

PARTIALLY-FLUORINATED POLYIMIDES

USING ALIPHATIC DIAMINES

THESIS

Presented to the Graduate Council of
Texas State University- San Marcos
in Partial Fulfillment
of the Requirements

for the Degree

Master of SCIENCE

by

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San Marcos, Texas

May 2010

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2010

DEDICATION

This work is dedicated to my grandparents, Janna Petrovna and Vladimir Platonovich Balakleets, who always supported and motivated me, especially in the sphere of education. Their love and enthusiasm gave me strength and encouragement along the way for which I am forever grateful. I am deeply honored to have their belief in me and the knowledge that they are proud of me.

ACKNOWLEDGEMENTS

I am very grateful to all the people who supported me during the course of my education. First of all, I would like to show my deep gratitude to my advisor and the chair of my committee, Dr. Chad Booth. Ever since I start working for him as an undergraduate student he always showed his support and confidence in me. His guidance in the research and academic sphere helped me to believe in myself. A special thanks goes to my other research adviser and a member of my committee, Dr. Patrick Cassidy. Dr. Cassidy provided me with an exceptional amount of knowledge and moral support. His openness and willingness to work on the solution to the problem inspired me on a number of occasions. I also would like to acknowledge another member of my committee, Dr. Luy Sun, who gave his valuable opinion in the course of the creation of this thesis. My deepest gratitude goes to all faculty members at Texas State University-San Marcos for providing me with the knowledge that enabled me to finish my education. I would like to thank to Summer Undergraduate Minority Research Award program that gave funding to Michael Sanchez and Alberto Cisneros, who helped me to do synthetic work on my project. I also would like to thank the ACS Petroleum Research Fund and its donors who provided funds for the project *via* ACS PRF# 46763.01-B7. I am forever grateful for my family and friends for their endless encouragement and motivation, especially my mother, Irene Freeman, and my fiancé, Chad Waxler.

This manuscript was submitted on 04/03/2010.

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ABSTRACT

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Two series of polyimides were created in order to address several of the existing problems with gas permeation membranes used today. These issues include the lack of flexibility and inverse ratio that exists between selectivity and permeation. The approach taken in order to solving the flexibility issue involved the incorporation of flexible spacers. The ratio of selectivity to permeation issue was addressed by the incorporation of titanium dioxide nanoparticles. Two series of partially-fluorinated polyimides made

using aliphatic diamines as the flexible component and titaniumdioxide nanoparticles were synthesized. All of the reactions were performed *via* condensation polymerization. Thermal data suggest that the obtained films have thermal stability between 395 – 490 °C. Mechanical data suggest that the resulting films have a dramatic increase in flexibility, when compared to existing materials, displaying storage modulus values of 1640 – 2740 MPa. In addition, both series show above normal molecular weights with values of 11 – 260 KDa for most of the films. This lends support to the justification for the above average mechanical performances reported.

I. INTRODUCTION

1.1 Background

The worldwide demand for natural gas continues to increase every day. Natural gas is an important fuel source and a major feedstock for fertilizers. So the demand for purification of partially depleted natural gas becomes more important. Typically carbon dioxide concentrations, in low quality natural gas, are in the range of 5 to 25%; however, some reservoirs contain much higher concentrations. The standard for pipeline specifications for transport of natural gas is less than 2% carbon dioxide concentration. In order to meet these standards one must to reduce the concentration of carbon dioxide present in the raw material.¹

Partially depleted natural gas reservoirs are currently being investigated as potential sources for supercritical carbon dioxide (sc-CO₂) sequestration for two purposes. The first purpose is to reduce the amount of carbon dioxide in the atmosphere that contributes to global warming. The second is to gain utility by using carbon dioxide to pressurize such reservoirs, through carbon dioxide injection, to enhance methane recovery. Clearly, this reinjection process greatly increases the carbon dioxide content of the recovered natural gas. For each of the above scenarios, membrane separation processes provide an attractive alternative to traditional absorption processes which are typically more expensive, much larger, and potentially harmful to the environment.¹

A membrane is an interphase between two adjacent phases acting as a selective barrier which regulates the transport of substances between the two compartments.² Typically membranes for gas separation are made from stiff polymers that have higher mobility selectivity. This creates a molecular sieve type behavior. Another benefit is that polymers with high glass transition temperatures can withstand high pressures without resulting in plastic deformation.³ Membranes are also considered a good choice for separation due to the fact that the upscaling and downscaling of membrane processes as well as their integration into other separation or reaction processes are easy. Most membranes are made using solid polymers because of the wide variability of barrier structures and properties.²

When examining the existing common membranes that are used for gas permeation, several issues come to light. These include the brittleness of typical films, and the fact that membranes typically display an inverse relationship between permeation and selectivity. Historically, increasing permeation rates of the polymer membranes used for separating gas mixtures decreases selectivity.^{4,5,6} This effect is further shown in Figure 1.

Polymeric membrane materials can be divided into rubbery and glassy polymers. With extended research in the area of gas separation, correlations between the polymer structure and the separation characteristics have been shown to exist. Generally, glassy polymers show attractive separation characteristics (high-mobility selectivity combined with medium permeability), whereas rubbery polymers show comparably low-mobility selectivity with high permeability for common gas pairs as O_2/N_2 , H_2/CH_4 , CO_2/CH_4 . This correlation is demonstrated for the CO_2/CH_4 separation in Table 1.⁷

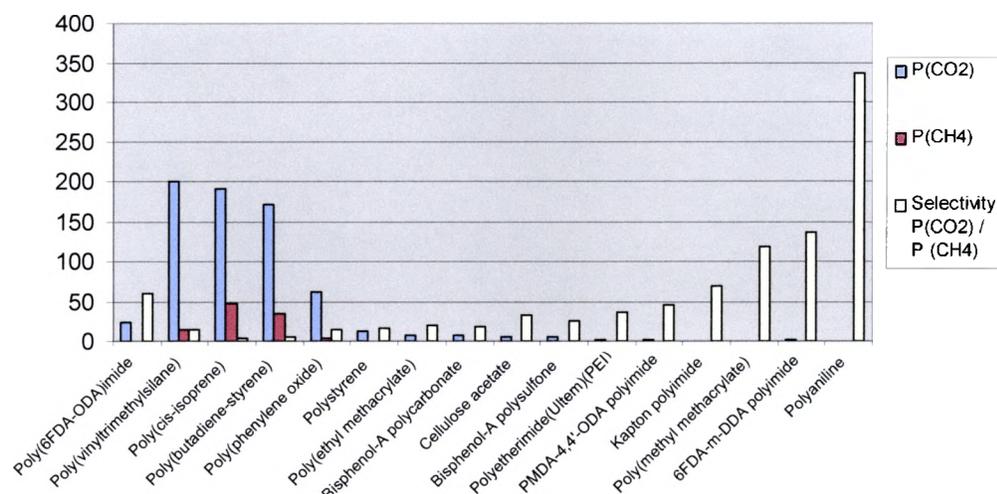


Figure 1. Comparison of common membranes with gas permeation of CO₂, gas permeation of CH₄, and selectivity.⁴

High selectivity is reached with glassy polymers due to several factors: the lower free volume, a more narrow distribution of the free volume, as well as the lower flexibility of the polymer chains, compared to the rubbery polymers.

Table 1. Comparison of glassy and rubbery polymer membranes in CO₂/CH₄ separation.⁷

Polymer	$\alpha_{ideal} = P(\text{CO}_2)/P(\text{CH}_4)$	P(CO ₂) [Barrer]
Polydimethylsiloxane	3	4550
Cellulose derivatives	11–33	75–75
Polycarbonates	15–25	110–6.5
Polyimides	55–65	23–0.6

Within the glassy polymers, polyimides (PI) are attractive as membrane materials because they have better separation characteristics, compared to other glassy polymers, for example polycarbonates, as also shown in Table 1. Additionally, polyimides offer good thermal and chemical resistance and are easy to process.⁷ The comparison graph (Figure 2) describes

different polyimide membranes used today.

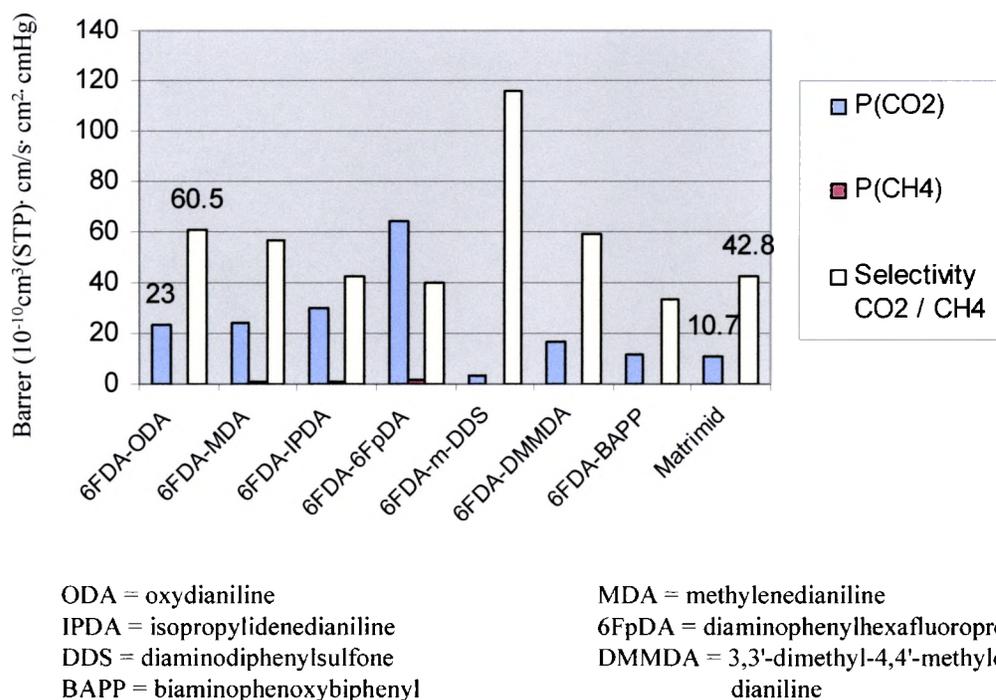


Figure 2. Comparison of permeation rates and selectivities of poly(6FDA-ODA)imide and other polyimides including Matrimid.^{4,8,9}

Polyimide membranes are manufactured by several companies and are applied mainly in gas separation processes and also in a few pervaporation and vapor recovery systems. In order to improve the separation characteristics of this polymer class, systematic studies have been performed over the last 10 years in order to find correlations between polyimide structure and separation performance. It had been shown that by using monomers with $-CF_3$ groups, such as hexafluoroisopropylidene diphthalic anhydride (6FDA dianhydride), shown in Figure 3, the chain mobility and, simultaneously, the chain packing can be restricted. Therefore, significantly improved selectivity as well as permeability can be reached.⁷

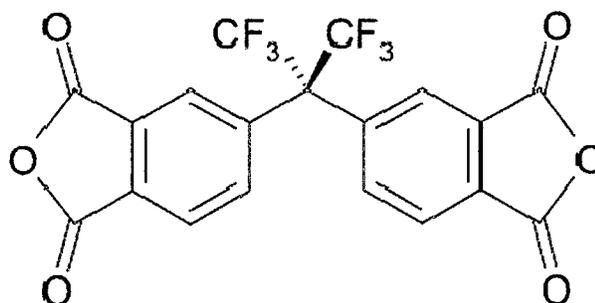


Figure 3. Chemical structure of 6FDA.⁷

Fluorine-containing groups in high performance polyimide materials have benefits that include low moisture absorptivity, low dielectric constant, resistance to wear and abrasion, low melt viscosity, low refractive index, and enhanced solubility in organic solvents.⁵

Although 6FDA polyimides show excellent separation characteristics for several gas pairs, in the presence of certain feed components, plasticization occurs. Plasticization leads to an increase in the intermolecular distance and to a decrease in the inter and intramolecular forces. As a consequence, the molecular motions and the permeability for all feed components increase with an associated selectivity decrease. Several studies have shown that plasticization occurs if polyimides are exposed to high CO₂ partial pressure, higher hydrocarbons, for example propylene and propane, or ethylene oxide.⁷

Despite the benefits of using CF₃ groups to help the selectivity and permeability; it does increase the brittleness of the polymer membrane. The ring structure of aromatic compounds provides a degree of rigidity upon the backbones of many polymers. Increased rigidity of a polymer backbone contributes to such properties as higher glass transition temperatures, increased structural integrity, as well as a greater toughness.¹⁰ However, one of the drawbacks to synthesizing polymers using all aromatic and cyclic monomers is that as one increases the structural rigidity, the brittleness tends to increase as well. The approach proposed herein

involves the use of loosely packed glassy polymers with high cohesive energy and semi-rigid structures. This can be done by using aliphatic diamine monomers with the 6FDA monomer in order to make a series polyimide membranes. Using the aliphatic spacer should decrease brittleness *via* increasing polymer chain flexibility.

A series of these polyimides was created previously using a different solvent system.¹¹ However, the purpose of the material was to determine its adhesive properties and was not studied as a film forming material for gas permeation. In addition, the use of TiO₂ nanoparticles to form nanocomposites should increase selectivity of the membranes, with minimal effect on permeation rate, by creating a selective surface flow effect.

II. PROSPECTUS OF RESEARCH

As natural gas passes through the membrane it undergoes the torturous path.

However, this permeation is nonselective, unless there is an interaction between the nanocomposite and the gas passing through, in which case diffusivity is changed in a way that enables less strongly adsorbed components to remain in the high pressure effluent stream while more strongly adsorbed components populate the permeant stream.⁵ (Figure

4)

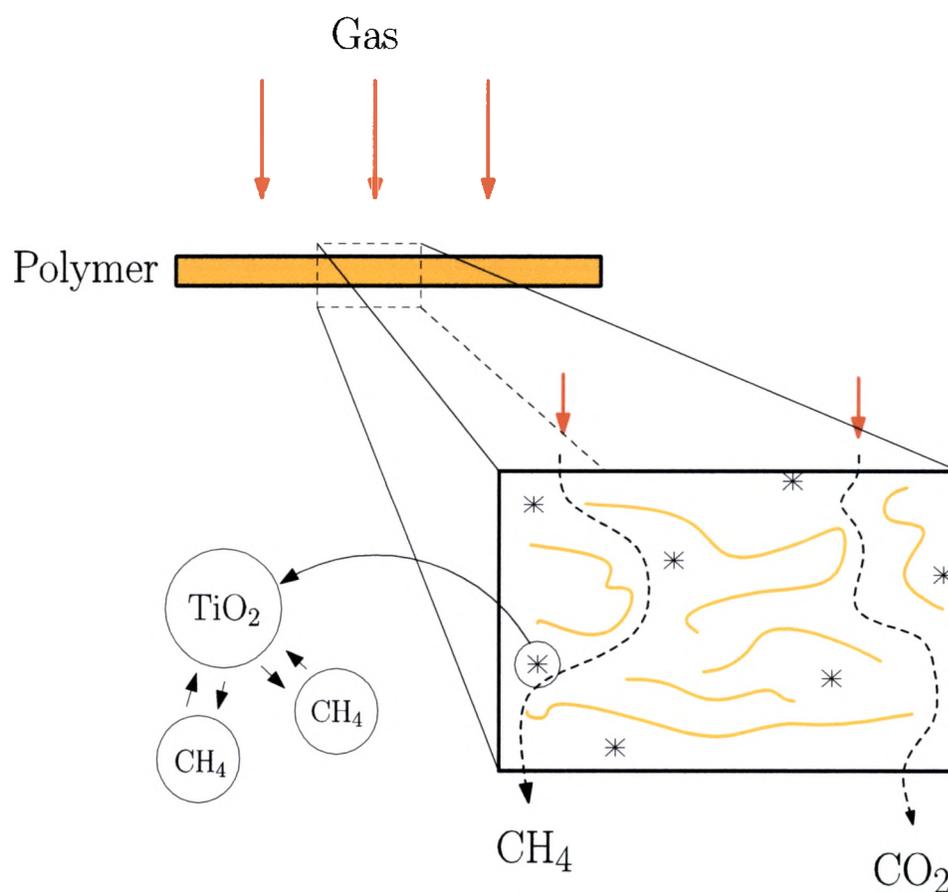


Figure 4. Selective surface flow diagram.

The focus of this project is the development and evaluation of loosely packed glassy polymers with high cohesive energy and semi-rigid structure materials with and without the incorporation of TiO₂ nanoparticles to form nanocomposites. These materials were tested using thermal and mechanical analysis. The data seek to show that there is a connection of the thermal, mechanical, and gas permeation properties of the polymers which depend on the length of the aliphatic spacer being used. These properties are gathered by using gel permeation chromatography for the determination of molecular weight, thermal gravimetric analysis for the determination of degradation temperatures, differential scanning calorimetry for the determination of the glass transition temperatures, and dynamic mechanical analysis for determination of the glass transition temperatures and storage moduli values. The conformation of the structure is achieved by analyzing the NMR results. Also the permeation properties of the resulting films are going to be studied in order to determine the importance of the length of the aliphatic spacers. The polymers are developed using a condensation reaction. Resulting polyamic acid undergoes thermal curing in order to become polyimide film when casted on the Teflon plate.

III. EXPERIMENTAL

3.1 Materials

The series of primary diamines, α,ω -aliphatic diamine, were obtained from Aldrich Chemical and used as supplied. 6-FDA, 2,2-bis(3,4-anhydrodicarboxyphenyl)hexafluoropropane was donated by Daikin Industries, LTD.(Japan). Dimethylacetamide (DMAc) was used as a solvent in the synthesis and was obtained from Aldrich Chemical. The TiO₂ used was obtained from Nanotechnologies, Inc. (Austin, TX).

3.2 Synthetic Methods

All polymers were synthesized at room temperature or at slightly elevated temperatures *via* a condensation polymerization reaction under protection of argon.¹² A 100 ml, round-bottom flask was flushed with argon, and about 5 ml of DMAc solvent was introduced with stirring. Then the specific diamine monomer, (0.700g) was introduced to the flask. Simultaneously the appropriate molar amount of 6FDA was dissolved in 10ml of DMAc. The calculated amounts used can be seen below (Table 2) where 1,6-diamine is used as an example. After a theoretical amount of polymer was calculated an approximate amount of solvent to be used is calculated to be about 80% of a total amount present in the flask.

After finishing the part of the project without the incorporation of TiO₂, there was a little modification to the theoretical calculations in order to account for the presents TiO₂, which was incorporated in 0.5% w/w. The mass of TiO₂ also was incorporated in a calculation for the amount of solvent.

Table 2. Theoretical amounts that need to be used in the reaction.

	H ₂ N(CH ₂) ₆ NH ₂	6FDA needed	Theoretical yield of polymer
Mass (g)	0.7000	2.6757	3.1586
Moles (mol)	0.0060235	0.0060235	0.0060235

Similar calculations were performed for each of the diamines with their appropriate molar weights which can be found in the Table 3.

Table 3. Characteristics of the chemicals used.

Name	State	MW (g/mol)	Purity (%)	Density (g/cm ³)	Boil. Point (°C)	Melt. Point (°C)
6FDA	s	444.21	N/A	N/A	N/A	N/A
1,2-diamine	l	60.1	99.5	0.897	117-118	N/A
1,3-diamine	l	74.13	99	0.886	136-138	N/A
1,4-diamine	s	88.15	99	0.874	60-61	25-27
1,5-diamine	l	120.18	97	0.869	78-80	N/A
1,6-diamine	s	116.21	99	N/A	N/A	39-42
1,7-diamine	s	130.24	98	N/A	223-225	26
1,8-diamine	s	144.26	98	N/A	N/A	N/A
1,9-diamine	s	158.29	98	N/A	258-259	35
1,10-diamine	s	172.32	98	N/A	N/A	59-61
1,12-diamine	s	200.37	98	N/A	N/A	68
DMAc	l	87.12	99.8	0.94	164-166	N/A

The resulting solution with 6FDA monomer was added slowly using a glass pipette to the flask to avoid the formation of clumps. After the addition of the solution was completed, the flask was left under the argon for eight hours to achieve full

polymerization. The resulting polyamic acid was cast on the Teflon plate and air dried for 48 hours before being placed into a vacuum oven at 53°C for four hours under increasing vacuum and for three hours under full vacuum to insure the absence of solvent. After the removal of the solvent was complete, the plate with the film was placed in an oven at 80°C where temperature was slowly increased to 200°C and left to cure for eight hours. The resulting PI film was removed from the Teflon plate for testing.

Films with the introduction of TiO₂ nanoparticles were made in the similar manner, except 0.5% w/w of TiO₂ nanoparticles were introduced in the solvent before the addition of monomers. The diamine was then introduced in full amount (0.700 g) and the appropriate molar amount of 6FDA was slowly added to the mixture.

3.3 Characterization Methods

The polymers were tested for thermal and mechanical properties via TGA, DSC, and DMA analysis. The molecular weight was obtained by using GPC analysis. The confirmation of the polymer structure was obtained using NMR analysis.

3.3.1 Gel Permeation Chromatography

Gel permeation chromatography (GPC) was obtained on a Waters model 600 GPC in conjunction with a Waters 2410 refractive index detector (410). Calibration was carried out using a series of ten polystyrene standards of varying molecular weights from 1.32×10^3 – 3.15×10^6 . Samples were prepared by mixing 20.00 mg of polyimide with 5.00 milliliter of HPLC grade chloroform. The samples were filtered using a 0.45 micron Teflon Cameo 30F syringe filter. Samples were injected at a volume of 50 μ L.

3.3.2 Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was measured on a TA Instruments Q50 thermal gravimetric analyzer from ambient to 800 °C at 20 °C/min on 5-10.00 mg samples. This analysis was carried out in both air and argon and was analyzed for 10% weight loss of the polyimide sample as well as its onset point.

3.3.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was measured on a TA Instruments Q200 DSC using a heat/cool/heat cycle at 10 °C/min on 5.00 mg samples. Data were taken on the first cool and second heat cycles of the run. An argon environment was maintained throughout the analysis. Data were analyzed to determine glass transition temperatures (T_g). Glass transition peak values were taken at the midpoint of the transitions.

3.3.4 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was measured on TA Instrument Q800 DMA. The response to the deformation was monitored as a function of temperature. The sample preparation is very critical and tedious. All the samples should be prepared within a certain range in their dimensions in order to achieve reproducibility and accurate comparison. The dimensions of samples were in the range of 20 mm to 30 mm in length, up to 6.5 mm in width, and up to 2 mm in thickness. The stainless steel standards were used for the calibration purpose. Data were analyzed to determine glass transition temperatures (T_g) and storage moduli values.

3.3.5 Nuclear Magnetic Resonance Spectroscopy

^1H -NMR spectra was obtained in solutions of deuterated chloroform in 10 mm tubes using a 400-MHz Oxford NMR 400 spectrometer. Samples were prepared by taking 1-2 mg of polyimide and dissolving it into approximately 0.75 ml of deuterated chloroform. NMR spectra were then run in the range of 0-9ppm as all significant peaks were in this range. Peaks were integrated for further analysis.

3.3.6 Membrane Permeability

The membranes had to be re-dissolved using N,N-dimethylacetamide and heated in order to get their thicknesses between 0.03 and 0.09 mm. The resulting solution was filtered and the membranes were reformed by casting inside a vacuum oven. The temperature was raised at 10°C per day from 30°C to 80°C, where they were kept for six more days. The most homogeneous areas were selected to perform the permeability measurements. The samples used had a diameter of 12.6 mm and thickness of 0.09 mm.

IV. RESULTS AND DISCUSSION

The series of partially-fluorinated polyimides was created using the aliphatic diamines as a flexible spacer. The synthesis was accomplished *via* condensation reaction with water being a byproduct. A second series was synthesized using the previous set up with the addition of nanoparticles which created nanocomposites within the polymer matrix. The reaction of the process can be observed below.

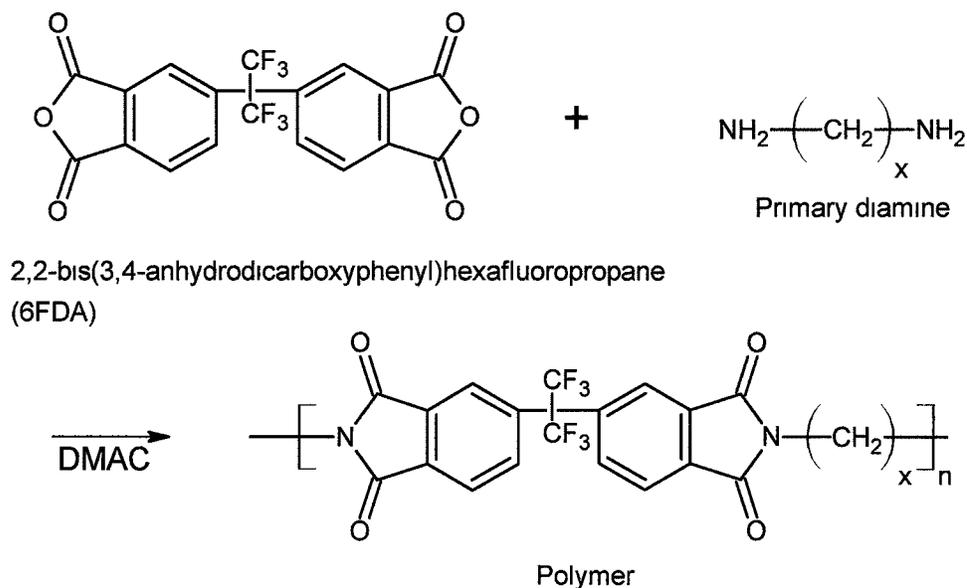


Figure 5. The synthesis of aliphatic polyimide.

4.1 Gel-Permeation Chromatography

Gel-permeation chromatography (GPC) was conducted for both polyimide series. Elution times were compared for all samples against a polystyrene standard. These peaks were then analyzed based on the weight average molecular weight (M_w), number weight

average molecular weight (Mn) and the polydispersity (PDI). The data are shown in Table 4 and Table 5, without and with the incorporation of TiO₂ nanoparticles respectively.

The range of the weight average molecular weight (Mw) from GPC for the series of partially-fluorinated polyimide with the aliphatic spacer is 11,000 to 200,000 Da. The range of the number average molecular weight (Mn) is 4,000 to 50,000 Da and the range for polydispersity (PDI) of the series is 2.00 to 4.00.

Table 4. Results from GPC for partially-fluorinated polyimide series.

Without TiO ₂ # of CH ₂	GPC		
	Mw	Mn	PDI
2	11409	5203	2.19
3	11576	4160	2.78
4	97600	44963	2.17
5	76140	23045	3.30
6	127575	44697	2.80
7	51804	22410	2.31
8	128636	41804	3.08
9	105939	25744	4.12
10	198095	48111	4.12
12	74995	31769	2.36

Due to such a narrow distribution of polydispersities, the molecular weights are considered accurate in their values. A general trend for the data show that the first two polymers with 1,2-diamine and 1,3-diamine aliphatic linkage did not form high quality films. The resulting films were fragile, which is reflected in their low Mw values. The reason for that might be that the diamines were not measured precisely since both monomers are in liquid form at room temperature which might have caused some evaporating issue that led to the inaccurate mass measurements. However, both films show PDI of about 2, which is ideal for condensation reaction. So another explanation

might be that these polyimides did not have enough time to react to their full potential in order to increase their Mw values. Similar problem can be seen with the use of 1,5-diamine, since it is also in the liquid form at room temperature. However, there is a definite improvement in the Mw as the number of the methylene groups goes pass three. There is an unexpected decrease of Mw with the use of 1,7-diamine and 1,12-diamine, which is most likely can be explained with the human error, but even in that case the Mw values are above 50,000 Da, which considered typical weight for polyimides. The literature values for similar films are in the range of 20,000 – 70,000 Da.¹³

Table 5. Results from GPC for partially-fluorinated polyimide series with the incorporation of TiO₂ nanoparticles.

With TiO ₂	GPC		
	# of CH ₂	Mw	Mn
2	19542	3284	6.00
3	11031	2459	4.49
4	41301	20875	1.98
5	84741	8411	8.00
6	269800	93207	2.89
7	75434	31825	2.37
8	182100	38118	4.00
9	55094	16599	3.32
10	28441	8420	3.38
12	142312	26878	5.29

The range of the weight average molecular weight from GPC for the series of partially-fluorinated polyimide with the aliphatic spacer and incorporation of TiO₂ nanoparticles is 11,000 to 270,000 Da. The range of the number average molecular weight (Mn) is 3,000 to 100,000 Da and the range for polydispersity of the series is 2.00 to 8.00. The similar trends are observed in this series comparing to the one that does not have TiO₂ nanoparticles incorporated. There are still good Mw values that are observed

making it hard to judge about the accuracy of the Mw values presented. One possible explanation is that some of the TiO₂ nanoparticles may have interacted with the some amine portion of the monomers changing the stoichiometry of the system that could potentially lead to the decrease in the Mw values and increase in PDI values.¹⁴ However, it is possible that this trend is nothing more than a coincidence based on slight variance in the way these polymers were synthesized. Slight differences in reaction time and temperature could account for this variance in the molecular weight.

4.2 Thermal and Mechanical Analysis

Thermal gravimetric analysis (TGA) was obtained in both air and argon. Decomposition temperatures (T_d) are defined as the temperature at which the polymer has lost ten percent of initial mass. Knowing this temperature allows for future studies to be made which utilize the decomposition temperature as a guide for processing the polymer. Degradation temperatures in both atmospheric and argon based conditions yielded good results for both series of polyimides. The data can be seen in Table 6 and Table 7 for the series of polyimides without and with the incorporation of TiO₂ nanoparticles respectively.

According to the data collected, as a number of aliphatic spacer was increased, degradation temperature decreased, as was expected. This trend occurs as the amount of methylene groups increases the easier they get oxidized during the degradation process. The difference in atmospheric conditions showed that in argon the T_d was approximately twenty degrees higher than in open-air conditions.

in most of the films; however, one can see that the polydispersity of the series increased,

Table 6. Data of thermal and mechanical results for series without TiO₂.

Without TiO₂	TGA	TGA	DSC	DMA	DMA
# of CH₂	T_d air (°C)	T_d Ar (°C)	T_g (°C)	St. Mod. (MPa)	T_g (°C)
2	493	507	189		
3	444	462	192		
4	465	484	186	2190	191
5	446	481	162	2127	184
6	460	480	152	2607	171
7	440	450	138	2373	163
8	421	470	123	1909	156
9	419	466	108	2256	133
10	432	483	112	2214	119
12	395	441	100		

Table 7. Data of thermal and mechanical results for series with TiO₂.

With TiO₂	TGA	TGA	DSC	DMA	DMA
# of CH₂	T_d air (°C)	T_d Ar (°C)	T_g (°C)	St. Mod. (MPa)	T_g (°C)
2	476	488	217		
3	447	469	192		
4	455	485	186		
5	441	467	165	2186	180
6	446	480	156	2740	172
7	452	478	143	2308	159
8	431	472	130	2149	152
9	441	470	122	1982	139
10	438	467	111	2158	131
12	429	460	102	1641	126

The literature value for the similar films is around 560 °C.⁵ The literature value is higher than the degradation temperature of the obtained films due to the fact that literature value is obtained from the polymer that has aromatic structure which allows it to have better thermal properties.

Differential scanning calorimetry (DSC) was carried out on all polymers in order to analyze for glass transition temperatures (T_g). The polymers show amorphous characteristics at all temperatures. Therefore on the first cool and the second heat only the glass transition was observed. All data for glass transition temperatures are tabulated in Table 6 and Table 7 for the series without and with the TiO_2 nanoparticles respectively. Also, data in Tables 6 and 7 were put in the graphs so one can easily see the trends in both series without and with the incorporation of TiO_2 nanoparticles. (Figure 6 and Figure 7). The literature values for the similar films are in the range of 124 – 142 °C.⁵ The literature values are higher than the glass transition temperatures of the obtained films due to the fact that literature values are obtained from the polymer that has aromatic structure which allows it to have higher T_g values.

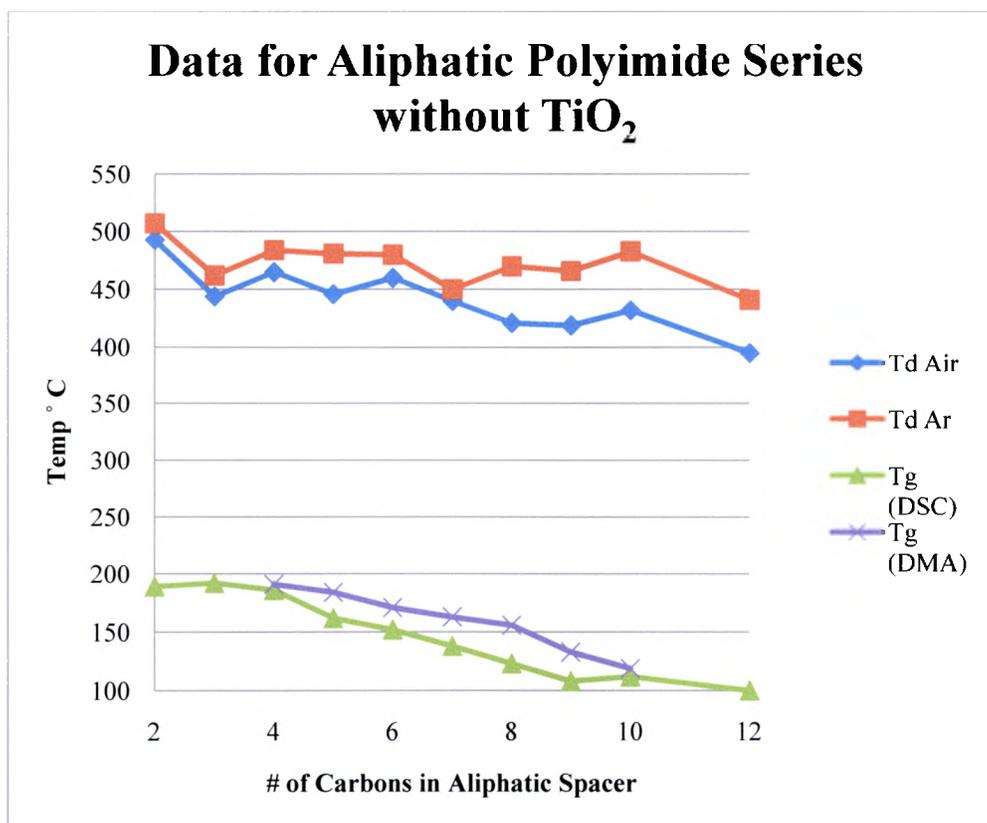


Figure 6. Data of thermal and mechanical results for series without TiO_2 .

Dynamic Mechanical Analysis (DMA) was carried out on most polymers in order to analyze for glass transition temperatures (T_g) and to obtain storage moduli values. The polyimides that were made with shorter aliphatic spacers were not tested due to their brittleness. The data can be seen in Tables 6 and 7 and they are graphically shown on Figures 6 and 7. The literature values for T_g in the similar films are in the range of 360 – 410 °C and 231 MPa for storage modulus.¹⁵ The literature values for T_g are higher than the glass transition temperatures of the obtained films due to the fact that literature values are obtained from the polymer that has aromatic structure which allows it to have higher T_g values. However, storage modulus values are higher in both synthesized series comparing to the literature value due to the high molecular weight of the obtained polymers.

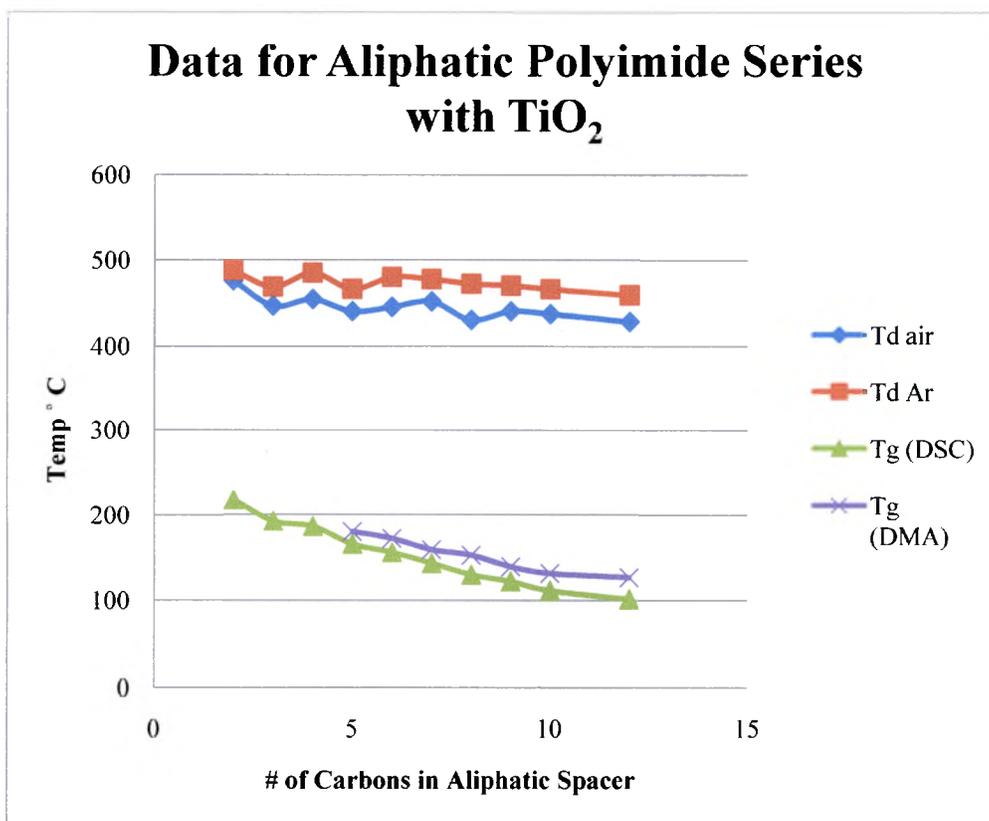


Figure 7. Data of thermal and mechanical results for series with TiO₂.

It might be hard to compare the two series with each other based on the graphs provides above. So, both series were compared and overlapped for TGA, DCS, and DMA responses individually. These data are shown on Figures 8, 9, 10, and 11.

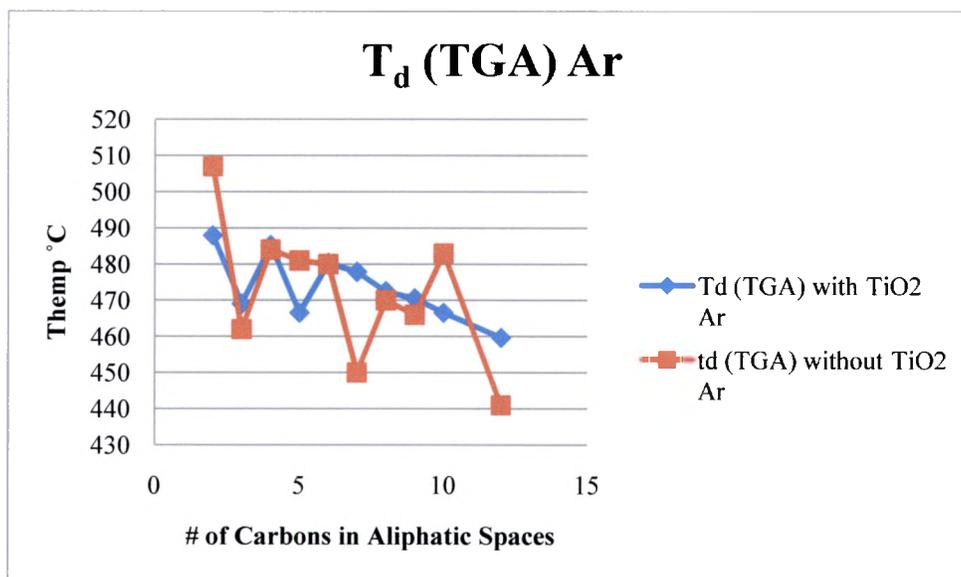


Figure 8. Data from TGA comparing T_d values of both series in Ar environment.

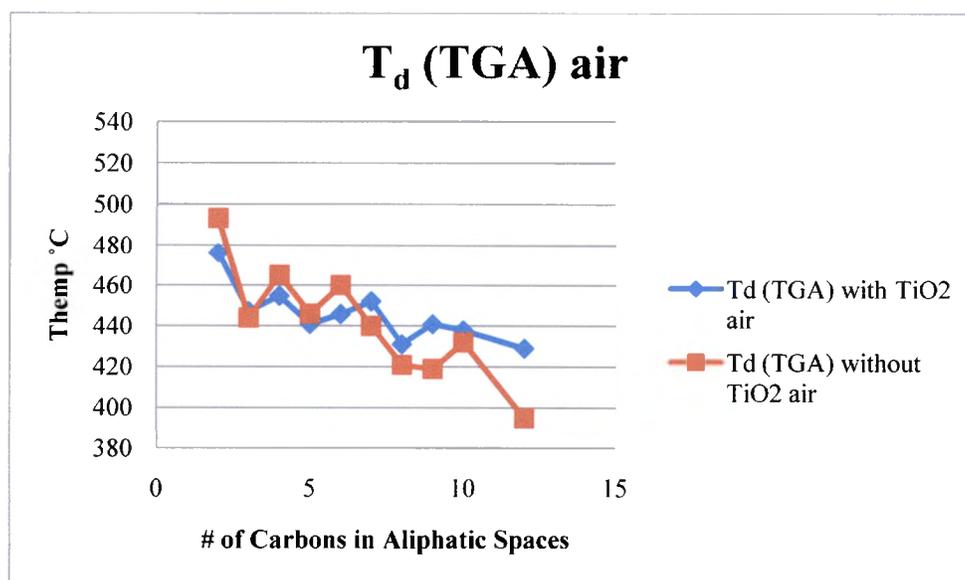


Figure 9. Data from TGA comparing T_d values of both series in atmosphere environment.

As one can see from the graphs above (Figure 8 – 11), the incorporation of TiO₂ nanoparticles did not contribute significantly to the thermal or mechanical properties. This result can be considered a positive one, since now one knows that TiO₂ nanoparticles can be incorporated in the polyimide films without a significant change, mainly without any significant loss, of the film's original properties.

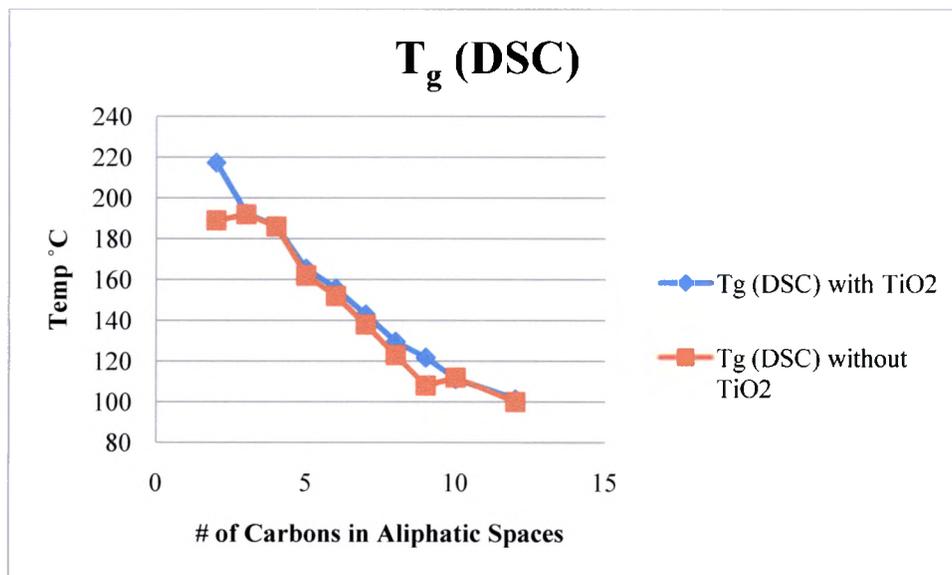


Figure 10. Data from DSC comparing T_g values of both series.

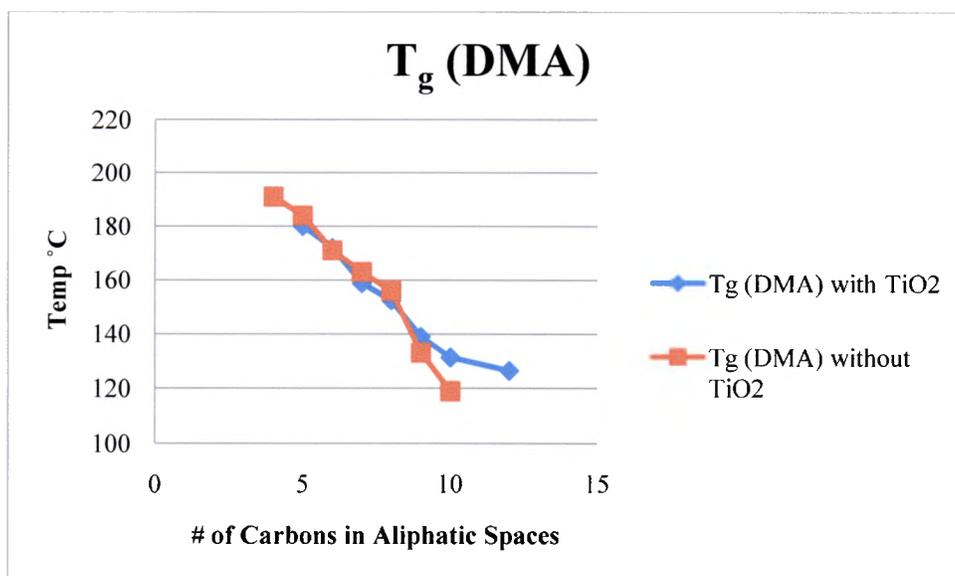


Figure 11. Data from DMA comparing T_g values of both series.

The T_g values that are in good agreement with each other based of the DSC and DMA testing. One can say that both series produced T_g values that are typical for the polyimides. However, it is evidential from Figures 12 and 13 that the films are durable and even can pass “crease test.” The trend in the storage modules values cannot be seen due to inconsistence in molecular weight and polydispersity between the films within both series.



Figure 12. Polyimide film passes “crease test.”



Figure 13. Flexibility of polyimide film.

The summary of all the thermal and mechanical properties of the polyimide films can be seen in Table 8.

Table 8. The summary of all the thermal and mechanical properties of the polyimides with the correspondent literature values.^{5,13,15,16}

	PI's without TiO₂	PI's with TiO₂	Literature
T_d TGA in air (°C)	395 – 490	430 – 475	560
T_d TGA in Ar (°C)	440 – 500	460 – 488	N/A
T_g DSC (°C)	100 – 190	102 – 217	124 – 142
T_g DMA (°C)	120 – 190	126 – 180	360 – 410
Storage Modulus DMA (MPa)	1909 – 2607	1640 – 2740	75 – 231
Molecular Weight GPC (KDa)	11 – 200	11 – 260	20 – 70

4.3 Conformation of the structure using ¹H NMR

Nuclear magnetic resonance spectroscopy was used in order to determine a structure of polyimide films. The ¹H NMR scan of polyimide film that was prepared using 1,10-diamine and 6FDA monomers is shown below. (Figure 14)

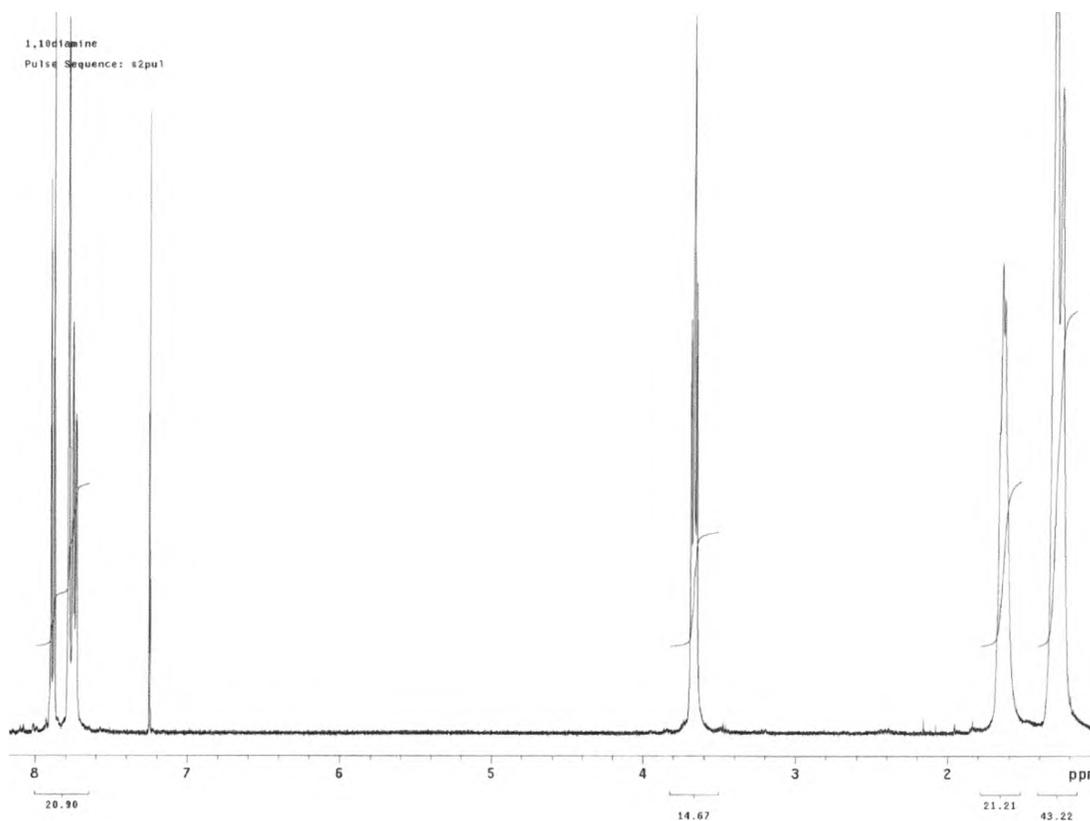


Figure 14. ^1H NMR scan of polyimide film.

4.4 Membrane Permeability

The reprocessed membranes showed some homogenous areas that were used for the permeability measurements. Data from those measurements are shown below in Table 9.

The homogenous areas of the films were completely dense without any pinholes in the area tested. This was confirmed by the constant H_2 permeability at different pressures, as it is indicated in the table below. The gas permeability data was obtained with an uncertainty of 4%. There were two polyimide films that were tested so far. Polyimide membrane of 1,5-diamine with 6FDA is more permeable to hydrogen gas (H_2)

and methane gas (CH₄) than the 1,6-diamine with 6FDA membrane; while both are equally permeable to carbon dioxide gas (CO₂).

Table 9. Gas permeability measurements.

Polymer	Gas permeability in Barrers at 35 °C				
	H ₂			CH ₄	CO ₂
	2 atm	3 atm	4 atm	2atm	2atm
1,5 diaminopentane + 6FDA	3.90	3.91	3.92	0.024	0.994
1,6 diaminohexane + 6FDA	3.76	3.73	3.72	0.017	0.993

These results make sense, since the increase of aliphatic portion of the polyimide increases the possible interactions between the aliphatic part of the polyimide and the H₂ gas and CH₄ gas that were tested. CO₂ gas travels at the same rate since the increase of aliphatic portion does not contribute to change of interactions of the gas travelled and the membrane. The selectivity values for 1,5-diamine with 6FDA membrane and 1,6-diamine with 6FDA membrane that are described above are 41.4 and 58.4 respectively. The literature values for the similar films are in the range of 32 – 59.7 which indicate that the resulting films have good selectivity.^{5,17}

V. CONCLUSIONS

Two series of partially-fluorinated polyimides using aliphatic diamines and incorporation of TiO₂ nanoparticles were synthesized *via* condensation polymerization. The identity of the resulting compounds was verified by ¹H NMR analyses. Degree of polymerization as well as polydispersity was obtained by GPC methods. Thermal and mechanical properties were determined using TGA, DSC and DMA.

The results show that as the length of the aliphatic diamine increases, the T_d values decrease. This is an expected trend, caused by the susceptibility to oxidation of the aliphatic portion of the back bone. In addition, the T_g values also decrease as the number of aliphatic spaces increases.

Mechanical data indicate that the incorporation of the aliphatic spacer has increased the flexibility of the polymer dramatically. The results for the series without the incorporation of the TiO₂ nanoparticles show that storage modulus is in the range of 1909 – 2607 MPa or 1.9 – 2.6 GPa. The series with the incorporation of TiO₂ nanoparticles show similar results, so it is fair to conclude that the incorporation of nanoparticles in the small amount does not affect the mechanical properties. Literature data report tensile strengths of similar films to be in the range of 75–231 MPa and tensile moduli of 1.46–1.95 GPa.^{15,16}

Data indicate that the increase of the aliphatic portion does not dramatically increase the molecular weight results. However, when dealing with the low numbers in aliphatic spacers the reaction time might need to be increased in order to drive the polymerization to completion.

The permeation studies suggest that as aliphatic portion of the polyimide increases, the permeation of the methane and hydrogen gases decreases. However, the additional tests need to be conducted in order to determine the effect of the incorporation of TiO_2 nanoparticles and their influence on the polymer matrix. As it was proposed earlier, TiO_2 nanoparticles form the nanocomposites within the polyimide which might have different permeation properties than the bulk of the material. So for future studies this area of the research needs additional work in order to fairly understand and evaluate it.

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