

A Bulk Dielectric Polymer Film with Intrinsic Ultralow Dielectric Constant and Outstanding Comprehensive Properties

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Supporting Information

ABSTRACT: A bulk dielectric polymer film with an intrinsic ultralow *k* value of 1.52 at 10 kHz has been successfully synthesized based on a novel polyimide FPTTPI. More importantly, such outstanding dielectric properties remain stable up to 280 °C. The excellent ultralow dielectric properties are mainly because of the larger free volume (subnanoscale), which intrinsically exists in the amorphous region of polymeric materials. Meanwhile, FPTTPI also shows excellent thermal stability and mechanical properties, with a glass-transition temperature (T_g) of 280 °C, 5 wt % loss temperature of 530 °C, and a residual of 63% at 800 °C under N₂. It was soluble in common solvents, which made it possible to undergo simple spin-on or efficient, low-cost, and continuous roll-to-roll processes.



■ INTRODUCTION

With the development of ultralarge-scale integration (ULSI) to high speed and high integration in the semiconductor industry, and with the continuing miniaturization in the dimensions of electronic devices utilized in ULSI circuits, an urgent need exists for high-performance low-k and ultralow-k dielectric materials (low-k: $k \leq 2.5$; ultralow-k: $k \leq 2.0$) has arisen.¹⁻⁴ Such dielectrics materials would reduce the capacitance between the metal interconnects, the resistance-capacitance delay, the line-to-line crosstalk noise, and the power dissipation;^{5–7} these materials also have important application prospects in the fields of interlayer dielectric, semiconductor packaging (chips modules, etc.), and high-frequency, low-loss boards etc. So far, research of low-dielectric materials as an alternative to the workhorse dielectrics silicon dioxide (k =3.9-4.3) are continually being pursued today, which mainly including organosilicates and organic polymers.⁸

Compared with inorganic dielectric materials, organic polymer materials often have a lower dielectric constant, because of the lower materials density and lower individual bond polarizability. Moreover, they show distinct advantages, in terms of easy chemical and geometric structural design.^{14–18} Thus, they have attracted much interest. Generally, by decreasing the dipole strength or the number of dipoles or a combination of both, the dielectric constant of full dense polymer materials can be lowered to 2.2–2.6.^{5,19–22} The most common way is fluorination of dielectric materials or increasing

the free volume by rearranging the material structure.²³⁻²⁷ However, it seems that no true dielectric generational extendibility to the ultralow-k region can be achieved without embracing the concept of porosity, either for organosilicates or organic polymers.^{28–32} The *k*-value of these porous materials can be less than 1.5,^{33–39} but the method itself is complicated, difficult to control, and expensive. Moreover, the pore structure, the size, and the distribution would greatly affect the homogeneity of the materials, which makes this technique difficult for large-area applications. In addition, the porosity tends to dramatically reduce the mechanical strength and increase the permeability of the materials, thereby making them too fragile for practical uses. Therefore, the switch to highperformance nonporous ultralow-k polymer insulators continues to be a formidable challenge to chemists, physicists, materials scientists, and integration engineers. Furthermore, as far as we know, homogeneous polymers with an *intrinsic k*-value of <2.0 have not ever been reported in the literature.

Polyimides have been widely used as materials for electronic packaging and electrical insulation in microelectronics industries, because of their excellent thermal, mechanical, and dielectric properties.^{40–42} It is one of the most promising polymer candidates for the next generation of high-perform-

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ance interlayer dielectrics. However, the k-value of the traditional polyimides, such as commercial DuPont Kapton polyimide films (see Figure 1), is typically 3.1–3.5, which



Figure 1. Chemical structure of the DuPont Kapton polyimide films, FPTTDA, and FPTTPI.

makes it difficult to meet the requirement of ultralow k-values of <2.0 for the technology nodes below 130 nm.⁴³ Hence, research on polyimides with ultralow dielectric constants is of great significance.

In this contribution, we present a new structural polymer (FPTTPI), which contains both a rigid polyimide main chain (PI MC) and a large rigid nonplanar conjugated side chain (LRNPC SC). It was synthesized by polycondensation between a novel diamine (FPTTDA) and a dianhydride (6FDA). Their chemical structures are shown in Figure 1. The solution-cast FPTTPI film shows an intrinsic k value of 1.52 with a dielectric loss on the order of 10^{-3} at 10 kHz. More importantly, the dielectric properties remain stable up to 280 °C. The excellent ultralow dielectric properties are mainly due to the larger free volume (subnanoscale) that intrinsically exists in the amorphous region of polymeric materials. Meanwhile, the FPTTPI shows excellent thermal stability and mechanical properties, with a glass-transition temperature (T_{a}) of 280 °C, 5 wt % loss temperature of 530 °C, and a residual of 63% at 800 °C under N2. In addition, it is soluble in common solvents, which made it possible to undergo simple spin-on or efficient, low-cost, and continuous roll-to-roll processes.

EXPERIMENTAL SECTION

Materials. 4-Bromobenzophenone, 4-bromobenzyl bromide, triethyl phosphate, 4-(trifluoromethyl)- phenylboronic acid, 4-aminophenylboronic acid hydrochloride, tetrakis(triphenylphosphine)palladium ($Pd[P(C_6H_5)_3]_4$), potassium *tert*-butanolate, Aliquat 336 (tricaprylylmethylammonium chloride), cesium fluoride (CsF), 1-fluoro-4-nitrobenzene, palladium 10% on carbon (10% Pd/C), and hydrazine monohydrate ($NH_2NH_2\cdot H_2O$), were purchased from Alfa Aesar and were used as received. 4,4'-(Hexafluoro-isopropylidene)-diphthalic anhydride (6-FDA) was purchased from Alfa Aesar and was heated at 140 °C under vacuum for 12 h prior to use. Analytical-grade dimethylformamide (DMF) was purified by distillation under an inert nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. All other solvents and reagents were purchased as analytical grade from the Guangzhou Dongzheng Company and were used without further purification.

Instrumentation. All NMR spectra were recorded on a Bruker Model AVANCE AV 400 spectrometer. Samples were composed of a solution of 5–15 mg of each compound in 0.5 mL of deuterated dimethyl sulfoxide (DMSO) using tetramethylsilane (TMS) as the internal reference. Mass spectra were measured on a Thermo EI mass spectrometer (DSQ II). Elemental analysis was performed on a CHNS elemental analyzer. Infrared spectra were recorded on a Bruker TENSOR 27 Fourier-transform infrared (FT-IR) spectrometer. Gel permeation chromatography (GPC) was performed with a Waters Model 717 plus autosampler and a Waters Model 1515 isocratic HPLC pump. Two Waters columns, connected in series, were used with DMF as the eluent and were calibrated with narrow polydispersity polystyrene standards. The intrinsic viscosity of the FPTTPI in DMF (0.5 g L^{-1}) was measured with an Ubbelohde viscometer. Thermogravimetric analyses (TGA) were performed with a TA Instruments Model Q50 thermal analyzer under N₂/air with a heating rate of 20 °C/min from 30 °C to 1000 °C; the samples were heated under flowing nitrogen/air (40 mL/min). Differential scanning calorimetry (DSC) curves were obtained with a Netzsch Model DSC 204 thermal analyzer at a heating rate of 25 °C/min from 30 °C to 400 $^{\circ}$ C under flowing nitrogen. The glass-transition temperature (T_{g}) was read at the midpoint of the transition in the heat capacity and was taken from the second heating trace after rapid cooling from 400 °C at a cooling rate of 40 °C/min. Thermal mechanical analysis (TMA) was used to study the thermal coefficient of expansion (CTE) of the FPTTPI film with a heating rate of 10 °C/min from 50 °C to 350 °C. A tensile test was performed on samples cut from a sheet $35-50 \ \mu m$ thick, and the test was performed using a SANS Model CTN6103 instrument according to Standard GB/T16421-1996. The specimen size was 10 mm \times 100 mm, and the jaw separation was 50 mm. The jaw speed was first set to 2 mm/min. When elongation reached 1 mm, the jaw speed was changed to 20 mm/min. The morphology of the surface of FPTTPI was studied using a field-emission scanning electron microscopy (FE-SEM) system (Hitachi, Model s4800, Japan) and an atomic force microscopy (AFM) system (Bruker, Model Multimode 8, Germany). The dielectric constant was measured at frequencies between 100 Hz and 1 MHz at 20 °C and 50% relative humidity, using a Solartron SI 1260 impedance/gain phase analyzer in conjunction with two copper electrodes (10.2 mm \times 10.2 mm). The amplitude of the ac electric field was ~ 1 V/cm. The samples were thin films with a size of 12 mm \times 12 mm. Silver paste was coated onto both surfaces of the PI film to ensure excellent contact between the electrodes and the PI film. Positron lifetime measurements were performed as follows: two identical samples with dimensions of 1.5 mm \times 10 mm \times 10 mm were sandwiched with a 1.1 \times 10⁶ Bq ²²Na positron source; the ²²Na nucleus emits a 1.28 MeV γ -ray simultaneously (within a few picoseconds) with the positron; the positron lifetime is determined from the time delay between the emission of the birth gamma (1.28 MeV) and one of the 0.511 MeV annihilation photons; lifetime measurements were conducted using a fast-fast coincidence system with a time resolution of ~220 ps and a channel width of 12.6 ps. We analyzed the lifetime spectra using the data processing program PATFIT. Before analyzing each spectrum, we subtracted the positron source components (392 ps/16.40%, 2.05 ns/ 0.70%). The variance of the fits was \sim 1.1. The film density was measured by a density balance (Mirage SD-200 L, Japan) with an accuracy of 0.1 mg.

Synthesis of Phenyl(4'-(trifluoromethyl)biphenyl-4-yl) Methanone (FPTC). 4-Bromobenzophenone (10.4444 g, 0.04 mol) and 4-(trifluoromethyl)phenyl-boronic acid (8.5469 g, 0.045 mol) were dissolved in THF (400 mL) and mixed in a 500 mL flask. Then, 2 M aqueous K₂CO₃ solution (120 mL) and 10 drops of Aliquat 336 were added. The mixture was stirred for 45 min under argon at room temperature. Tetrakis(triphenylphosphine) palladium $(Pd(Pph_3)_4)$ (catalytic amount) was subsequently added as a catalyst, and the reaction mixture was stirred at 75 °C for 24 h. After cooling to room temperature, the product was concentrated and purified by silica-gel column chromatography using dichloromethane/*n*-hexane (v/v = 1/1). The yield of the product was ~92%. mp: 160 °C; ¹H NMR (400 MHz, DMSO- d_6): δ 8.00 (d, J = 8.2 Hz, 2H), 7.95 (d, J = 8.3 Hz, 2H), 7.88 (d, J = 8.2 Hz, 4H), 7.79 (d, J = 7.2 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H); ¹³C NMR (100 MHz, DMSO- d_6): δ 195.25, 142.89, 142.37, 136.936, 136.63, 132.71, 130.37, 129.52, 128.57 (q, ${}^{2}J$ = 31.8 Hz), 128.56, 127.82, 127.20, 125.88 (q, ${}^{3}J$ = 3.3 Hz) 124.20 (g ${}^{-1}I$ = 270.4 Hz): IR (KBr): 1647 cm⁻¹ (C=O Hz), 124.20 (q, ${}^{1}J = 270.4$ Hz); IR (KBr): 1647 cm⁻¹ (C=O stretching), 1177 cm⁻¹ (C-F stretching), 1100-700 cm⁻¹ (Ar-H stretching). UV/vis: λ_{max} 282 nm; HRMS (*m/z*): [M]⁺ calcd for C₂₀H₁₃F₃O, 326.0913; found, 326.0907. Analysis for C₂₀H₁₃F₃O: calcd, C, 73.61; H, 4.02; found: C, 73.14; H, 4.09.

Synthesis of (E)-4-(2-(4-bromophenyl)-1-phenyl-vinyl)-4'-(trifluoromethyl)biphenyl (FPTBr). 4-Bromo-benzyl bromide (12.4965 g, 0.05 mol) and triethyl phosphite (24.924 g, 0.15 mol) were mixed in a 500 mL flask. The mixture was stirred for 24 h under argon at 150 °C. After the mixture was cooled to room temperature, FPTC (13.0524 g, 0.04 mol) and THF (400 mL) were added. Then, potassium tert-butanolate (8.4158 g, 0.075 mol) was added, and the reaction mixture was stirred at room temperature for 12 h. After reaction, the product was concentrated and purified by silica-gel column chromatography, using *n*-hexane. The yield of the product was ~72%. mp: 149 °C; ¹H NMR (400 MHz, DMSO- d_6): δ 7.91 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.48-7.40 (m, 5H), 7.35 (d, J = 8.5 Hz, 2H), 7.22-7.16 (m, 3H), 6.97 (d, J = 8.5 Hz, 2H); ¹³C NMR (100 MHz, DMSO- d_6): δ 143.36, 142.06, 141.84, 139.18, 137.62, 135.97, 131.07, 130.79, 129.52, 128.95, 128.09 $(q, {}^{2}J = 32.1 \text{ Hz}), 127.75, 127.60, 127.15, 126.86, 126.77, 125.61 (q, {}^{3}J$ = 3.4 Hz), 124.23 (q, ${}^{1}J$ = 275 Hz), 119.96; IR (KBr): 3045 cm⁻¹ C-H stretching), 1482 cm⁻¹ (C=C stretching), 1164 cm⁻¹ (C-F stretching), 1100–700 cm⁻¹ (Ar–H stretching), 698 cm⁻¹ (C–Br stretching). UV/vis: λ_{max} 323 nm; HRMS (m/z): [M]⁺ calcd for C27H18BrF3, 478.0538; found, 478.0533. Analysis for C27H18BrF3: calcd, C, 67.65; H, 3.79; found: C, 67.99; H, 3.95.

Synthesis of (E)-4'-(2-phenyl-2-(4'-(trifluoromethyl) biphenyl-4-yl)vinyl)biphenyl-4-amine (FPTPA). FPTBr (9.5866 g, 0.02 mol) and 4-aminophenylboronic acid hydrochloride (3.4682 g, 0.02 mol) were dissolved in THF (100 mL) and mixed in a 250 mL flask. Then, 2 M aqueous K₂CO₃ solution (30 mL) and 10 drops of Aliquat 336 were added. The mixture was stirred for 45 min under argon at room temperature. Tetrakis(triphenylphosphine) palladium (Pd- $(Pph_3)_4$ (catalytic amount) was subsequently added as a catalyst, and the reaction mixture was stirred at 75 °C for 24 h. After cooling to room temperature, the product was concentrated and purified by silica gel column chromatography using dichloromethane/n-hexane (v/v = 1/1). The yield of the product was ~85%. mp: 188 °C; ¹H NMR (400 MHz, DMSO- d_6): δ 7.97 (d, J = 7.5 Hz, 2H), 7.82 (d, J = 7.5 Hz, 4H), 7.33 (dd, J = 14.3, 7.5 Hz, 11H), 7.13-7.04 (m, 3H), 6.60 (d, J = 8.4 Hz, 2H), 5.16 (s, 2H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 148.93, 143.99, 143.04, 140.97, 140.81, 139.63, 137.92, 134.57, 131.17, 130.24, 128.85, 128.51, 128.40 (q, ${}^{2}J$ = 31.6 Hz), 127.97, 127.92, 127.80, 127.56, 127.37, 127.03, 126.24 (q, ${}^{3}J$ = 3.7 Hz), 125.13, 124.84 (q, ${}^{1}J$ = 270.2 Hz), 114.67; IR (KBr): 3375 cm⁻¹ (N-H stretching), 1617 cm⁻¹ (δ N-H), 1284 cm⁻¹ (C-N stretching), 1165 cm⁻¹ (C-F stretching), 1100–700 cm⁻¹ (Ar–H stretching); UV/vis: λ_{max} 352 nm; HRMS (m/z): [M]⁺ calcd for C₃₃H₂₄F₃N, 491.1855; found, 491.1848. Analysis for C33H24F3N: calcd: C, 80.63; H, 4.92; N, 2.85; found: C, 81.08; H, 4.99; N, 2.82.

Synthesis of (E)-N,N-bis(4-nitrophenyl)-4'-(2-phenyl-2-(4'-(trifluoromethyl)biphenyl-4-yl)vinyl) biphenyl-4-amine (FPTTDN). FPTPA (9.831 g, 0.02 mol), 1-fluoro-4-nitrobenzene (5.644 g, 0.04 mol), and cesium fluoride (6.0764 g, 0.04 mol) were mixed in a 500 mL flask, and DMSO (150 mL) was added. The mixture was stirred for 24 h under argon at 150 °C. After reaction, the product was concentrated and purified by silica-gel column chromatography using dichloromethane/n-hexane (v/v = 1/1). The yield of the product was ~76%. mp: 210 °C; ¹H NMR (400 MHz, DMSO- d_6): δ 8.23–8.15 (m, 8H), 7.97 (d, J = 8.2 Hz, 2H), 7.91 (d, J= 8.2 Hz, 2H), 7.82 (dd, J = 11.8, 6.1 Hz, 6H), 7.79-7.70 (m, 6H), 7.53 (dd, J = 8.4, 6.8 Hz, 4H), 7.48-7.30 (m, 12H), 7.29-7.17 (m, 18H), 7.13 (d, J = 8.5 Hz, 2H); ¹³C NMR (100 MHz, DMSO- d_6): δ 151.96, 144.26, 143.98, 143.90, 142.88, 142.83, 142.67, 142.00, 141.78, 140.72, 140.22, 138.15, 138.07, 138.05, 137.73, 137.69, 136.77, 136.70, 131.15, 130.50, 130.46, 130.18, 129.63, 128.91, 128.81, 128.55 (q, ${}^{2}J$ = 19.2 Hz), 128.33, 128.24, 128.16, 128.07, 127.95, 127.80, 127.75, 127.69, 127.48, 126.61, 126.54, 126.27 (q, ${}^{3}J = 5$ Hz), 126.05, 126.05, 124.82 (q, ${}^{1}J$ = 269.9 Hz), 123.15; IR (KBr): 1582 cm⁻¹, 1495 cm⁻¹ (-NO₂ stretching), 1165 cm⁻¹ (C–F stretching), 1100–700 cm⁻¹ (Ar–H stretching); UV/vis: λ_{max} 372 nm; HRMS (m/z): [M]⁺ calcd for $C_{45}H_{30}F_3N_3O_4$, 733.2183; found, 733.2189. Analysis for $C_{45}H_{30}F_3N_3O_4$: calcd: C, 73.66; H, 4.12; N, 5.73; found: C, 73.79; H, 4.23; N, 5.66.

Synthesis of (E)-N¹-(4-aminophenyl)-N¹-(4'-(2-phenyl-2-(4'-(trifluoromethyl)biphenyl-4-yl)vinyl) -biphenyl-4-yl)benzene-1,4-diamine (FPTTDA). A mixture of FPTTDN (14.6746 g, 0.02 mol), 10% Pd/C catalyst (0.5 g), hydrazine monohydrate (16 mL), and ethanol (300 mL) was placed in a three-necked flask and heated at 80 °C for 24 h. The mixture was then filtered to remove the Pd/C catalyst. After the mixture cooled to room temperature, the precipitated crystals were isolated by filtration, recrystallized from ethanol twice, ground into powder, and dried under vacuum. Yield: 89%. mp: 228 °C; ¹H NMR (400 MHz, DMSO- d_6): δ 7.88 (t, J = 13.8 Hz, 2H), 7.82 (t, J = 8.6 Hz, 4H), 7.75 (dd, J = 13.2, 8.5 Hz, 4H), 7.62 (d, J = 8.2 Hz, 2H), 7.51-7.12 (m, 26H), 7.05 (t, J = 1.5 Hz, 2H), 6.83 (dd, J = 8.1 Hz, 8H), 6.63 (d, J = 7.0 Hz, 4H), 6.56 (dd, J = 8.5, 3.6)Hz, 8H), 4.98 (s, 8H); ¹³C NMR (100 MHz, DMSO-d₆): δ 149.69, 149.35, 146.28, 146.14, 145.66, 144.96, 144.36, 144.03, 143.05, 143.04, 140.73, 140.42, 139.09, 138.40, 138.09, 137.86, 136.75, 136.25, 136.05, 134.91, 130.35, 130.20, 129.85, 129.62, 129.54, 129.03, 128.84, 128.57 $(q, {}^{2}J = 23.6 \text{ Hz}), 128.38, 128.30, 128.23, 128.05, 127.94, 127.82,$ 127.71, 127.46, 127.08, 126.60, 126.21 (q, ${}^{3}J$ = 3.8 Hz), 126.18 (q, ${}^{3}J$ = 3.8 Hz), 125.66, 125.36, 125.05 (q, ¹J = 310.0 Hz), 117.24, 117.04, 115.30; IR (KBr): 3371 cm⁻¹ (N–H stretching), 1617 cm⁻¹ (δ N–H), 1264 cm⁻¹ (C-N stretching), 1100-700 cm⁻¹ (Ar-H stretching). UV/vis: λ_{max} 322 nm; HRMS (m/z): [M]⁺ calcd for C₄₅H₃₄F₃N₃, 673.2699; found, 673.2707. Analysis for C₄₅H₃₄F₃N₃: calcd, C, 80.22; H, 5.09; N, 6.24; found: C, 80.26; H, 5.12; N, 6.18.

Synthesis and Preparation of Polyimide Film (FPTTPI). To a solution of FPTTDA (1.3475 g, 2 mmol) in purified DMF (15.8 mL) in a 50 mL flask, 6FDA (0.8885 g, 2 mmol) was added in one portion. Thus, the solid content of the solution was \sim 15 wt %. The mixture was stirred at room temperature under argon for ~12 h to produce a viscous poly(amic acid) (PAA) solution. The weight-average molecular weight (M_w) values and the polydispersity (PDI) of the resultant PAA (FPTTPAA) estimated from GPC were 29.7 \times 10⁴ and 2.23, respectively, measured in DMF at a concentration of 4 mg/mL at 50 °C. The PAA solution was subsequently uniformly coated onto a clean and dry glass (film thickness could be controlled), and thermal imidization was performed in a vacuum drying oven to produce the FPTTPI film. The polyimide film was subsequently removed from the glass substrate after the oven had cooled to room temperature. ¹H NMR (400 MHz, DMSO- d_6): δ 8.11 (d, J = 7.0 Hz, 2H), 7.96 (d, J =16.9 Hz, 3H), 7.86-7.54 (m, 10H), 7.49-7.33 (m, 10H), 7.30-7.04 (m, 11H); IR (film): 1774 and 1719 cm⁻¹ (C=O stretching), 1100-700 cm^{-1} (Ar–H stretching).

RESULTS AND DISCUSSION

Synthesis and Characterization of FPTTDA. The FPTTDA diamine was synthesized via the Wittig–Horner reaction and Suzuki coupling reaction, as shown in Scheme 1. The chemical structures of all the intermediate products and the target diamine were confirmed by ¹H NMR, ¹³C NMR (H–H COSY, C–H QC, and C–H BC) spectra, mass spectra, FT-IR, and elemental analysis; the results are shown in Figures S1–S5 in the Supporting Information. The thermal properties of FPTTDA were studied by DSC and TGA. These results revealed that the diamine exhibited good thermal stability. The 5% and 10% weight-loss temperatures (T_d) of FPTTDA in nitrogen were 404 and 417 °C, respectively.

Synthesis and Characterization of FPTTPI. The FPTTPI polyimide was prepared in a conventional two-step procedure by the reaction of equal molar amounts of diamine FPTTDA with commercially available aromatic tetracarboxylic dianhydride (6FDA) in dimethylformamide (DMF) to form the precursor poly(amic acid) (FPTTPAA), followed by thermal cyclodehydration to obtain the novel polyimide FPTTPI, as





shown in Scheme 2. The chemical structure of FPTTPI was confirmed by FT-IR spectra, as shown in Figure S6 in the Supporting Information. Compared with the spectrum of FPTTDA, the characteristic absorption at 3371 and 1617 cm⁻¹ (N–H stretching) in the spectrum of FPTTPI disappeared.

Scheme 2. Preparation of the FPTTPI Based on FPTTDA and 6FDA by a Conventional Two-Step Procedure



Meanwhile, the characteristic absorption peaks of the imide group at 1774 cm⁻¹ (asymmetrical stretching of carbonyl) and 1719 cm⁻¹ (symmetrical stretching of carbonyl), and the C–N bond at ~1264 cm⁻¹ were clearly shown in the FT-IR spectra of the polyimide, which indicated the successful reaction between FPTTDA and the dianhydride 6FDA and the complete imidization reaction of the FPTTPAA. In addition, the desired formation of the polyimide was further confirmed by ¹H NMR, as shown in Figure S7 in the Supporting Information.

The molecular weight of the FPTTPI was determined by GPC, and the qualitative solubility behavior of the corresponding polyimide is summarized in Table 1. The inherent viscosity

Table 1. (GPC Results	and the	Solubility	of	FPTTPI
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GPC Results ^a					
value					
8.96					
3.50					
Solvent Data					
solubility ^b					
+ +					
+					
+					
+					
+					

"With respect to polystyrene standards, with DMF as the eluent. Flow rate, 1 mL/min; test temperature, 50 °C. ^bLegend: (++) soluble at room temperature; (+) partially soluble at room temperature, soluble on heating (90 °C). The solubility was determined using 10 mg of PI in 1 mL of solvent.

of FPTTPI in DMF (0.5 g L⁻¹) is 0.31 g dL⁻¹, as measured by an Ubbelohde viscometer at 30 °C. The M_n and M_w of the polyimide was 2.56×10^5 and 8.96×10^5 , respectively, and thus a polydispersity index of 3.50 was observed, as determined by GPC. The polyimide was soluble in many common polar solvents such as *N*-methylpyrrolidone (NMP), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), DMF, and mcresol. The enhanced solubility can be attributed to the introduction of the rigid large nonplanar conjugated side chain into the polymer. Such structures may increase the steric hindrance effect, thus reducing the interactions between the polymer macrochains. The excellent solubility makes the polymer a potential candidate for practical applications in microelectronics by simple spin-on or efficient, low-cost and continuous roll-to-roll processes.

The polyimide could be processed to a flexible and tough film via solution casting or spin-on processes. Its thermal properties were investigated by TGA and DSC (see Table S1 in the Supporting Information), and the results of the TGA revealed that the polyimide exhibited good thermal stabilities in the atmospheres of N₂ and air. The 10% weight-loss temperatures (T_{d5} % and T_{d10} %) were 530 °C in N₂ and 512 °C in air, respectively. The amount of carbonized residue (char yield) in N₂ was 63% at 800 °C. In addition, the polyimide film exhibited a high T_g of 280 °C and showed no clear endothermic melting peaks up to the decomposition temperatures in the DSC thermograms. These results are in agreement with the WAXD results (see Figure S8 in the Supporting Information), which demonstrated the amorphous nature and isotropic properties of the material. Moreover, the polyimide film

showed excellent mechanical properties (see Table S1); the tensile strength and tensile modulus of the as-cast film were 92.1 MPa and 2.5 GPa, respectively. The thermal coefficient of expansion (CTE) of the FPTTPI film was measured by a thermomechanical analyzer (TMA Q400), which is $60 \ \mu m/(m^{\circ}C)$ within the range of 100–200 °C (see Figure S9 in the Supporting Information). The high $T_{g'}$ the excellent thermal stability, and the good mechanical properties of the soluble PI could be due to the aromatic rigid nonplanar structure and low polarity of the diamine monomer FPTTDA and are expected to meet the requirements of heat resistance and high processing and application temperatures in the microelectronics industry.

Dielectric Properties of the FPTTPI Film. The dielectric properties of the polyimide film were measured at the frequencies between 100 Hz and 1 MHz at 20 °C and 50% relative humidity using a Solartron SI 1260 impedance/gain phase analyzer (Solartron Group Ltd., U.K.). A commercial insulating material, DuPont Kapton polyimide film, was also measured for comparison. The measurement was carried out as follows. First, a capacitance measurement was carried out; then the dielectric constant of the FPTTPI and Kapton film was calculated using eq 1:

$$\varepsilon' = \frac{C}{\varepsilon_0} \left(\frac{l}{A} \right) \tag{1}$$

Here, ε' is the dielectric constant of the material between the plates, *C* the capacitance of the material (in Farads), ε_0 the electric constant ($\varepsilon_0 \approx 8.854 \times 10^{-12}$ F m⁻¹), *l* the thickness of the film (in meters), and *A* the area of overlap of the two plates (in square meters); the results are shown in Figure 2. The



Figure 2. Dielectric properties of the FPTTPI film and a DuPont Kapton polyimide film; inset shows a plot of the dielectric constant of FPTTPI versus temperature at 10 kHz.

FPTTPI provided good electrical properties, with a dielectric constant of 1.52 and a dissipation factor of ~0.008 at 10 kHz, which is much lower than that of the commercial Kapton film (dielectric constant of 3.49) and the most of the reported ultralow-*k* nanoporous organosilicate dielectric films (with *k* values in the range of 1.66–1.71) to date.³³ Moreover, these outstanding dielectric properties remain stable up to 280 °C (see inset in Figure 2), which is near the T_g of this polymer.

Morphology of the FPTTPI Film and Mechanisms Studies. The exciting results caused us to examine the morphology of the polymer film. Figure 3a showed a rolled sample demonstrated the film flexibility, which was produced



Figure 3. Morphology of the FPTTPI film: (a) image of the flexible FPTTPI film produced by a solution casting process; (b) a typical AFM image of the FPTTPI film surface.

by a solution casting process. The film surface was smooth and compact, with a surface roughness (R_q) of 2.88 Å (see Figure 3b), which was confirmed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The polyimide film contained no nanoporous structures, which prompted us to consider the fact of larger free volume (subnanoscale) that intrinsically exists in the amorphous region of polymeric materials. The rigid nonplanar conjugated side chain of the polymer may lead to structural (static or dynamic) disorder and contribute to the local free volume, which may play an important role in the ultralow-*k* properties of the polymer.

Positron annihilation lifetime spectroscopy (PALS) is a useful method for studying atomic- and subnanometer-sized holes in materials,^{44–46} and is often used to characterize the free volume of polymer materials. In liquids and porous solids, a fraction of the positrons injected from a radioactive source form positronium, which can annihilate from the para state (*p*-Ps, singlet spin state) or the ortho state (*o*-Ps, triplet spin state), with a relative formation probability of 1:3. p-Ps decays mainly via self-annihilation by emitting two γ -rays with a lifetime of \sim 125 ps, whereas the self-annihilation lifetime of o-Ps, which emits three γ -rays, is as long as 142 ns. The lifetime of o-Ps confined in local free volumes will be reduced to a typical value of 1-5 ns, because of collisions of Ps with molecules. The o-Ps will pick off one electron from the surrounding molecules and annihilate it by emitting two γ -rays, which are called pick-off annihilation. The pick-off annihilation lifetime of o-Ps is highly sensitive to the size of the free volume.

The positron lifetime spectra measured for FPTTPI and Kapton films are shown in Figure 4. From a detailed analysis of the lifetime spectra using the PATFIT routine (see Table 2),⁴⁵ we found two exponential decay components (τ_1 and τ_2) for the Kapton film and three exponential decay components (τ_1 , τ_2 , and τ_3) for the FPTTPI film. The shortest lifetime τ_1 was 0.29 ns for Kapton and 0.24 ns for FPTTPI, which is due to the *p*-Ps lifetime and the free annihilation lifetime of the positrons. The second lifetime component τ_2 is attributed to positron annihilation in the amorphous region, which is 0.41 ns for Kapton and 0.50 ns for FPTTPI. The long-lifetime component τ_3 is attributed to pick-off annihilation of *o*-Ps at holes in the



Figure 4. Positron lifetime spectra measured for the FPTTPI film and a DuPont Kapton polyimide film.

Table 2. An	alyzed I	Data fo	r the	Positron	Lifetime	in	the
DuPont Ka	pton and	I FPTT	PI F	ilms			

	Kapton	FPTTPI		
density (g/cm ³)	1.4406	1.3221		
exponential decay (ns)				
$ au_1$	0.29	0.24		
$ au_2$	0.41	0.50		
$ au_3$		2.47		
intensity (%)				
I_1	34.4	46.1		
I_2	65.6	41.8		
I_3		12.1		

amorphous phase and can be used to estimate the size of local free volumes in amorphous phases by eq $2:^{46,47}$

$$\tau_{o-\mathrm{Ps}} = 0.5 \,\mathrm{ns} \left[1 - \frac{r}{r+\Delta r} + \frac{1}{2\pi} \,\mathrm{sin} \left(\frac{2\pi r}{r+\Delta r} \right)^{-1} \right] \tag{2}$$

where the prefactor of 0.5 ns is the spin-averaged Ps annihilation lifetime, which is also observed in densely packed molecular crystals; a value of $\Delta r = 0.166$ nm is obtained by fitting eq 2 to the observed porous materials and was determined by Eldrup and Jean.⁴⁷

Compared with Kapton, FPTTPI shows a long-lifetime component (τ_3) (12.1%) of 2.47 ns, whereas the Kapton film shows no τ_3 component. The mean hole radius (r) of free volume in the FPTTPI film is 3.25 Å, and the diameter of the free-volume size is ~6.50 Å. Compared with the commercial Kapton film, which contains linear molecular structures without the nonpolar, large rigid side chain (Scheme 1), the appearance of these Ångström-scale free volumes decreases the density of the FPTTPI film by 8.2%. The density of the FPTTPI is 1.3221 g/cm³, whereas that of Kapton is 1.4406 g/cm³. As a result, the FPTTPI film shows ultralow-k properties.

CONCLUSION

In summary, by controlling the chemical, steric, and aggregation structures of the polymer at the molecular level, we obtained a subnanoscale porous, flexible polyimide dielectric film with outstanding ultralow-k and excellent comprehensive properties. The k value of the dielectric film is as low as 1.52 at 10 kHz. More importantly, such properties are an intrinsic

characteristic of the material formed only through a simple solution casting process, and they are stable up to 280 °C. Its excellent collective properties, such as high thermal stability and mechanical properties, as well as good solubility, make it a promising candidate for the ULSI industry. It is also our belief that such a design strategy is beneficial for lowering the k value and simultaneously maintaining the overall properties of polymers, and it also can be extended to other novel high-performance polymer systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.5b01798.

NMR results of all the intermediate products, FPTTDA and FPTTPI; WAXD patterns of the FPTTPI film; mechanical and thermal proterites of FPTTPI; experimental setup for the dielectric constant measurement (PDF)

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Notes

The authors declare no competing financial interest.

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