

Highly Soluble Polyimide Based on Asymmetric Diamines Containing Trifluoromethyl Group for High Performance Dielectric Material

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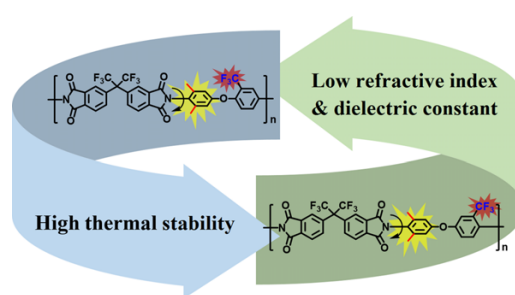
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Received May 22, 2017 / Revised September 11, 2017 / Accepted September 16, 2017

Abstract: In this study, we report the newly synthesized asymmetric diamine monomers and polyimides (PIs). The new diamines containing a trifluoromethyl group, 4-(4-amino-3-(trifluoromethyl)phenoxy)-2,6-dimethylaniline (ARFPA) and 4-(4-amino-2-(trifluoromethyl)phenoxy)-2,6-dimethylaniline (ALFPA) were synthesized by the nucleophilic aromatic substitution reaction, followed by reduction of nitro groups. The new PIs were synthesized by the conventional polycondensation from the newly synthesized diamines and 6FDA (4,4'-(hexafluoroisopropylidene)diphthalic anhydride). The all PI films showed the improved thermal stability (a temperature of 5% loss in weight) in the range of 523-562 °C and high glass transition temperature ($T_g > 307$ °C). The all PIs also exhibited good solubility in several solvents including chloroform, dimethyl sulfoxide, ethyl acetate, and acetone. Additionally, the PIs showed a low refractive index (1.5470-1.5475 at 637 nm) as well as a low dielectric constant.

Keywords: polyimide, trifluoromethyl groups, polymer optics, refractive index, dielectric constant.



1. Introduction

Aromatic polyimides (APIs)¹⁻⁸ are high performance polymers with several remarkable properties,^{9,10} including chemical resistance, excellent thermal dimensional stability, and low dielectric constant. Because of their reliable and superior mechanical and thermal properties, APIs are widely applied in a variety of engineering fields, including electric and microelectronic applications,¹¹ in liquid crystal displays (LCDs) and other valuable industries such as roll-up displays, portable devices, plastic substrates and color filters. Generally, aromatic polyimides have a poor solubility in aromatic solvents unmanageable and high melting temperature, due to a structurally rigid backbone, and strong interchain interactions between the polymer chains. Accordingly, polyimides (PIs) have thus far had only limited application in the optical and electrical fields. Polyimide's mechanical and thermal properties make it a valuable choice in a range of applications that require a low dielectric constant polymer,¹²⁻¹⁵ notably, the dielectric layers in electronic materials and microelectronics. However, the dielectric constant of typical polyimides is too high for use in electronic devices.¹⁶⁻²⁰

A number of synthesis approaches have been developed to improve polyimides' solubility, processability and flexibility, as

well as other favorable properties, for example, by inflowing non-coplanar units, bulky substituents or flexible linkages. Nonetheless, there is still a need for a low dielectric constant polymer that is appropriate for the fabrication process conditions in ordinary production lines.

Fluorinated PIs²¹⁻²⁵ were developed because the low polarizability of the C-F bonds and increasing fractional free volume of the PIs improve the material's hydrophobic, optical, and dielectric performance. However, fluorinated PIs have some limitations which can lead to processing difficulties, such as their low solubility in various organic solvents, and high processing temperature.

In this study, we state the synthesis of 4-(4-amino-3-(trifluoromethyl)phenoxy)-2,6-dimethylaniline (ARFPA) and 4-(4-amino-2-(trifluoromethyl)phenoxy)-2,6-dimethylaniline (ALFPA) as a new class of asymmetric^{26,27} diamine monomers containing trifluoromethyl and methyl groups,^{28,29} for high performance fluorinated PIs. The PIs were obtained by two-step polycondensation followed by chemical imidization derived from ARFPA, ALFPA, and 6FDA anhydride (4,4'-(hexafluoroisopropylidene)diphthalic anhydride). The synthesized PIs exhibited high thermal stability (>500 °C), a high glass transition temperature (>307 °C), and especially high solubility in organic solvents. The listed enhancements occurred by the trifluoromethyl group and methyl groups of the amino groups obstructed the intermolecular close packing and free rotation of the C-N bond in imide group was disturbed by same reason.³⁰ Furthermore, the PIs exhibited not only a low refractive index (1.547 at 633 nm) but also a low dielec-

Acknowledgments: This work was supported by a grant from the Korea Institute of Science and Technology (KIST) institutional program and by a grant from the Ministry of Trade, Industry & Energy of Korea (2MR6150, 2MR6190).

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tric constant (2.63). The structural property relationships of the PIs, such as their solubility, thermal and optical properties, dielectric constant and refractive index of the polyimides are discussed in detail.

2. Experimental

2.1. Measurements

NMR spectra of ^1H (600 MHz), ^{13}C (150 MHz) were measured by DMSO or CDCl_3 as a solvent included TMS (tetramethylsilane) as an internal standard using NMR spectrometer (Agilent 600 MHz Premium COMPACT). The FT-IR Spectrophotometer (Fourier transform-infrared spectroscopy, Nicolet IS10, USA) were analyzed functional groups of the polymer. TGA (Thermogravimetric analysis) was measured decomposition temperature (T_d) using TA 50 (TA Instruments, USA) at a $10\text{ }^\circ\text{C}/\text{min}$ heating rate under nitrogen atmosphere. DSC (Differential scanning calorimetry, TA Instruments Q 20, USA) measured the glass transition temperature (T_g) of the synthetic compounds under nitrogen gas flow at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. DMA (Dynamic mechanical thermal analysis, TA Instruments Q 800, USA) also measured T_g of PI films at a $3\text{ }^\circ\text{C}/\text{min}$ heating rate with a 1 Hz load frequency in air atmosphere and sample size for measurement was approximately 5 mm wide, 30 mm length, and ca. 50 μm thickness. The refractive indices of the polymer films such as in-plane (n_{TE}) and out-of-plane (n_{TM}) were measured with a prism coupler (Metricon PC-2000) with a wavelength: 637 nm He-Ne laser light source. The birefringence (Δn) was calculated between the n_{TE} and n_{TM} and the average refractive index (n_{av}) was calculated by the equation: $n_{av} = [(2n_{TE}^2 + n_{TM}^2)/3]^{1/2}$ and the dielectric constants were calculated by the formula: $\epsilon = 1.1n_{av}^2$.

2.2. Materials

Monomers such as 4-amino-3,5-xyleneol, 5-chloro-2-nitrobenzotrifluoride and 2-chloro-5-nitrobenzotrifluoride were prepared by Sigma-Aldrich and TCI. Aromatic dianhydride, 6FDA (4,4'-(hexafluoroisopropylidene)diphthalic anhydride) was obtained from TCI. The solvents such as *n*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylformamide (DMF) were purified by purification system using a two-column solid state (Glass contour system, Joerg Meyer, Irvine, CA).

2.3. Monomer synthesis

2.3.1. Synthesis of 4-(4-amino-3-(trifluoromethyl)phenoxy)-2,6-dimethylaniline (ARFPA)

To synthesize a new amine,³¹ all the necessary materials such as 4-amino-3,5-xyleneol (7.0 g, 51.0 mmol), equivalent amount of 5-chloro-2-nitrobenzotrifluoride (11.5 g, 51.0 mmol), K_2CO_3 (10.6 g, 76.5 mmol), and 120 mL of DMF were added to a 200 mL two-neck round flask. The mixed solution was responded at $120\text{ }^\circ\text{C}$ under an Ar atmosphere for 12 h. After, the solution was slowly poured into brine and extracted with ethyl acetate and brine. This work used MgSO_4 to remove the remaining water in the solution, and evaporated the solution in order to remove

the solvent, and then to separate the pure product using column chromatography consisting of solvent ethyl acetate and hexane at a ratio of one to four ($R_f=0.3$). The product 2,6-dimethyl-4-(4-nitro-3-(trifluoromethyl)phenoxy)aniline (12.7 g, 76% yield) was a brown solid. MS (+ESI): calculated for $\text{C}_{15}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_3 + \text{H}^+$: 327.09; found: 327.10.

The next step was to reduce the nitro groups to amino groups. The 2,6-dimethyl-4-(4-nitro-3-(trifluoromethyl)phenoxy) aniline (12.7 g, 38.9 mmol) and 10% Pd/C catalyst (0.05 g) and hydrazine (12.2 mL) were added to 120 mL ethanol, and the hydrazine was added by dropwise for about 1 h. After that the mixed solution was refluxed for a day at room temperature, and then to remove the Pd/C poured into a celite filter, and subsequently refined by column chromatography at a ratio of ethyl acetate to hexane of one to five ($R_f=0.3$), followed by recrystallization in ethanol.

The resulting ARFPA (5.2 g, 22.8 mmol, 58.6% yield) was a pale-yellow crystal product. ^1H NMR (600 MHz, CDCl_3): $\delta=7.07$ (d, $J=2.82$ Hz, 1H), 6.94 (dd, $J=8.15, 2.25$ Hz, 1H), 6.69 (d, $J=8.77$ Hz, 1H), 6.61 (s, 2H), 3.95 (s, 2H, $-\text{NH}_2$), 3.46 (s, 2H, $-\text{NH}_2$), 2.16 (s, 6H) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta=150.21, 148.96, 139.66, 138.74, 127.18, 125.37, 123.57, 123.17, 118.69, 116.18, 114.74, 17.78$ ppm. MS (API+): calculated for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{N}_2\text{O} + \text{H}^+$: 297.11; found: 297.2.

2.3.2. Synthesis of 4-(4-amino-2-(trifluoromethyl)phenoxy)-2,6-dimethylaniline (ALFPA)

4-Amino-3,5-xyleneol (7.0 g, 51.0 mmol), an equal amount of 2-Chloro-5-nitrobenzotrifluoride (11.5 g, 51.0 mmol), K_2CO_3 (10.6 g, 76.5 mmol), and 120 mL of DMF were blended by stirring for 12 h at $120\text{ }^\circ\text{C}$ under Ar atmosphere. After that reaction time, the solution was extracted more than twice using brine and ethyl acetate, and dried with MgSO_4 to remove the water in the solution, and evaporated to eliminate solvent. The product was refined by chromatography (ethyl acetate:hexane=1:3, $R_f=0.3$). The product 2,6-dimethyl-4-(4-nitro-2-(trifluoromethyl)phenoxy) aniline (12.3 g, 74% yield) was a brown solid. MS (+ESI): calculated for $\text{C}_{15}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_3 + \text{H}^+$: 327.09; found: 327.08.

After this step, the 2,6-dimethyl-4-(4-nitro-2-(trifluoromethyl)phenoxy) aniline (14.3 g, 37.7 mmol) and 0.05 g of 10% Pd/C and EtOH (120 mL) were synthesized using an autoclave (Buchiglasuster, Switzerland). The reaction conditions were kept pressure at roughly at room temperature 6 bar for 12 h under hydrogen gas and then the output solution was poured into a celite filter to remove the Pd/C catalyst. To refine the pure product, the product was separated by column chromatography using silica gel and recrystallized over ethyl acetate with hexane. The column chromatography development solvent was ethyl acetate and hexane at a ratio of one to three ($R_f=0.3$). The product ALFPA (4.3 g, 14.5 mmol, 38.5% yield) was a yellow crystal. ^1H NMR (600 MHz, $\text{DMSO}-d_6$): $\delta=6.87$ (s, 1H), 6.73 (d, $J=8.78$ Hz, 1H), 6.67 (d, $J=8.53$ Hz, 1H), 6.46 (s, 2H), 5.18 (s, 2H, $-\text{NH}_2$), 4.28 (s, 2H, $-\text{NH}_2$), 2.04 (s, 6H) ppm. ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$): $\delta=148.12, 145.95, 144.55, 140.49, 125.14, 123.33, 122.52, 121.20, 119.14, 118.16, 111.15, 18.26$ ppm. MS (API+): calculated for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{N}_2\text{O} + \text{H}^+$: 297.11; found: 297.23.

2.4. Polymer synthesis and preparation of polyimide films

The PI films were prepared using the chemical imidization method. The diamine monomers ARFPA and ALFPA were polymerized with 6FDA dianhydride. In addition, ODA was polymerized with 6FDA as a reference PI film. The films were designated 6FDA-ARFPA, 6FDA-ALFPA and 6FDA-ODA, respectively. The polyimide polymerization was performed with a one pot solution method. All of the materials, that is, the diamine monomer ARFPA, ALFPA (1.0 g, 4.4 mmol) and 6FDA (1.51 g, 4.4 mmol), were mixed in a purified NMP solvent (solid content in 20 wt%) in a 50 ml two-neck round flask along with a Dean-Stark trap and stirred for about 12 h under an argon atmosphere. After approximately 5 drops of isoquinoline was added to the mixture as a catalyst, it was stirred for 1 h at room temperature.

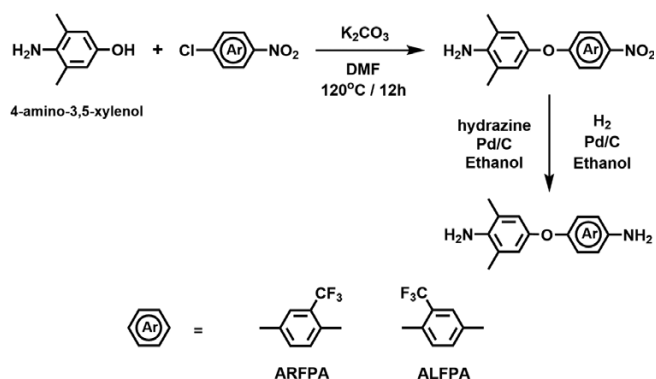
The mixed solutions were then stirred at room temperature for 12 h to obtain viscous PAA solutions. After that, the reaction temperature was slowly raised up to 190 °C and the solutions were kept at 190 °C for 12 h. During this time, distillation using a toluene and water azeotrope removed the water generated by the imidization process. Then the solutions were poured into a stirred solvent consisting of methanol and distilled water in order to precipitate a fiber-like polyimide. The obtained fiber-like solid polymer was gathered by filtration and dried under vacuum at 80 °C for over 12 h.

The polymers were dissolved in approximately 15 wt% triglyme. Then the Tri-GL solutions were filtered and cast on a clean glass, quartz and silicon wafer substrate, using a spin coater. The solutions were dried in a vacuum oven at room temperature for 1 h and then at increasing temperatures to 150 °C for 5 h to eliminate the remaining solvent. After drying, the substrates were placed in distilled water to remove them from the plates, then finally flexible polyimide free standing films were prepared.

3. Results and discussion

3.1. Synthesis and characterization of monomer

The new asymmetric diamine monomers, ARFPA and ALFPA, which contains a dimethyl groups and trifluoromethyl group, these monomer synthesis methods were described in the Scheme 1. To be specific, the monomers were synthesized by



Scheme 1. Synthesis of diamine monomers.

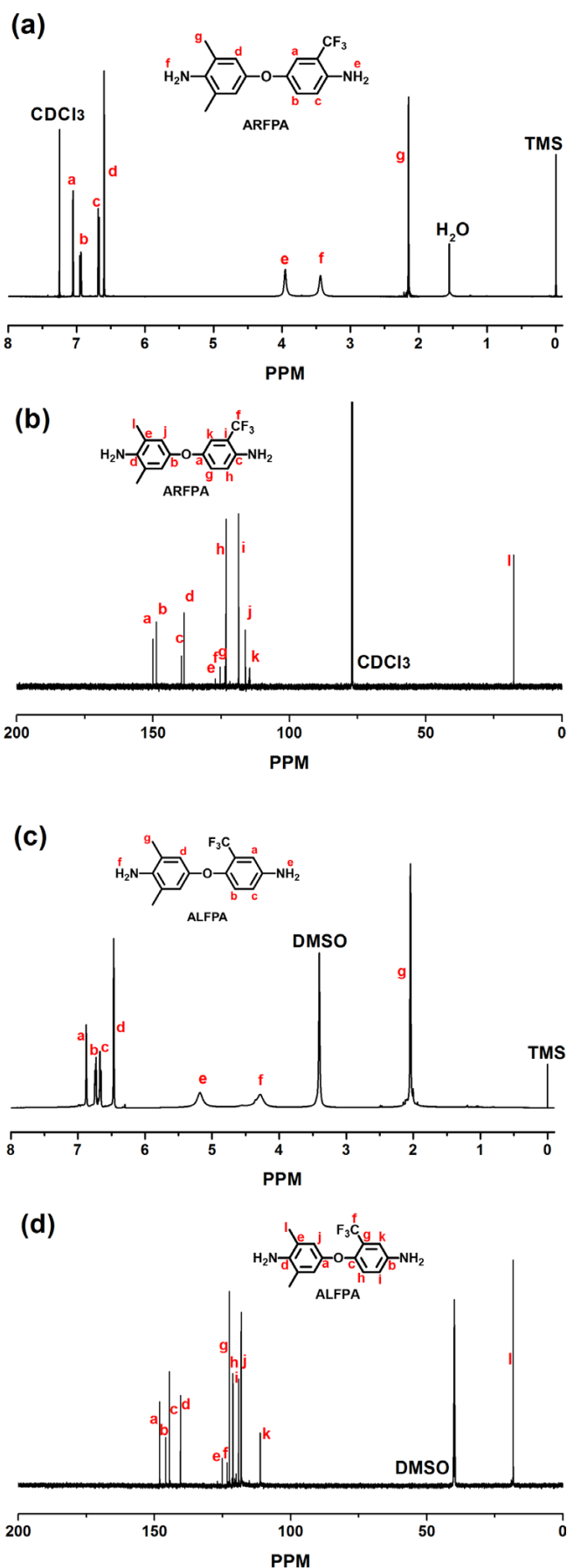
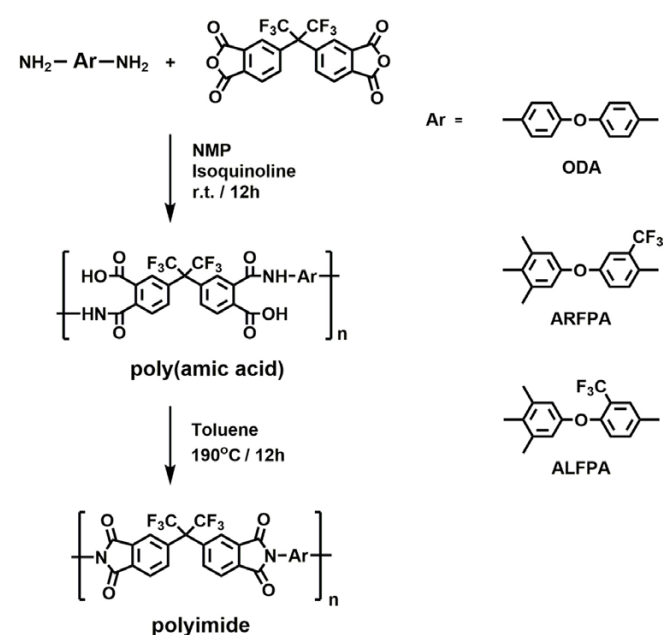


Figure 1. NMR spectra of ARFPA, (a) ^1H NMR (b) ^{13}C NMR, and ALFPA, (c) ^1H NMR (d) ^{13}C NMR.

the S_NAr reaction (nucleophilic aromatic substitution reaction) using 4-amino-3,5-xyleneol and 5-chloro-2-nitrobenzotrifluoride or 2-chloro-5-nitrobenzotrifluoride. The second step was reduction. The nitro group was changed into an amino group by the palladium on carbon catalyst (Pd/C) and hydrazine or another method using H_2 gas with Pd/C *via* autoclave equipment. Then the chemical structures of the synthesized diamines were confirmed by 1H and ^{13}C NMR spectroscopies and mass measurement.

The 1H and ^{13}C NMR spectra of ARFPA and ALFPA are shown in Figure 1. To be specific, NMR data of the ARFPA was measured by deuterated chloroform solvent ($CDCl_3$). The aromatic proton peaks in the 1H NMR of the ARFPA monomer were indicated at 7.07, 6.94, 6.69, 6.61 ppm. The peak at 2.16 ppm was shown to be the methyl groups of the ARFPA monomer, and the amine signals were observed as two points, at 3.95 and 3.46 ppm. The carbon peaks of the ARFPA monomer in ^{13}C NMR appeared in the range of 114–150 ppm. Additionally, the 17.9 ppm peak was the benzylic carbons peak.

The ALFPA NMR data was measured by deuterated DMSO solvent. The proton peaks of the ALFPA monomer were indicated at 6.87, 6.73, 6.67, 6.46 ppm and the proton peak of the methyl groups in the ALFPA monomer appeared at 2.04 ppm in the 1H NMR. Moreover, the typical amine signs of the ALFPA monomer were measured at 5.18 and 4.28 ppm. The carbon peaks of the ALFPA monomer appeared in the range of 118–148 ppm.



Scheme 2. Synthesis of polyimides.

Additionally, the benzylic carbons peak was at 18.3 ppm in the ^{13}C NMR. The identified results using NMR analysis conformed to the predicted structures of ARFPA and ALFPA.

3.2. Synthesis and characterization of polymer

The new polyimides (PIs) synthesis method by chemical imidization were shown in Scheme 2. First, the monomers, the ARFPA and ALFPA diamine with 6FDA as a dianhydride in stoichiometric amounts of the diamine, were dissolved in NMP, respectively, and isoquinoline was added as catalyst. The solutions were proceeded at room temperature for about 12 h to get a viscous polyamic acid (PAA) solution *via* ring-opening polyaddition. After the reaction temperature was elevated to 190 °C the mixture was stirred at that temperature for 12 h, and at the same time the water was eliminated by azeotropic distillation using toluene. Then the solution was poured into a mixed solvent consisting of methanol and distilled water in order to precipitate a fiber-like polyimide.

The molecular weights of the polyimide films, such as weight-average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC). The weight-average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (PDI) were in the range of 89.5 – 293.4×10^3 , 50.6 – 208.8×10^3 and 1.42–1.93, respectively (Table 1).

The chemical structure of the polyimide films made from the ARFPA or ALFPA monomer was estimated by FT-IR spectroscopy, as shown in Figure 2. All of the polyimide films exhibited similar absorptions typical of the imide structure. The observed

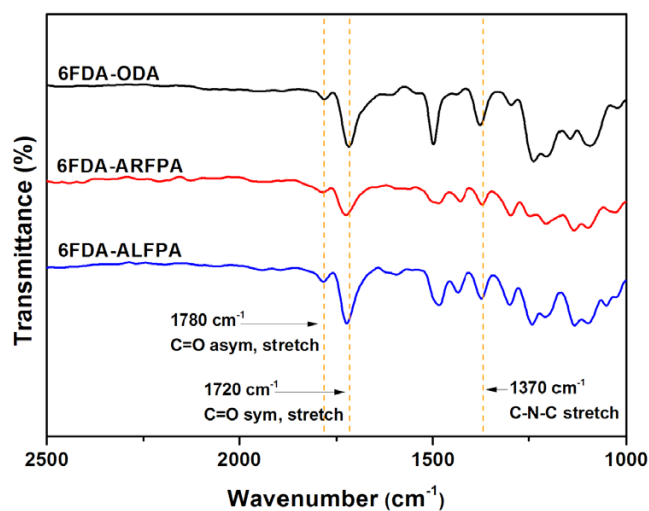


Figure 2. FT-IR spectra of polyimides.

Table 1. Molecular weights of polyimides and thermal properties of polyimide films

	$M_w (\times 10^3)$	$M_n (\times 10^3)$	PDI (M_w/M_n) ^a	T_g^b (°C)		$T_{5\%}^c$ (°C)	$T_{10\%}^c$ (°C)	Char Yield ^d (%)
				DSC	DMA			
6FDA-ODA	293.4	208.8	1.42	307	317	562	581	57
6FDA-ARFPA	105.8	54.4	1.93	314	305	528	554	54
6FDA-ALFPA	89.5	50.6	1.94	313	307	523	553	54

^aDetermined by GPC in DMF with polystyrene standards at 80 °C. ^b T_g : glass transition temperature measured by DSC and DMA. ^c $T_{5\%}$, $T_{10\%}$: temperatures at 5% and 10% loss in weight measured by TGA. ^dResidual weight % at 800 °C after TGA analysis under N_2 atmosphere.

Table 2. Solubility of the synthesized polyimide films^a

	6FDA-ODA	6FDA-ARFPA	6FDA-ALFPA
THF	+	++	++
DMF	+	++	++
Chloroform	+	++	++
DMSO	+	+	++
NMP	+	+	++
DMAc	+	+	++
Acetone	-	++	++
Ethyl Acetate	-	++	++
Toluene	-	-	-
n-Hexane	-	-	-
Methanol	-	-	-

^aSolubility level: ++, soluble at room temperature; +, soluble on heating; -, insoluble. Abbreviations: THF, tetrahydrofuran; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; DMAc, *N,N*-dimethylacetamide; NMP, *N*-methylpyrrolidone.

peaks at 1780 cm⁻¹ (carbonyl asymmetric) and 1720 cm⁻¹ (symmetric stretching) were the absorption of imide groups, and the peak at 1370 cm⁻¹ was C-N stretching vibration.

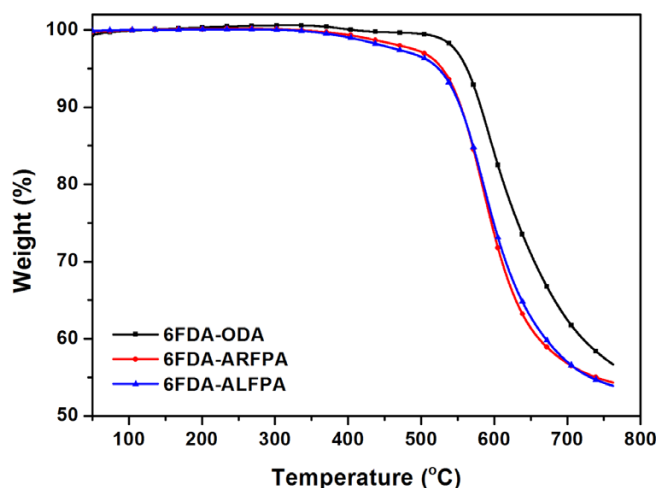
3.3. Solubility of polyimides

The solubility of the synthesized polyimide in various solvents is briefly presented in Table 2. The new PIs demonstrated excellent solubility in numerous solvents, including chloroform, *N,N*-dimethylformamide and tetrahydrofuran at room temperature. Additionally, the PIs of 6FDA-ARFPA and 6FDA-ALFPA were soluble in ethyl acetate and acetone. The solubility of the polyimides was greatly influenced by several factors, such as the ether linkage flexibility on the polymer chains, the bulkiness of the CF₃ group, and also the asymmetrical structure of the diamine monomer.

As a result, the ALFPA containing methyl groups and the bulky trifluoromethyl group in its polymer structure showed the best solubility among all the PIs. On balance, the ARFPA had a lower solubility than the ALFPA. This can be explained in the following way. Since the trifluoromethyl group of the ARFPA was located on the *ortho* position of the amine, this position interrupted the free rotation of the polymer chain and resulted in less flexibility in the polymer structure. Accordingly, the ARFPA had lower solubility than the ALFPA. Relatively speaking, the 6FDA-ODA had the lowest solubility because the 6FDA-ODA had no functional groups in the polymer structure. At the same time, all of the polyimides were practically insoluble in *n*-hexane, toluene and methanol.

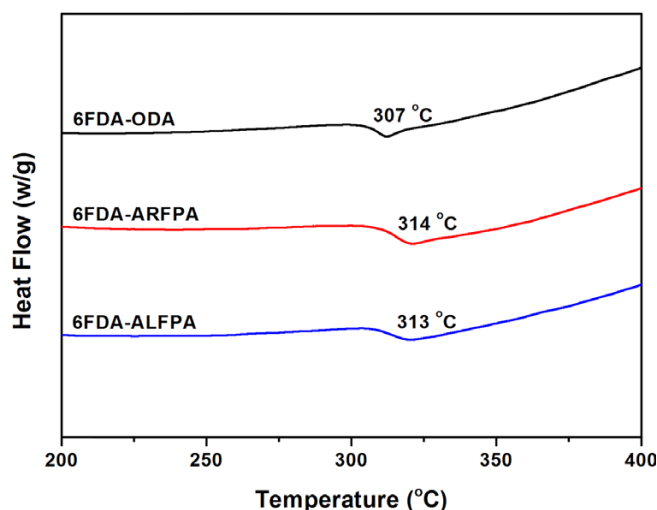
3.4. Thermal properties of polyimides

The thermal properties of the polyimides were examined by several methods, including TGA, DSC, and DMA, and the results for the polyimide films are arranged in Table 1. Commonly the TGA used to check thermal stability (Figure 3), the synthesized PI films were exposed to a maximum heat of 800 °C at a 10 °C/min heating rate in nitrogen atmosphere. All of the PI films exhib-

**Figure 3.** TGA curve of polyimides (in N₂ atmosphere, 10 °C/min).

ited a high decomposition temperature (T_d) without a change in weight up to 400 °C, and the 5% weight-loss temperature ($T_{5\%}$) was measured at around 523–562 °C. Accordingly, the char yield of the polyimide was above 54% at 800 °C. The 6FDA-ODA film in particular exhibited a high $T_{5\%}$ and $T_{10\%}$, since it had no functional groups in the polymer structure. In other words, the polymer chain structure of 6FDA-ODA was more linear than the other polyimide structures.

The curves of the thermal properties measured by DSC and DMA are presented in Figures 4 and 5, respectively. One of the important thermal properties of polyimides is the glass transition temperature (T_g), and this property was regulated by the DSC and DMA process. In more detail, the DSC measurement of the polyimide film was registered at a 10 °C/min heating rate in nitrogen atmosphere. The DMA measurement was executed in air atmosphere at a 3 °C/min heating rate with a load frequency of 1 Hz, and T_g was decided by the $\tan \delta$ curve peak. The T_g s measurement were indicated at 307–314 °C by DSC and 305–317 °C by DMA. Consequently, the glass transition temperature for each was measured at around 300 °C, and these results were influenced by the chain rigidity of the synthesized diamine

**Figure 4.** DSC curve of polyimides (in N₂ atmosphere, 10 °C/min).

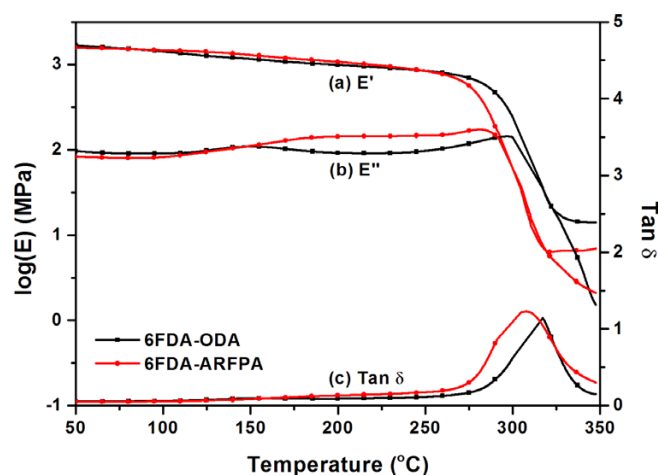


Figure 5. DMA curve of polyimides. (a) Storage modulus (E'), (b) loss modulus (E''), and (c) $\tan \delta$ (1 Hz, 3 °C/min).

structure. The free rotation of the polymer chain was inhibited by the bulky trifluoromethyl group in the diamine. Because of this, the rigidity of the polymer chain increased more than the polymer with no functional group. The polymer with the most rigid backbone structure exhibited the highest T_g . In addition, the 6FDA-ARFPA and 6FDA-ALFPA polymers exhibited higher T_g values in results of DSC measurement. The bulky trifluoromethyl groups in the polymers influenced the interactions between intra- and intermolecular chains, which caused higher T_g of the polyimide films with the CF_3 groups than 6FDA-ODA.

3.5. Optical and electrical properties of polyimides

The refractive index of the PIs was examined with a prism coupler using several laser beam wavelengths, 637 nm, 1306.5 nm, and 1549.5 nm. The graph showing the relation between the average refractive index (n_{av}) and each wavelength is provided in Figure 6. The values of the refractive index for the in-plane (n_{TE}), out-of-plane (n_{TM}) and average refractive index (n_{av}), and optical properties of the PI films are listed in Table 3. The n_{TE} , n_{TM} , and n_{av} of the PIs at 637 nm were in the range of 1.5554–1.5946, 1.5300–1.5860 and 1.5470–1.5917 respectively.

In each case, the refractive index of the polymer was influenced by various elements, including the linearity or flexibility of the polymer structure, molecular packing, and molecular geometry. In this work, the molecular packing of the polymer chains in ARFPA and ALFPA declined under the influence of the methyl groups and trifluoromethyl groups. Accordingly, the 6FDA-ALFPA polymer appeared to have the lowest refractive index (1.5470) at 637 nm. The bulky trifluoromethyl groups in

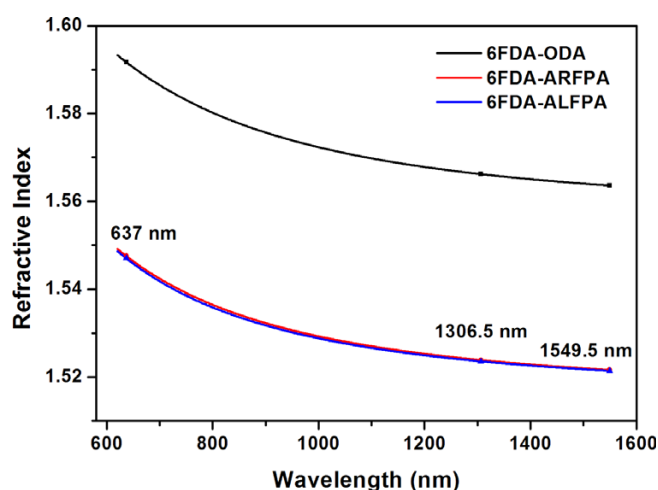


Figure 6. Refractive indices of polyimides.

the amine monomer increased the polymer free volume and interrupted the intermolecular packing, and as a result showed a high refractive index.

The dielectric constant of the synthesized polyimides was reduced, and the relatively bulky groups in the polymer structure increased, as shown in Table 3. The dielectric constant of the newly synthesized polymers were in the range of 2.633–2.787. This performance is better than those reported for typical polyimides such as Kapton® from DuPont™ (3.2). There are several possible reasons for the reduction in the dielectric constant. The dielectric constant depends on hydrophobicity, polarizability and is inversely proportional to the structural free volume of the polymer. For this reason, the polymers which contained the asymmetric diamine monomer trifluoromethyl group, such as 6FDA-ARFPA and 6FDA-ALFPA exhibited a decreased dielectric constant compare to commercial polyimide films. The low dielectric constant can be attributed to the asymmetrical trifluoromethyl groups, which induce a reduction in the intermolecular force and packing of the polymers of the polymer backbone. These results were confirmed that the polyimides containing asymmetric functional groups elevated free volume and loosened polymer intermolecular packing, which subsequently led to the reduction in dielectric constant.

4. Conclusions

In summary, a method for synthesizing polyimide using new diamines was demonstrated. The new diamines were ARFPA and ALFPA containing *ortho* or *meta*-position trifluoromethyl groups in the phenylene ring. The ARFPA and ALFPA were polymerized with 6FDA aromatic dianhydrides, using the gen-

Table 3. Optical properties of polyimide films

	λ_{cutoff}^a (nm)	Refractive Index and Birefringence at 637 nm ^b			Dielectric Constant ^c (ϵ')	n_{∞}^d	D^e ($\times 10^4$)
		n_{TE}	n_{TM}	n_{av}			
6FDA-ODA	394	1.5946	1.5860	1.5917	2.787	1.5580	1.3670
6FDA-ARFPA	349	1.5558	1.5309	1.5475	2.634	1.5164	1.2636
6FDA-ALFPA	356	1.5554	1.5300	1.5470	2.633	1.5162	1.2488

^aCut-off wavelength measured by UV-vis. ^bMeasured by prism coupler at 637 nm. ^cDielectric constant measured by formula ($\epsilon = 1.1n_{av}^2$). ^dRefractive index at the infinite wavelength. ^eDispersion coefficient of refractive index fit by the Cauchy formula ($n_{\lambda} = n_{\infty} + D\lambda^{-2}$).

eral chemical imidization method. The synthesized polyimides designated ALFPA, which contained bulky methyl groups and trifluoromethyl groups in the polymer structure, exhibited the best solubility among all the synthesized PIs. The glass transition temperatures (T_g) of the synthesized polyimide films were found to be about 307–314 °C. The decomposition temperatures ($T_{d10\%}$) were measured at 553–581 °C. In particular, the synthesized polymers derived from ARFPA and ALFPA, containing bulky trifluoromethyl groups, had lower rigidity than the other polymers with no functional groups. In addition, the refractive index of 6FDA-ALFPA at 637 nm was 1.5470. These enhanced optical properties were produced by the methyl and trifluoromethyl groups on the diamine structure, these structures led to less intermolecular stacking and chain rigidity. The dielectric constant of the synthesized 6FDA-ALFPA was 2.633. This low dielectric constant was attributed to the trifluoromethyl group which caused the asymmetric structure, which resulted in looser intermolecular packing of the polymer and elevated free volume. This design of molecule provides a new approach to the synthesis of advanced organic materials.

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