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# Colorless polyimides from 2,3,3′,4′-biphenyltetracarboxylic dianhydride (α-BPDA) and various aromatic bis(ether amine)s bearing pendent trifluoromethyl groups

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## Abstract

A series of organosoluble and light-colored polyimides (**III**) was prepared from 2,3,3′,4′-biphenyltetracarboxylic dianhydride (α-BPDA) with various fluorinated aromatic bis(ether amine)s via two-step method with thermal or chemical imidization of poly(amic acid)s yielded polyimides. The **III** series had inherent viscosity of 0.74–1.01 dl/g and showed excellent solubility in a variety of organic solvents. They were soluble in the amide polar solvent, ether-type solvent, and chlorinated solvent. These polyimide films also showed a high optical transparency and less color intensity, with an ultraviolet-visible absorption edge of 369–382 nm and low $b^*$ values (a yellowness index) of 5.0–11.7. Glass-transition temperature of the **III** series was recorded at 244–319 °C and higher than the isomeric polyimides **V** series. Compared with the nonfluorinated polyimides **IV**, the **III** series showed lighter-colored and lower dielectric constants and moisture absorptions. The good tensile properties and excellent thermal properties of the **III** series were also observed.

*Keywords:* 2,3,3′,4′-Biphenyltetracarboxylic dianhydride; Fluorine-containing polyimide; Bis(ether amine)

## 1. Introduction

Aromatic polyimides are well accepted as high-performance polymeric materials because of their excellent thermal and mechanical properties at elevated temperatures. They are widely used in the aerospace and electronic industries in the form of films and moldings [1–3]. In addition, optical transparency of polyimide films is of special importance in some application such as flexible solar radiation protectors [4], orientation films in liquid crystal display devices [5] and optical half-waveplates for planar lightwave circuits [6].

However, most of the conventional polyimide films show considerable coloration from pale yellow to deep brown mainly due to charge-transfer complexing between alternating electron-donor (diamine) and electron-acceptor (dianhydride) segments [7]. Besides, solubility and processability are generally major concerns when working with polyimides. Considerable efforts have been made to improve the solubility and/or melting processability of polyimides while maintaining their positive properties. Therefore, great efforts have been expended to develop advanced polyimide material with both good solubility and transparency. The solubilization and processing of rigid-chain polymers have been made through the synthetic modification of the flexibilizing linkages [8–10] or introducing of bulky side group [11–13] or molecular asymmetry (*ortho*, *meta* versus linkages) [14,15] into the backbone. Optical transparency polyimides could be prepared by the dianhydride moiety with hexafluoroisopropylidene group [16] or diamine containing trifluoromethyl-substituted [17–20]. It have been proved that polyimide with trifluoromethyl-substituted benzene in the side chain can enhance the solubility and thermal stability, reduce dielectric constant and moisture absorption, raise the optical transparency and decrease color intensity [21–27]. Thus, it is expected that fluorinated polyimides will be widely applied in electro-optical and semiconductor industries.

Generally, polyimides deriving from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA) with diamine were

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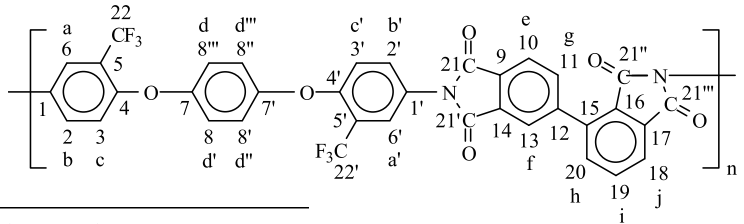
possessed of good mechanical properties and thermal stability such as Upilex. However, these polymers showed limited solubility in organic solvents. It has been reported that incorporation of unsymmetrical diamine or dianhydride and hindered moieties would disturb the coplanarity of the aromatic unit to reduce packing efficiency. The resulting lead to enhance solubility and maintain high $T_g$'s through controlled segmental mobility, such as polyimides based on α-BPDA [28], 2,3,3′,4′-beznophenonetetracarboxylic dianhydride (α-BTDA) [29] or mellophanic dianhydride (MPDA) [30]. Polyimides derived from α-BPDA have higher $T_g$ and transmittances, and possess lighter colored than the corresponding symmetric polyimides based on s-BPDA, but the improvement of solubility is limited [28]. Besides, we also found that the diamine with the trifluoromethyl group ($CF_3$) could contribute to polyimide films' optical transparency, low color, and enhance solubility [30–32]. Thus, a novel series of fluorinated polyimides (**III**) was synthesized from α-BPDA and $CF_3$-containing bis(ether amine)s $\mathbf{I_{a-g}}$ in this study. These polymers were subjected to solubility, optical, thermal, mechanical, and dielectric properties. Moreover, we also compared the **III** series with the analogous nonfluorinated polyimides **IV** and the isomeric polyimides **V** derived from s-BPDA to investigate the structure of dianhydride affected coloration, solubility and $T_g$.

## 2. Experimental

### 2.1. Material

Aromatic anhydride: 2,3,3′,4′-biphenyltetracarboxylic dianhydride (α-BPDA; Ube Industries Ltd) was recrystallized from toluene/acetic anhydride before use. Fluorinated bis(ether amine)s were synthesized according to the literature [31,32–37] and its melting point as follows, 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene ($\mathbf{I_a}$) [22,33] (mp: 132–133 °C), 1,2-bis(4-amino-2-trifluoromethylphenoxy)benzene [34] ($\mathbf{I_b}$) (mp: 116–117 °C), 2,5-bis(4-amino-2-trifluoromethylphenoxy)-*tert*-butylbenzene [35] ($\mathbf{I_c}$) (mp: 164–165 °C), 4,4′-bis(4-amino-2-trifluoromethylphenoxy)biphenyl [31] ($\mathbf{I_d}$) (mp:155–156 °C), 4,4-bis(4-amino-2-trifluoromethylphenoxy)3,3′,5,5′-tetramethylbiphenyl [25] ($\mathbf{I_e}$) (mp: 256–257 °C), 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane [36] ($\mathbf{I_f}$) (mp: 131–132 °C), 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane [32] ($\mathbf{I_g}$) (mp:



65–66 °C). Others included *N*-methy-2-pyrrolidone (NMP; Fluka), *N*,*N*-dimethylacetamide (DMAc; Fluka), *N*,*N*-dimethylformamide (DMF; Fluka) and pyridine (Py; Wako).

### 2.2. Synthesis of polyimides

#### 2.2.1. Thermal imidization method

The general polymerization procedure is illustrated by the following example. Diamine $\mathbf{I_a}$ (0.429 g; 1 mmol) was dissolved in dried DMAc (5.6 ml) in a 20 ml flask. After the diamine was completely dissolved, α-BPDA (0.294 g, 1 mmol) was added in one portion. The mixture was stirred at room temperature for 10 h to afford a highly viscous poly(amic acid) (PAA) solution. Then PAA solution was poured into a glass culture dish, which was placed in a 80 °C oven for 1 h to remove the solvent. The semidried PAA film was further dried and imidized by sequential heating at 120–210 °C at the rate of 30 °C/10 min, and 250 °C for 30 min. The polyimide film was stripped from the glass substrate by soaked in water. Inherent viscosity ($\eta_{inh}$) in DMAc of $\mathbf{III_a}$ was 0.82 dl/g, as measured at a concentration 0.5 g/dl at 30 °C.

IR (film): 1779, 1725 (imide C=O), 1619–1481 (aromatic C=C stretch), 1378 (C–N stretch), 1240 (C–O), 1135, 740 $cm^{-1}$ (imide ring deformation), 1100–1300 $cm^{-1}$ (C–O and C–F stretching) (Fig. 1). $^1H$ NMR (500 MHz, DMSO-$d_6$, δ, ppm): 8.26 (1H, $H_f$), 8.17, 8.15 (1H, $H_e$), 8.05–8.08 (2H, $H_{i,j}$), 8.00, 7.98 (2H, $H_{g,h}$), 7.95, 7.93 (2H, $H_{a,a'}$), 7.74–7.78 (2H, $H_{b,b'}$), 7.26–7.29 (6H, $H_{c,c',d,d',d'',d'''}$). $^{13}C$ NMR (100 MHz, DMSO-$d_6$, δ, ppm): 166.6, 166.5, 166.3, 166.2 ($C^{21,21',21'',21'''}$), 154.5, 154.4 ($C^{7,7'}$), 152.0 ($C^{4,4'}$), 142.2 ($C^{12}$), 137.7 ($C^{15}$), 135.8 ($C^{14}$), 134.9 ($C^{17}$), 133.4 ($C^{19}$), 132.7 ($C^{1,1'}$), 131.4, 131.3 ($C^{9,16}$), 127.8 ($C^{11,20}$), 126.8, 126.7 ($C^{13,18}$), 126.3 ($C^{10}$), 124.6 ($C^{2,2'}$), 124.3 ($C^{3,3'}$), 123.5, 123.3 ($C^{6,6'}$), 121.6 ($C^{8,8',8'',8'''}$), 119.2 ($C^5$, quartet, $^2J_{C-F}=31$ Hz), 119.1 ($C^{22,22'}$).

#### 2.2.2. Chemical imidization method

The method of synthesizing PAA was similar to thermal imidization. Then a mixture of 1 ml of acetic anhydride/pyridine (volume ratio 2/1) were added to the PAA solution. The PAA solution was heated at 80 °C for 1 h to effect a complete imidization and then poured into a glass culture dish, which was placed in an 80 °C oven for 1 h to evaporate the solvent and form a thin solid film. The polyimide film was sequentially heated to 200 °C and held at that temperature for 2 h to remove the residual solvent.

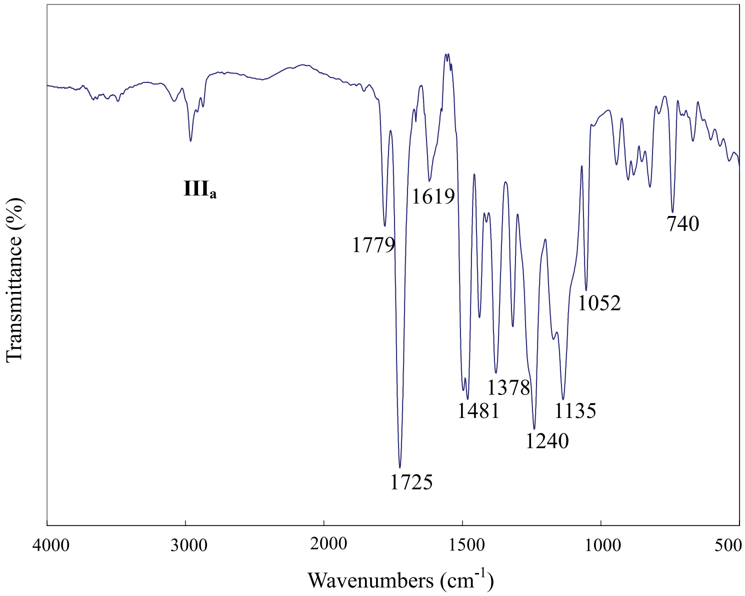


Fig. 1. FT-IR spectra of polyimide **III$_a$**.

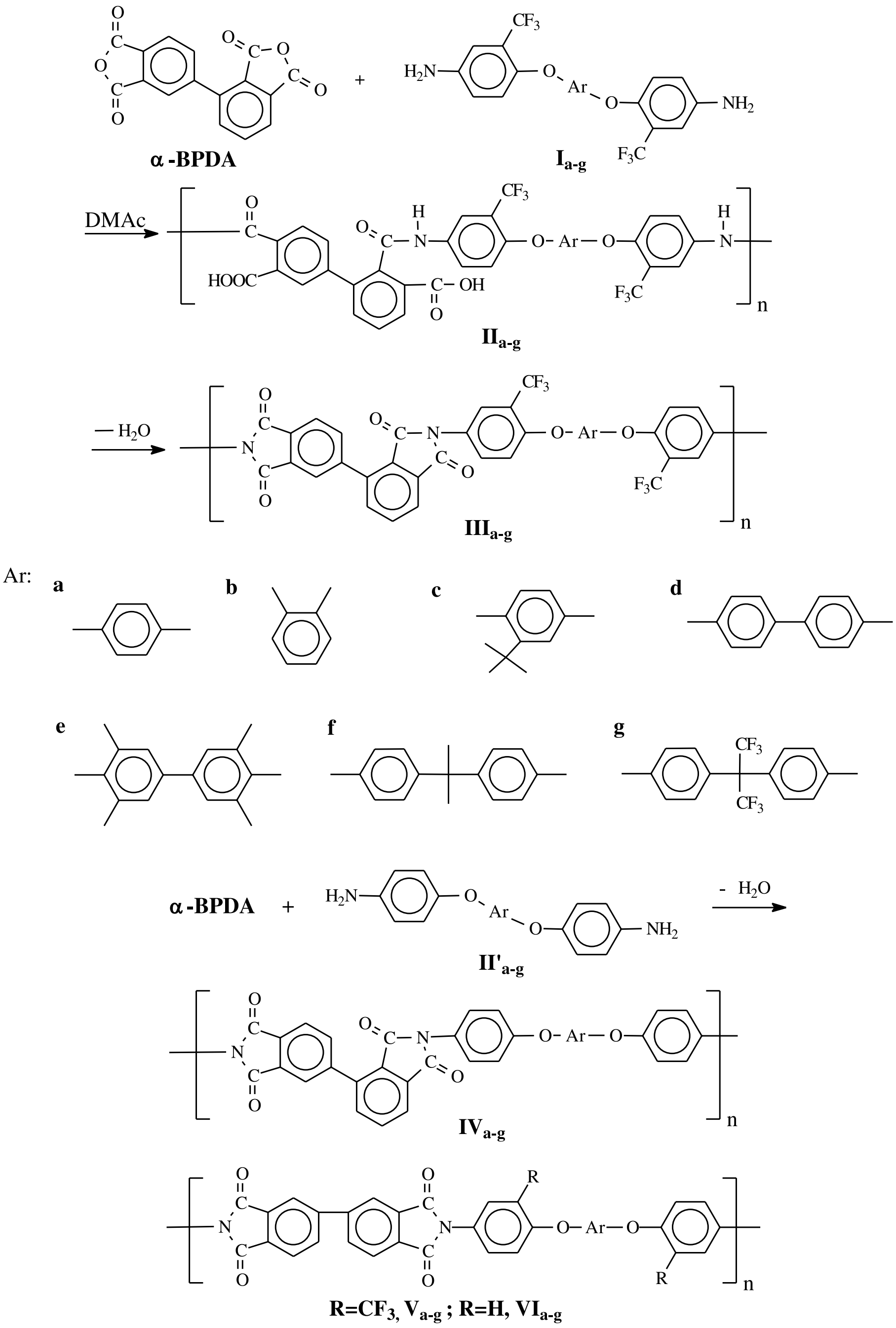
### 2.3. Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run on a Heraeus VarioEL-III for CHN analyzer. $^1$H and $^{13}$C NMR spectra were measured on a Bruker AV-500 FT-NMR spectrometer. Inherent viscosities were determined at a 0.5 g/dl concentration with an Ubbelohde viscometer at 30 °C. Weight-average molecular weights ($\bar{M}_w$'s) and number-average molecular weights ($\bar{M}_n$'s) were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration using Waters 2410 as an apparatus and tetrahydrofuran (THF) as the eluent. Qualitative solubility was determined with as 100 mg of polymer in 1 ml of solvent soluble (10%), and added solutions to 5 or 1%. Color intensity of the polymers was evaluated on a Macbeth color-eye colorimeter. Measurements were performed for the films at an observational angle of 10° and with a Commission International de l'Eclairage (CIE)-D illuminant. A CIE LAB color difference equation was used. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer. Mechanical properties of the films were measured on an Instron model 1130 tensile tester with a 5 kg load cell at a crosshead speed of 5 cm/min on strips approximately 30–60 μm thick and 0.5 cm wide with a 2 cm gauge length. An average of at least five individual determinations was used. Glass-transition temperature ($T_g$) of the polymer was measured on TA Instrument DSC 2010, in flowing nitrogen 40 cm$^3$/min at a heating rate of 15 °C/min. Rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so $T_g$ of all the polyimide could be easily read in the subsequent heating DSC traces. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. Measurements were carried out on 9–11 mg film samples heated in flowing nitrogen or air (90 cm$^3$/min) at a heating rate of 20 °C/min. Dielectric property of the polymer films was tested by the parallel-plate capacitor method with a Hewlett Packard 4194A dielectric analyzer. Gold electrodes were vacuum-deposited on both surfaces of dried films. Experiments were performed at 25 °C in a dry chamber. Equilibrium moisture absorption was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.

## 3. Results and discussion

### 3.1. Polymer synthesis

The synthetic route of a novel polyimides (**III$_{a\text{–}g}$**) derived from α-BPDA is shown in Scheme 1. The synthesis was that the various bis(ether amine)s (**I$_{a\text{–}g}$**) bearing pendent CF$_3$ groups were dissolved in DMAc, then added an equivalent α-BPDA via a conventional two-step procedure of ring-opening polyaddition at room temperature to form PAA (**II**) solution, followed by a thermal or chemical imidization and directly cast film. The merits of the former were sequential heating to 250 °C and were easy to handle by directly casting of the polymer into thin film. The latter method was added the mixture of Ac$_2$O/Py to obtain the corresponding polymers, and was suited to prepare soluble polyimide. However, the synthesis of polyimide **III$_e$** showed unusual phenomenon. Although the inherent viscosity of PAA **II$_e$** was 1.12 dl/g at a concentration of 12% in DMAc, the thermally cured polyimide film **III$_e$(H)**



Scheme 1. Synthesis of polyimides.

from their PAA solutions were brittle with inherent viscosity of 0.29 dl/g. If the polyimides **III$_e$(C)** were prepared via the chemical imidization of their PAA solutions by means of acetic anhydride and pyridine, they had a relatively higher inherent viscosity value (0.75 dl/g) and could be cast into flexible and tough films. The relatively lower inherent viscosities of the thermally cured polyimides may be attributed to the reversible reaction took place on thermal imidization process. Thus, causing PAA with the result that revert to anhydrides and amines end side occurred again [37]. Though the process of reversion exists in all PAA films, the anhydride and amine end group could recombine during thermal imidization, but due to the influence of chain angle on α-BPDA–PAA, the ring-like polyimide with low molecular weight formed easily during rearrangement. In contrast, the inter-molecular imidization reaction of polyamide–anhydride did not occur reversion process and would not rearrangement. Therefore, high molecular weight of its predecessor PAA could be maintained to produce polyimide via chemical imidization.

Table 1
Inherent viscosity, elemental analysis and GPC data of the polyimides **III**

| Polymer[a] | $\eta_{inh}$ (dl/g) | Elemental analysis (%) | | | | | GPC data[b] | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Formula of PI (formula weight) | | C | H | N | $\bar{M}_n \times 10^4$ | $\bar{M}_w \times 10^4$ | PDI[c] |
| **III$_a$** | 0.82 | $(C_{36}H_{16}F_6N_2O_6)_n$ | Calcd | 62.98 | 2.35 | 4.08 | 7.76 | 9.93 | 1.3 |
| | | $(686.52)_n$ | Found | 62.48 | 2.37 | 4.06 | | | |
| **III$_b$** | 0.75 | $(C_{36}H_{16}F_6N_2O_6)_n$ | Calcd | 62.98 | 2.35 | 4.08 | 8.28 | 10.49 | 1.3 |
| | | $(686.52)_n$ | Found | 62.64 | 2.37 | 4.04 | | | |
| **III$_c$** | 0.74 | $(C_{40}H_{24}F_6N_2O_6)_n$ | Calcd | 64.69 | 3.26 | 3.77 | 6.74 | 9.05 | 1.3 |
| | | $(742.63)_n$ | Found | 64.15 | 3.29 | 3.75 | | | |
| **III$_d$** | 1.01 | $(C_{42}H_{20}F_6N_2O_6)_n$ | Calcd | 66.15 | 2.64 | 3.67 | 7.25 | 9.66 | 1.3 |
| | | $(762.62)_n$ | Found | 65.86 | 2.67 | 3.65 | | | |
| **III$_e$** | 0.75 | $(C_{46}H_{28}F_6N_2O_6)_n$ | Calcd | 67.48 | 3.45 | 3.42 | 8.02 | 10.24 | 1.3 |
| | | $(818.73)_n$ | Found | 66.93 | 3.46 | 3.42 | | | |
| **III$_f$** | 0.76 | $(C_{45}H_{26}F_6N_2O_6)_n$ | Calcd | 67.17 | 3.26 | 3.48 | 7.03 | 9.31 | 1.3 |
| | | $(804.70)_n$ | Found | 66.82 | 3.29 | 3.47 | | | |
| **III$_g$** | 0.74 | $(C_{45}H_{20}F_{12}N_2O_6)_n$ | Calcd | 59.22 | 2.21 | 3.07 | 6.87 | 9.29 | 1.4 |
| | | $(912.64)_n$ | Found | 59.02 | 2.22 | 3.05 | | | |

[a] Taking polymer films from thermal imidization.

[b] Inherent viscosity and GPC data of **III$_e$** were measured by the polyimide film of chemical imidization.

[c] The polydispersity index (PDI) was obtained by $\bar{M}_w/\bar{M}_n$.

The results of elemental analysis of **III$_{a–g}$** are listed in Table 1 showing that the measured values are close to the calculated ones. All **III$_{a–g}$** can dissolve in THF and measure the GPC curves. $\bar{M}_w$ and $\bar{M}_n$ values were available in the range of $9.05\times10^4$–$10.49\times10^4$ and $6.74\times10^4$–$8.28\times10^4$, respectively, relative to standard polystyrene. The polydispersity index (PDI) of the **III** series is in the range of 1.3–1.4, and had inherent viscosity in range of 0.74–1.01 dl/g (Table 1). $^1$H and $^{13}$C NMR spectra of **III$_a$** are shown in Fig. 2. In $^1$H NMR spectrum, all the aromatic protons of **III$_a$** resonated in the region of 7.26–8.27 ppm. $H_f$ appeared the farthest downfield because of the resonance of imide group, $H_{c,c',d,d',d'',d'''}$ shifted to a higher field due to the electron donating property of ether group. In $^{13}$C NMR spectrum should be exhibited 22 main peaks for **III$_a$**. However, there are only 19 main signals appeared, it seems the carbon $C^{11}$ and $C^{18}$ are overlapping with $C^{20}$ and $C^{13}$, respectively, and the numbers of C were still conformed to **III$_a$**. $C^{21,21',21'',21'''}$ was of the carbonyl groups and they showed in the downfield. The quartet centered at about 119 ppm was the $CF_3$-attached carbon ($C^{5,5'}$) with a smaller coupling constant of about 31 Hz due to two-bond C–F coupling. Above-cited results evidence that the **III** series has been synthesized successfully.

## *3.2. Properties of polymers*

### *3.2.1. Solubility*

The solubility properties of the **III** series are reported in Table 2. All polymers **III$_{a–g}$(H)** could be dissolved at a concentration of 5–10 wt/v% in the amide-type solvents, such as NMP, DMAc, DMF, in the basic solvent of pyridine, in ether-type solvents such as Dioxane and THF, and were also soluble in chlorinated solvents such as $CH_2Cl_2$ and $CHCl_3$. Most of the **III(H)** series were also soluble in the phenolic solvent of *m*-cresol except **III$_d$(H)** and **III$_e$(H)**. The difference in solubility of DMSO and Acetone between the **III(H)** series is much. **III$_b$** can be dissolved in DMSO at a concentration of 5 wt/v%, others are soluble at 1% except **III$_{d,e}$**. Only **III$_c$(H)** could be dissolved in Acetone at a concentration of 5 wt/v%. The solubility of most of the **III(C)** series were improved or the same as thermal imidization ones. However, **III$_d$(C)** showed lower solubility in $CH_2Cl_2$ and $CHCl_3$ than **III$_d$(H)** due to the inherent viscosity of **III$_d$(C)** was higher than **III$_d$(H)** as shown in Table 2.

Compared with the nonfluorinated polyimides **IV** series, the solubility of **III** is better than **IV** except **III$_e$(H)** in $CH_2Cl_2$ and $CHCl_3$. This difference in solubility between the **III** and **IV** series can be attributed to the presence of bulky $CF_3$ groups, which inhibit close packing, thus reducing the inter-chain interaction to enhance solubility. Comparing the **III** series with the isomeric polyimides **V** series, the **III** series also showed better solubility and may be attributed to asymmetric structure, creating a steric hindrance effect and enhancing solubility, furthermore, the imide groups inhabit inter-chain interaction and chain packing, thus increase solubility. Moreover, compared with the common polyimides (**VI**) based on s-BPDA, the **VI** series was obviously insoluble. It can be said that the solubility of the **III** series is raised much, and retain the good properties of BPDA–polyimide.

### *3.2.2. Optical property*

The color intensities of polyimide films were elucidated from the yellowness ($b^*$), redness ($a^*$), and lightness ($L^*$) indices observed on a Macbeth color-eye colorimeter. In this case, we based our judgment of the degree of

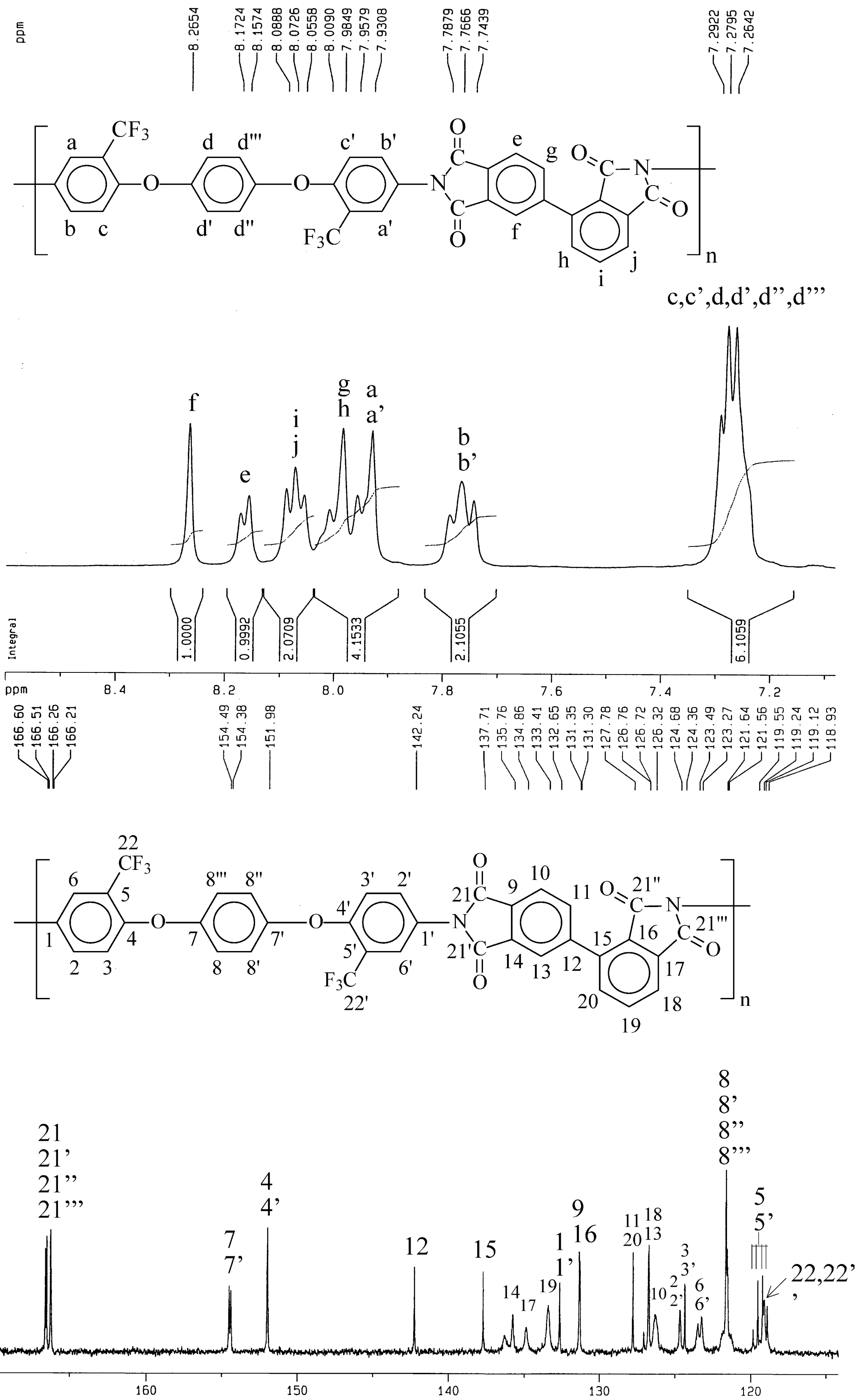


Fig. 2. $^1$H and $^{13}$C NMR spectrum of polyimide **III$_a$** in DMSO-$d_6$.

Table 2
Solubility of polyimides

| Polymer Code[c] | Solvent [b] | | | | | | | | | | | $\eta_{inh}$ (dL/g) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | NMP | DMAc | DMF | DMSO | *m*-Cresol | Py | Dioxane | THF | $CH_2Cl_2$ | $CHCl_3$ | Acetone | |
| $\mathbf{III_a(H)}$ | ◎ | ◎ | ◎ | + | ○ | ◎ | ◎ | ◎ | ◎ | ◎ | − | 0.82 |
| $\mathbf{III_b(H)}$ | ◎ | ◎ | ◎ | ○ | ◎ | ○ | ◎ | ◎ | ◎ | ◎ | − | 0.75 |
| $\mathbf{III_c(H)}$ | ◎ | ◎ | ◎ | + | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | 0.74 |
| $\mathbf{III_d(H)}$ | ◎ | ◎ | ◎ | − | + | ◎ | ○ | ◎ | ◎ | ◎ | − | 1.01 |
| $\mathbf{III_e(H)}$ | ◎ | ◎ | ◎ | − | + | ◎ | ◎ | ○ | ○ | ○ | − | d |
| $\mathbf{III_f(H)}$ | ◎ | ◎ | ◎ | + | ◎ | ◎ | ◎ | ○ | ◎ | ◎ | − | 0.76 |
| $\mathbf{III_g(H)}$ | ◎ | ◎ | ◎ | + | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | + | 0.74 |
| $\mathbf{III_a(C)}$ | ◎ | ◎ | ◎ | + | ○ | ◎ | ◎ | ◎ | ◎ | ○ | − | 0.78 |
| $\mathbf{III_b(C)}$ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | +− | 0.69 |
| $\mathbf{III_c(C)}$ | ◎ | ◎ | ◎ | ○ | ○ | ◎ | ○ | ○ | ◎ | ◎ | ◎ | 0.67 |
| $\mathbf{III_d(C)}$ | ◎ | ◎ | ◎ | − | + | + | ◎ | ◎ | − | − | − | 1.12 |
| $\mathbf{III_e(C)}$ | ◎ | ◎ | ◎ | − | ○ | ◎ | ◎ | ○ | ○ | ○ | − | 0.75 |
| $\mathbf{III_f(C)}$ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | + | 0.68 |
| $\mathbf{III_g(C)}$ | ◎ | ◎ | ◎ | + | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | + | 0.65 |
| $\mathbf{IV_a(H)}$ | + | + | − | − | + | ○ | − | − | − | − | − | |
| $\mathbf{IV_b(H)}$ | ◎ | ◎ | + | − | − | ○ | − | − | ○ | ○ | − | |
| $\mathbf{IV_c(H)}$ | ◎ | ◎ | ◎ | − | − | ◎ | + | ○ | ○ | ○ | − | |
| $\mathbf{IV_d(H)}$ | + | + | − | − | − | + | − | − | − | − | − | |
| $\mathbf{IV_e(H)}$ | ◎ | ◎ | ◎ | S | + | ◎ | + | ○ | ◎ | ◎ | − | |
| $\mathbf{IV_f(H)}$ | ◎ | ◎ | ◎ | − | ○ | ◎ | S | S | ○ | ○ | − | |
| $\mathbf{IV_g(H)}$ | ◎ | ◎ | ◎ | − | + | ◎ | ◎ | ◎ | ◎ | ◎ | − | |
| $\mathbf{V_a(H)}$ | − | − | − | − | +− | + | − | − | − | − | − | |
| $\mathbf{V_b(H)}$ | ◎ | ◎ | ○ | ○ | + | ○ | + | + | + | + | − | |
| $\mathbf{V_c(H)}$ | − | − | − | − | − | − | − | − | − | − | − | |
| $\mathbf{V_d(H)}$ | + | + | − | − | + | − | S | − | − | − | − | |
| $\mathbf{V_e(H)}$ | + | + | + | S | − | ○ | ○ | ○ | − | − | S | |
| $\mathbf{V_f(H)}$ | ◎ | ◎ | ◎ | + | ◎ | ◎ | ○ | + | − | − | S | |
| $\mathbf{V_g(H)}$ | ◎ | ◎ | ◎ | + | ◎ | ◎ | ○ | + | − | − | − | |
| $\mathbf{VI_a(H)}$ | − | − | − | − | − | − | − | − | − | − | − | |
| $\mathbf{VI_b(H)}$ | +− | − | − | − | +− | − | − | − | − | − | − | |
| $\mathbf{VI_c(H)}$ | +− | − | − | − | +− | + | − | − | +− | − | − | |
| $\mathbf{VI_d(H)}$ | − | − | − | − | − | − | − | − | − | − | − | |
| $\mathbf{VI_e(H)}$ | − | − | − | − | − | − | − | − | − | − | − | |
| $\mathbf{VI_f(H)}$ | + | − | − | − | +− | + | − | − | − | − | − | |
| $\mathbf{VI_g(H)}$ | + | + | + | − | + | + | − | − | − | − | − | |

Qualitative solubility was determined with as: ◎, 100 mg of polymer in 1 ml of solvent soluble (10%); ○, 5%; +, 1%; +− = partial soluble, − = insoluble, S = swelling. $\mathbf{III_e(H)}$ was brittle as casting into film and inherent viscosity ($\eta_{inh}$) of polyimide films was 0.29.

[a] (H): polyimides were obtained by the thermal imidization. (C): polyimides were obtained by the chemical imidization.

[b] DMSO, dimethyl sulfoxide; Py, pyridine.

[c] $III_e(H)$ was brittle as casting into film and inherent viscosity ($\eta_{inh}$) of polyimide films was 0.29.

yellowness on the $b^*$ value. Table 3 shows that all the **III**(**H**) with a low $b^*$ value range from 5.0 to 11.7. The insignificant difference of $b^*$ value ($\Delta b^*$) in the **III** series arose from either the purity and colorness of diamines or the thickness of polyimide films. As for the influence on color by the chemical or thermal imidization method, the former can avoids oxidization in the air and thus reduces $b^*$ value, such that $\mathbf{III_f(C)}$ is lower than $\mathbf{III_f(H)}$ by 3.4. All the fluorinated polyimide **III** series was lighter-colored and revealed a lower $b^*$ value and than their respective nonfluorinated analogues **IV** series, the difference in $b^*$ value ($\Delta b^*$) is between 8 and 15.9 even. The bulky and electron-withdrawing $CF_3$ groups in diamine $\mathbf{I_{a–g}}$ were effective in decreasing the charge-transfer complexing (CTC) formation between polymer chains through steric hindrance and the inductive effect. Contrasting the $b^*$ value of the **III** series and common polyimide, Kapton based on PMDA or light-colored fluorinated polyimide (**V** series) based on s-BPDA, the $b^*$ value of the **V** series ranging 12.5–28.3 is much lower than that of Kapton which shows deep yellow to brown. In this study, we synthesized the **III** series, whose $b^*$ values were much lower than the **V** series'. Fig. 3 shows the comparing results of the **III** and **V** series. Due to the dianhydride moiety of the **III** series was α-BPDA, its structure was more asymmetric than s-BPDA did, which can reduce the electron-conjugation on the imide ring and these

Table 3
Color coordinates and the cut-off wavelength ($\lambda_0$) from UV–visible spectra for both **III**, **IV** and **V** series polyimide films

| Polymer code[a] | Film thickness (μm) | Color coordinates[b] | | | | $\lambda_0$ (nm) | Ref. |
|---|---|---|---|---|---|---|---|
| | | $b^*$ | $\Delta b^{*c}$ | $a^*$ | $L^*$ | | |
| Standard | | 1.0 | | −0.4 | 100 | | |
| **III$_a$(H)** | 36 | 7.5 | | −3.1 | 99.6 | 378 | |
| **III$_b$(H)** | 76 | 10.3 | | −3.5 | 99.0 | 377 | |
| **III$_c$(H)** | 56 | 10.0 | | −.39 | 99.2 | 376 | |
| **III$_d$(H)** | 36 | 11.7 | | −5.0 | 98.6 | 381 | |
| **III$_f$(H)** | 58 | 11.4 | | −3.9 | 98.8 | 382 | |
| **III$_g$(H)** | 52 | 5.0 | | −1.9 | 99.7 | 369 | |
| **III$_a$(C)** | 32 | 6.8 | −0.7 | −2.6 | 99.8 | 371 | |
| **III$_b$(C)** | 63 | 9.9 | −0.4 | −4.2 | 98.6 | 383 | |
| **III$_c$(C)** | 53 | 8.5 | −1.5 | −3.7 | 99.7 | 379 | |
| **III$_d$(C)** | 42 | 10.1 | −1.6 | −4.0 | 99.6 | 380 | |
| **III$_e$(C)** | 56 | 12.1 | | −5.4 | 99.8 | 384 | |
| **III$_f$(C)** | 68 | 8.0 | −3.4 | −3.7 | 99.3 | 381 | |
| **IV$_a$(H)** | 19 | 23.4 | +15.9 | −7.7 | 97.6 | 387 | |
| **IV$_b$(H)** | 23 | 19.6 | +10.3 | −7.7 | 98.9 | 383 | |
| **IV$_c$(H)** | 33 | 18.0 | +8.0 | −7.3 | 99.4 | 390 | |
| **IV$_d$(H)** | 21 | 27.4 | +15.7 | −7.9 | 99.4 | 390 | |
| **IV$_e$(H)** | 43 | 30.7 | | −8.7 | 97.2 | 382 | |
| **IV$_f$(H)** | 41 | 20.7 | +9.3 | −8.0 | 98.1 | 388 | |
| **IV$_g$(H)** | 38 | 14.6 | +9.6 | −5.4 | 98.8 | 381 | |
| **V$_a$(H)** | 34 | 22.5 | +15.0 | −7.4 | 93.3 | 399 | |
| **V$_b$(H)** | 43 | 22.8 | +12.5 | −7.2 | 98.9 | 394 | 34 |
| **V$_c$(H)** | 30 | 19.1 | +9.1 | −7.8 | 99.5 | 392 | 35 |
| **V$_d$(H)** | 40 | 27.0 | +15.3 | −8.2 | 98.2 | 400 | 31 |
| **V$_e$(H)** | 34 | 28.3 | | −9.3 | 98.8 | 395 | 25 |
| **V$_f$(H)** | 34 | 19.9 | +8.5 | −8.1 | 99.6 | 391 | 36 |
| **V$_g$(H)** | 25 | 12.5 | +7.5 | −4.7 | 99.4 | 383 | 36 |
| Kapton | 41 | 83.8 | | 5.0 | 88.1 | 444 | |

**III$_e$(H)** and **III$_g$(C)** was brittle as form thin film.

[a] (H): polyimides were obtained by the thermal imidization. (C): polyimides were obtained by the chemical imidization with DMAc as solvent.

[b] The color parameters were calculated according to a CIE LAB equation, using paper as a standard. $L^*$ is lightness; 100 means white, while 0 implies black. A positive $a^*$ means red color, while a negative $a^*$ indicated green color. A positive $b^*$ means yellow color, while a negative $b^*$ implies blue color.

[c] $\Delta b$ are the value of camparing **III(H)** difference.

results were attributed to the reduction of the intermolecular CTC effect. Therefore, the **III** series was more colorless than the **V** series. The **III** series also shows their $L^*$ values over than 98.6%, indicate these polyimides are with higher lightness.

Moreover, the color intensity of the **III** series could also be elucidated from the cutoff ($\lambda_0$) observed in UV–vis absorption spectra. The $\lambda_0$ of the **III** series in the range of 369–382 nm is listed in Table 4. Fig. 4 shows the UV–vis spectra of the **III** series, the **III** series is the kind of polyimide with high transmittances and are even higher than **IV** series' and kapton's. To summarize, the colorlessness of the **III** series stems from the structures of dianhydride and diamine. The asymmetrical dianhydride α-BPDA is effective in preventing the CTC formation between the polymer chain through steric hindrance. Bis(ether amine) with the pendent $CF_3$ group also can reduces CTC formation to form colorless polyimide. Therefore, the **III** series combines hindering from CTC formation to obtain colorless characteristic.

### 3.2.3. Thermal property

DSC and TGA were used to evaluate the thermal properties of these polyimides. As shown in Table 4, $T_g$ values of **III$_{a–g}$** were in the range of 244–319 °C, **III$_{a,b,e}$** were over than 300 °C, and **III$_e$** containing tetramethylbiphenyl group showed the highest $T_g$. However, the $T_g$ values of **III$_a$**, **III$_c$**, **III$_f$** and **III$_g$** showed the unusual phenomenon. Compared **III** series with nonfluorinated **IV** series and fluorinated s-BPDA–polyimides (**V** series), the $T_g$ values raised because of the t-butyl group make the chain rotate uneasily such as **IV$_c$**>**IV$_a$** and **V$_c$**>**V$_a$**, but the $T_g$ value of **III$_a$** is higher than **III$_c$**. In addition, as the structure containing isopropyl or hexfluoroisopylidene groups are compared, **IV$_g$** and **V$_g$** are higher than **IV$_f$** and **V$_f$**, respectively. Because of the bonding energy of C–F is higher. However, this phenomenon is not showed in **III** series (**III$_g$** and **III$_f$**). Slightly lower $T_g$'s for the **III** series in comparison with the **IV** series except **III$_{a,b}$**, this might be a result of reduced chain–chain interaction and poor chain packing due to the bulky pendant $CF_3$ groups. In addition, **III$_{a–g}$** exhibited higher $T_g$ than **V$_{a–g}$** ones that was attributed to the asymmetric structure requiring a larger sweep volume for the crank shaft motion and higher temperature to obtain this motion.

The temperatures for 10% weight loss ($T_{10}$) and a char

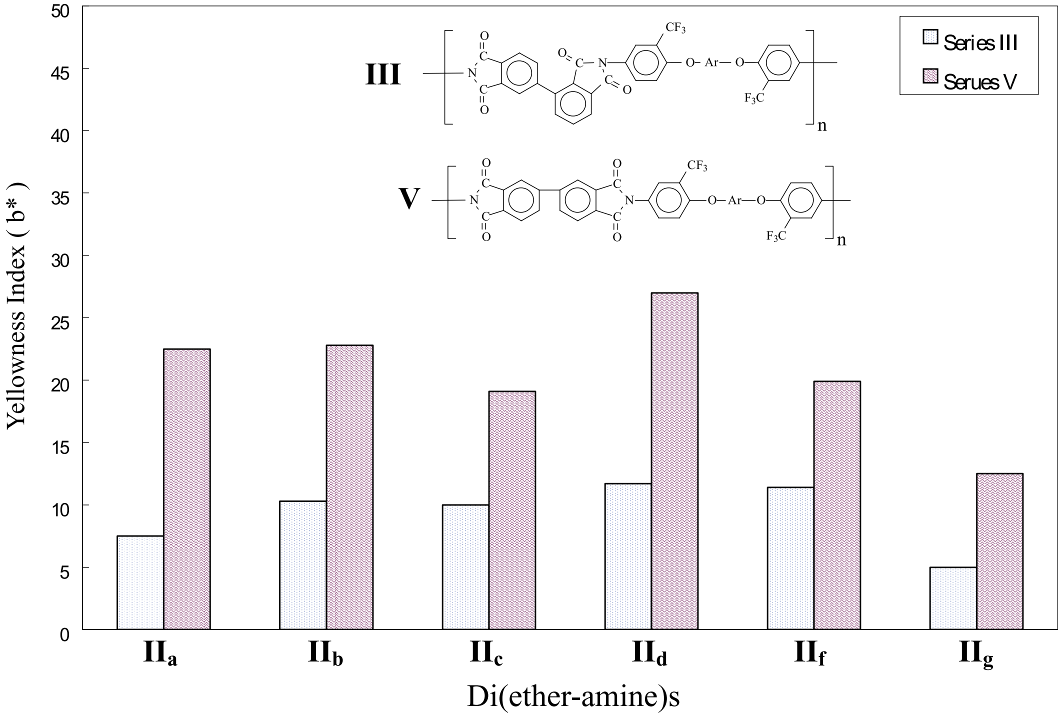


Fig. 3. Comparison of the yellowness index ($b^*$ value) between polyimides **III** and **V**.

yield were determined from original TGA thermograms and are also tabulated in Table 4. The $T_{10}$ values of **III$_{a–g}$** stayed within 515–608 °C in nitrogen and within 505–597 °C in air atmosphere. They left more than 54% char yield at 800 °C in nitrogen. **III$_d$** showed the highest $T_{10}$ values either in nitrogen or in air and residual, due to containing the rigid structure of biphenyl. **III$_e$** show lowest $T_{10}$ either in nitrogen or in air. It might be due to tetramethylbiphenyl group is decomposed easily by heating process.

### 3.2.4. Tensile property

The thin film tensile properties for the **III** series are shown in Table 5. They had strengths at break of 96–123 MPa, elongations to break of 7–19%, and initial moduli of 1.9–2.5 GPa. These films showed distinct yield points on stress–strain curves (yield strengths = 100–128 MPa) except **III$_b$**. **III$_d$** with the highest molecular weight possess yield strengths and largest elongation at break and initial modulus, which indicated high toughness. **III$_e$(H)** was turned into oligomer and was brittle in the production of thermal imidization, but **III$_e$(C)** via chemical imidization possessed good tensile property. The fluorinated **III** series not only increased solubility and reduced colored intensity, but also retained the well mechanical property as compared with the **IV** series.

### 3.2.5. Moisture absorption and dielectric constants

The moisture absorption of the **III** series is summarized

Table 4
Thermal properties of polyimides

| Polymer | $T_g$ (°C)[a] | $T_{10}$ (°C)[b] | | Char yield (%)[c] | Polymer | $T_g$ (°C)[d] | Ploymer | $T_g$ (°C)[d] |
|---|---|---|---|---|---|---|---|---|
| | | In $N_2$ | In Air | | | | | |
| **III$_a$** | 310 | 602 | 587 | 58 | **IV$_a$** | 285 | **V$_a$** | 260 |
| **III$_b$** | 311 | 600 | 589 | 56 | **IV$_b$** | 256 | **V$_b$** | 249 |
| **III$_c$** | 286 | 544 | 542 | 54 | **IV$_c$** | 291 | **V$_c$** | 262 |
| **III$_d$** | 283 | 608 | 597 | 65 | **IV$_d$** | 298 | **V$_d$** | 276 |
| **III$_e$** | 319 | 500 | 490 | 56 | **IV$_e$** | 338 | **V$_e$** | 351 |
| **III$_e$(C)** | 305 | 515 | 505 | 62 | | | | |
| **III$_f$** | 250 | 556 | 553 | 61 | **IV$_f$** | 262 | **V$_f$** | 243 |
| **III$_g$** | 244 | 566 | 562 | 55 | **IV$_g$** | 269 | **V$_g$** | 245 |

[a] Baseline shift in the second heating DSC traces, with a heating rate of 15 °C/min.

[b] Temperatures at which 10% weight loss were recorded by TG at a heating rate of 20 °C/min.

[c] Residual weight (%) when heated to 800 °C in nitrogen.

[d] Polyimides were obtained by the thermal imidization.

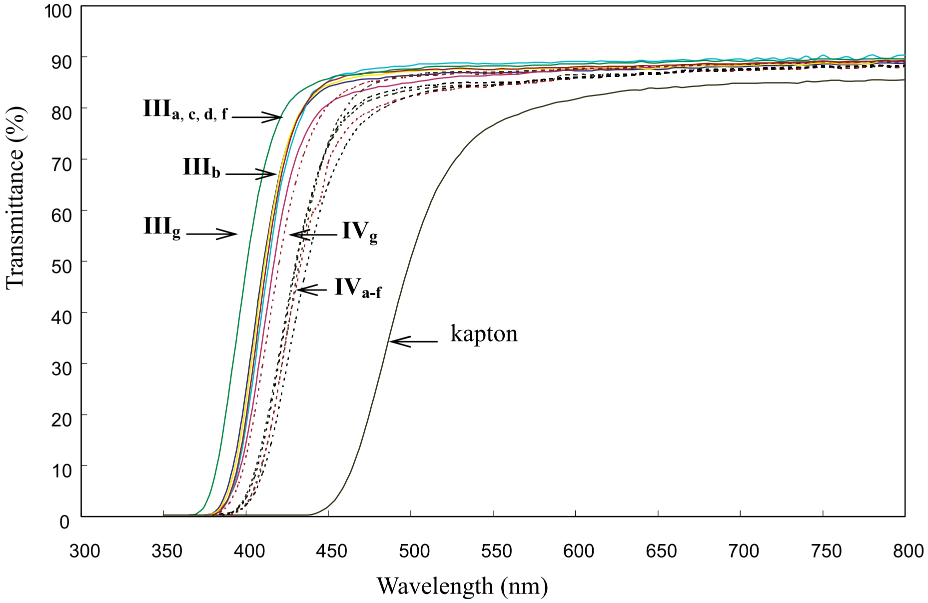


Fig. 4. UV–visible spectra of polyimide films $\mathbf{III_{a-g}}$, $\mathbf{IV_{a-g}}$ and Kapton.

in Table 6. $\mathbf{III_{a-g}}$ exhibited lower moisture absorption in range of 0.11–0.36% than the corresponding nonfluorinated homologues $\mathbf{IV_{a-g}}$ (0.46–0.64%) and commercial polyimide Kapton film (0.52%) because of the hydrophobicity of $CF_3$ group. Moreover, $\mathbf{III_g}$ exhibited the lowest moisture absorption due to the higher fluorine content in the repeat unit. Table 6 also summarizes the results of dielectric constants. $\mathbf{III_{a-g}}$ showed lower dielectric constants (3.16–3.36 at 1 kHz) than the **IV** series (3.44–3.77 at 1 kHz) and Kapton (3.89 at 1 kHz). The decreased dielectric constants might be attributed to the presence of the bulky $CF_3$ groups, the strong electronegativity of fluorine results in very low polarizability of the C–F bonds, thus decreasing the dielectric constant. Thus, $\mathbf{III_g}$ also exhibited the lowest dielectric constants.

## 4. Conclusions

A series of colorless polyimide $\mathbf{III_{a-g}}$ is synthesized from α-BPDA with various aromatic bis(ether amine)s ($\mathbf{I_{a-g}}$) bearing the pendent trifluoromethyl group via a thermal or chemical imidization. The **III** series shows excellent solubility in the organic solvents. They are all soluble in the amide-type solvent like NMP, DMAc, DMF, ether-type solvents like Dioxane, THF and chloronated-solvent of $CH_2Cl_2$ and $CHCl_3$. These films ($\mathbf{III_{a-g}}$) are colorless and transparent with cutoff wavelengths ($\lambda_0$) in the range of 369–382 nm and $b^*$ value (a yellowness index) ranging from 5–11.7. $T_g$'s of the **III** series are raised higher and the **III** series also show lighter-colored than symmetrical structure of polyimides deriving from s-BPDA (**V**). The resulting of

Table 5
Tensile properties of polyimide films

| Polymer code[a] | Strength at yield (MPa) | Strength at break (MPa) | Elongation to break (%) | Initial modulus (GPa) |
|---|---|---|---|---|
| $\mathbf{III_a}$ | 119 | 110 | 19 | 2.1 |
| $\mathbf{III_b}$ | – | 98 | 7 | 2.3 |
| $\mathbf{III_c}$ | 100 | 96 | 10 | 2.1 |
| $\mathbf{III_d}$ | 128 | 123 | 13 | 2.5 |
| $\mathbf{III_e}$ | – | 106 | 14 | 1.9 |
| $\mathbf{III_f}$ | 111 | 109 | 15 | 2.2 |
| $\mathbf{III_g}$ | 105 | 102 | 11 | 2.0 |
| $\mathbf{IV_a}$ | – | 113 | 10 | 2.3 |
| $\mathbf{IV_b}$ | – | 159 | 13 | 2.9 |
| $\mathbf{IV_c}$ | – | 128 | 11 | 2.2 |
| $\mathbf{IV_d}$ | – | 116 | 10 | 2.2 |
| $\mathbf{IV_e}$ | – | 57 | 10 | 1.5 |
| $\mathbf{IV_f}$ | 107 | 101 | 14 | 1.8 |
| $\mathbf{IV_g}$ | 101 | 99 | 9 | 2.3 |

$\mathbf{III_e}$(**H**) was brittle as casting to film.

[a] Polyimides were obtained by the thermal imidization except $\mathbf{III_e}$ was obtained by the chemical imidization with DMAc as solvent.

Table 6
Moisture absorption and dielectric constants of polyimides

| Polymer[a] | Film thickness (μm) | Moisture absorption (%) | Dielectric constant (Dry) | | | |
|---|---|---|---|---|---|---|
| | | | 1 kHz | 10 kHz | 1 MHz | 40 MHz |
| $\mathbf{III_a}$ | 92 | 0.33 | 3.30 | 3.27 | 3.24 | 3.24 |
| $\mathbf{III_b}$ | 71 | 0.22 | 3.16 | 3.12 | 3.10 | 3.08 |
| $\mathbf{III_c}$ | 69 | 0.36 | 3.36 | 3.34 | 3.32 | 3.31 |
| $\mathbf{III_d}$ | 79 | 0.30 | 3.29 | 3.22 | 3.21 | 3.20 |
| $\mathbf{III_e}$ | 85 | 0.35 | 3.35 | 3.34 | 3.31 | 3.29 |
| $\mathbf{III_f}$ | 95 | 0.24 | 3.25 | 3.22 | 3.18 | 3.17 |
| $\mathbf{III_g}$ | 90 | 0.11 | 3.16 | 3.11 | 3.09 | 3.07 |
| $\mathbf{IV_a}$ | 24 | 0.54 | 3.66 | 3.58 | 3.54 | 3.53 |
| $\mathbf{IV_b}$ | 28 | 0.58 | 3.57 | 3.50 | 3.47 | 3.48 |
| $\mathbf{IV_c}$ | 37 | 0.64 | 3.72 | 3.64 | 3.60 | 3.60 |
| $\mathbf{IV_d}$ | 25 | 0.55 | 3.62 | 3.53 | 3.51 | 3.50 |
| $\mathbf{IV_e}$ | 49 | 0.49 | 3.77 | 3.66 | 3.64 | 3.63 |
| $\mathbf{IV_f}$ | 39 | 0.46 | 3.60 | 3.55 | 3.53 | 3.52 |
| $\mathbf{IV_g}$ | 42 | 0.50 | 3.44 | 3.36 | 3.33 | 3.32 |
| Kapton | 28 | 0.52 | 3.89 | 3.85 | 3.67 | 3.69 |

[a] Polyimides were obtained by the thermal imidization except $\mathbf{III_e}$ was obtained by the chemical imidization with DMAc as solvent.

these polyimides exhibit easy dissolved, more colorless, lower dielectric constants and moisture absorption than the corresponding nonfluorinated **IV** series together with good mechanical properties and thermal stability.

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