37, 3683.
- [21] Takekoshi, T., 1996. *Polyimides- Fundamentals and Applications*, ed. M.K Ghosh, and K.L. Mittal, Chapter 2. New York: Marcel Dekker.
- [22] Lee, C.J. 1989. *J. Macromol. Sci.- Rev. Macromol. Chem. Phys.* 29 (4), 431.
- [23] Soo, C.Y, Jo, H.J, Lee, Y.M, Quay, J.R and Murphy, M.K. 2013. Effect of the chemical structure of various diamines on the gas separation of thermally rearranged poly(benzoxazole-co-imide) (TR-PBO-co-I) membranes. *Journal of Membrane Science*. pp. 444: 365-377.
- [24] Han, S.H. Misdan, N. Kim, S. Doherty, C.M. Hill, A.J and Lee, Y.M. 2010. Thermally rearranged (TR) polybenzoxazole: Effects of diverse imidization routs on the physical properties and gas transport behaviours. *Macromolecules*. 43(18): 7657-7667.
- [25] Adewole, J.K., Ahmad, A.L., Ismail, S., Leo, C.P., Sultan, A.S. 2015. Comparative studies on the effects of casting solvent on physico-chemical and gas transport properties of dense polysulfone membrane used for CO₂/CH₄ separation. *J Appl Poly Sci*. 132: 1-10
- [26] Van Krevelen, D.W., and Te Nijenhuis, K. 2009. *Properties of Polymers Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions* 4th edition. New York: Elsevier.
- [27] Lee, H.R., and Lee, Y.D. 1990. Solubility behavior of an organic soluble polyimide. *J of Apl Poly Sci*. 40, 2087-2099
- [28] Liu, Y. and Shi, B. 2008. Determination of Flory interaction parameters between polyimide and organic solvents by HSP theory and IGC. *Polymer Bulletin*, 61, 501-509

- [29] Jwo, S.L., Whang, W.T., and Liaw, W.C. 1999. Effects of the solubility parameter of polyimides and the segment length of siloxane block on the morphology and properties of poly(imide siloxane). *J of Appl Polyr Sci*, 74, 2832-2847
- [30] Kim, Y. J., Glass, T. E., Lyle, G. D., and McGrath, J. E. 1993. Kinetic and mechanistic investigations of the formation of polyimides under homogeneous conditions. *Macromolecules*. 26 (6), 1344-1358
- [31] Gowariker, V.R. Viswanathan, N.V and Sreedhar. 1986. *Polymer science*. New Delhi: New Age International (P) Ltd.
- [32] Grubb, T.L. Ulery, V.L. Smith, T.J. Tullos, G.L. Yagci, H. Mathias, L.J. and Langsam, M. 1999. Highly soluble polyimides from sterically hindered diamines. *Polymer*. 40: 4279-4288.
- [33] Calle, M, Chan, Y. Jo, H.J. and Lee, Y.M. 2012. The relationship between the chemical structure and thermal conversion temperatures of thermally rearranged (TR) polymers. *Polymer*. 48(7): 1313-1322.
- [34] Chen, C.F., Qin, W.M., and Huang, X.A. 2008. Characterization and Thermal Degradation of Polyimides Derived from ODPa and Several Alicyclic-Containing Diamines. *Polymer engineering and Science*. 48: 1151-1156.
- [35] Chung, T. S., Ren, J., Wang, R., Li, D., Liu, Y., Pramoda, K. P., Cao, C., and Loh, W. W. 2003. *J. Membr. Sci*, 214, 57.