HIGHLY TRANSPARENT AND COLORLESS POLYIMIDE FILM WITH LOW DIELECTRIC CONSTANT BY INTRODUCING META-SUBSTITUTED STRUCTURE AND TRIFLUOROMETHYL GROUPS

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Abstract

An effective design strategy for preparing highly transparent polyimide film with low dielectric constant is presented. The key to the strategy is to simultaneously introduce meta-substituted structure and trifluoromethyl in polymer chains. By using this design strategy, a highly transparent polyimide film with low-k was synthesized from 3,5-diaminobenzotrifluoride (m-TFPDA) and 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) through a two-step method. The obtained m-TFPDA/6FDA (CPI) film (∼30 μm) possesses high optical transparency (Tλ=334 nm, Tλ=450 nm,90% =85.26%, Haze=0.31) and is close to colorless (L*=-96.03, a*=-0.34, b*=2.12, yellow index=-3.96). The intrinsic k and dielectric loss value of the film are 2.27 and 0.0013 at 10 kHz, respectively. More importantly, such low dielectric performance could remain stable up to 280 °C and the film shows a good moisture rate (∼0.51%), which helps to maintain the low-k property stability in different humid environments. Meanwhile, the film also shows good thermal stability and mechanical properties, with a glass transition temperature (Tg) of 295 °C and the 5 wt% decomposition temperature (T5%) of 522 °C under N2. The tensile strength and tensile modulus of the film are 85.1 MPa and 1.96 GPa, respectively. In addition, the film is soluble in common solvents, which allows simple solution processing and low-cost, continuous roll-to-roll processes. This design strategy is beneficial to improving the transparency, lightening yellow color, lowering the dielectric constant and meanwhile maintaining the comprehensive properties of polyimide films, which is mainly due to the introduced meta-substituted and trifluoromethyl structures effectively inhibiting the transfer of charge transfer complex (CTC) effects and increasing the free volume of film. This design strategy could also be extended to other high-performance polymer systems.

Keywords

Polyimide film; Translucent; Colorless; Low dielectric constant

INTRODUCTION

With the development of photoelectric devices presenting the trend of light-weight, flexibility and high-integration, glass as a traditional transparent substrate material cannot meet the requirements of flexible packaging technology. High-transparency polymer materials are an attractive choice due to the advantages of flexibility and light-weight, of which polyimide (PI) has become a research focus due to its good mechanical properties, chemical resistance as well as good heat resistance, which can meet the high-temperature manufacturing requirements such as electrode film deposition and annealing process. However, traditional aromatic PI generally presents the characteristics of yellow color owing to the existence of intra- and inter-molecular charge transfer complex (CTC), making PI get absorption in ultraviolet-visible or near-infrared regions, and limiting its application in some photoelectric materials, optical communication industry and other associated fields.

To improve the transparency of PI films, researchers have focused on designing the molecular structure of diamine or dianhydride. A direct approach is to introduce alicyclic structures in polymer backbone to destroy the CTC effects, which could damage the heat resistance of PI to some extent. It is to be solved that improving the transparency meanwhile as far as possible maintaining the excellent characteristics of PI films. Some studies have shown that the introduction of fluorine atoms or fluorine-containing substituents in aromatic PI can improve its transparency and lighten the yellow color due to the fluorine atom possessing high electronegativity. Although the transparency of PI film could increase, the syn-
thetic methods are usually complex with high cost due to the increased proportion of fluorine atoms in the monomer.\textsuperscript{[19]} It is also proved that incorporating meta-substitution structures,\textsuperscript{[20]} non-coplanar structures,\textsuperscript{[21]} asymmetric structures\textsuperscript{[22]} or bulky side groups\textsuperscript{[23]} to PI chains can impede the flow of charges along the molecular chains, and reduce the conjugation among molecules, which also could effectively reduce the absorption of visible light and improve the transparency of PI films.

Meanwhile, with the upcoming of fifth generation (5G) mobile communication technology, low-k materials (k<3) or ultra-low-k materials (k<2) are demanded for the high-speed and high-frequency transmission.\textsuperscript{[24]} Typically, the dielectric constant of normal PI is approximately 3.1–3.5 depending on the chemical structures,\textsuperscript{[25]} which cannot meet the requirements of low-k materials. According to the Clausius-Mossotti equation, the most effective method for reducing the dielectric constant is to increase the internal space of materials.\textsuperscript{[26]} Air is the substance with the smallest dielectric constant in nature (about 1.0), so introducing air into the polymer matrix can reduce the density of polarized units and effectively reduce its dielectric constant, even below 2.0.\textsuperscript{[27]} However, it is difficult to regulate the trade-off of the porosity with mechanical properties, as ordinary porous materials usually have poor mechanical properties and are easy to absorb water due to their porosity, which could deteriorate the low-k properties during the subsequent processing and applications. It is confirmed that increasing the free volumes can obtain intrinsic low-k PI materials,\textsuperscript{[28]} and the effective methods are introducing asymmetric structures or bulky side groups in PI chain segments, which breaks the tight packing of molecular chains.\textsuperscript{[29,30]}

It is momentous to prepare PI films with high transparency and low-k for applications in the field of electronics or communications, whereas few studies were reported due to the complicated molecular structure and high manufacturing cost.\textsuperscript{[31,32]} In this work, we present a facile and effective strategy for synthesis of highly transparent PI film with low-k by simultaneously introducing meta-substituted structure and trifluoromethyl in polymer chains. A highly transparent PI film with intrinsic low-k was synthesized from 3,5-diaminobenzotrifluoride (m-TFPDA) and 4,4′-(hexafluoroisopropyridine) diphthalic anhydride (6FDA) (CPI) through a two-step method (Scheme 1). The effects of meta-substituted structure and the introduction of trifluoromethyl units on optical transparency and dielectric properties of CPI were also studied by comparing with p-phenylenediamine/6FDA (p-PDA/6FDA) and m-phenylenediamine/6FDA (m-PDA/6FDA).

**EXPERIMENTAL**

**Materials**

3,5-Dinitrobenzotrifluoride was purchased from Shanghai adamas reagent corporation. p-Phenylenediamine (p-PDA) and m-phenylenediamine (m-PDA) were provided by Changzhou sunshine pharmaceutical corporation. 4,4′-(Hexafluoroisopropyridine) diphthalic anhydride (6FDA) was supplied by Tianjin zhuongai chemical technology corporation and recrystallized from acetic anhydride and then dried in vacuum at 150 °C for 10 h prior to use. 10% Palladium on activated carbon (Pd/C) was provided by Shanghai titan technology corporation. N,N-dimethylacetamide (DMAc) was purified by distillation under reduced pressure over CaH\textsubscript{2} and stored in 4Å molecular sieves. All other solvents (analytical grade) were purchased from Sinopharm chemical reagent Shanghai corporation and used without further purification.

**Characterization**

Inherent viscosities (\(\eta_{inh}\)) of poly(amide acid) (PAA) were measured with an Ubbelohde viscometer at 25 °C in DMAc at a concentration of 0.5 g/dL. FTIR spectra were recorded on a Nicolet 8700 spectrometer (Perkin Elmer, USA) at a resolution of 4 cm\textsuperscript{-1}. Elements analysis (EA) was conducted on a Vario EL III element analyzer (Elementar, GER). \(^1\)H- and \(^13\)C-NMR spectra were recorded on an Avance III HD 600 MHz spectrometer (Bruker, SUI) operating at 600 MHz in DMSO-d\(_6\). Wide-angle X-ray diffraction (WAXD) was conducted on a Rigaku D/max-2550 PC X-ray diffractometer (Rigaku, Japan) using Cu Ka radiation, 2\(\theta\) ranging from 5° to 60°. The density of the polyimide film was measured by a XS204 densimeter (METTLER TOLEDO, Swiss). Color intensities of the films were assessed by a CS-720 colorimeter (Hangzhou color spectrum Co. LTD., China). The transmittance of the films was determined by a Lambda 950 Ultraviolet-visible

![Scheme 1](https://doi.org/10.1007/s10118-021-2514-2)
(UV-Vis) spectrometer (Perkin Elmer, USA). Differential scanning calorimetry (DSC) was performed with a DSC1 differential scanning calorimeter (NETZSCH, Germany) at a heating rate of 10 °C/min under nitrogen with 50 mg/min gas flow. Thermal mechanical analysis (TMA) was carried out with a Q400 thermal mechanical analyzer (TA, USA) at a heating rate of 5 °C/min under nitrogen ranged from 50 °C to 400 °C with the preloading force set as 0.05 N. Thermogravimetric analysis (TGA) was performed using a TG209F3 thermogravimetric analyzer (Netzsch, Germany) at a heating rate of 10 °C/min under nitrogen ranged from 40 °C to 800 °C. The mechanical properties were tested with an Instron 5969 universal testing instrument (USA) at crosshead speed of 5 mm/min in accordance with GB/T 1040.3-2006. The dielectric constant and dielectric loss were measured by a Novocontrol concept 40 wideband dielectric impedance spectrometer (Germany). The free volume of the films was analyzed by positron annihilation lifetime spectroscopy (PALS) with a fast-slow coincidence system. Water uptake was calculated by the weight change of the films before and after immersed in deionized water at 45 °C for 48 h.

**Synthesis of 3,5-Diaminobenzotrifluoride**

To a 250 mL three-neck round-bottom flask fitted with a mechanical stirrer, a dropping funnel and a condenser was added a mixture of 3,5-dinitrobenzotrifluoride (7.083 g, 30 mmol), absolute ethyl alcohol (80 mL) and 10% Pd/C (0.5 g). The mixture was heated to reflux under nitrogen and 85% hydrazine hydrate (10 mL) was added dropwise over a period of 1 h. After a further 18 h of refluxing, the hot mixture was filtered to remove Pd/C, and most of the solvent in filtrate was removed by vacuum rotary evaporation. The obtained mixture was poured into 300 mL of stirring water to produce a solid precipitate which was filtered out, washed with water, and dried under vacuum. Yield: 3.25 g (65%). Melting point: 88−90 °C (DSC). FTIR (KBr, cm⁻¹): 3453, 3414, 3324, 3217, 1612. PyGC-MS (EI) m/z: 176.10 (M⁺) calculated for C₇H₇F₄N₂O; 176.14. ¹H-NMR (DMSO-d₆, δ, ppm): 6.03 (s, 2H), 5.98 (s, 1H), 5.15 (s, 4H). ¹³C-NMR (DMSO-d₆, δ, ppm): 150.32, 130.96, 130.76, 130.56, 130.36, J_C,F=30 Hz), 128.00, 126.20, 124.39, 122.59, J_C,F=270 Hz), 102.27, 99.09. Elemental analysis: Calculated for C₇H₇F₄N₂: C, 47.22%, H, 4.81%, N, 15.90%, Found: C, 47.24%, H, 4.80%, N, 15.98%.

**Synthesis of Polyimides**

Three kinds of PI films were synthesized by two-step procedure via PAA precursors, followed with heat imidization by gradient heating process. The optimum imidization temperature was determined by temperature-dependent FTIR spectra of PAA (Fig. S1 in the electronic supplementary information, ES1). The preparation of CPI film was described as an example. The PAA solution was synthesized by firstly dissolving 0.7046 g (4 mmol) of 3,5-diaminobenzotrifluoride (m-TFPA) in 10 g of dimethylacetamide (DMAc), and then 1.78 g of 4,4′-(hexafluorosulfonyl) diphthalic anhydride (6FDA) and extra 12.33 g of DMAc were successively added to adjust the solid content of 10 wt%. The solution was stirred at 200 r/min with a mechanical stirrer for 24 h at room temperature. PI films were prepared by casting PAA solutions on glass substrates, followed by a preheating procedure (60 °C/12 h, 80 °C/2 h) and an imidization procedure (100 °C/1 h, 200 °C/1 h, 300 °C/1 h) in a vacuum oven. The films were obtained by soaking casted glass substrates in deionized water and dried.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of PI Films**

As shown in Scheme 1, a series of polyimide (PI) films are synthesized via a two-step procedure with poly(amic acid) (PAA) as precursors, followed by thermal imidization at elevated temperature to 300 °C. The inherent viscosities of the PAA precursors are 0.84–1.60 dL/g, and the high viscosities provide the possibility for the subsequent film-forming. The chemical structures of PI films are firstly studied by FTIR spectra and ¹H-NMR. As shown in Fig. 1(a), FTIR spectra display that the imide characteristic bands appear at around 1780, 1730 and 1380 cm⁻¹.

![Fig. 1](https://doi.org/10.1007/s10118-021-2514-2)
1390 cm\(^{-1}\), and the C–O and C–F stretching vibration absorption bands present in the region of 1300–1100 cm\(^{-1}\). There is no existence of the characteristic absorption bands of the amide at 3200 and 1520 cm\(^{-1}\), which indicates the complete imidization reaction of PI films. In the \(^1\)H-NMR spectra of PI films in Figs. 1(b) and 1(c), all the protons can be assigned for various samples. The results of the element analysis of PI films are listed in Table 1, and the detected values could be well in agreement with the calculated ones of the proposed structures, which confirms that the PI films have been successfully synthesized.

### Optical Properties of PI Films

The physical appearances of the PI films are shown in Fig. 2. Compared with the commercially aromatic polyimide film (Kapton), the obtained samples in our work demonstrate better transparency and lighter color. The color intensities of PI films are further assessed by colorimeter and the values are summarized in Table 2.

There are some color characteristic parameters including \(L^*\) (0-100, black-white), \(a^*\) (negative-positive, green-red), \(b^*\) (negative-positive, blue-yellow), the yellow index (YI) and haze values to assess the color index of films. As shown in Table 2, it is noticed that CPI film exhibits a high \(L^*\) value of 96.03, showing a good lightness. It also exhibits a low \(a^*\) value of \(-0.34\) and \(b^*\) value of 2.12 with the YI value of 3.96, which are much lower than those of \(m\)-PDA/6FDA (18.11) and \(p\)-PDA/6FDA (9.96) films, indicating good colorless properties.

The optical transparency of the films is also evaluated by UV-Vis spectra as displayed in Fig. 3. It is shown that the cutoff wavelength (\(\lambda_{\text{cutoff}}\)) of CPI film is about 334 nm, lower than those of \(m\)-PDA/6FDA (366 nm) and \(p\)-PDA/6FDA (357 nm) films, and the transmittance at the wavelength of 450 nm for CPI film is about 85.26%, which is higher than those of \(m\)-PDA/6FDA (83.27%) and \(p\)-PDA/6FDA (80.41%). Meanwhile, CPI shows a low haze value of 0.31, demonstrating that the introduction of both meta-substituted and trifluoromethyl structures could lighten the color and increase the optical transmittance of PI film.

To explore its mechanism, the geometry structures and molecular orbital energies are further analyzed by theoretical calculations. Fig. 4 describes the theoretical conformation of as-prepared PI films derived from geometry optimization calculation of density functional theory (DFT) based on a large basis-set function of M06-2X/def2-SVP. In Fig. 4, the position of amino group changing from \(para\)-substituted to \(meta\)-substituted makes the molecular chains more bent. In addition, further introduction of trifluoromethyl increases the dihedral angle between phenyl and imide ring (\(p\)-PDA/6FDA=140°, \(m\)-PDA/6FDA=140°, CPI=143°), which distorts the molecular chains. The introduction of \(meta\)-substituted and trifluoromethyl units makes the molecular chains twisted, impeding the flow of charge transfer along the molecular chains and improving the transparency of PI films,\(^{[15]}\) which are consistent with the results of UV-Vis.

It is well known that the intramolecular and intermolecular

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**Table 1** General properties of PAA solutions and PI films.

| Code      | \(n_{\text{inh}}\) of PAA (dL/g) | Repeating unit             | Density (g/cm\(^3\)) | Elemental analysis (%) |
|-----------|----------------------------------|----------------------------|----------------------|------------------------|
|           |                                  |                            |                      | C                | H    | N    |
|           |                                  |                            |                      | Calculated          |      |      |
|           |                                  |                            |                      | Found              |      |      |
| p-PDA/6FDA| 1.60                             | \(\text{C}_3\text{H}_3\text{O}_3\text{F}_4\text{N}_2\)     | 1.40                 | 58.15              | 1.95 | 5.42 |
| m-PDA/6FDA| 1.54                             | \(\text{C}_3\text{H}_3\text{O}_3\text{F}_4\text{N}_2\)     | 1.37                 | 58.15              | 1.95 | 5.42 |
| CPI       | 0.84                             | \(\text{C}_3\text{H}_3\text{O}_3\text{F}_4\text{N}_2\)     | 1.34                 | 57.83              | 2.17 | 5.52 |

**Fig. 2** Physical appearance of various polyimide films.

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**Table 2** Optical properties of polyimide films.

| Code      | \(L^*\)       | \(a^*\)      | \(b^*\)      | YI      | \(\lambda_{\text{cutoff}}\) (nm) | \(T_{450}\) (%) | Haze |
|-----------|---------------|--------------|--------------|---------|-------------------------------|-----------------|------|
| p-PDA/6FDA| 94.73         | −3.25        | 10.96        | 18.11   | 366                           | 80.41           | 0.49 |
| m-PDA/6FDA| 95.16         | −1.44        | 5.67         | 9.96    | 357                           | 83.27           | 0.29 |
| CPI       | 96.03         | −0.34        | 2.12         | 3.96    | 334                           | 85.26           | 0.31 |
| Kapton    | 88.13         | −10.06       | 66.35        | 85.87   | 447                           | 1.255           | 1.37 |

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CTC effects between electron-donating diamines and electron-withdrawing dianhydrides result in the poor light transmittance in visible light area and the yellow characteristics of PI films, which mainly depend on the molecular structures of the polymers. Thus, the density functional theory (DFT) calculations based on a large basis-set function of M06-2X/def2-SVP are further applied to evaluate the molecular orbital energies of various PI structures in our work. The $E_{\text{LUMO}}$ values are related to the electrophilicity of dianhydrides moieties, and the larger $E_{\text{LUMO}}$ values indicate stronger electron acceptable ability of the compounds. As shown in Fig. 5. The $E_{\text{LUMO}}$ values of p-PDA/6FDA, m-PDA/6FDA and CPI are $-1.91$, $-1.92$ and $-2.06$ eV, respectively, while the $E_{\text{LUMO}}$ value of Kapton film is $-2.38$ eV, indicating that 6FDA unit with electron-withdrawing groups ($\text{CF}_3$) possesses a stronger electrophilicity. Meanwhile, the $E_{\text{HOMO}}$ values represent the nucleophilicity of diamine moieties, and there is a decreased trend from p-PDA/6FDA ($-7.90$ eV) to m-PDA/6FDA ($-8.05$ eV) and CPI ($-8.43$ eV), illustrating that the position of the amino changed from para-substituted to meta-substituted and the introduction of trifluoromethyl both reduce the electron donating ability of diamines moieties, thus benefiting the weakening of CTC effects in PI films. Furthermore, the energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) determines the degree of CTC effects between intra- and/or inter-molecular chains and a larger $\Delta E$ value indicates weakened CTC effects between intramolecular and intermolecular PI chains. It is clearly noticed in Fig. 5 that CPI film displays higher $\Delta E$ value than those of p-PDA/6FDA (5.99 eV), m-PDA/6FDA (6.13 eV) and Kapton film (5.04 eV), confirm-
ing that the diamine changing from para-substitution to meta-substitution and the introduction of trifluoromethyl could be an effective strategy to inhibit the formation of CTC effects in PI films and lighten its color characteristics.

**Dielectric Properties of PI Films**

As shown in Fig. 6, the dielectric constant and dielectric loss of polyimide films are measured at the frequencies from $10^2$ Hz to $10^6$ Hz at 25 °C and 30% relative humidity. As shown in Fig. 6(a), the intrinsic dielectric constant decreased according to the following sequence: Kapton (3.48) > p-PDA/6FDA (2.66) > m-PDA/6FDA (2.56) > CPI (2.27), exhibiting a decreased dielectric constant with the diamine changing from para-substitution to meta-substitution and the introduction of trifluoromethyl groups. Besides, the dielectric loss value of CPI film is 0.0013 at 10 kHz. More importantly, the low-k performance of CPI film could remain stable up to 280 °C as displayed in Fig. 6(c), illustrating its great application potentials at high temperatures. To probe the deep possible reasons, PALS is used to characterize the free volume of polymer materials.\(^{[15,36]}\) Positrons from a radioactive source, in addition to being annihilated by the electron, could combine with an electron in material to form a metastable atom called positronium, with the premise that the electron density in a material must be low enough. The positronium will annihilate from $p$-Ps (singlet spin state, electron and positron have reverse spin) by emitting two $\gamma$-rays with a lifetime of 125 ps or $o$-Ps (triplet spin state, electron and positron have the same spin) by emitting three $\gamma$-rays with a lifetime of 142 ns. The formed $o$-Ps in a material would pick up an electron around it and the positron in $o$-Ps annihilate by emitting two $\gamma$-rays, greatly shortening the lifetime of $o$-Ps to a typical value of 1–10 ns. This annihilation is called pick-off annihilation, with which the lifetime is highly sensitive to the size of the free volume in material.

The positron lifetime spectra of different polyimide films are shown in Fig. 7(a) and the detailed data of the lifetime spectra analyzed by the PATFIT routine\(^{[28]}\) are listed in Table 3.

**Fig. 6** (a) Dielectric constant and (b) dielectric loss of the polyimide films versus frequency, and (c) the dielectric constant and loss versus temperature of CPI film at 10 kHz.

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Three exponential decay components ($\tau_1$, $\tau_2$, and $\tau_3$) were detected for each sample. $\tau_1$ is the positron annihilation lifetime of $p$-Ps due to free annihilation and $\tau_2$ is attributed to positron annihilation in the amorphous region. The long-lifetime component $\tau_3$ is attributed to pick-off annihilation of $o$-Ps at holes in the amorphous phase, which can be used to estimate the size of the free volumes in the amorphous phases of PI by Eq. (1):[35,37]

Table 3 Analyzed data for the positron lifetime in $p$-PDA/6FDA, $m$-PDA/6FDA, CPI and Kapton PI Films.

| Sample       | $\tau_1$ (ns) | $I_1$ (%) | $\tau_2$ (ns) | $I_2$ (%) | $\tau_3$ (ns) | $I_3$ (%) | $r_{PLAS}$ (Å) | $V_{PLAS}$ (Å$^3$) | $f_v$ (%) |
|--------------|---------------|-----------|---------------|-----------|---------------|-----------|----------------|---------------------|-----------|
| $p$-PDA/6FDA | 0.23          | 41.2      | 0.46          | 55.3      | 2.59          | 3.50      | 3.33           | 154.95              | 0.98      |
| $m$-PDA/6FDA | 0.24          | 42.7      | 0.47          | 52.9      | 2.80          | 4.39      | 3.49           | 177.91              | 1.41      |
| CPI          | 0.23          | 29.8      | 0.42          | 68.9      | 2.59          | 1.29      | 3.33           | 150.23              | 0.36      |

$^a$ Calculated by Eq. (1). $^b$ Calculated by the formula for the volume of the sphere: $V_{PLAS}=\frac{4}{3}\pi r_{PLAS}^3$. $^c$ Calculated by the formula: $f_v=C V_{PLAS} I_3$, $C=0.0018$. [24,28]

Fig. 8 (a) DSC curves, (b) TMA curves, (c) TGA curves, (d) tensile stress-strain curves, and (e) moisture rate and water contact angles of polyimide films.
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\tau_{\text{Ps}} = 0.5 \text{ ns} \left[ 1 - \frac{r}{r + \Delta r} + \frac{1}{2\pi} \sin \left( \frac{2\pi r}{r + \Delta r} \right) \right]^{-1}
\]

where the prefactor of 0.5 ns is the spin-averaged Ps annihilation lifetime, a value of \( \Delta r = 0.166 \) nm is obtained by fitting Eq. (1) to the observed porous materials, which was determined by Eldrup and Jean.\(^{[25,27]}\)

As summarized in Table 3, CPI film shows a long life-time component (\( \tau_3 \)) (5.95%) of 2.83 ns and the mean volume (\( V_{\text{PLAS}} \)) of the free-volume size is about 180.83 Å\(^3\). The relative free-volume fraction (\( \Delta \)) of the CPI film is about 1.94%, much larger than those of p-PDA/6FDA film (0.98%), m-PDA/6FDA film (1.41%) and the control sample of Kapton film (0.36%). This is well consistent with the changes of the dielectric constant for various PI films, indicating that a larger Ångström-scale free volume in CPI film greatly contributes to the reduced dielectric properties.

Furthermore, the broad WAXD peaks in Fig. 7(b) indicate that all the PI films present amorphous phases and the CPI film displays the largest interlayer distance according to the Bragg equation. Meanwhile, the densities of the p-PDA/6FDA, m-PDA/6FDA and CPI are 1.34, 1.37 and 1.40 g/cm\(^3\), respectively (\( \rho_{\text{Kapton}}=1.42 \) g/cm\(^3\)). It indicates that the introduction of meta-substituted structure and trifluoromethyl groups is favorable to the decrease of packing density of the molecules in PI films, which is beneficial to reducing the CTC effects and thus leads to a highly colorless film with a low dielectric property.

**Thermal and Mechanical Properties of PI Films**

The thermal properties of prepared PI films were also investigated by DSC, TMA and TGA. As displayed in Fig. 8(a), DSC results show that all the obtained PI films possess high service temperature above 280 °C. The glass transition temperatures (\( T_g \)) of p-PDA/6FDA, m-PDA/6FDA and CPI are 332, 298 and 296 °C, respectively. It is exhibited that the \( T_g \) decreased with the introduction of meta-substituted structures or trifluoromethyl groups, indicating the reduced trend of the tight packing for molecule chains with different structures of diamines. CTE values are also related to the linearity and rigidity of molecular chains. TMA results in Fig. 8(b) show that all the films expand as the temperature increases, and the curves show sharp expansion near the \( T_g \). Afterwards, the sizes of PI films remain constant with the temperature rising due to the straightened molecular chains. The CTE values (in the range of 50–250 °C) of p-PDA/6FDA, m-PDA/6FDA and CPI are 37, 39 and 48 ppm/K, respectively. p-PDA/6FDA shows the lowest CTE value due to the linearity of p-PDA, while the m-PDA makes molecular chains bent, increasing the CTE of m-PDA/6FDA, and the further introduction of trifluoromethyl with large volume makes the molecular chains twisted and increases the CTE of CPI. Furthermore, TGA curves show that PI films possess good thermal stability, with a \( T_{d,5}\%), of 514–522 °C, \( T_{d,10}\%) of 535–541 °C and their residual mass is 45%–51% at 800 °C in N\(_2\) atmosphere. \( T_{d,5}\%) and \( T_{d,10}\% \) and the residual mass of p-PDA/6FDA are almost identical with those of m-PDA/6FDA, illustrating that the meta-substituted structure has little effects on the heat resistance of the PI film. CPI film displays the highest values of \( T_{d,5}\%) and \( T_{d,10}\% \) with the lowest residual mass, which might be attributed to strong strength of C—F bond as the trifluoromethyl would be fractured from the main chain when the temperature is high.\(^{[34]}\)

The mechanical properties of PI films including tensile strength, tensile modulus and elongation at break were further examined, and all of the films present high tensile strength values of 85–105 MPa, tensile modulus values of 1.9–2.4 GPa and elongation at break values of 6.1%–7.3%, indicating that these PI films are tough and flexible. Additionally, moisture rates and water contact angles of three PI films are shown in Fig. 8(a), which display that the PI films possess good hydrophobicity. The introduced fluorine atoms possess small radius and low surface energy, which could migrate and enrich into the film surface during the process of the film formation, thus reducing the surface energy and improving the hydrophobicity of the films. Therefore, the moisture rate of CPI film is 0.51%, basically conforming to the request of water-resistant materials. The solubility behavior of CPI is also summarized (Table S1 in ESI), which shows that CPI has good solubility in many common organic solvents such as DMAc, dimethyl formamide (DMF), N-methylpyrrolidone (NMP), dichloromethane (DCM), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and m-cresol. The good solubility enables the feasibility of simple spin-on or continuous roll-to-roll processes to fabricate PI films during the device manufacturing process, making CPI a potential candidate in microelectronics.

**CONCLUSIONS**

In summary, an effective design strategy for preparing highly transparent PI film with low-k is presented. The key to this strategy is simultaneously introducing meta-substituted structure and trifluoromethyl groups in polymer chains. By using this strategy, a highly transparent polyimide film (CPI) with low-k was synthesized from m-TFPDA and 6FDA. The CPI film (~30 μm) possesses high optical transparency (\( \lambda_{\text{cut-off}}=334 \) nm, \( T_{450 \text{ nm}}=85.26\%, \text{Haze}=0.31 \)) and is close to colorless (\( L^*=96.03, a^*=-0.34, b^*=2.12, \text{yellow index}=3.96 \)). The intrinsic \( k \) and dielectric loss value of the film are 2.27 and 0.0013 at 10 kHz, respectively. More importantly, such outstanding low-k performance remains stable up to 280 °C and the film shows a low moisture rate (~0.51%), which could maintain the low-k property stability in different humid environments. Moreover, CPI film possesses high maximum service temperature with the \( T_g \) of 296 °C, good dimensional stability with the CTE of 48 ppm/K and good thermal stability with the \( T_{d,5}\%) of 522 °C. Besides, CPI also shows good mechanical properties with the tensile strength and tensile modulus of 85.1 MPa and 1.96 GPa, respectively. The CPI film with high \( T_g \) good thermal stability and mechanical properties is promising to meet the requirements of heat resistance and high application temperatures in the microelectronics industry, and has a potential to be applied as the flexible transparent substrate and dielectric layer material of integrated devices or transparent insulating panel of advanced transparent display devices.

**Electronic Supplementary Information**

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-021-2514-2.
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