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ARTICLE

## Novel soluble poly(ether imide)s with trifluoromethyl and chloride pendant groups for optical materials

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A new bis(ether dianhydride) monomer [4,4'-(2-(3'-trifluoromethyl-4'-chlorophenyl)-1,4-phenylenedioxy)-diphthalic anhydride (3)] was designed and prepared through a multistep reaction sequence. The new monomer 3 was polymerized with typical diamines, such as PDA, ODA, APB, 6FAPB and 9F-Cl-APB, using a two-step chemical imidization method to obtain the corresponding poly(ether imide)s (PEIs) (4a-4e). All the PEIs had high glass transition temperatures, excellent thermal stability, good solubility, and could be made into transparent and flexible films. The cast films showed UV-Vis absorption edges at 346-369 nm, low birefringences of 0.0052-0.0131, low dielectric constants of 2.69-2.80, and low water uptakes of 0.30-0.52 wt%. Based on the characterization results, a series of optical materials with tunable refractive indices were obtained by copolymerization in the range of 1.6217-1.5523 at 650 nm.

### 1 INTRODUCTION

2 Aromatic polyimides (PI) are widely known as high performance materials originally developed for the aerospace industry.  
3 High thermal stability combined with chemical resistance and excellent electrical and mechanical properties make PIs attractive  
4 as versatile high performance materials for a variety of applications such as composites, coatings, electric materials and  
5 membranes.<sup>1,2</sup> High optical transparency is one of the most desirable properties of PI materials for a wide diversity of  
6 applications like flexible solar cell arrays, or micro-optical devices in the field of displays and waveguides.<sup>3-7</sup> Despite their  
7 widespread use, their rigid backbones and strong intermolecular interactions restrict their applications in some fields. Most of  
8 them have high melting or softening temperatures, and limited solubility in most organic solvents. Another shortcoming is the  
9 pale yellow or deep brownish-yellow color of PI films due to their highly conjugated aromatic structures and the formation of  
10 intermolecular charge-transfer complexes (CTC) and electronic polarization interactions.<sup>8,9</sup>  
11 To solve these problems, considerable research effort has been focused on the synthesis of soluble and transparent PIs in a fully  
12 imidized form without deterioration of their excellent properties. In the past decades, many attempts have been made to  
13 improve the optical properties of PIs by incorporating fluorine, chlorine or sulfone groups, introducing unsymmetrical and bulky  
14 pendent units, as well as adopting alicyclic moieties in the polymer structure.<sup>10-14</sup> Therefore, the development of soluble PIs has  
15 attracted major interest in the research of aromatic polymers. Fortunately, progress has been achieved with considerable efforts  
16 on improving the capacity and the solubility of PIs through structure design, modification of aromatic dianhydride and diamine  
17 monomers.<sup>15,16</sup> Among many approaches, the incorporation of trifluoromethyl (CF<sub>3</sub>) groups into polymer chains is considered an  
18 effective means of realizing soluble and transparent PIs without deteriorating their excellent properties, not only because the  
19 bulky CF<sub>3</sub> groups disturb the interactions and chain packing between the polymer chains, but also because the C-F bond is one of  
20 the strongest single bonds. Thus, this method can optimize the trade-off between processability and color properties of aromatic  
21 PIs.<sup>17-22</sup>

22 At present, most dissoluble aromatic PIs containing fluorine were prepared by using different kinds of aromatic diamines  
23 containing fluorine rather than fluorinated aromatic dianhydrides, except for 6FDA, which is currently commercially available.<sup>23-</sup>  
24 <sup>26</sup> However, the widespread applications and commercialization of 6FDA are also hampered by the synthetic procedure. Our  
25 previous research on fluorinated aromatic PIs demonstrated that the incorporation of bulky trifluoromethyl groups into diamines  
26 and dianhydrides resulted in an enhanced solubility and a lower dielectric constant, as well as an improved optical  
27 transparency.<sup>27-30</sup>

28 Besides the carbon-fluorine bonds (C-F bonds), the introduction of carbon-chlorine bonds (C-Cl bonds) can also improve the  
29 polymer optical properties. Because the C-Cl bond is reported to have low loss at 1310 and 1550 nm (optical telecommunication

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region) like the C-F bond based on the calculation, and has larger polarizability than the C-F bond, incorporation of the C-Cl bond into the polymer backbone may yield good refractive index controllability without additional optical loss.<sup>31,32</sup> In addition, the introduction of bulky moieties (CF<sub>3</sub> and Cl groups) into the polymers would increase the chain-packing distances and decreased intermolecular interactions further. It has been demonstrated that the introduction of bulky pendant groups into polyimide backbones resulted in enhanced solubility and optical transparency. Thus, chlorofluorinated polyimides for copolymerization for controlling the refractive index can be a potential candidate for optical application.

As part of our continuing efforts to gain colorless and soluble PIs with high thermal stability and a wide application potential in optoelectronics, novel bis(ether dianhydride) [4,4'-(2-(3'-trifluoromethyl-4'-chlorophenyl)-1,4-phenylenedioxy)-diphthalic anhydride (3)] was designed and prepared. A series of soluble poly(ether imide)s (PEI) (4a-4e) were prepared by polycondensation of bis(ether dianhydride) (3) with various aromatic diamines (a-e). From the characterization results, the prepared PEIs exhibited good solubility, excellent thermal and mechanical properties, low water uptake, low dielectric constants and high optical properties, including high optical transparency, low birefringence, and low NIR absorptions loss at the communication windows. Moreover, a series of PEIs optical materials with tunable refractive indices were obtained by copolymerization.

## Experimental

### Materials

The (3-fluoromethyl-4-chlorophenyl)-1,4-hydroquinone was synthesized according to the literature.<sup>33</sup> 4-Nitrophthalodinitrile (TCI), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, Aldrich) and acetic anhydride were obtained from commercial sources used as received. *N,N*-dimethylformamide (DMF, Aldrich), *N,N*-dimethylacetamide (DMAc, Aldrich) and pyridine (Py, Aldrich) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) (TCI), *p*-Phenylenediamine (PDA) (TCI), 4,4'-oxydianiline (ODA) (TCI) and 1,4-bis(4-aminophenoxy)benzene (APB) (TCI) were used without further purification. 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) and 1,4-(4-amino-2-trifluoromethylphenoxy)-2-(3'-trifluoromethyl-4'-chlorophenyl)benzene (9F-Cl-APB) was synthesized in our laboratory according to the previously reported.<sup>34</sup>

### Measurements

Gel permeation chromatograms (GPC) were obtained on a Waters 410 instrument with *N,N*-dimethylformamide (DMF) as an eluent at a flow rate of 1 mL min<sup>-1</sup> using polystyrene as a standard. FTIR spectra were measured on a Nicolet Impact 410 Fourier transform infrared spectrometer. <sup>1</sup>H NMR spectra were recorded on a Bruker 510 NMR spectrometer (500 MHz) with tetramethyl silane as a reference. Elemental analysis was performed on an Elemental Analyses MOD-1106. Inherent viscosity was determined on an Ubblohe viscometer in thermostatic container with the polymer concentration of 0.5 g dL<sup>-1</sup> in DMAc at 25 °C. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 821<sup>e</sup> instrument at a heating rate of 20 °C min<sup>-1</sup> under nitrogen. Thermal gravimetric analyses (TGA) were determined in nitrogen atmosphere using a heating rate of 10 °C min<sup>-1</sup> and polymers were contained within open aluminum pans on a PERKIN ELMER TGA-7. The refractive indices of the polymer were studied using a Gaertner L116B spectroscopic ellipsometer. The birefringences of the polymer films, at the 650 nm wavelength, were determined from coupling angles of TE (transverse electric) of TM (transverse magnetic) optical guided modes with a gadolinium gallium garnet (GGG) prism. UV-visible transparency was measured by a Shimadzu UV 2501-PC spectrophotometer. Wide-angle X-ray diffraction (WAXD) measurements were made at room temperature using a Rigaku/max-rA diffractometer equipped with a Cu Kα radiation source. The mechanical tests in tension were carried out using a SHIMADZU AG-I at a constant crosshead speed of 10 mm min<sup>-1</sup>. The equilibrium moisture absorption was determined by weighing the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days. The photographs of the PIs films were taken by Canon EOS 6D.

### Monomer Synthesis

As shown in Scheme 1, the bis(ether dianhydride) monomer 3 was synthesized from the nitro-displacement reaction of 4-nitrophthalodinitrile with (3-fluoromethyl-4-chlorophenyl)-1,4-hydroquinone in *N,N*-dimethylformamide (DMF) in the presence of potassium carbonate as the base, followed by the alkaline hydrolysis of the intermediate bis(ether dinitrile)s and the cyclodehydration of the resulting bis(ether diacid)s. The synthesis details have been described in a previous article.<sup>28</sup> The characterization of the target bis(ether anhydride) (3) is listed as follows:

Compound 1: Yield: 90%, m.p. 192-194 °C. IR (KBr, cm<sup>-1</sup>): 2236 (-CN), 1245 (C-O), 1122 (C-F). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, δ, ppm): 8.19 (d, J=8.8 Hz, 1H), 8.14 (s, 2H), 8.10 (t, J=8.9 Hz, 2H), 7.93 (d, J=2.5 Hz, 1H), 7.82 (d, J=2.5 Hz, 1H), 7.73 (d, J=2.1 Hz, 1H), 7.63 (dd, J=6.2 Hz, 1H), 7.50 (d, J=2.7 Hz, 1H), 7.46 (s, 2H). (Supporting Information, Fig. S1)

Compound 2: Yield: 85%, m.p. 164-166 °C. IR (KBr, cm<sup>-1</sup>): 2500-3500 (O-H), 1700 (C=O), 1272 (C-O-C), 1120 (C-F). <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, δ, ppm): 13.14 (br, 4H, -COOH), 8.21 (d, J=7.4 Hz, 2H), 8.06 (s, H), 7.81 (d, J=9.3 Hz, 1H), 7.70 (t, J=8.1 Hz, 2H), 7.35 (d, J= 9.5 Hz, 2H), 7.22 (s, 2H), 7.06 (s, 2H). (Supporting Information, Fig. S2)

1 Compound 3: Yield: 81%, m.p. 173-175 °C. IR (KBr,  $\text{cm}^{-1}$ ): 1854 (asym. C=O), 1772 (sym. C=O), 1276 (C-O-C), 1120 (C-F).  $^1\text{H}$  NMR  
2 (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.97 (d,  $J = 8.2$  Hz, 1H), 7.86 (d,  $J = 6.5$  Hz, 2H), 7.64 (d,  $J = 8.2$  Hz, 1H), 7.58 (dd,  $J = 8.4, 2.2$  Hz, 1H),  
3 7.51 (d,  $J = 2.1$  Hz, 1H), 7.39 (dd,  $J = 8.4, 2.2$  Hz, 1H), 7.37 – 7.34 (m, 1H), 7.33 (s, 1H), 7.31 (d,  $J = 9.3, 2.5$  Hz, 2H), 7.29 (dd,  $J = 9.3,$   
4 2.5 Hz, 2H). Elem. Anal. Calcd for  $\text{C}_{29}\text{H}_{12}\text{ClF}_3\text{O}_8$  (580.85): C 59.97, H 2.08. Found: C 60.02, H 2.03.

#### 5 Polymer Synthesis

6 Utilizing monomer 3 as dianhydride, five kinds of PEIs were synthesized by polycondensation with diamine monomers PDA,  
7 ODA, APB, 6FAPB and 9F-CI-APB, respectively. The resulting PEIs were abbreviated to 4a-4e, respectively.

8 In a typical experiment, PEI-4c was derived from dianhydride 3 and diamine APB (c). To a 50 mL thoroughly dried three-neck  
9 flask, 2 mmol dianhydride monomer 3 was dissolved in 8 mL of DMAc. To this dianhydride solution, 2 mmol diamine APB and an  
10 additional 5 mL of DMAc were added. The mixture was stirred for 24 h at room temperature under nitrogen to yield a viscous  
11 poly(amic acid) PAA solution. Chemical imidization was performed via the addition of 1.5 g triethylamine and 4.5 g of acetic  
12 anhydride into the PAA solution at ambient temperature. The mixture was stirred at 60 °C for 6 h to yield a PEI solution. Then,  
13 the solution was poured into anhydrous ethanol to give a precipitate and washed thoroughly with anhydrous ethanol before  
14 drying at 80 °C in vacuum. IR (KBr,  $\text{cm}^{-1}$ ): 1779 and 1721 (asymmetric, symmetric imide C=O stretch), 1619–1480 (aromatic C=C  
15 stretch), 1382 (C-N stretch), 1100–1300 (C–O and C–F stretching).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.97 (d, 1H), 7.86 (d, 2H),  
16 7.64 (d, 1H), 7.55 (s, 1H), 7.50 (dd, 2H), 7.37 (dd, 4H), 7.32 (s, 1H), 7.25 (ddd, 4H), 7.12 (m, 8H).

17 The other PEIs (4a, 4b, 4d and 4e) (Scheme 2) were prepared by a similar procedure, adding the corresponding diamine (PDA,  
18 ODA 6FAPB and 9F-CI-APB) instead of APB.

## 19 RESULTS AND DISCUSSION

### 20 Synthesis and Characterizations of the Monomer

21 The bis(ether anhydride) monomer 3 was prepared by a three-step reaction sequence, as shown in Scheme 1. First, the  
22 intermediate bis(ether dinitrile) was obtained from the nucleophilic nitro-displacement of 4-nitrophthalonitrile with the  
23 phenoxide ions of hydroquinones in DMF. The bis(ether diacid) was prepared by ethanolic potassium hydroxide, and then the  
24 generated bis(ether diacid) was cyclodehydrated to yield the final bis(ether anhydride). The structures of the bis(ether  
25 anhydride) products were confirmed by elemental analysis, IR and  $^1\text{H}$  NMR spectra.

26 In the IR spectra, after the cyano group was hydrolyzed to give the carboxyl group, the sharp absorption near 2230  $\text{cm}^{-1}$   
27 characteristic to the cyano group disappeared, and the carbonyl stretching absorption around 1700  $\text{cm}^{-1}$  and the broad O-H  
28 absorption in the region between 2550 and 3500  $\text{cm}^{-1}$  appeared. After the bis(ether diacid) was cyclodehydrated to the bis(ether  
29 anhydride), the broad O-H absorption disappeared, and the spectrum showed characteristic cyclic anhydride absorptions near  
30 1850 and 1770  $\text{cm}^{-1}$ , suggesting the asymmetric and symmetric stretching vibrations of C=O. Fig. 1 shows the  $^1\text{H}$  spectrum of the  
31 bis(ether anhydride) monomer 3, in which the proton ortho-positioned from the C=O groups ( $\text{H}_1$ ) appeared in the downfield of  
32 the spectrum (8.00 ppm) owing to the strong electron-withdrawing effect of the C=O group, the proton ortho-positioned from  
33 the ether group ( $\text{H}_4, \text{H}_5$ ) appeared in the upfield of the spectra (7.28 ppm) owing to the strong electron-donating effect of the –  
34 O– group. The corresponding protons on the “phthalic anhydride” units (1, 1'; 2, 2'; 3, 3') should appear two slightly different  
35 chemical shifts because of different electronic nature.

### 36 Synthesis and characterization of polymers

37 The PEIs 4a-4e in Scheme 2 were prepared via the conventional two-step method by first reacting equimolar amounts of the  
38 dianhydride monomer 3 with diamines monomers (a-d) to form the poly(amic-acid) at ambient temperature, and sequential  
39 chemical imidization by adding the mixture of acetic anhydride and triethylamine into a PAA solution at ambient temperature.  
40 This was followed by heating at 60 °C to obtain the PEIs 4a-4e.

41 The elemental analysis of the PEIs is listed in Table S1, and shows that the experimental values are close to the calculated  
42 ones. As shown in Table 1, the molecular weights of the resulting PEIs were in the range of 82,000-172,000 for  $M_w$  with the  
43  $M_w/M_n$  values of 1.5-1.7, relative to the polystyrene standards. The inherent viscosities were evaluated in DMAc at 25 °C with an  
44 Ubbelohde viscometer, and the results fell within the 0.70-0.86 dL/g range. The structures of the PEIs were characterized by FTIR  
45 (Fig. S3) and H-H COSY spectra (Fig. 2). The FTIR spectra of PEIs exhibited characteristic imide group absorptions at around 1781  
46 and 1726  $\text{cm}^{-1}$  (typical of imide carbonyl asymmetrical and symmetrical stretch), and did not show an amide carbonyl peak at  
47 1650  $\text{cm}^{-1}$ , indicating complete imidization during polycondensation. Also in the spectra there were peaks seen at 1375  $\text{cm}^{-1}$  (C-N  
48 stretch), 1090 and 730  $\text{cm}^{-1}$  (imide ring deformation), and some strong absorption bands in the region of 1100-1300  $\text{cm}^{-1}$  which  
49 were due to the C-O and C-F stretch.

50 Fig. 2 illustrates the H-H COSY spectra of soluble PEI-4c. Assignments of each proton are also given in these figures, and agree  
51 well with the proposed molecular structure. In H-H COSY spectra, the correlated pairs at 7.98/7.50 ppm, 7.87/7.30 ppm,  
52 7.65/7.50 ppm and 7.38/7.13 ppm. The aromatic protons 1 appeared at the most downfield (7.98 ppm) owing to the strong  
53 electron-withdrawing effect of the C=O groups as a doublet. Accordingly, the connected doublet signal at 7.50 ppm is assigned to  
54 the protons 2. The corresponding protons on the “phthalic anhydride” units (1, 1'; 2, 2'; 3, 3') should appear two slightly different

1 chemical shifts because of different electronic nature. The aromatic protons 11 appeared at the most upfield (7.13 ppm) owing  
2 to the strong electron-donating effect of the -O- groups as a triplet, is also connected with multiple signal at 7.38 ppm arising  
3 from protons 10.

4 Fig. S4 shows the WAXD patterns of the PEIs 4a-4e. The curves of all the PEIs were broad and without obvious peak features,  
5 because of the polymer backbones with multiple trifluoromethyl groups and bulky aromatic side moieties which would increase  
6 the disorder of the polymer chains. The amorphous structure endows the obtained PEIs 4a-4e with good solubility.

#### 7 Solubility of the PEIs

8 The solubility of synthesized PEIs 4a-4e was tested in various organic solvents and the results are summarized in Table S2. All  
9 the PEIs showed excellent solubility in aprotic polar solvents such as NMP, DMAc and DMSO, and were also soluble in less polar  
10 solvents like Py and acetone at room temperature. The excellent solubility of PEIs could be attributed to the presence of flexible  
11 ether structure, CF<sub>3</sub> and Cl groups, and bulky phenyl substitutes in the dianhydrides, which appeared to force the two phenyl  
12 rings into adopting noncoplanar conformation, resulting in inhibition of close packing and reduced interchain interactions to  
13 enhance solubility. The PEIs 4d and 4e exhibited better solubility than PEI 4a-4c. PEI-4d and 4e even exhibited excellent solubility  
14 in acetone. The good solubility of PEI-4d and 4e was attributed to the high fluorine and ether content in the polymer backbone.

#### 15 Thermal Properties of the PEIs

16 The thermal behavior data of all the PEIs are listed in Table 1. In general, the decreasing order of T<sub>g</sub> correlated with both  
17 molecular packing and chain conformation (chain rigidity and linearity) of the polymer. The T<sub>g</sub> values of PEIs 4a-4e were in the  
18 ranges of 208-245 °C, which decreased in the order of 4a>4b>4c>4d>4e. As we expected, the T<sub>g</sub> values of these PEIs depended  
19 on the structure of the diamine component and decreased with increasing flexibility of the PEI backbones according to the  
20 applied structure of the diamine. PEI-4e derived from 9F-Cl-APB exhibited the lowest T<sub>g</sub> because of the presence of two flexible  
21 ether units and three -CF<sub>3</sub> groups, which would lead to an internal plasticization in addition to the geometry and free volume  
22 factors.

23 Thermal stabilities of the PEIs were evaluated by TGA as shown in Fig. 3. All the PEIs had excellent thermal stability, and no  
24 obvious decomposition was observed below 500 °C as shown in Table 1. Film samples of PEIs underwent 5 % weight losses at  
25 507-591 °C in nitrogen when subjected to TGA with a heating rate of 10 °C /min. Their char yield at 800 °C in nitrogen was in the  
26 range of 53-59 wt%. The TGA data indicated that these PEIs had fairly high thermal stabilities regardless of the introduction of  
27 the pendant groups, even though they showed high solubility and optical transparency.

#### 28 Mechanical and Electrical Properties of the PEIs

29 The mechanical properties of the PEI films were summarized in Table 2. The PEI films have tensile strength of 88-120 MPa,  
30 tensile modulus of 2.11-2.70 GPa, and elongation at breakage of 15-27 %, respectively.

31 The dielectric constants of the PEI films were evaluated by capacitance method and were also listed in Table 3. All the PEIs  
32 showed low k values in the range of 2.69-2.80 at 1 MHz due to the existence of CF<sub>3</sub>, Cl groups, and bulky phenyl substitutes  
33 groups in the main chain, which brought about less efficient chain packing and an increased free volume. As expected, the  
34 fluorinated PEI-4e exhibited lower water absorption (0.30 %) than PEI-4a (0.52 %), PEI-4b (0.50 %), PEI-4c (0.43 %) and PEI-4d  
35 (0.32 %), due to the content of hydrophobic CF<sub>3</sub> and Cl groups. The low water absorptions ensure that these polymers have  
36 stable dielectric performance.

#### 37 Optical Properties of the PEIs

38 Optical transparency of the PEI films was evaluated by their physical appearance, UV-Vis spectra and color intensities. Fig. 4  
39 shows the UV-visible transmittance spectra of the PEI films with thickness of 80 μm, while the cut-off wavelength (absorption  
40 edge, λ<sub>0</sub>) values and the percentages transmittance at different wavelength are listed in Table 3. All the PEIs had shorter λ<sub>0</sub> than  
41 370 nm, and exhibited high optical transparency of 76-88 % at 450 nm, 85-93 % at 550 nm and 87-94 % at 800 nm. This  
42 contrasted sharply with the typical Kapton film derived PMDA and 4,4'-ODA, which showed a deep yellow color and exhibited λ<sub>0</sub>  
43 of 455 nm and transmittance at 450 nm of 0 % and at 550 nm of 54 %. Because of the highly conjugated aromatic structures and  
44 intermolecular charge-transfer complex (CTC) formation of PI, most polymers between the UV and the visible area have strong  
45 absorption. However, these PEIs which had flexible groups like ether linkages and CF<sub>3</sub> groups with bulky side groups in the center  
46 of the dianhydride, reduced the intermolecular CTC between alternating electron-donor (diamine) and electron-acceptor  
47 (dianhydride) moieties. The PDA, ODA, APB, 6FAPB and 9F-Cl-APB produced nearly colorless PEI films, which could be explained  
48 from the decreased intermolecular interactions. Moreover, the CF<sub>3</sub> group might weaken the chain-to-chain cohesive force due to  
49 a lower polarizability of the C-F bond. For comparison, another photograph of a commercial Kapton film is shown in Fig. 5. The  
50 films were photographed against a special background to highlight the transparency. It is easy to see that the PEIs films were  
51 much lighter in color than the Kapton film. Wherein, the color of PEI 4c-4e films is close to colorless compared with PEI 4a and 4b.  
52 Furthermore, we also investigated the relationship between the transparency of the films and their thickness. According to the  
53 data from Fig. 6, with the increase of the thickness of PEI-4d film from 19 to 78 μm, the λ<sub>0</sub> increased from 325 to 358 nm. The  
54 results indicated that the transparency of the PEI films was heavily dependent on their thickness.

1 The refractive indices of the PEIs 4a-4e were studied using a Gaertner L116B spectroscopic ellipsometer, and the values were  
2 in the range of 1.6268-1.5962 at 650 nm, 1.5595-1.6039 at 1310 nm, 1.5541-1.6022 at 1550 nm, respectively, as shown in Fig. 7.  
3 In addition, the refractive index decreased with the increase of the wavelength from 600 nm to 1600 nm. In fact, a good linear  
4 relationship between the refractive index of the polymer and the feed ratio of the dianhydride (monomer 3 and 6FDA) and  
5 diamine (6FAPB and 9F-CI-APB) was observed as shown in Fig. 8. When the feed ratio of 6FDA was increased from 0 to 100 mol%,  
6 the refractive index decreased from 1.5962 to 1.5523. (as shown in Fig. 8a) This was attributed to the fluorinated and chlorinated  
7 content of the diamine monomer. On the other hand, we can control the refractive index by controlling the ratio of diamine:  
8 when the feed ratio of 6FAPB was increased from 0 to 100 mol%, the refractive index decreased from 1.6217 to 1.5962. (as  
9 shown in Fig. 8b) Thus, this method may be better suited for copolymerization for controlling the refractive index in greater  
10 scope. A similar chemical structure to ensure that the core and the cladding materials having similar CTE, to prevent cracking  
11 between the core and cladding materials due to temperature changes. Since the design and fabrication of waveguide structures  
12 depend on the difference in the refractive index between the core and the cladding materials, this linearity of refractive index  
13 over such a large range provides tremendous flexibility in the fabrication of waveguide devices using these PEIs.

14 The birefringences ( $\Delta n = n_{TE} - n_{TM}$ ) of the PEIs were studied using the prism coupling technique at 650 nm on thin films, and  
15 showed low values in the range of 0.0052-0.0131 as shown in Table 3. The fact that  $n_{TE}$  values were slightly higher than the  $n_{TM}$   
16 ones for all PEIs films reflects the preferential chain orientation parallel to the film plane. It is well known that the birefringence  
17 of polymers can be affected by chain flexibility and geometry of the repeat units.<sup>35,36</sup> The values of  $\Delta n$  were far lower than  
18 conventional aromatic PIs.<sup>37</sup> The negligibly small birefringence implied that these polymers with pendant groups had low  
19 anisotropy, and the polymer chains were randomly oriented in the film.

20 It was reported that the replacement of C-H bonds with C-F bonds gave high optical transparency of the polymeric material in  
21 the near-infrared (NIR) telecommunication region.<sup>38</sup> The propagation losses of the fluorinated PEIs 4a-4e were measured by the  
22 NIR absorption spectra, and the spectra are shown in the Fig. 9. In these spectra, the C-H bond vibrational absorption peaks ( $2\nu_{C-H}$ ,  
23  $1650\text{ nm}$ , and  $3\delta_{C-H}$ ,  $1100\text{ nm}$ ) and a related peak ( $2\nu_{C-H} + \delta_{C-H}$ ,  $1400\text{ nm}$ ) can be observed. However, they had small light  
24 absorptions at the telecommunication wavelengths of 1310 and 1550 nm due to high fluorine content. The wavelength of 1310  
25 nm or 1550 nm will be used for optical telecommunication, so these PEIs are expected to be applicable to optoelectronic  
26 materials.<sup>39</sup>

## 27 CONCLUSIONS

28 A series of novel PEIs (4a-4e) with ether linkages and bulk side groups in the backbone have been successfully synthesized  
29 from the novel dianhydride monomer 3 with  $CF_3$  and Cl groups and diamines (a-e). It was proved to be a successful process for  
30 reducing overall charge transfer complex formation due to either inter- or intramolecular electronic interactions. Thus, the  
31 prepared PEIs displayed excellent solubility, high thermal stability, good mechanical properties, and low dielectric constants. It  
32 was very interesting that they also had excellent optical properties, including high optical transparency, low birefringence, and  
33 low NIR absorptions losses at the communication windows. Moreover, the refractive indices could be controlled precisely by the  
34 copolymerization in the range of 1.6217-1.5523. All the characterizations proved that the resulting PEIs were potential  
35 candidates for optical devices and microelectronic applications.

## 36 Acknowledgements

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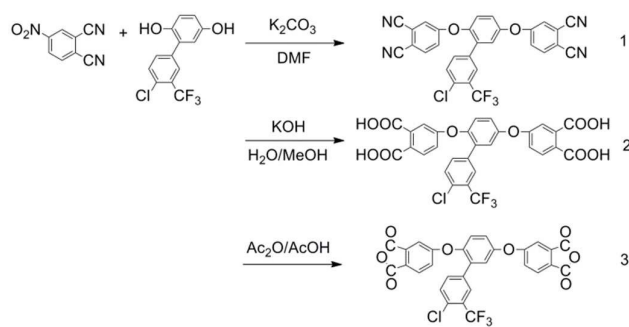
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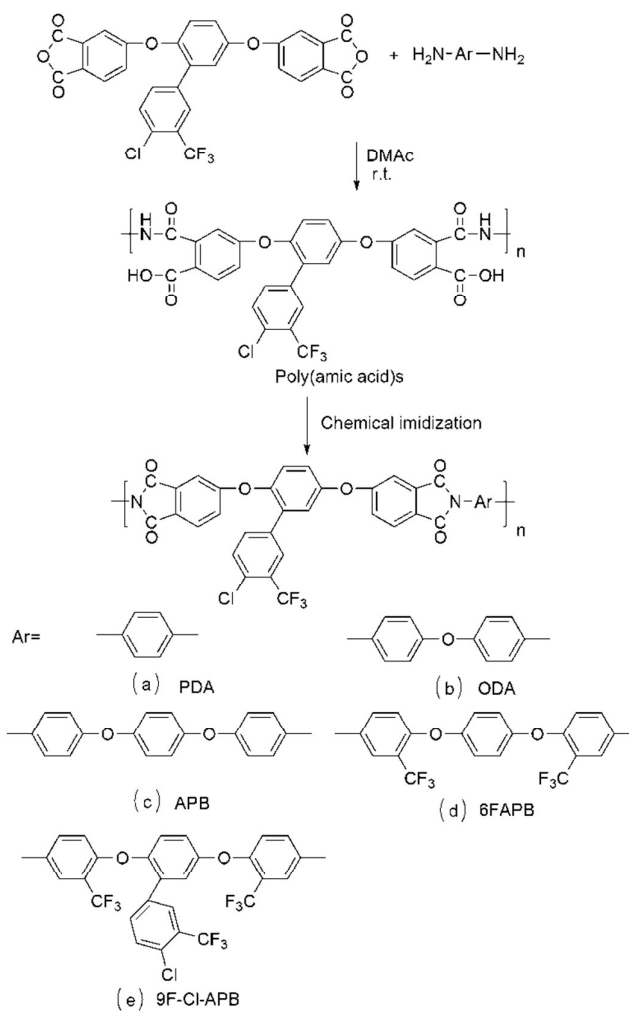
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**1 Figure and Table Captions****2 Scheme 1.** Synthesis of dianhydride monomer.**3 Scheme 2.** Synthesis of the PEIs.**4 Fig. 1** <sup>1</sup>H NMR spectra of dianhydride monomer 3 in CDCl<sub>3</sub>.**5 Fig. 2** H-H COSY spectra of PEI-4c in CDCl<sub>3</sub>.**6 Fig. 3** The TGA curves of PEIs.**7 Fig. 4** UV-visible spectra of the PEI films.**8 Fig. 5** Photograph of the PEI films (4a-4e) and Kapton film.**9 Fig. 6** Cutoff wavelength curves of PEI-4d film with different thickness.**10 Fig. 7** The refractive index curves of PEIs.**11 Fig. 8 a.** Variation of refractive index at 650 nm with dianhydride 6FDA content. **b.** Variation of refractive index at 650 nm with  
**12 diamine 6FAPB content.****13 Fig. 9** Near-IR spectra of the PEIs.**14 Table 1.** Inherent Viscosity, GPC Data and Thermal Properties of the PEIs**15 Table 2.** Mechanical Properties, Dielectric Constant and Water Absorption of the PEIs**16 Table 3.** Optical Properties and Dielectric Constants of the PEIs**17****18**



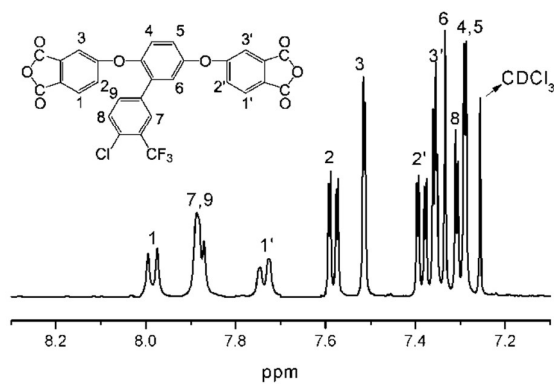


**Scheme 1.** Synthesis of dianhydride monomer.



**Scheme 2.** Synthesis of the PEIs.

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**Fig. 1** <sup>1</sup>H NMR spectra of dianhydride monomer 3 in CDCl<sub>3</sub>.

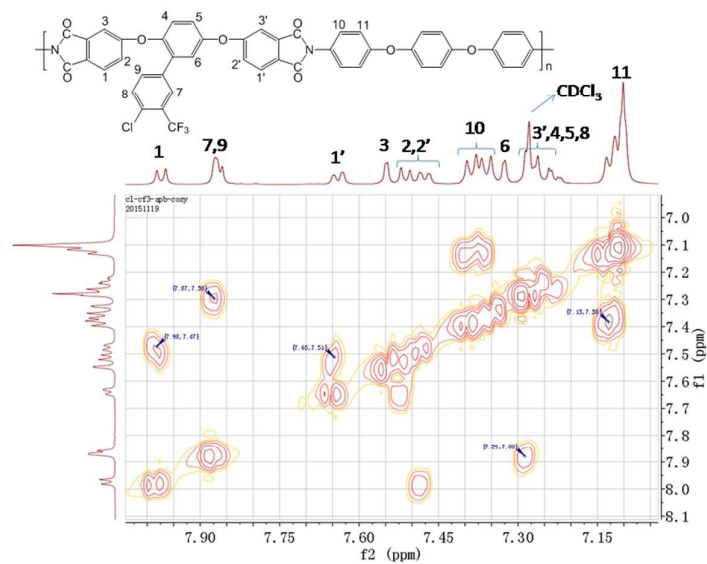
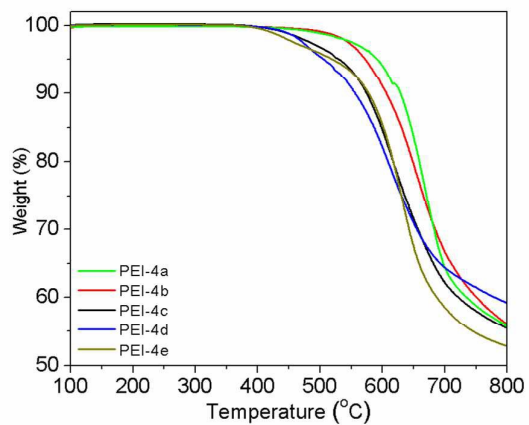


Fig. 2 H-H COSY spectra of PEI-4c in CDCl<sub>3</sub>.

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**Fig. 3** The TGA curves of PEIs.

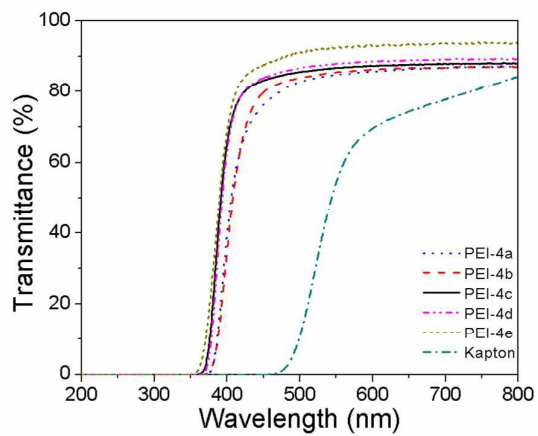
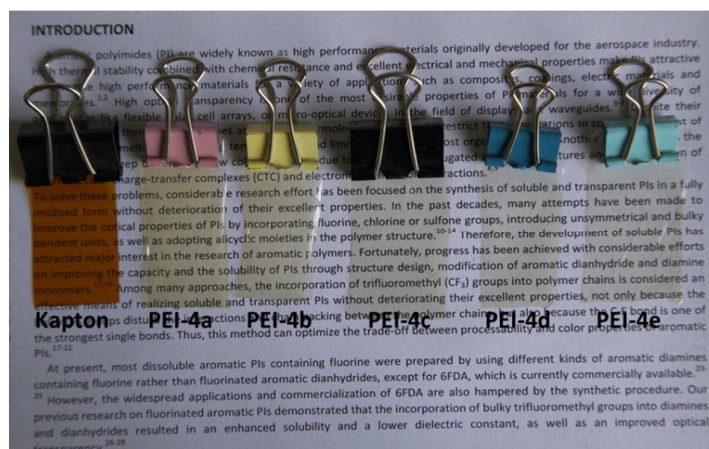


Fig. 4 UV-visible spectra of the PEI films.

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**Fig. 5** Photograph of the PEI films (4a-4e) and Kapton film.

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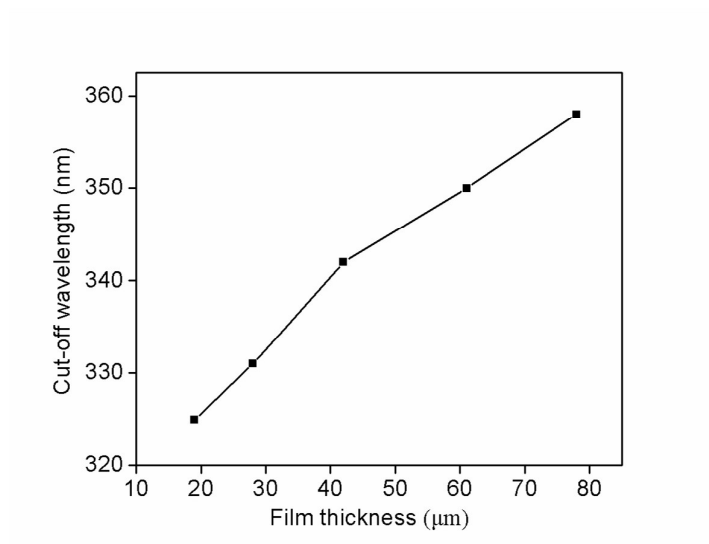


Fig. 6 Cutoff wavelength curves of PEI-4d film with different thickness.



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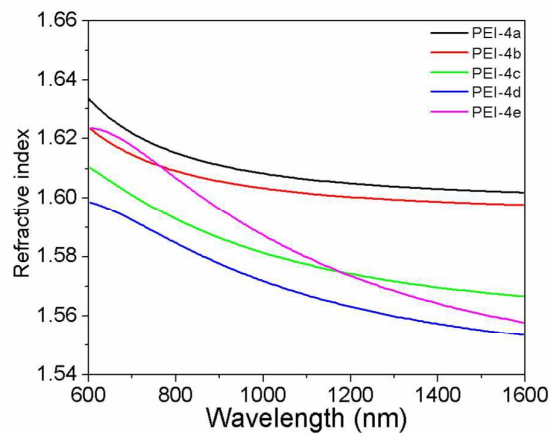
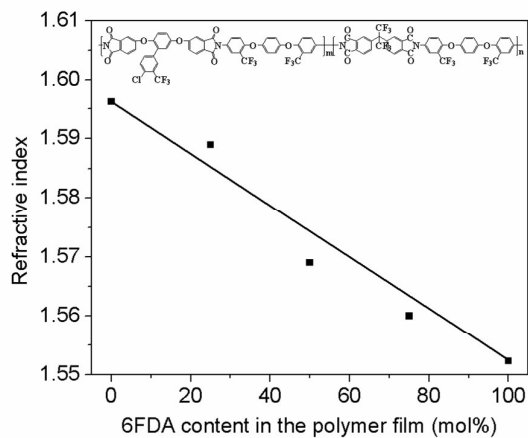
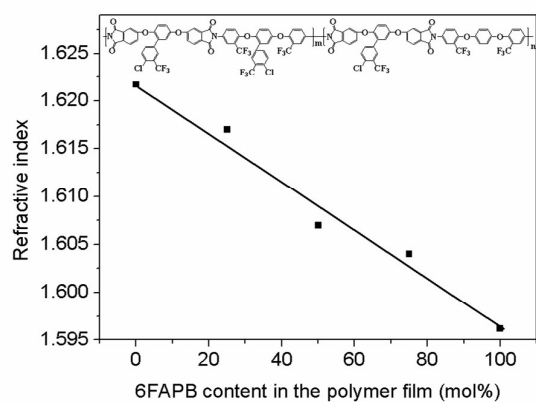


Fig. 7 The refractive index curves of PEIs.



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(b)

**Fig. 8 a.** Variation of refractive index at 650 nm with dianhydride 6FDA content. **b.** Variation of refractive index at 650 nm with diamine 6FAPB content.

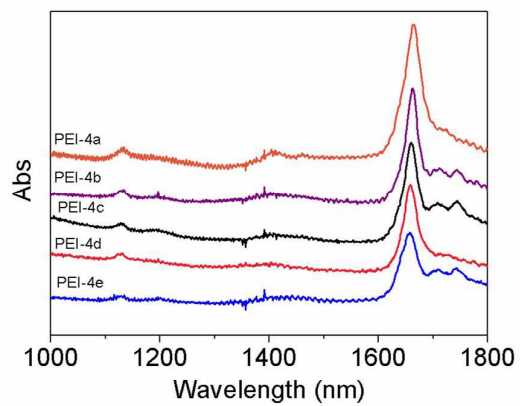


Fig. 9 Near-IR spectra of the PEIs.

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**Table 1.** Inherent Viscosity, GPC Data and Thermal Properties of the PEIs

Polymer	Inherent Viscosity $\eta_{inh}$ (dL/g) <sup>a</sup>	GPC data		DSC	TGA		
		$M_w^b \times 10^4$	$M_w/M_n^b$	$T_g^c$ (°C)	$T_{5\%}^d$ (°C)	$T_{10\%}^d$ (°C)	Char yield <sup>e</sup> (%)
PEI-4a	0.84	13.5	1.7	245	591	629	55
PEI-4b	0.86	16.2	1.6	228	573	606	56
PEI-4c	0.85	17.2	1.6	222	531	575	55
PEI-4d	0.75	9.3	1.5	220	507	556	59
PEI-4e	0.70	8.2	1.7	208	520	578	53

<sup>a</sup> Determined with 0.5% solutions in a solvent (DMAc) at 25 °C.

<sup>b</sup> Relative to polystyrene standard, using DMF as the eluent.

<sup>c</sup> Baseline shift in the second heating DSC traces, with a heating rate of 20 °C / min in nitrogen.

<sup>d</sup> Temperature at 5% and 10% weight loss were recorded by TGA at a heating at 10 °C / min in nitrogen.

<sup>e</sup> Residual weight (%) when heated to 800 °C .

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**Table 2.** Mechanical Properties, Dielectric Constant and Water Absorption of the PEIs

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Polymers	Film thickness (μm)	Tensile strength (MPa)	Elongation at break (%)	Youngs' modulus (GPa)	Dielectric Constant <sup>a</sup>	Water Uptake (%)
PEI-4a	82	120	15	2.70	2.80	0.52
PEI-4b	80	91	25	2.41	2.75	0.50
PEI-4c	79	89	27	2.25	2.73	0.43
PEI-4d	80	92	20	2.20	2.69	0.32
PEI-4e	80	88	18	2.11	2.77	0.30

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<sup>a</sup> Dielectric constant of PEIs at 1 MHz.

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**Table 3.** Optical Properties of the PEIs

polymer	Refractive Index				$\lambda_0$ (nm)	Transmittance at 450 nm (%)	Transmittance at 550 nm (%)	Transmittance at 800 nm (%)
	$n_{TE}^a$	$n_{TM}^b$	$n_{AV}^c$	$\Delta n^d$				
PEI-4a	1.6312	1.6181	1.6268	0.0131	369	76	85	87
PEI-4b	1.6237	1.6122	1.6186	0.0115	366	80	86	87
PEI-4c	1.6092	1.5990	1.6058	0.0102	360	83	87	88
PEI-4d	1.5992	1.5901	1.5962	0.0091	358	84	88	90
PEI-4e	1.6234	1.6182	1.6217	0.0052	346	88	93	94

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5 <sup>a</sup> In-plane refractive index at 650 nm:  $n_{TE}$ .6 <sup>b</sup> Out-of-plane refractive index at 650 nm:  $n_{TM}$ .7 <sup>c</sup> Average refractive index:  $n_{AV} = (2n_{TE} + n_{TM})/3$ .8 <sup>d</sup> Birefringence  $\Delta n = n_{TE} - n_{TM}$ .

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A series of novel PEIs (4a-4e) with ether linkages and bulk side groups in the backbone have been successfully synthesized. It was very interesting that they also had excellent optical properties, including high optical transparency, low birefringence, and low NIR absorptions losses at the communication windows. Moreover, the refractive indices could be controlled precisely by the copolymerization in the range of 1.6217-1.5523 at 650 nm.

