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Synthesis and characterization of highly-fluorinated colorless polyimides derived from 4,4'-((perfluoro-[1,1'-biphenyl]-4,4'-diyl) bis(oxy))bis(2,6-dimethylaniline) and aromatic dianhydrides

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ABSTRACT

The authors report the synthesis and characterization of a polyimide (PI) series derived from 4,4'-((perfluoro-[1,1'-biphenyl]-4,4'-diyl)bis(oxy))bis(2,6-dimethylaniline) (8FBPODMA). The 8FBPODMA monomer containing a perfluorobiphenyl group with two 2,6-dimethylaniline units connected by an ether bond was synthesized and polycondensed with several aromatic dianhydrides, including 4,4'biphthalic anhydride (BPDA), 4,4'-oxydiphthalic anhydride (ODPA), pyromellitic dianhydride (PMDA), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), by the traditional two-step imidization procedure. All PIs shows high optical transparency, higher than 80% at 500 nm for a thickness of *ca*. 10 μ m and good thermal properties. The thermal decomposition temperatures (T_{10x}) of the PIs are in the range of 507–527 °C and the glass transition temperatures (T_g) are in the range of 280–345 °C. In addition, the PIs have low refractive indices because of their high fluorine contents. In particular, 8FBPODMA–6FDA shows a very low refractive index (1.5389) and a low birefringence (0.0054) at 637 nm.

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1. Introduction

Aromatic polyimides (PIs) have been developed for a wide range of applications, including automobile, aviation, aerospace, and electronic industries, owing to their excellent chemical resistance, thermal stability, and electrical properties [1–10]. However, polyimides which have strong absorption in the visible region, a deep reddish color, and a high dielectric constant, are the main obstacles that limit any optoelectronic and microelectronic applications [11,12]. This is because PIs have not only conjugated aromatic structures but also form charge transfer complexes between electron donor and electron acceptor moieties in the polymer chains [13–15]. To overcome these problems of PIs, many effort has been focused on synthesis of Low-k and colorless PIs, without deterioration of the resulting PIs [16–20]. There are several approaches to prepare colorless PIs, including the introduction of flexible and unsymmetrical linkages or noncoplanar monomers and bulky or fluoro-containing substituents [21,22]. Fluorination is one of the most widely used methods to reduce the dielectric constant while lowering moisture absorption and improving solubility and optical properties [23-26]. However, the aforementioned procedure results in a decrease of packing density of the polymers that may reduce thermal properties. Thus, a breakthrough in the tradeoff between solubility/transparency and positive properties such as high thermal properties has remained challenging [27]. The introduction of aromatic diamine containing methyl groups at the ortho position is common and is considered an effective method to improve optical transparency and thermal properties, not only because the introduction of methyl groups at the ortho position of aromatic diamine can induce a twisted structure between C-N imide bonds which prevents formation of an intermolecular charge-transfer complex (CTC), but also because methyl groups at the ortho position of aromatic diamine which can prevent free rotation of the C–N imide bond, which is effective in increasing the glass transition temperature [28]. Moreover, incorporation of fluorine atoms which have low electric polarity and high electronegativity can result in low refractive index, dielectric constant, optical loss, and moisture absorption characteristics for many applications, such as electronic coating and in electronic devices [29–31]. In particular, to reduce dielectric properties and optical





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opaqueness is necessary for application to transparent optoelectronics.

In this study, we design a new diamine which contains eight fluorine atoms and methyl groups at the ortho position. It was expected that the methyl groups at the ortho position of the diamines would enhance glass-transition temperature (T_g) while improving optical transparency because the methyl groups can prevent intermolecular packing and free rotation between C–N imide bonds in the polymer chains. Moreover, the highly fluorinated diamine can endow a low refractive index and low-dielectric constant for the resulting PIs. The structure–property relationships, dielectric constant, and thermal properties of the polyimides are investigated in detail.

2. Experimental section

2.1. Measurements

¹H (600 MHz), ¹³C (150 MHz) NMR spectra were recorded on an Agilent 600 MHz Premium COMPACT NMR spectrometer. ¹H and ¹³C NMR spectra were obtained by using tetramethylsilane (TMS) as an internal standard and CDCl₃ as a solvent. Elemental analysis and mass spectrum analysis were performed at the Center for University-wide Research Facilities at Jeonbuk National University. The surface functional groups of the PI films were analyzed by using a Fourier transform-infrared spectroscopy (FT-IR Spectrophotometer, Nicolet IS10, USA), Thermogravimetric analysis (TGA) was carried out with a TA 50 (TA Instruments, USA) under nitrogen gas flow at a heating rate of 10 °C/min. Glass transition temperatures of the PI films were measured by DSC analysis with a Q 50 (TA Instruments, USA) under nitrogen gas flow at a heating rate of 10 °C/min. Dynamic mechanical thermal analyses (DMA) were evaluated from PI films (30 mm length, 10 mm wide, and ca. 50 µm thickness) on a DMA (TA Instruments, DMA Q800, USA) at a heating rate of 3 °C/min with a load frequency of 1 Hz in air. The UV-visible spectra were recorded on a JASCO V-670 spectrometer. Inherent viscosities of the PAA precursors in NMP solution (0.5 g/ dL) at 30 °C were measured using a Malvern Y510 viscometer. The densities of the films were measured by digital readout density gradient column (Ray-Ran, UK). The out-of-plane ($n_{\text{TM}} = n_{xy}$) and in-plane $(n_{\text{TE}} = n_z)$ refractive indices of PI films were measured with a Metricon PC-2000 prism coupler with a He-Ne laser light source (wavelength: 637, 1306.5, and 1549.5 nm). The birefringence (Δn) was calculated to measure the difference between n_{TE} and n_{TM} . The average refractive index was calculated according to the equation: $n_{\text{AV}} = [(2n_{\text{TE}}^2 + n_{\text{TM}}^2)/3]^{1/2}$. The dielectric constant (ε) was calculated by the estimated n_{AV} according to Maxwell's equation: $\varepsilon = n^2$.

2.2. Materials

Decafluorobiphenyl, 4-amino-3,5-xylenol, and 4-aminophenol were obtained from TCI, and used without further purification. Aromatic dianhydrides, 4,4'-biphthalic anhydride (BPDA), 4,4'-oxydiphthalic anhydride (ODPA), pyromellitic dianhydride (PMDA), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were purchased from TCI, and used after sublimation. Other commercially available chemicals were used as received. Dime-thylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) were purified by a two-column solid-state purification system (Glass-contour System, Joerg Meyer, Irvine, CA). All reactions were performed under an argon atmosphere.

2.3. Monomer synthesis

2.3.1. 4,4'-((Perfluoro-[1,1'-biphenyl]-4,4'-diyl)bis(oxy))bis(2,6dimethylaniline) (8FBPODMA)

Decafluorobiphenyl (7.83 g, 23.4 mmol), 4-amino-3,5-xylenol (6.76 g, 49.3 mmol), K₂CO₃ (5.38 g, 38.9 mmol), and DMF (50 ml) were mixed, and the solution was stirred at 120 °C overnight. Following concentration of the solution by evaporation, the crude products were then diluted with methyl tert-butyl ether and washed with NaHCO₃ (aq) and brine. After drying over MgSO₄, the products were concentrated. After purification by flash chromatography on silica gel ($12:1 = CHCl_3:EtOAc$, $R_f = 0.35$) and recrystallization in ethanol, the compound **8FBPODMA** (11.5 g, 20.3 mmol, 86.7%) was obtained as a white powder. ¹H NMR $(600 \text{ MHz}, \text{CDCl}_3)$: $\delta = 6.70$ (s, 4H, Ar–H), 3.48 (s, 4H, –NH₂), 2.18 (s, 12H, Ar–CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 149.21, 145.59,$ 143.87, 142.63, 140.90, 139.31, 136.58, 123.00, 116.10, 101.85, 17.88 ppm. MS (p-ESI): m/z: calcd for $C_{28}H_{20}F_8N_2O_2 + H^+$: 569.15; found: 569.10. Elemental analysis: calcd for C₂₈H₂₀F₈N₂O₂: C 59.16, H 3.55, N 4.93; found: C 59.10, H 3.62, N 4.85.

2.3.2. 4,4'-((Perfluoro-[1,1'-biphenyl]-4,4'-diyl)bis(oxy))dianiline (8FBPOA)

Similarly to the synthetic procedure of **SFBPODMA**, the **SFBPOA** was synthesized from decafluorobiphenyl (2.00 g, 5.99 mmol), 4aminophenol (1.37 g, 12.6 mmol), K₂CO₃ (1.08 g, 7.81 mmol), and DMF (10 ml) as a yellow solid (2.25 g, 4.40 mmol, 73.5%). ¹H NMR (600 MHz, CDCl₃): δ = 6.90 (d, *J* = 8.7 Hz, 4H), 6.66 (d, *J* = 8.7 Hz, 4H), 3.61 (s, 4H) ppm. MS (API+): *m/z*: calcd for C₂₄H₁₂F₈N₂O₂ + H⁺: 513.08; found: 512.99. Elemental analysis: calcd for C₂₄H₁₂F₈N₂O₂: C 56.26, H 2.36, N 5.47; found: C 56.26, H 2.47, N 5.34.

2.4. Polymer synthesis

The PI films were fabricated by a conventional two-step method. First, a NMP solution of the diamine monomer and a dianhydride was stirred for 1 day under inert atmosphere to obtain viscous poly(amic acid) (PAA) precursor. Second, the prepared PAA solution was cast on the several substrates and thermally annealed at 150 °C for 30 min, 200 °C for 30 min, 250 °C for 1 h. Subsequently, the films were used, as is, in optical measurements and thermal analysis after removal from substrates. The monomer, **8FBPODMA**, was polymerized with 4 kinds of dianhydrides, PMDA, BPDA, ODPA, and 6FDA, and **8FBPOA** was reacted only with PDMA. The polyimides, 8FBPODMA-PMDA, -BPDA, -ODPA, -6FDA, and 8FBPOA-PDMA were named PMDA, BPDA, ODPA, 6FDA, PMDA', respectively. For preparation of the PAA solution, the following polymerization method was used. 8FBPODMA (0.50 g, 0.88 mmol) and NMP (2.00 ml) were put into a 10 ml flask under an argon atmosphere. After the monomer was dissolved by stirring, dianhydride, 6FDA (0.39 g, 0.88 mmol), was added in the flask. Additionally, NMP (1.47 ml) was added in order to adjust the monomers content to 20 wt%. The mixture was stirred at room temperature for 1 day to obtain a viscous PAA solution. Other PAA solutions were prepared by similar procedure to **6FDA** and their inherent viscosities were in the range of 0.26–1.26 (measurement condition: NMP (0.5 g/dL) solution, 30 °C).

3. Results and discussion

3.1. Synthesis and characterization of monomer

The novel diamine monomer, 4,4'-((perfluoro-[1,1'-biphenyl]-4,4'-diyl)bis(oxy))bis(2,6-dimethylaniline) (**8FBPODMA**), containing a perfluorobiphenyl group having two 2,6-dimethylaniline units connected by an ether bond was synthesized (Scheme 1). In addition, 4,4'-((perfluoro-[1,1'-biphenyl]-4,4'-diyl)bis(oxy))dianiline

(8FBPOA) was prepared for the fabrication of a reference PI that is a known compound, but the optical properties of its resulting-PI have been not properly investigated [32]. The monomers were synthesized by the similar reaction of decafluorobiphenvl and aminophenol derivatives. The structural analysis of the monomers was carried out by ¹H and ¹³C NMR spectroscopies, mass measurement, and elemental analysis. In particular, the remarkable differences seen between the two types of the monomers are due to whether there are the methyl substituents around the amine or not. We believe this is the key determinant for inhibition of the molecular packing in the resulting-PI that promotes the anisotropy of chain arrangement, the decrease of molecular free-volume, and the generation of the intermolecular charge transfer (CT) complexes. In other words, the additional methyl groups of **8FBPODMA** are able to induce the improvement of optical properties, including low birefringence, low refractive index, and high transparency of the resulting-PI.

The ¹H and ¹³C NMR spectra of **8FBPODMA** measured in the CDCl₃ solution and the all peaks are assigned (Fig. 1). In ¹H NMR spectrum, the three peaks is observed at 6.71, 3.49, 2.19 ppm. The peak at 6.71 ppm is assignable to aromatic protons and the peak of the benzylic protons is shown at 2.19 ppm. In addition, the broad singlet peak of the amine-protons is observed at 3.49 ppm. In ¹³C NMR spectrum, the ten signals of aromatic carbons are observed in the range of 101–150 ppm due to the carbons bonded to fluorine atoms having split signals. In addition, the peak of the benzylic carbons is shown at 17.9 ppm. In NMR studies, all the observed peaks show good correspondence with the expected structure. In addition, mass measurement and elemental analysis supported that the desired compound was synthesized.

3.2. Preparation and characterization of polyimides

Polyimide films were fabricated by the typical two-step thermal imidization procedure (Scheme 2) [33]. First, the PAA precursors were synthesized by polymerization with diamine, **8FBPOA** or **8FBPODMA**, and dianhydride monomers such as 6FDA, PMDA, BPDA, ODPA in NMP as shown in Scheme 2. Second, the prepared PAA solutions were casted or spin-coated on silicon wafers or quartz plates to adjust the film thickness. Finally, the substrates were annealed by gradual heat treatment at 150 °C for 30 min, 200 °C for 30 min, 250 °C for 1 h to obtain the resulting PI films under inert atmosphere. The degrees of polymerization were determined by measuring inherent viscosities of the PAA and their



Fig. 1. NMR spectra of **8FBPODMA** (a) ¹H NMR (b) ¹³C NMR.

inherent viscosities were in the range of 0.26–1.26 at 30 °C in 0.5 g/ dL NMP solution (Table 1).

Thermal conversions of PAAs to PIs were tracked by FT-IR spectroscopy (Fig. 2). All PI films show a similar waveform and the characteristic absorption of the PIs originated from imide moieties. The absorption peaks nearby 1780 cm⁻¹, 1720 cm⁻¹, and 1370 cm⁻¹ are assigned to C=O symmetric stretching, C=O asymmetric stretching, and C–N–C stretching vibration, respectively. These typical peaks of imide groups clearly indicate that the PAAs are converting to the expecting PIs.



[8FBPODMA]

Scheme 1. Synthesis of **8FBPOA** and **8FBPODMA**.



Scheme 2. Synthesis of polyimides.

 Table 1

 Inherent viscosities of PAA and thermal properties of resulting-PIs.

Polymer	$[\eta]_{inh}^{a} [dl/g]$	$T_{\rm g}^{\rm b} [^{\circ}{\rm C}]$		$T_{5\%}^{c} [^{\circ}C]$	$T_{10\%}^{c} [^{\circ}C]$	Char yield ^d [%]
		DSC	DMA			
6FDA	0.72	286	303	481	507	50
PMDA	0.94	345	363	478	518	53
BPDA	1.26	300	324	484	522	55
ODPA	0.26	280	302	480	527	53
PMDA'	0.72	338	-	559	592	48

^a Inherent viscosity of PAAs in 0.5 g/dL NMP solution at 30 °C.

^b T_{g} : glass transition temperature.

^c $T_{5\%}$, $T_{10\%}$: temperatures at 5% and 10% weight loss, respectively.

 $^{\rm d}$ Remaining weight percentage after TGA analysis at 800 $^\circ \text{C}$ under N_2 atmosphere.



Fig. 2. FT-IR spectra of PI films.

3.3. Thermal properties

The thermal properties of the PIs were investigated by ThermoGravimetric Analysis (TGA), Differential Scanning Calorimetry

(DSC), and Dynamic Mechanical Analysis (DMA). Analysis results are summarized in Table 1. First, the thermal stabilities and decomposition behaviors of the PIs were investigated by TGA (Fig. 3). The PIs synthesized from **8FBPODMA** exhibited similar thermal decomposition behavior. However, the pyrolysis of PMDA' begins at slightly higher temperatures and the weight loss is more rapid than for other PIs. All PIs did not exhibit any weight loss up to 400 °C and the 5%-weight-loss temperatures ($T_{5\%}$) of **PMDA** that has lowest $T_{5\%}$ among the PIs is 478 °C. The $T_{5\%}$ s and $T_{10\%}$ s of the PIs synthesized from **8FBPODMA** are in the range of 478–484 °C and 507–527 °C, respectively. In addition, their char yields after pyrolysis at 800 °C are the more than 50%. The PIs derived from **8FBPODMA** show thermal stability of a similar degree to Kapton[®], although that was slightly inferior compared to PMDA'. The superior thermal stability of PMDA' might be originated from stabilization effect of intermolecular stacking that would be suppressed in the PIs derived from 8FBPODMA.

Next, the glass transition temperatures (T_{gs}) were measured by DSC (Fig. 4) and DMA (Fig. 5). The DSC measurements were



Fig. 3. TGA curves of PI films (in nitrogen atmosphere, 10 °C/min).

accomplished using a heating rate of 10 °C/min in a nitrogen atmosphere and the DMA were recorded at a heating rate of 3 °C/min with a load frequency of 1 Hz in air. The T_g data are summarized in Table 1. The T_{gs} were determined from the peak temperature of the tan δ plot in DMA measurement and the values are slightly higher than those estimated by DSC, but the trend shows a good correlation in both. In addition, the T_gs of the PIs derived from **8FBPODMA** were estimated by both of DSC and DMA in the increasing temperature order ODPA < 6FDA < BDPA < PMDA. The T_g values measured from DSC and DMA are in the range of 286-345 °C and 302–363 °C, respectively. With increased rigidity of dianhydrides, the resulting PIs have a correspondingly more rigid polymer mainchain [34]. Interestingly, in comparison with the PIs synthesized from **8FBPOA**, **PMDA** has high T_g than **PMDA**' and the T_g of **6FDA** is higher than that of the PI prepared from **8FBPOA** and 6FDA [32]. These improvements in T_g might be due to the ortho-substituted methyl groups on the diamine monomer reducing the flexibility of the chain and increase the chain stiffness in the crystalline state.

3.4. Optical properties

All PIs were visually observed as a light yellow except for PMDA'. In particular, 6FDA has a substantially transparent color. The relatively transparent color of PI films prepared from **8FBPODMA** is due to the reducing effect of intermolecular stacking by orthosubstituted methyl groups of the diamine. The UV-vis spectroscopy was carried out to investigate the precise optical transparency of the synthesized PI films (Fig. 6 and Table 2). The thickness of PI films on guartz plate was adjusted to ca. 10 μ m by the control of a casting rate for UV-vis measurement. The cutoff wavelength (λ_{cutoff}) is in the increasing wavelength order 6FDA < ODPA < PMDA = PMDA ' < **BDPA**. The λ_{cutoff} of **GFDA** is the shortest wavelength, which results in the conclusion that **6FDA** is the most transparent among the synthesized PIs. Because BPDA has a more the planar structure than the others, its λ_{cutoff} is shown to be the most red-shifted. In addition, the transmittances of the PI films measured at 500 nm were in the order of 94.2% (6FDA), 85.9% (ODPA), 83.1% (BPDA), 81.6% (PMDA), 66.8% (PMDA'). The transmittance values show a similar trend with the order of λ_{cutoff} , except for **PMDA**'. This result could be explained by differences in the molecular structure of PIs. While the PI films synthesized from 8FBPODMA, 6FDA, ODPA, PMDA, and BDPA, have ortho-substituted methyl groups on the amine that would inhibit the stacking of polymer chain and increase steric hindrance to interfere with formation of the CT complex, and because PMDA' does not have the substituents it would be tinged with yellow in the procedure of thermal imidization. After all, considering that they are aromatic



Fig. 4. DSC curves of PI films (in nitrogen atmosphere, 10 °C/min).



Fig. 5. DMA curves of PI films (1 Hz, 3 °C/min): (a) storage modulus (E'), (b) loss modulus (E''), (c) tan δ .



Fig. 6. Wavelength dependent transmittance of PI films (film thickness: ca. 10 µm).

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Optical	properties	of PI	films.

Polymer	Fluorine content [%]	$\lambda_{cutoff} a [nm]$	Transmittance ^b [%]
6FDA	28.28	310	94.2
PMDA	20.25	352	81.6
BPDA	18.39	362	83.1
ODPA	18.04	339	85.9
PMDA'	21.82	352	66.8

^a Cut-off wavelength.

^b Transmittance at 500 nm and film thickness: *ca.* 10 μm.

polyimides, the PI films derived from **8FBPODMA** exhibit excellent transparency in visible region. In particular, **6FDA** achieves considerably high transparency without any bleaching process.

The refractive indices of the PI films were measured by prism coupling method to investigate the effects of fluorine atoms on the refractive index, because of the possibility of the PIs having a low polarizability due to their high fluorine atom content [35]. The inplane (n_{xy}), out-of-plane (n_z), average refractive indices (n_{av}), inplane/out-of-plane birefringences (Δn), refractive indices at the infinite wavelength (n_{∞}), and dispersion coefficients of refractive index (D) of the PI films (thickness < 10 µm) are summarized in Table 3. The refractive indices of the PIs are in the range of 1.5389–1.6168 measured at 637 nm and those values are significantly lower than that of a conventional PI, such as Kapton [PMDA-ODA] and Upilex-S [BPDA-PDA] [33]. In addition, the n_{av} of the PIs at 637 nm are in the order of **6FDA** < **PMDA** < **ODPA** < **BPDA** < **PMDA**', which tended to match the high order of fluorine content except for **PMDA**'. Especially, **6FDA** containing the fluorine atoms on the

Table 3	
Refractive indices and densities of PI films.	

Polymer	Density at 23 °C [g/ml]	Refractive inc	Refractive indices ^a					
		n _{xy}	nz	n _{av}	Δn	$n_{\infty}^{\mathbf{b}}$	D^{b} [×10 ⁴]	
6FDA	1.4225	1.5407	1.5353	1.5389	0.0054	1.5193	0.7912	
PMDA	1.3869	1.5818	1.5666	1.5767	0.0152	1.5459	1.2033	
BPDA	1.3841	1.5983	1.5917	1.5961	0.0066	1.5554	1.6140	
ODPA	1.3824	1.5868	1.5818	1.5851	0.0050	1.5546	1.2546	
PMDA'	1.4887	1.6314	1.5872	1.6168	0.0442	1.5911	1.0157	

^a Measured at 637 nm, see Section Measurements.

^b n_{∞} is refractive index at the infinite wavelength and *D* is dispersion coefficient of refractive index obtained from the fitting by the simplified Cauchy formula $(n_{\lambda} = n_{\infty} + D\lambda^{-2})$.

dianhydride unit exhibited extremely low refractive index and the $n_{\rm av}$ value is 1.5389. In general, a refractive index decreases in the film of a low density because a low density causes large free volume. However, there was no significant difference in densities of the synthesized PIs compare to those of commercial PIs. These result means that low refractive indices of the PI films are achieved by the low polarizability of fluorine atom. Hongham et al. reported a series of PIs of low refractive indices synthesized from 6FDA and a highly fluorinated diamine [36]. However, because the resulting-PAA solutions of Hongham's PIs had an extremely low viscosity because the polycondensation had been inhibited by steric influences and the electronic effects of excessively substituted fluorine on diamine monomers, they had no choice but to prepare the PI films by solid-state chain extension methods. By contrast, **6FDA** is producible using the traditional PI preparation method. In addition, 6FDA has a similar refractive index despite of a lower fluorine content compared to Hongham's PIs. In the comparison between PMDA and PMDA' synthesized from the same dianhydride, **PMDA** has lower n_{av} and Δn than those of **PMDA**'. The *ortho*substituted methyl groups of 8FBPODMA make the resulting PI have a large molar volume which causes structural suppression of intermolecular packing. As a result, **PMDA** exhibits lower n_{av} and Δn than **PMDA**' and the resulting-PIs of **8FBPODMA** have relatively low n_{av} and Δn compared to other PIs. In particular, the low birefringence values in the PI films are observed in the range of 0.0054-0.0152, which have been achieved by low optical anisotropy due to their large free volume due to substituents, such as ortho-substituted methyl groups and perfluorinated phenylene units.

The wavelength dispersions of the average refractive indices measured at 637, 1306.5, and 1549.5 nm of the PI films (Fig. 7). In addition, the solid lines are fitted with the simplified Cauchy formula. The infinite refractive indices (n_{∞}) of the PIs are in the range



Fig. 7. Wavelength dispersion of the refractive indices of PI films.

of 1.5193–1.5911 and the order of the values is same as that measured at specific wavelengths. In addition, all PIs show low *D* values because there is a linear relationship between n_{∞} and *D* [37]. In particular, **6FDA** has the lowest n_{∞} and *D* value due to the effect by large free volume of their highly-fluorinated backbone.

4. Conclusions

We synthesized a novel diamine monomer, 8FBPODMA, containing a perfluorobiphenyl group containing two 2,6dimethylaniline units connected by an ether bond. A series of PIs were prepared from **8FBPODMA** and the aromatic dianhydrides PDMA, ODPA, BPDA, and 6FDA by a classical two-step thermal imidization. All PIs exhibited high thermal stability, i.e. T_{g} (>280 °C) and $T_{10\%}$ (>500 °C). In comparison with the PIs derived from **8FBPOA**. the PIs from **8FBPODMA** are more optically transparent and have lower refractive indices and birefringences due to structural hindrance of intermolecular packing by their orthosubstituted methyl groups. In particular, the PI from 8FBPODMA and 6FDA are almost completely visually transparent (Transmittance: 94.2% at 500 nm) and exhibited a very low refractive index (1.5389) and birefringence (0.0054) at 637 nm, which originate from steric hindrances and the atomic effect of a highlyfluorinated structure. These PIs are good candidates as a substrate for advanced optoelectronics. In addition, this research provides a novel strategy from the perspective of molecular design for optoelectronic applications.

Author contributions

Hyeonuk Yeo and Nam-Ho You contributed equally to this work.

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